

Safe and high-performing bio-based alternatives to NMP

FABIEN DESWARTE, CIRCA
ÁNGEL PUENTE, NOVA-INSTITUTE

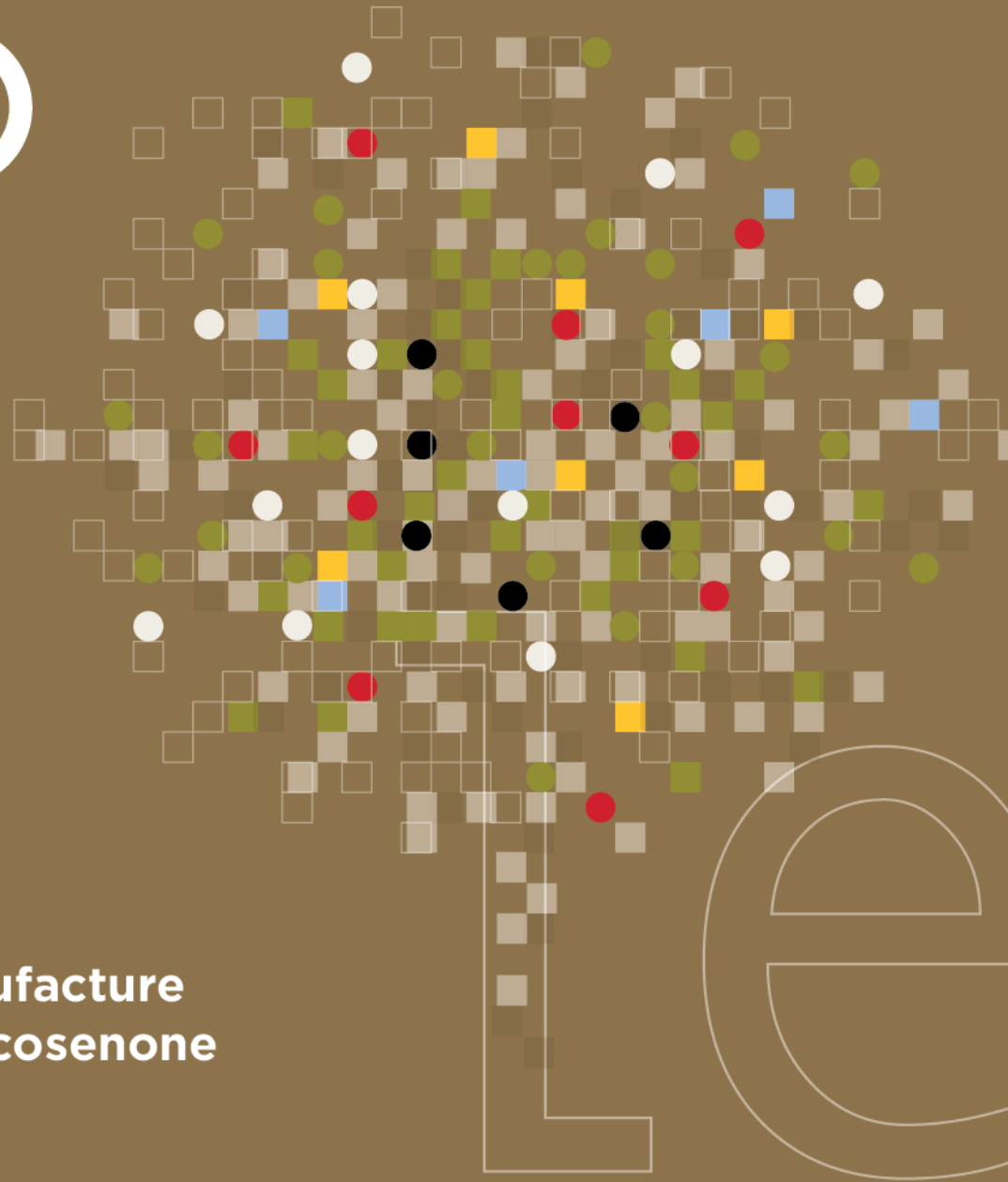


This project has received funding from the Bio Based Industries Joint Undertaking under the European Union's Horizon2020 research and innovation programme under agreement No 745450

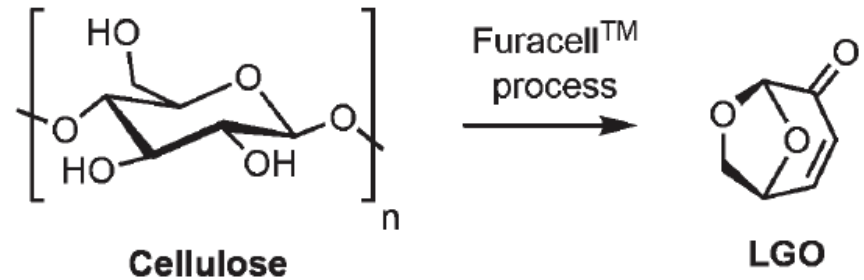
What is Circa Group?



Developers of world's first continuous process to manufacture platform molecule Levoglucosenone from waste cellulose



Our Furacell™ technology



- Proven over **10 years** and **4 pilot plants**
- **Demonstration plant successfully commissioned** and **operating end-to-end**

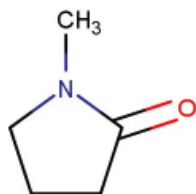
- Ubiquitous solvent used in wide range of applications
- Global market value:
 - \$1.18bn in 2017
 - \$1.54bn in 2022 (CAGR of 5.40%)
- Under intense regulatory pressure due to its toxicity

Substance identity

EC / List no.: 212-828-1

CAS no.: 872-50-4

Mol. formula: C₅H₉NO



Hazard classification & labelling



Danger! According to the **harmonised classification and labelling** (ATP09) approved by the European Union, this substance may damage the unborn child, causes serious eye irritation, causes skin irritation and may cause respiratory irritation.

Additionally, the classification provided by companies to ECHA in **REACH registrations** identifies that this substance may damage fertility or the unborn child.

Properties of concern



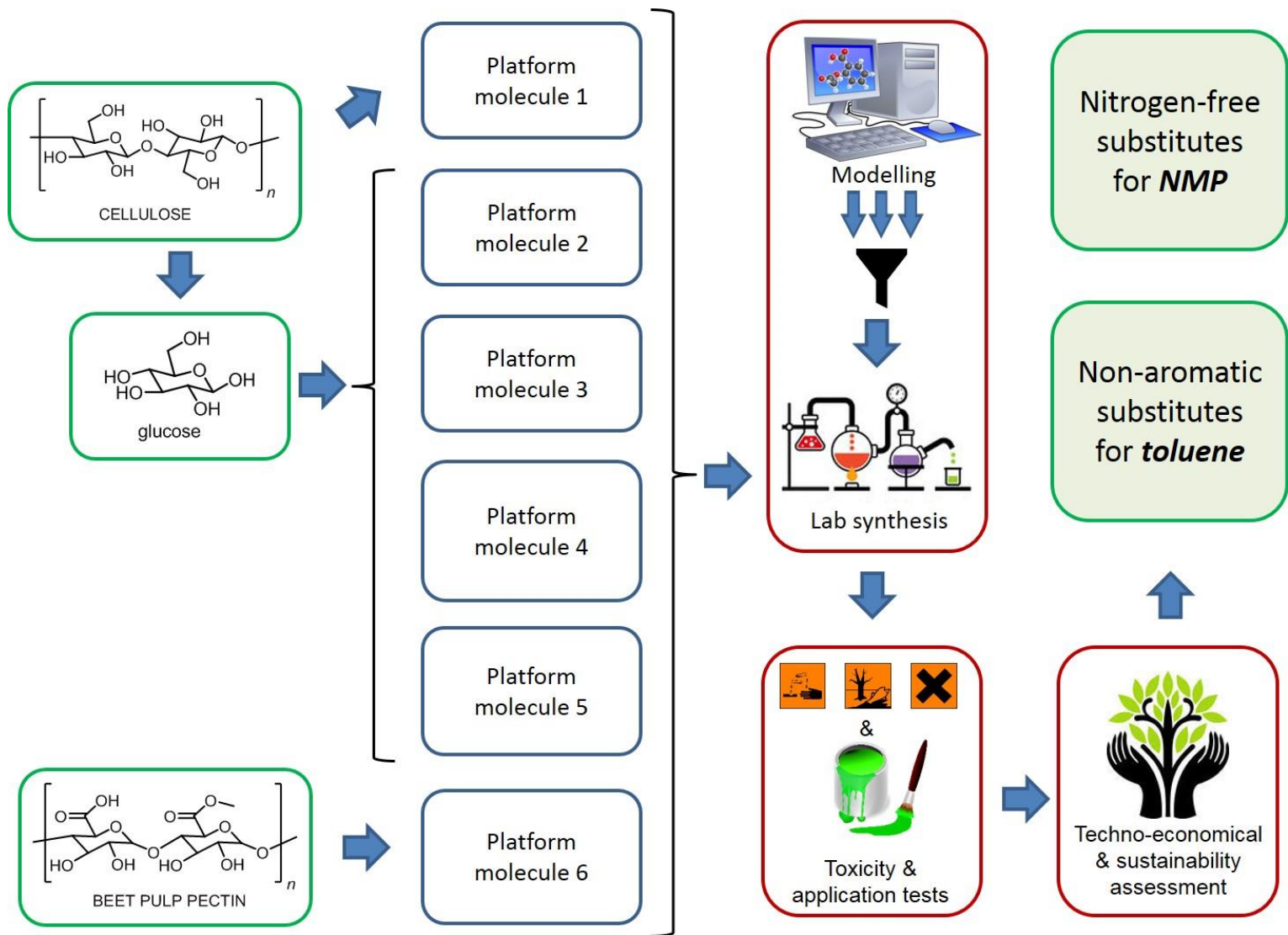
Toxic to Reproduction

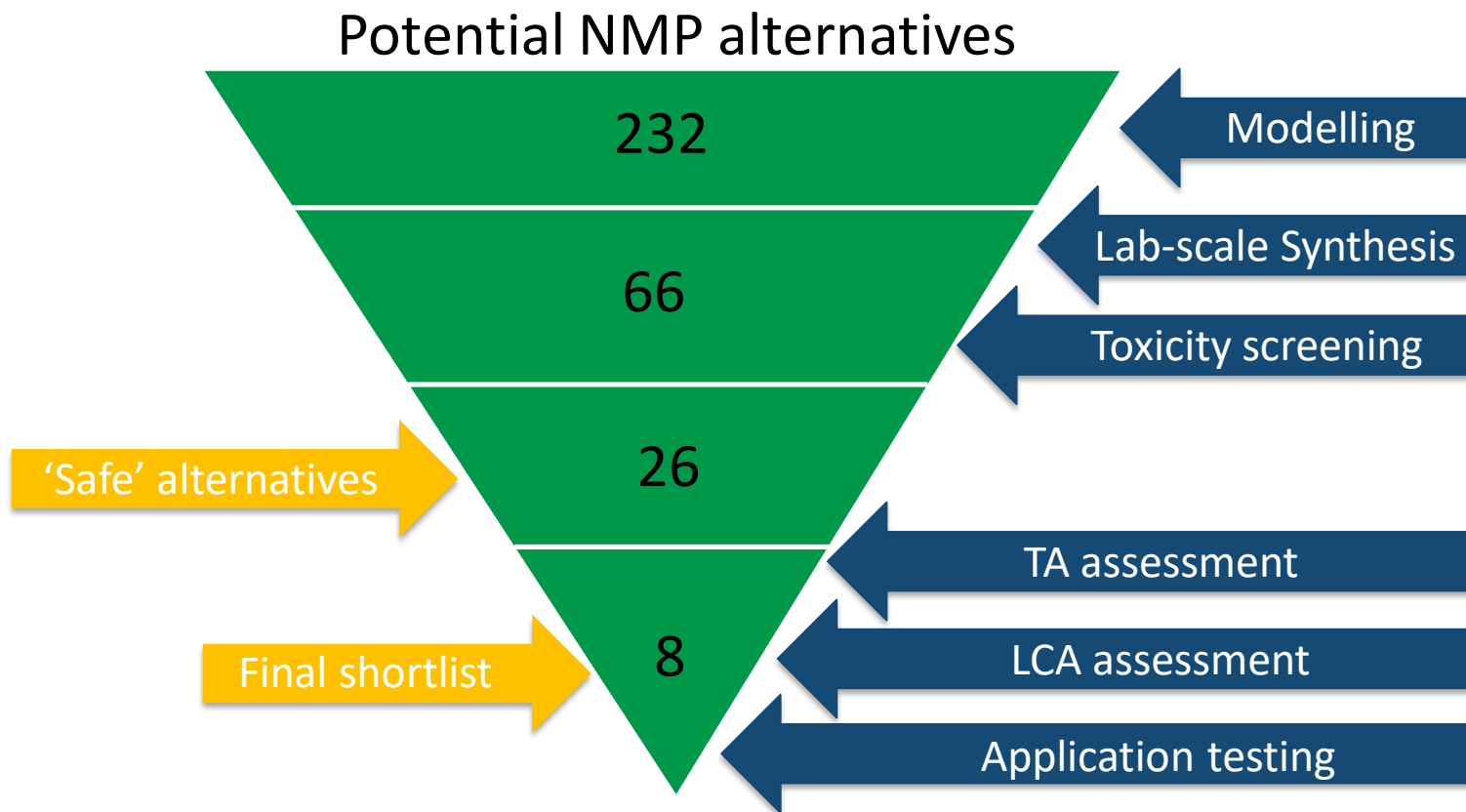
Important to know



- Substance of very high concern (SVHC) and included in the [candidate list](#) for authorisation.
- Some uses of this substance are restricted under [Annex XVII of REACH](#).

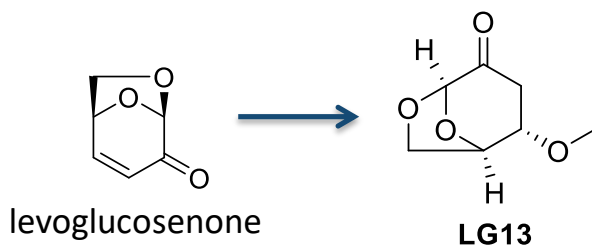
The concept



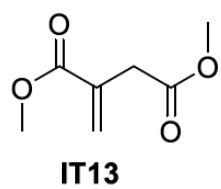


Toxicity screening


Code	compound	In vitro											bioavailability			In silico				
		Cytotox20%	Eba	AR-anti	PR-anti	PXR	PPARδ	Ahr	AP1	ESRE	Nrf2	p53 GENTOX	[max tested]	max [medium]	Volatility	Carcinogenicity	Gentox	Reprotox	Skin sens	
LGO	LG1	Cyrene	-3.0						-3.3		-3.5		-1.0	-1.0	N		EXP		EXP	
	LG6		-1.1			-1.6						-1.1	-1.1	L	TBC	TBC	TBC	TBC		
	LG64		-1.5									-1.2	-1.2	M	TBC	TBC	TBC			
	LG13	2-Methoxy-6,8-dioxabicyclo[3.2.1]octan-4-one	-4.3					-5.1	-5.1		-5.4		-1.1	-1.1	L					
	LG23	6,8-Dioxabicyclo[3.2.1]octan-4-yl methyl ether	-1.2		-2.7	-2.7	-3.7		-2.7	-1.7		-2.9	-1.2	x	L					
isosorbide	IS1		-1.2		-2.2	-2.5						-2.0	-2.0	N		RAX	RAX	RAX		
	IS2					-2.0						-2.0	-2.0	N		RAX	RAX	RAX		
	IS3					-2.2					-1.2	-1.2	-1.2	N		EXP	EXP	EXP		
	IS15					-2.2						-2.2		L	TBC	TBC	TBC	TBC		
levulinic acid /HMF	LV34	Butyl levulinate			-2.8	-2.5	-3.0			-2.5	-2.2	-2.2	-1.2	-1.2	L		EXP		EXP	
	OT16				-2.2		-2.2				-3.2		-1.2	-1.2	N	TBC				
itaconic acid	IT13	dimethyl itaconate	-3.4				-4.0					-3.0	-2.0	-3.0	M		EXP	EXP	GHS	
	IT14	diethyl itaconate	-3.2				-3.9				-3.3	-3.2	-3.3	-1.3	-2.7	M				
	IT15	dipropyl itaconate	-2.9				-4.7	-3.7			-3.7	-3.3	-3.9	-3.8	-1.3	-2.8	M			
	IT18	dibutyl itaconate	-3.3				-4.3	-4.3			-4.1	-3.4	-4.1	-4.7	-1.4	-3.5	M	EXP	RAX	EXP
	IT16	dipentyl itaconate	-3.6				-5.0	-4.0			-4.0	-2.4	-4.4	-4.4	-1.4	-3.4	M			

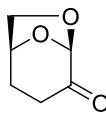
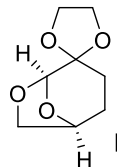
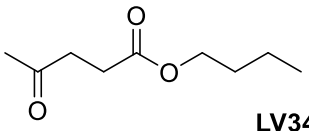


Easy and selective synthesis ✓
Toxic ✗



1,4-acceptor

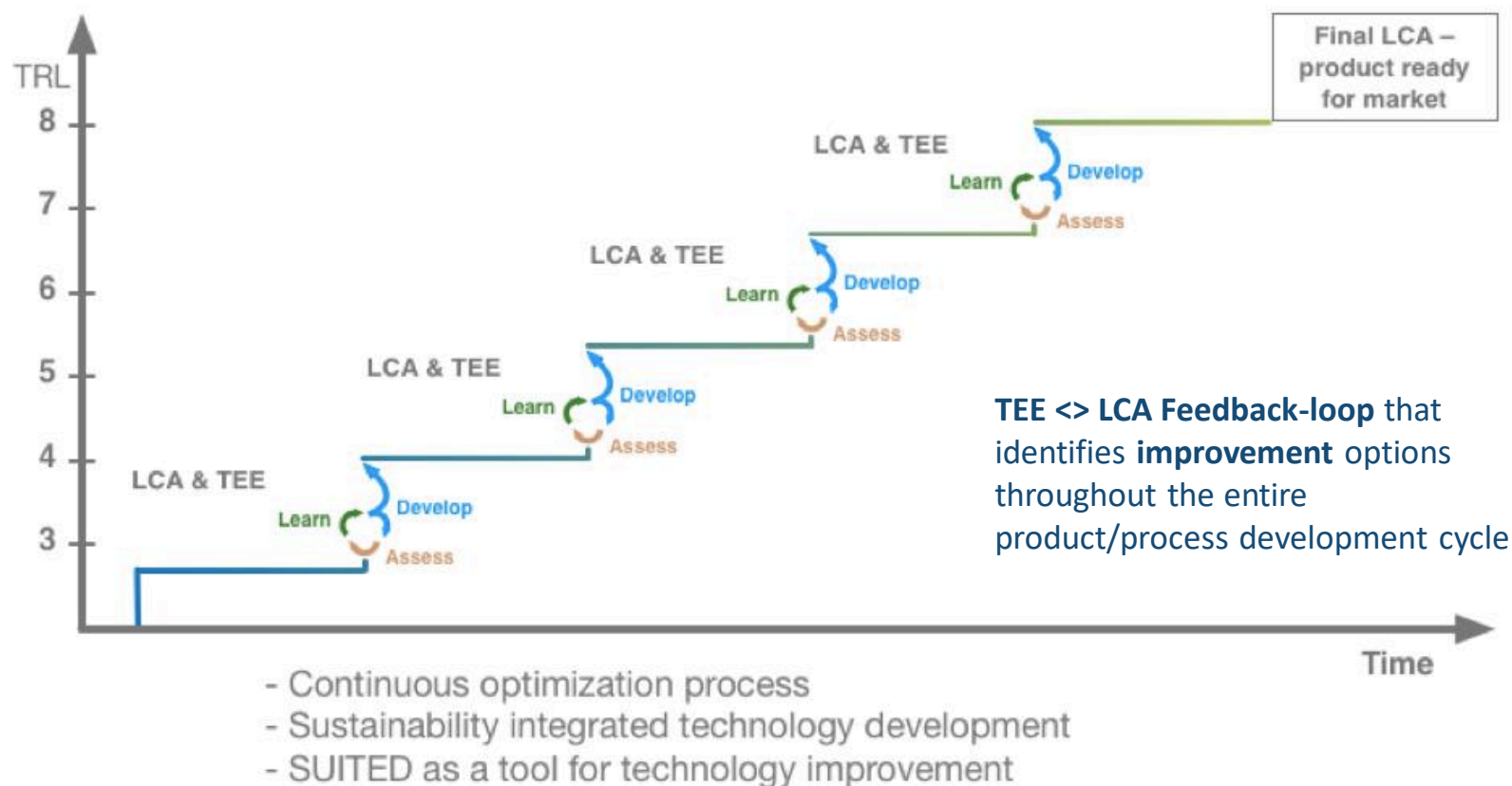

 Mutagenicity ✗
 (reaction with DNA) ?

Platform	Top candidates
Levogluosenone	  <p>LG1 LG2</p> <p>LG6 LG64</p>
Isosorbide	<p>IS1 IS2</p>
Levulinic acid / HMF	 <p>LV34 OT16</p>
Itaconic acid	None – all derivatives were suspected to be toxic
Pyrone	None – unselective synthesis
Alkenes	N/A

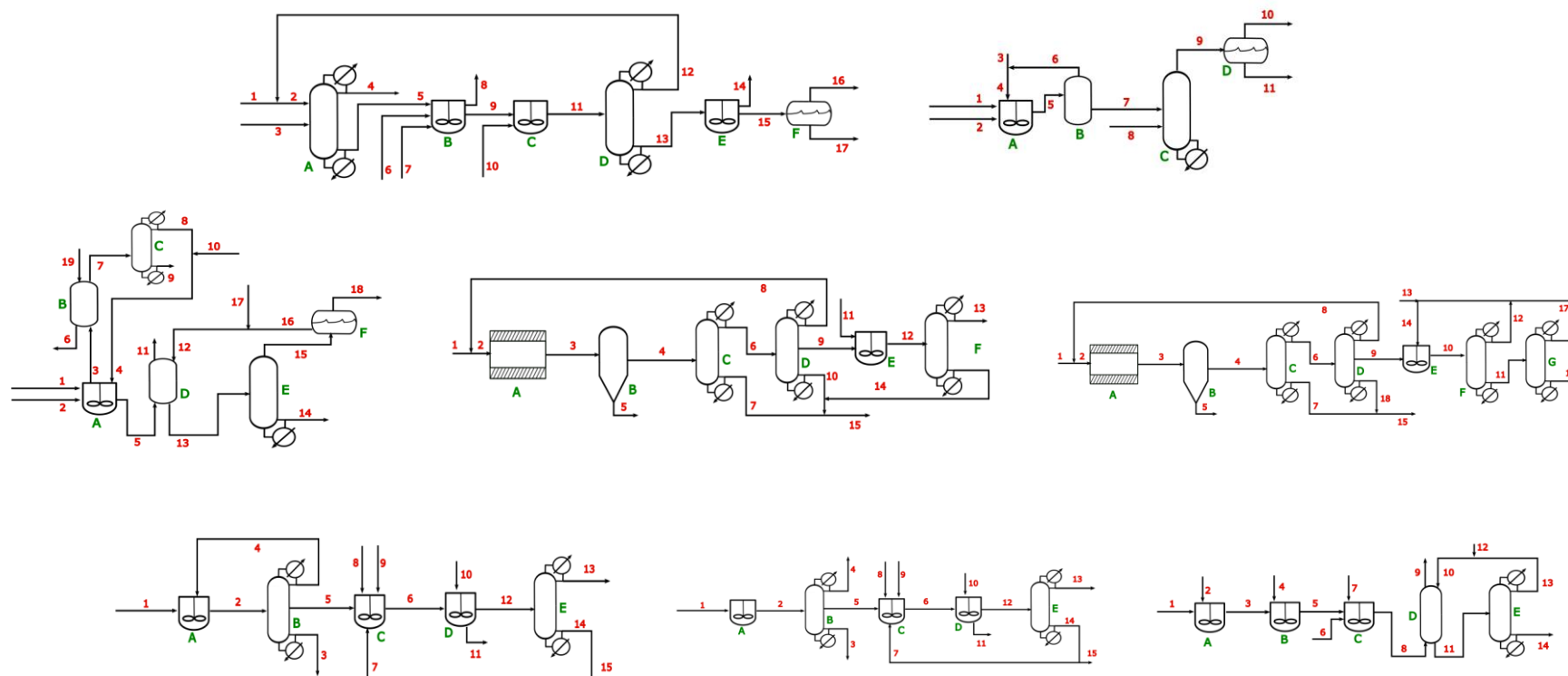
Economic and environmental performance



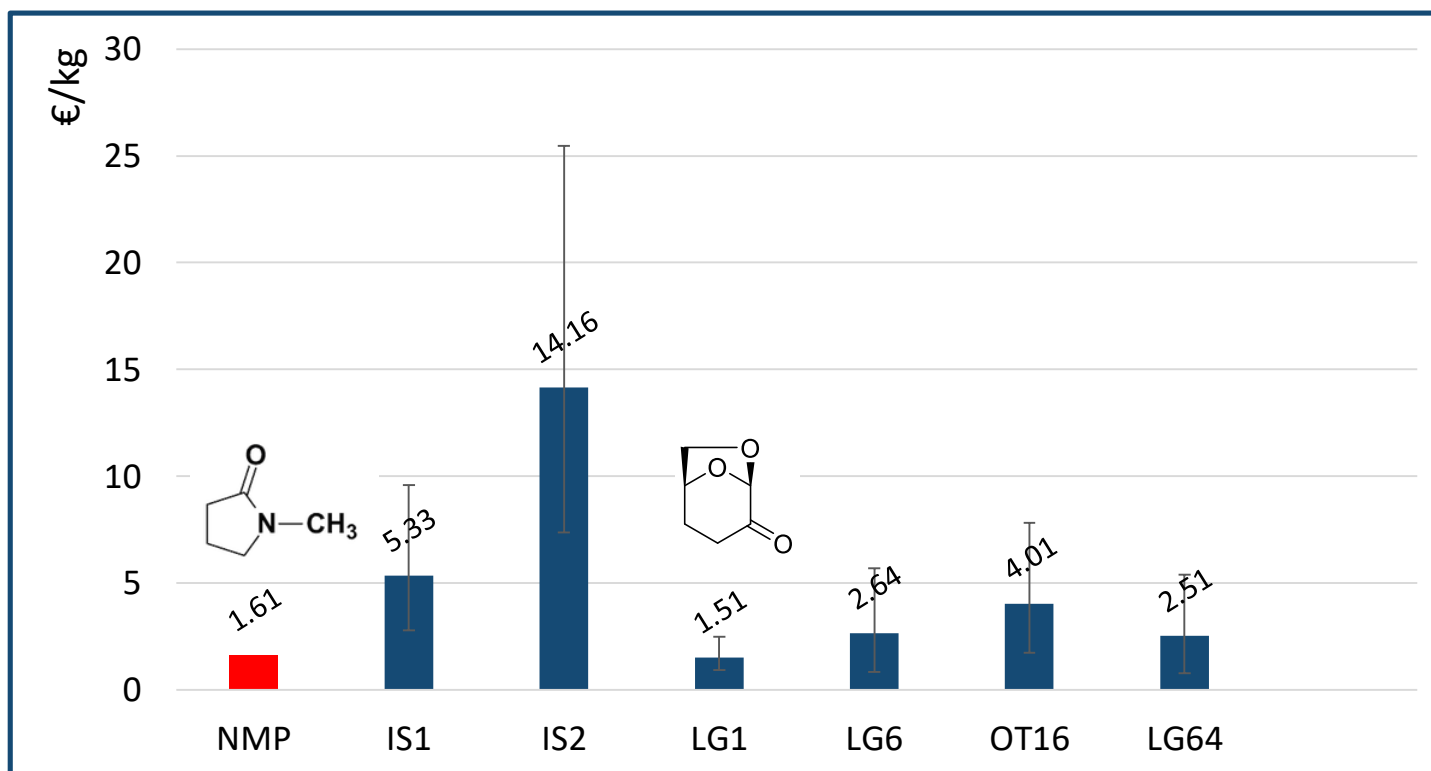
SUITED: SUstainability Integrated Technology Development



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



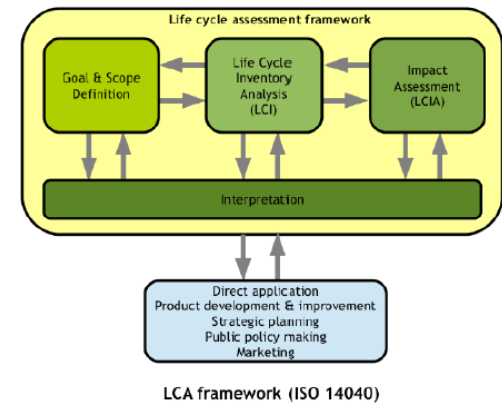
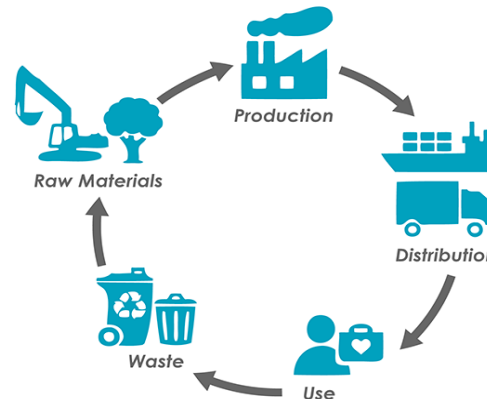
- Together with market analysis CAPEX and OPEX to give insight on production costs for selected candidates
- Most of the solvents we have looked at are well under 10 €/kg



Bio-based content & BUE

NMP replacements	Bio-based content, %	BUE, %
LG1	98%	70%
LG6	85%	62%
LG64	65%	62%
IS1	84%	81%
OT16	79%	70%
LV34	56%	53%

Life Cycle Assessment



- **Reference flow:** 1 kg of solvent
- **System boundaries: cradle-to-gate**
 - infrastructure is excluded
 - apart from gaseous **emissions** to the air it is assumed that all emissions are controlled as **solid wastes** and effluents will go to **wastewater treatment**
 - **use phase** not part of this study (very variable)
 - **end-of-life** are not considered either
- **Data source and quality:** primary data from CPD, LCI databases, literature, estimations, data quality assessment was carried out
- Scope: hotspot analysis, scenario analysis, comparative analysis and benchmarking
- **Multi-functionality:** partition by allocation method, products and co-products are allocated based on the **economic value**. Preferred when there is a substantial difference in the price between products and co-products

Impact categories

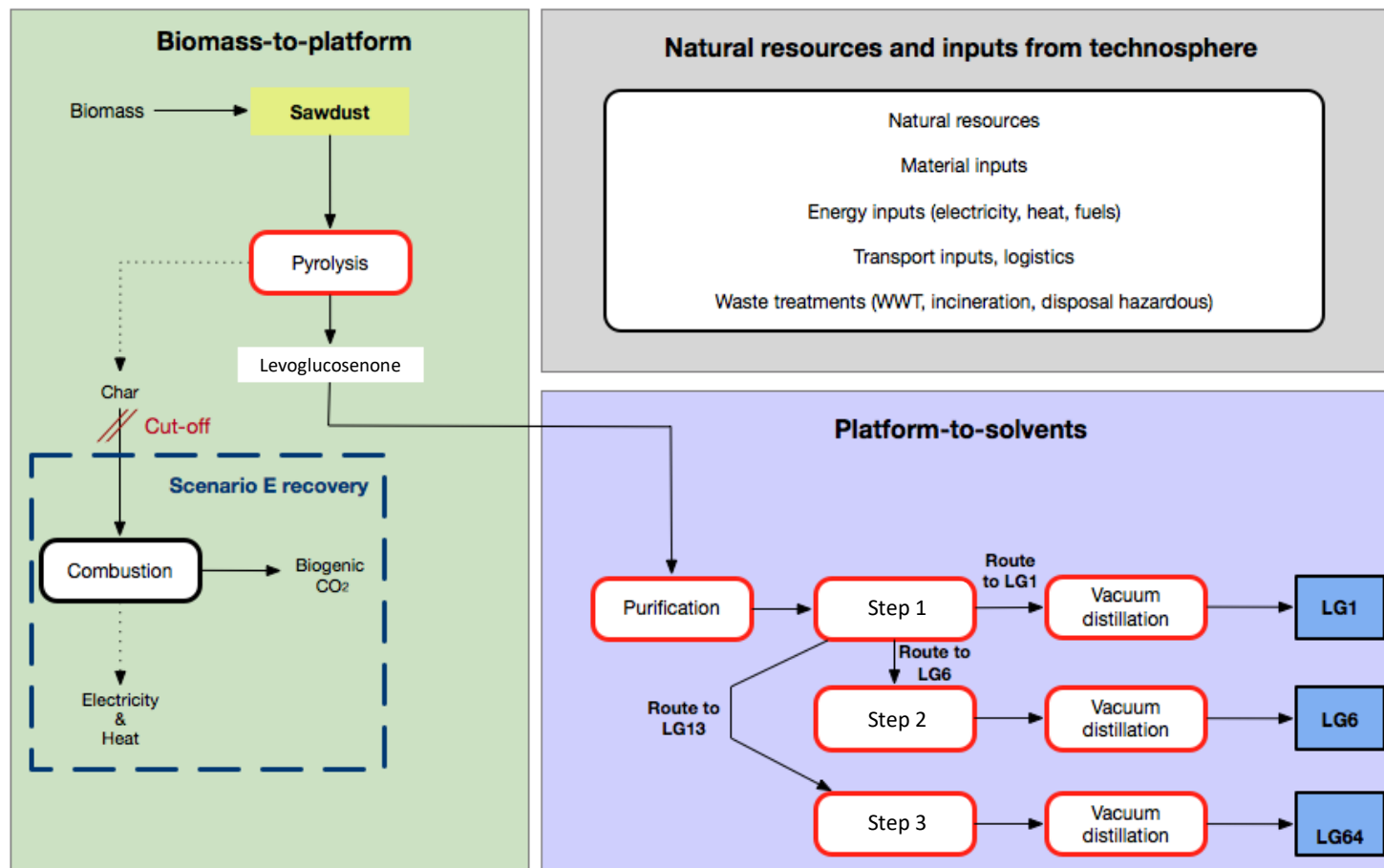
Single point indicators covering depletion of **resources**, **ecotoxicity** and **human toxicity** aspects


No **weighting** was applied


- Global warming potential with a timeframe of 100 years (**GWP100a**) kg CO₂ eq.
- Abiotic depletion potential (**ADP**) (**fossil fuels**) MJ
- Abiotic depletion potential (**ADP**) (**minerals**) kg Sb eq.
- Stratospheric Ozone layer depletion (**ODP**) kg CFC-11 eq.
- Photochemical oxidation potential (**POCP**) kg C₂H₄ eq.
- Acidification potential (**AP**) kg SO₂ eq.
- Eutrophication potential (**EP**) kg PO₄³⁻ eq.
- Human toxicity potential (**HTP**), Freshwater aquatic ecotoxicity (**FAETP**), Marine aquatic ecotoxicology (**MAETP**) and Terrestrial ecotoxicity (**TETP**) 1,4-dichlorobenzene eq.

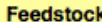
Describe the fate, exposure and effects of toxic substances in humans o ecosystems for an infinite time horizon

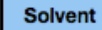
cradle → gate 0 → gate 1




 From primary data (PDC)

 Datasets from LCI databases

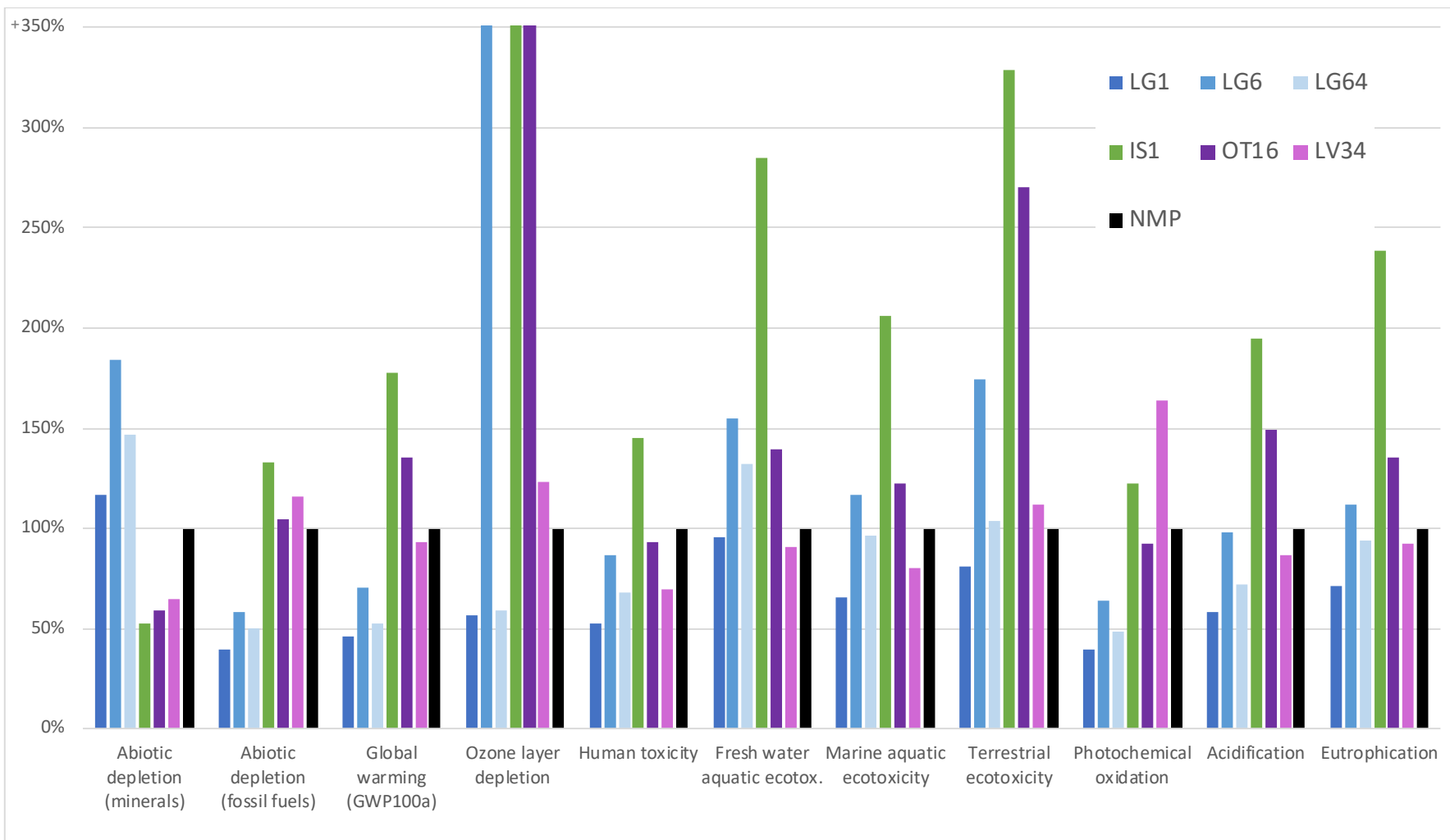
 Feedstock

 Solvent

 Co-products

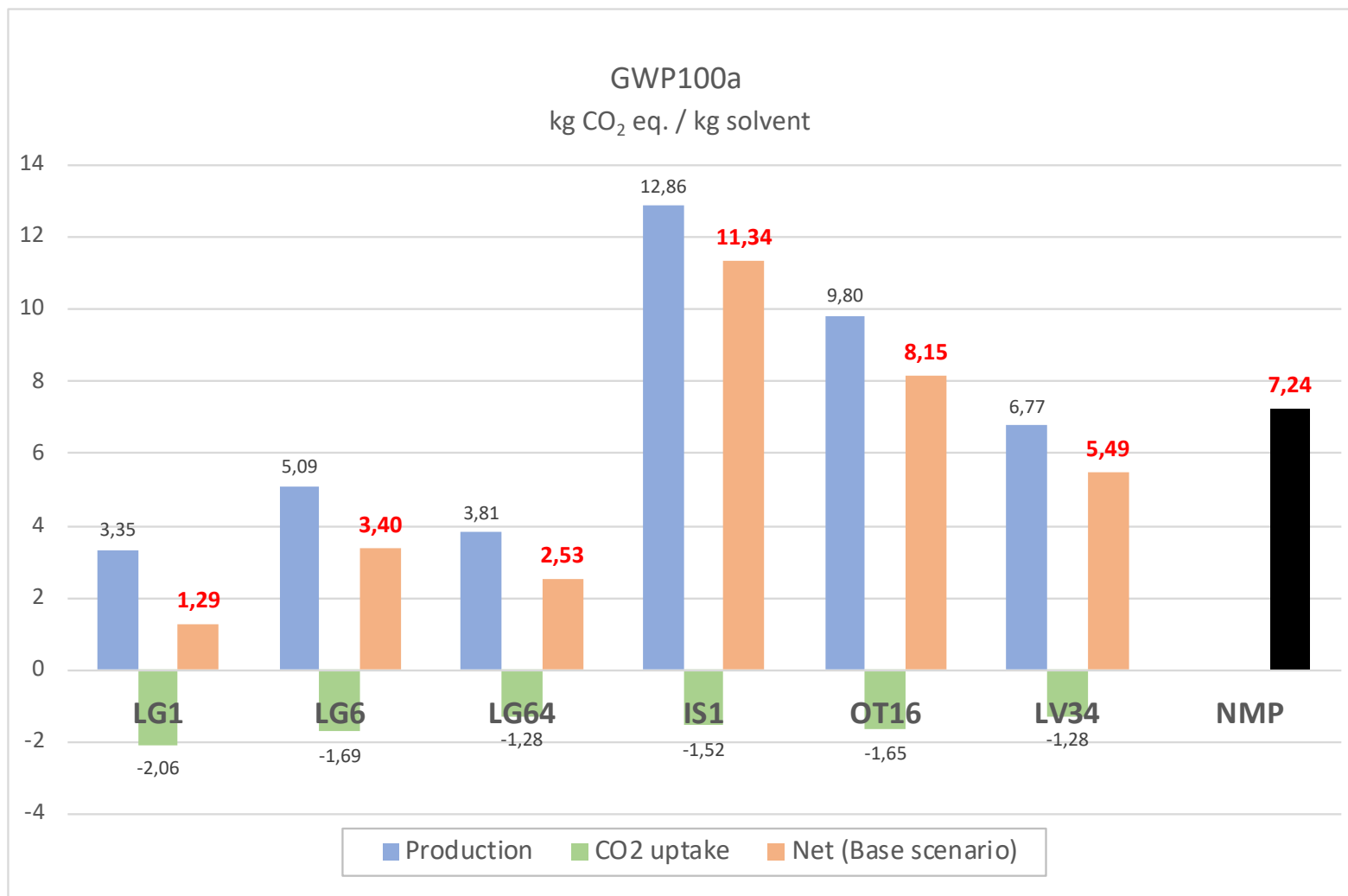
NMP replacements

Comparative analysis

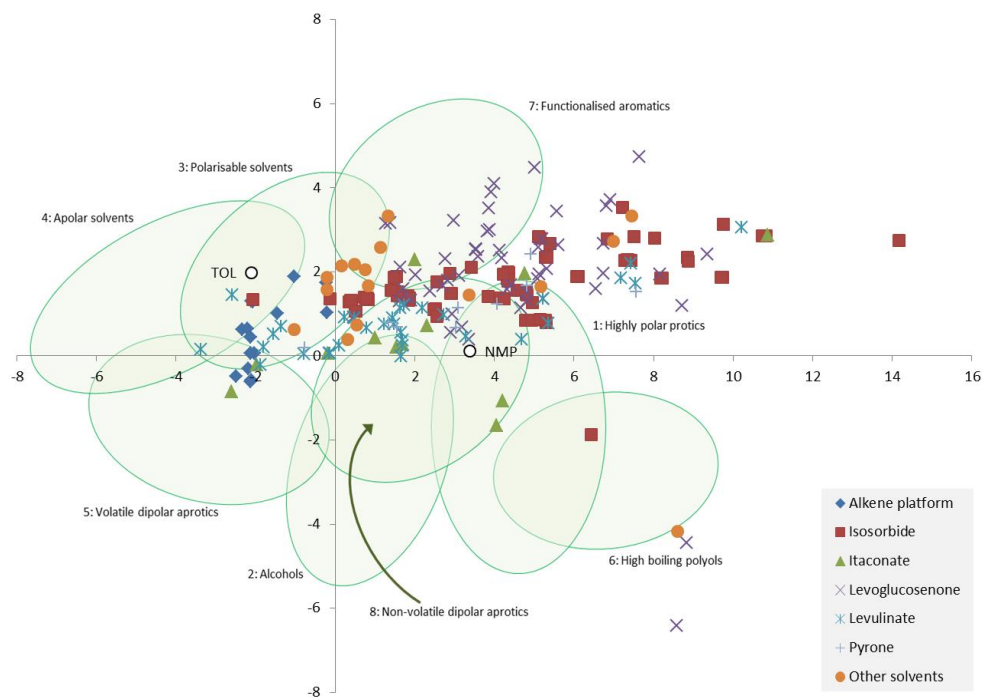
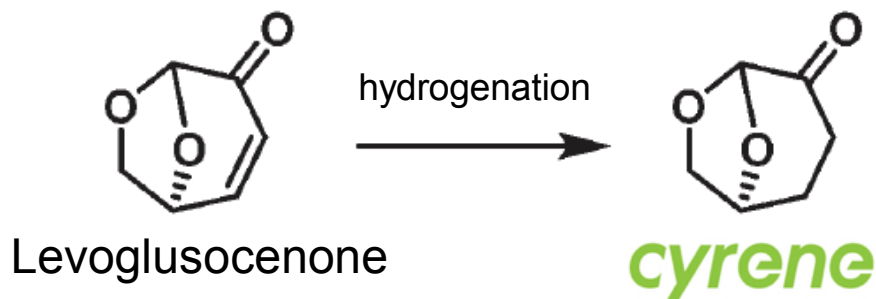


GWP NMP replacements

CO₂ uptake



Dihydrolevoglucosenone (LG1)



	Cyrene	NMP
δD (MPa) ^{1/2}	18.8	18.4
δP (MPa) ^{1/2}	10.6	12.3
δH (MPa) ^{1/2}	6.9	7.2
b.p. (°C)	227	202
η (mPa·s)	14.5	1.9

J. Sherwood *et al.*, *Chem. Commun.*, 2014, 50, 9650

Test	Method	Result
Toxicity to reproduction	OECD 422	Negative
Mutagenicity	OECD 471/476/487	Not mutagenic
Acute toxicity (oral)	OECD 423	LD ₅₀ >2,000mg/kg*
Repeated dose toxicity	OECD 422	NOAEL = 1,000mg/kg/day*
Skin sensitisation	OECD 429	not sensitising
Skin irritation	OECD 404/435	not irritating
Eye irritation	OECD 437/ Ocular Irritaction®	Mild eye irritant
Toxicity to fish	OECD 203	96h LC ₅₀ >100 mg/l*
Toxicity to aquatic invertebrates	OECD 202	48h EC ₅₀ >100 mg/l*
Toxicity to algae & cyanobacteria	OECD 201	72h EC ₅₀ >100 mg/l*
Toxicity to microorganisms	OECD 209	3h EC ₅₀ >1000 mg/l*
Biodegradability	OECD 301	Readily biodegradable

* maximum concentration tested

REACH registration to allow sales into EU:

- **Annex VII (1-10T)**
- completed
- **Annex VIII (10-100T)**
- completed
- **Annex IX (100-1,000T)**
- Dossier submission in 2020

Registration in the US and other jurisdictions to follow

Polyamide-imides production

- PAIs production – largest user of NMP in European Union¹
- Wide range of application incl. corrosion resistant coatings
- Cyrene showed to provide a number of benefits vs NMP
- Additional advantage – doesn't produced NOx during curing

¹ EU Restriction report for NMP

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(71) Applicant: HUNTSMAN ADVANCED MATERIALS LICENSING (SWITZERLAND) GMBH [CH/CH]; Legal Services Department, Klybeckstrasse 200, 4057 Basel (CH).

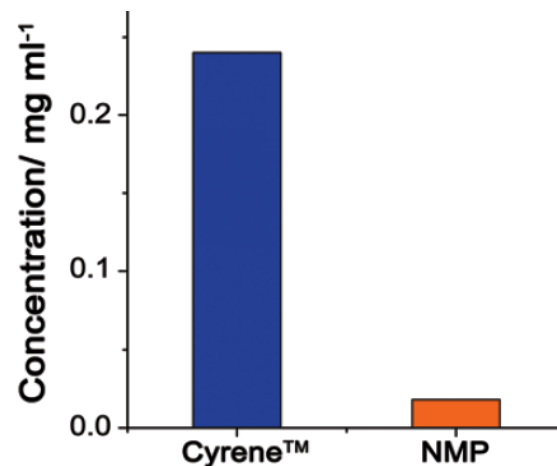
(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Title: PREPARATION OF POLYAMIDOIMIDES

“It has surprisingly been found that the application of dioxabicycloalkane derivatives [and in particular pure Cyrene] instead of conventional polar aprotic solvents like NMP [...] not only facilitates rapid curing but also provides coatings having enhanced solvent resistance.”

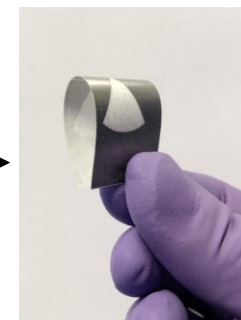
Graphene processing

- NMP widely used to disperse graphene for downstream use
- Wide range of application incl. composites, coatings, batteries, 3D printed materials, etc.
- Cyrene has been shown to have “near ideal physical properties” for the exfoliation of graphite and, crucially, the production of stable, high concentration graphene dispersions and inks



Graphene ink

Printing
→



Wireless connectivity antenna

Salavagione *et al.*, *Green Chem.*, 2017, 19, 2550
Pan *et al.*, *Nature Communications*, 2018, 9, 5197

Cyrene – commercialisation



MERCK



CIRCA GRANTS WILL & CO EXCLUSIVE BENELUX DISTRIBUTION RIGHTS FOR CYRENE®

November 13, 2017



MELBOURNE, AUSTRALIA and YORK, UK – 8 November 2017, Circa Group Pty Ltd. and Will & Co B.V. have entered into an exclusive distribution agreement in Benelux for commercial quantities of Circa's bio-based solvent and platform molecule Cyrene®.

"Our 50 tonnes per year prototype plant for producing Cyrene® is just coming online in Tasmania, and this distribution agreement with Will & Co is a major step forward in bringing our new product to Europe", explains Tony Duncan, CEO of Circa. "We are excited to be

will&co®



Winner Bio-based Chemical Innovation of the year 2017

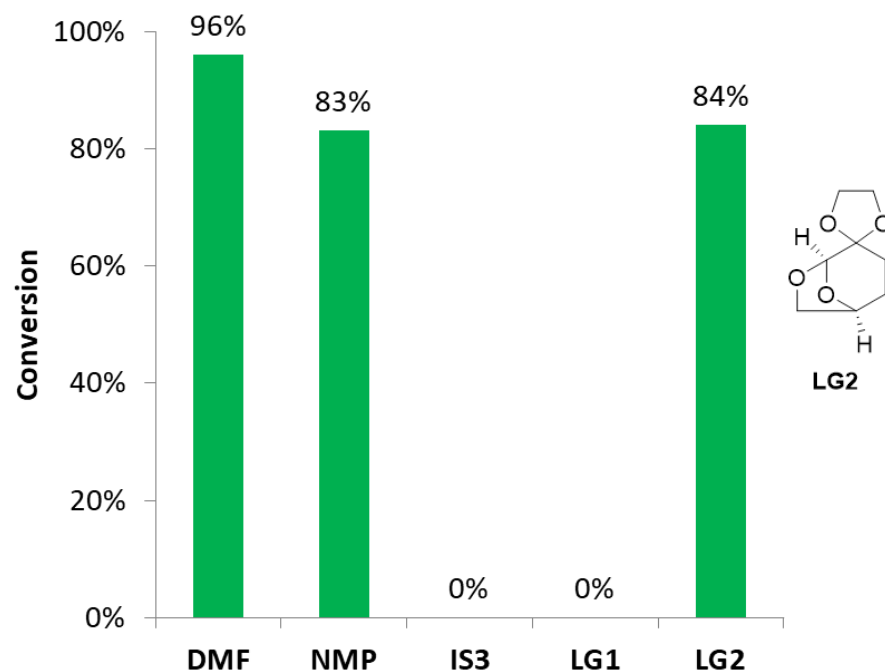
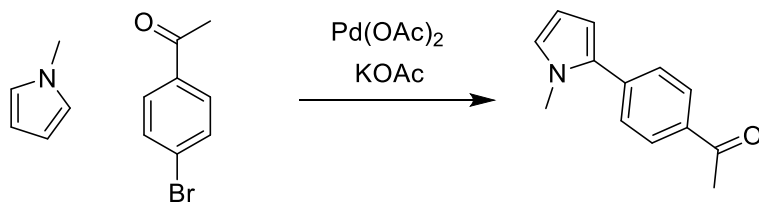
Cyrene



Amsterdam, June 1st, 2017



Potential applications for other NMP alternatives is still being assessed



There is no such things as a drop-in replacement in the solvent sector!

- One of the key objectives of ReSolve was to develop at least one safe bio-based alternative to hazardous solvent NMP
- Using a combination of computational modelling, toxicity testing, LCA, TEA and performance evaluation, ReSolve was able to identify 8 safer NMP alternatives, starting from a “long list” of 232 candidates
- Circa is progressing with the commercialisation of ‘lead target’ Cyrene, with a first commercial plant expected to be operational in 2022
- The performance of other ‘safe’ bio-based alternatives developed by ReSolve are currently being evaluated
- The approach developed by ReSolve could be applied to other applications/sectors

The background features a series of concentric circles in shades of gray and black, centered on the left side. On the right side, there is a large, stylized green shape resembling a leaf or a petal, with a white curved section on its upper edge.

Thank you.

circagroup.com.au