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ECH polymerization Qualification of a solvent compatible with REACh regulation

G. Eck, M. Fourdinier, T. Alaime, C. Bedos, V. Chauffour

- Introduction / Context

- Middle term replacement of DCE
  - Lab scale results
  - Process file for scaling up to industrial scale

- Conclusion

INTRODUCTION / CONTEXT

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REACh

EUROPE has to face to different regulations

ITAR

(US/DoD or US/DoC regulations)

EAR

- Registration, Evaluation, Authorization and Restriction of Chemicals
- Adopted to improve the protection of human health and the environment from the risks that can be posed by chemicals

- International Traffic in Arms regulations / Export Administration Regulation
- Designed to help ensure that defense related technology does not get into the wrong hands

REACh regulation

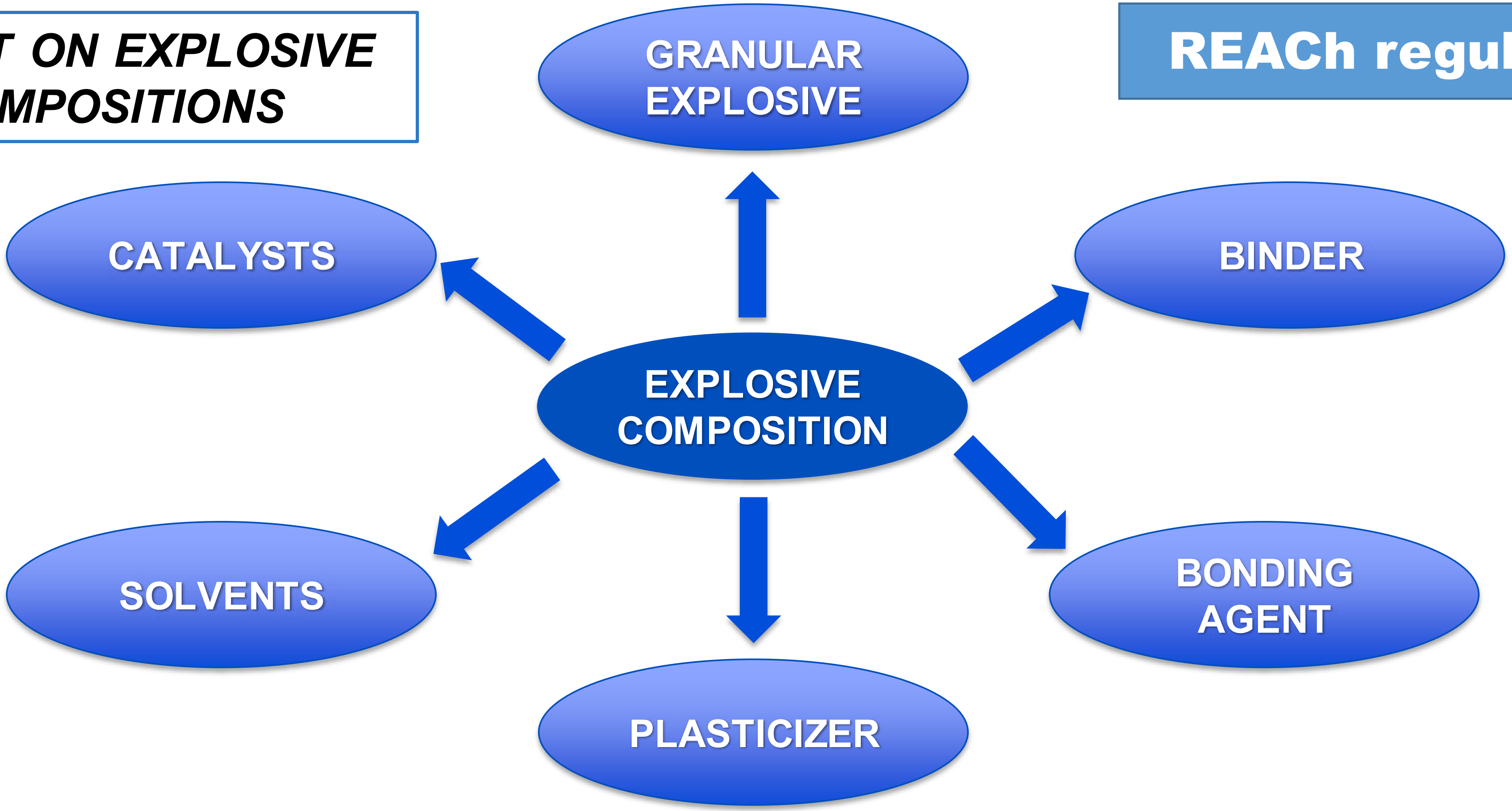
- **REACH applies to all chemicals (except polymers)**
  - Chemicals involved in industrial process
  - Chemicals in our day-to-day lives : cleaning products, paints, clothes, furniture, electrical appliances,…

- **Companies must identify and manage the risks linked to the substances they manufacture and market in the EU as manufacturers, importers or downstream users**

- **In the long run, the most hazardous substances should be substituted with less dangerous ones**

IMPACT ON EXPLOSIVE COMPOSITIONS

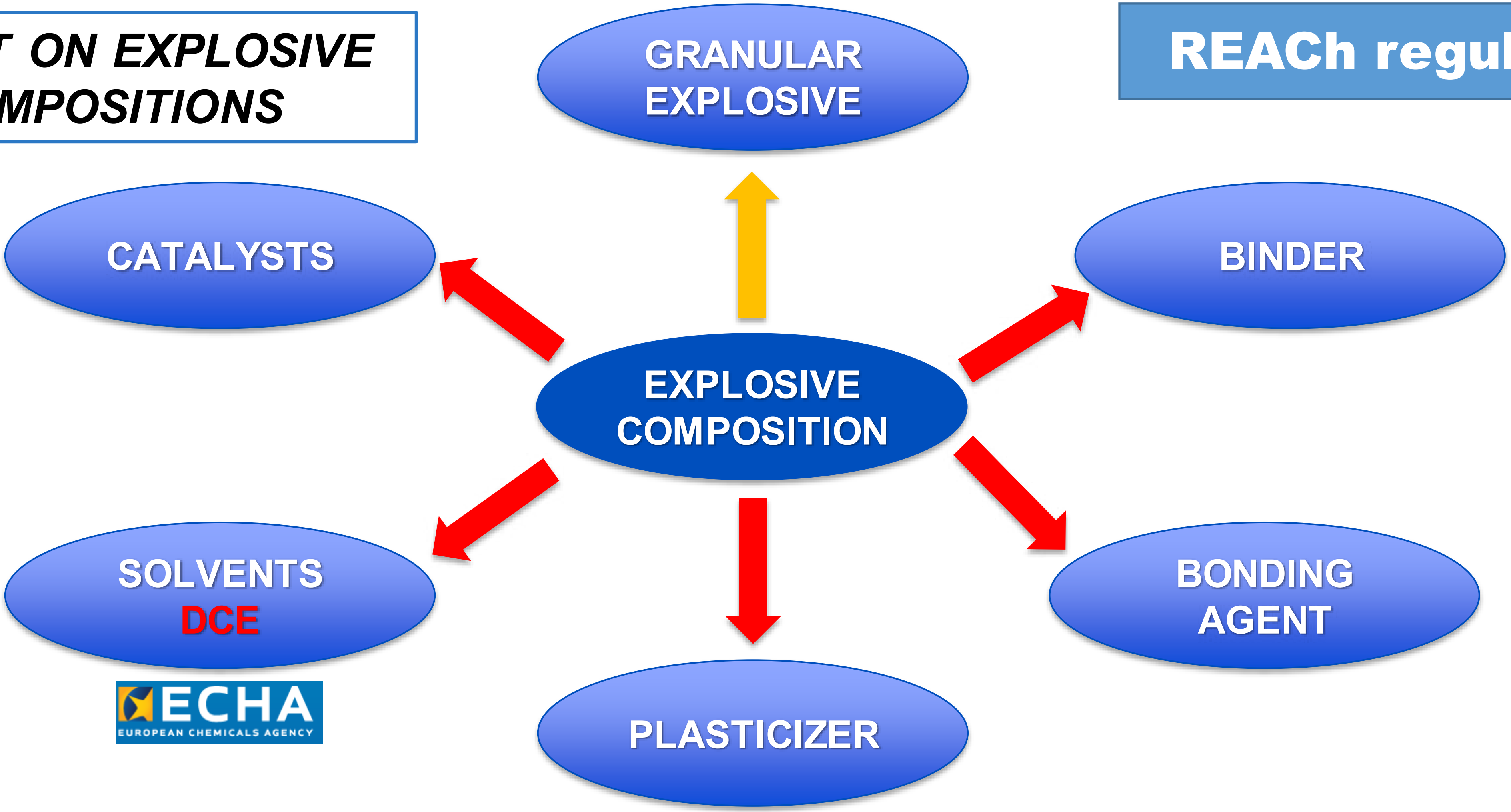
REACh regulation



INTRODUCTION / CONTEXT

IMPACT ON EXPLOSIVE COMPOSITIONS

REACh regulation



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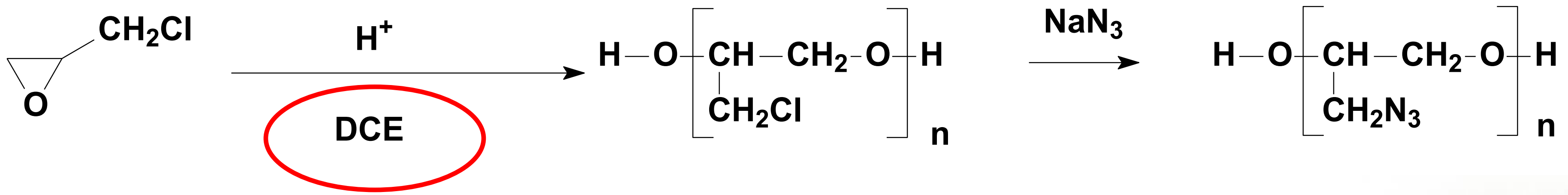
Impact on PECH / GAP synthesis



ECH

PECH

- **Impact of REACH regulation on DCE use as a solvent**
  - ➔ Authorized for use up to the end of 2021
  - ➔ Prohibited after that

Impact on PECH / GAP synthesis

- **Middle term replacement**
  - Organic solvent not yet impacted by REACh
  - Process file ready for scale up to the industrial workshop

- **Long term replacement**
  - Research studies to find new ways to polymerize ECH

- **Introduction / Context**

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LAB SCALE RESULTS

- **Experiments performed on 350 g. of ECH in DCE, solvents A and B**
  - Reaction medium T° set between TR1 and TR2
  - Double jacket T° set at T1 or T2
  - Addition rate of ECH regulated by the reaction medium T°

- **Special attention to**
  - The initiation of the polymerization and the temperature peak that is observed when the reaction starts.
  - The propagation phase of the polymerization
  - The characterization of the polymer PECH: Mn / Mw and hydroxyl content

LAB SCALE RESULTS

Ref.	Solvent	Double Jacket T° (°C)	PECH characterizations			
			Mn	Mw	I	OH content (eq/kg)
Average at industrial scale			*1790*	*1890*	*1.05*	*0.80*
DCE-1	DCE	T_2	1670	1890	1.13	0.80
DCE-2	DCE	T_1	1750	1890	1.08	0.75
A-1	A	T_2	1690	1910	1.13	0.86
A-2	A	T_1	1770	1910	1.08	0.84
A-3	A	T_1	1820	1960	1.08	0.80
B-1	B	T_1	1770	1900	1.08	0.83
B-2	B	T_2	1750	1910	1.09	0.78
B-3	B	T_1	1770	1910	1.08	0.81

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→DCE-2 seems representative of the industrial scale

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→ Reproducible results for experiments performed in the same conditions

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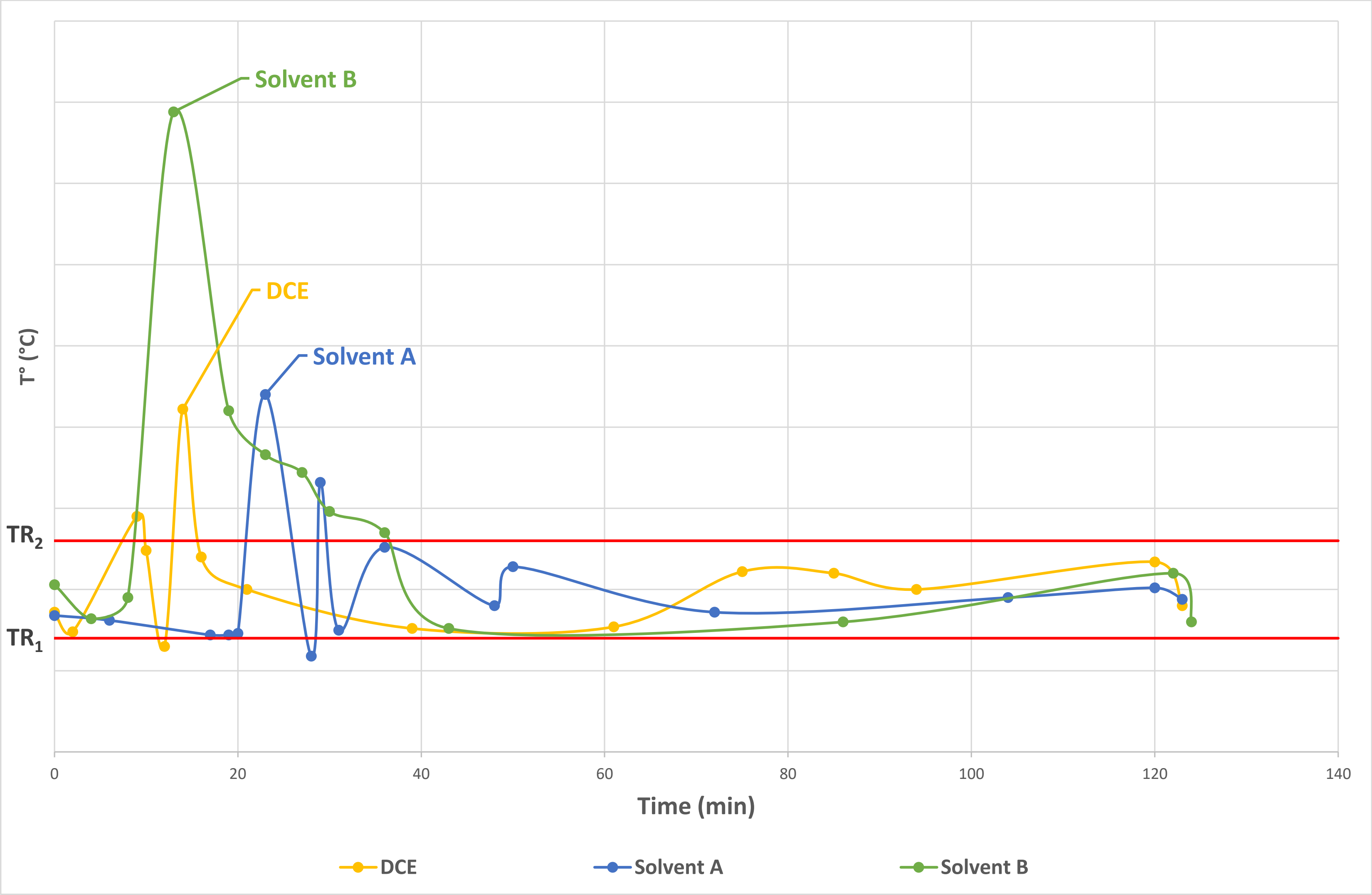
→ **At lab scale, no significant impact of polymerization conditions on PECH characteristics**

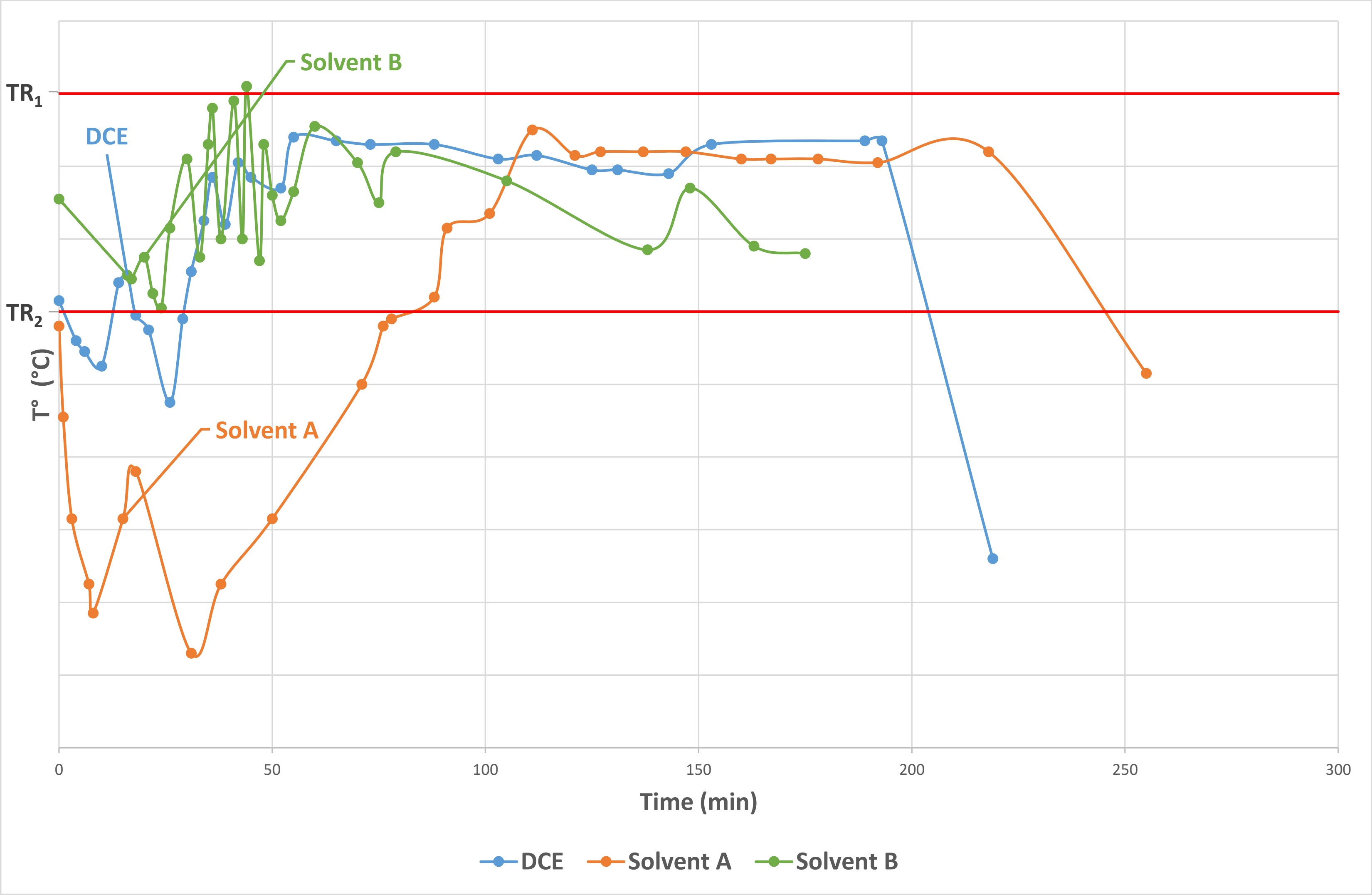
LAB SCALE RESULTS



COOLING AT T_1

- ➔ Exothermic phenomenon for all solvents
- ➔ Peak T° slightly shifted in time for solvent A

LAB SCALE RESULTS



COOLING AT T_2

- ➔ Good control for DCE and solvent B
- ➔ More difficult to control in solvent A

CONCLUSION

Based on lab scale experiments, solvent B seems to be the best candidate to replace DCE

Double Jacket T° (°C)	PECH characterizations		
	Mn	Mw	OH content (eq/kg)
T_1	1770	1900	0.83
T_2	1750	1910	0.78

Scale up to industrial scale to be made

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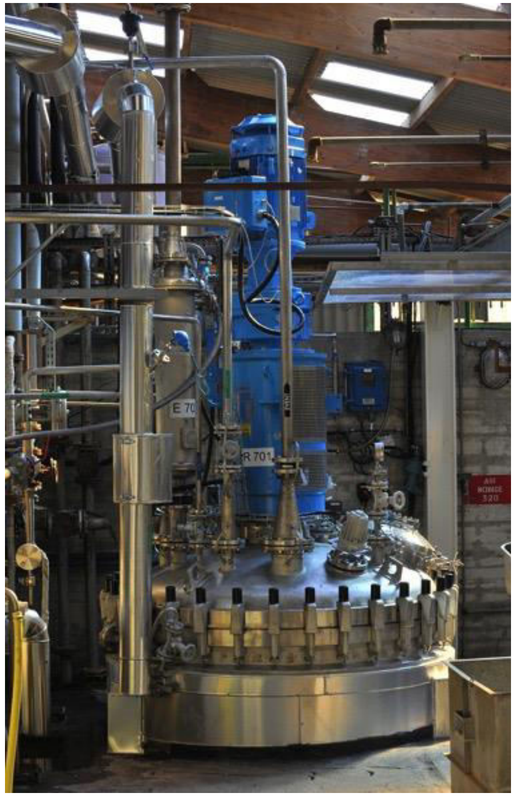
PROCESS FILE

- Material balance
- Heat balance
- Sequence of manufacturing steps
- Production time



Comparison for solvent B and DCE

Material balance

Raw materials	Vessel N°1 Initial loading	Vessel N°2 Recovered or engaged quantities
ECH	M1	0 kg
Solvent B	M2	M2
Initiator	M3	0 kg
Catalyst	M4	Reacted
PECH		M1
Washing ingredients		M5

Heat balance

- **Heat exchange capacity of reactors (kcal/h) :** $\phi = K\,x\,S\,x\,\Delta T$
  - K = Heat transfer coefficient (kcal/h/m^2.k)
  - S = Exchange area (m^2)
  - ΔT = Mean logarithmic temperature Cold fluid / Hot fluid

- **Amount of heat (J.) :** $Q = m\,x\,Cp\,x\,\Delta T$
  - m = Mass of components (kg)
  - Cp = Specific heat of the components (J/kg.K)
  - ΔT = Temperature difference Initial state / Final state

Heat balance

Synthesis phase	Heat balance (compared to DCE in %)	
Loading and heating	Q_{Total} (kcal)	72%
	t (min)	80%
	$\Phi_{cooling\ medium}$ (kg/h)	100%
Polymerization	Q_{Total} (kcal)	99.8%
	t (min)	100%
	$\Phi_{cooling\ medium}$ (kg/h)	100%
Solvent extraction	Q_{Total} (kcal)	97.6%
	t (min)	96%
	$\Phi_{heating\ medium}$ (kg/h)	100%

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  - Scale up
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CONCLUSION

- **One of the most important issue induced by REACh regulation is the replacement of DCE, the polymerization solvent for the synthesis of PECH.**
- **A middle term solution has already been found**
  - DCE could be replaced by solvent B.
  - The obtained PECH has the same characteristics than the current one produced at industrial scale.
- **Long term research studies are in progress in order to find a sustainable replacement product.**

ACKNOWLEDGEMENTS

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AND

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Thank you for your attention

Questions ?

Member of

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