

CHEMICAL RECYCLING OF POLYURETHANE

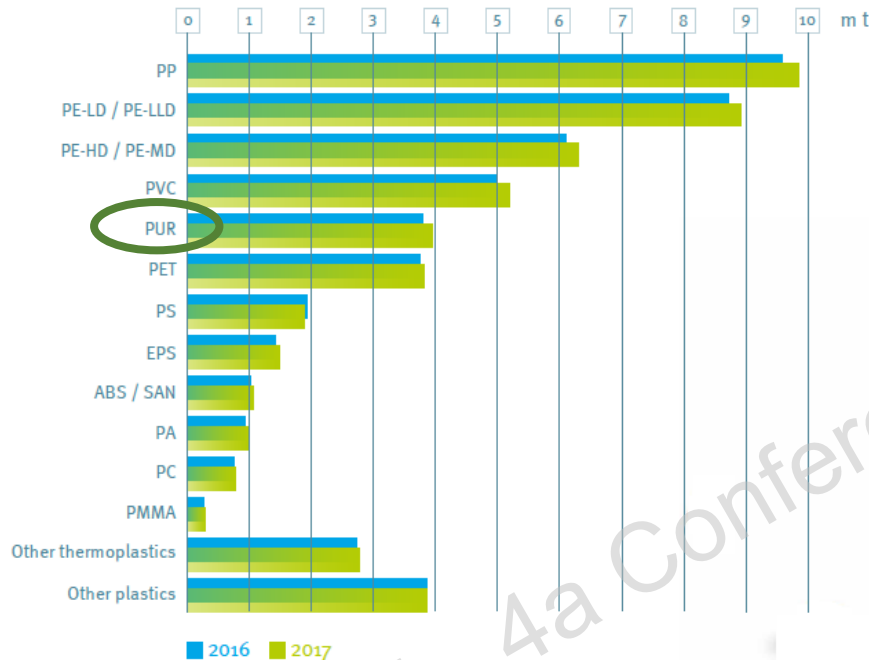
Francesca Piovesan



ROME, 10th October 2019

- Polyurethane market and wastes;
- The need of a circular economy strategy;
- Chemical recycling of polyurethane by glycolysis;
- Application of the glycolysis product in the synthesis of new rigid PU foams.

Distribution of European plastic converter demand by resin type (2017)



Source: PlasticsEurope Market Research Group (PEMRG) / Consultic Marketing & Industrieberatung GmbH

51.2 mt
Total converter
demand

18.4 mt
Polyurethane
converted in the world

3.6 mt
Polyurethane converted in
EU in 2017





Thermosetting material

High volumes

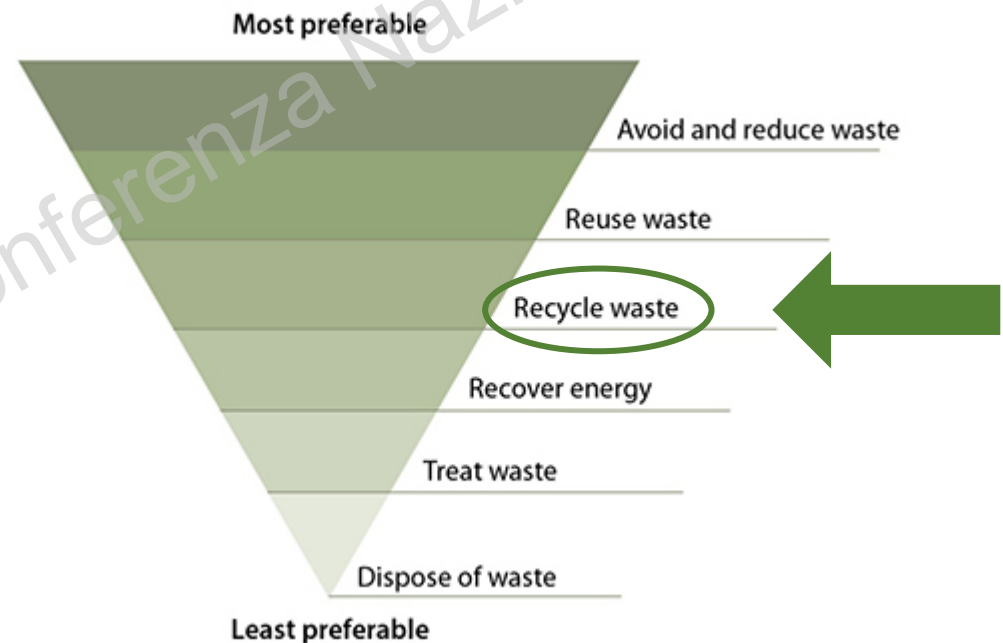
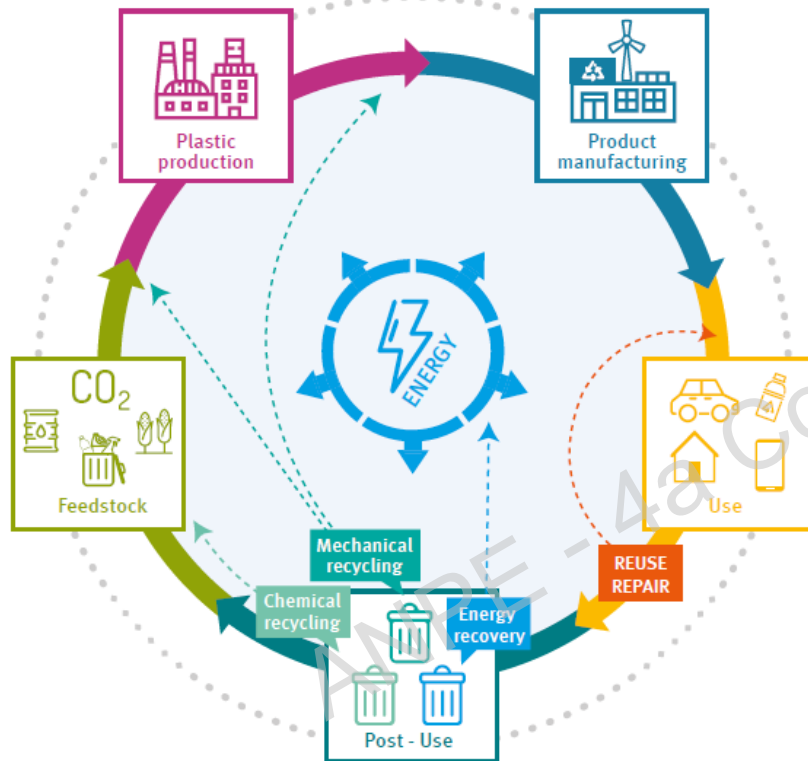
Mixed with others materials (es. coatings in insulation panels)

Presence of blowing agents and flame retardants

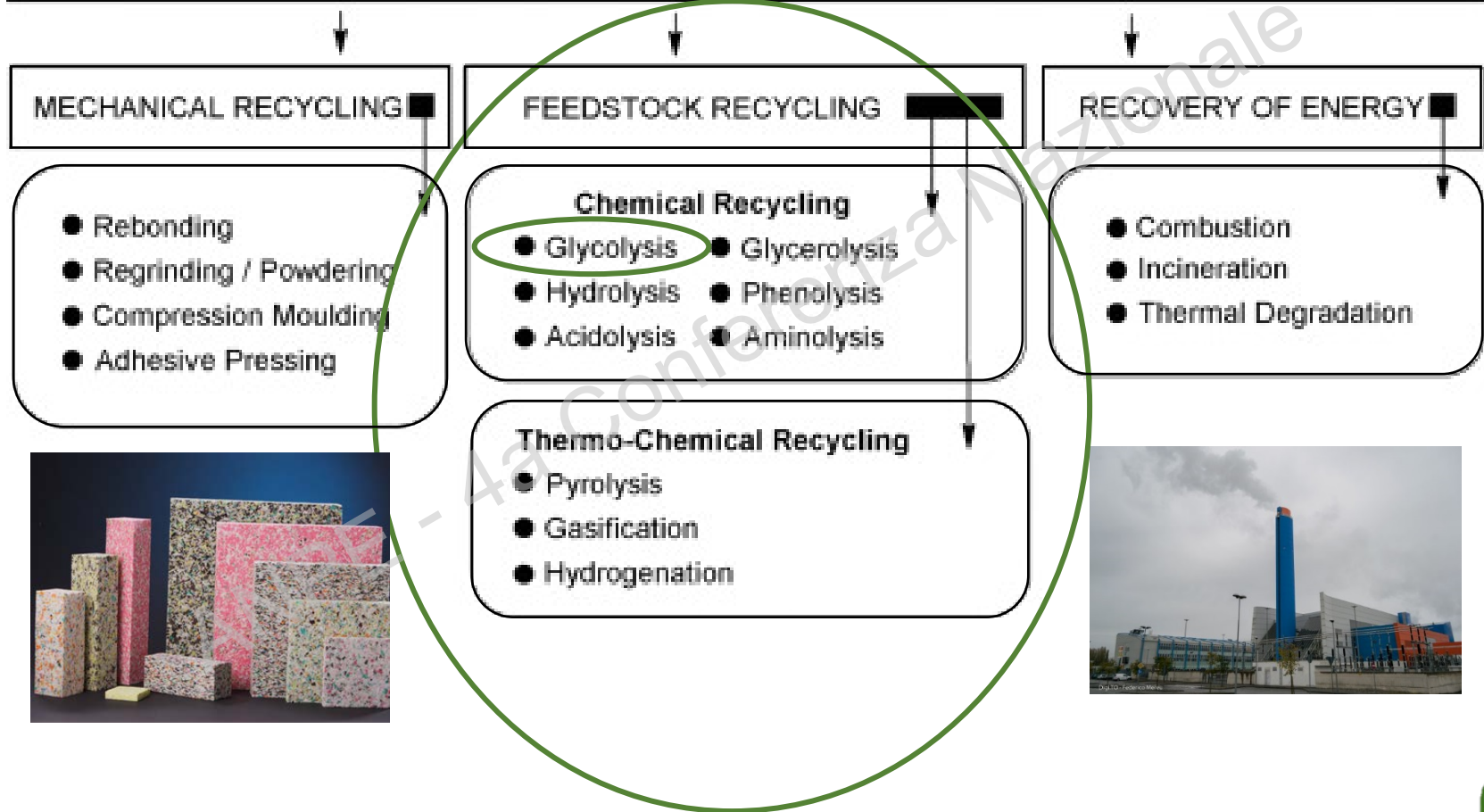
High cost for disposal

EU restrictions in landfill disposal

Waste legislation and policy of the EU Member States shall apply as a priority order the following waste management hierarchy:



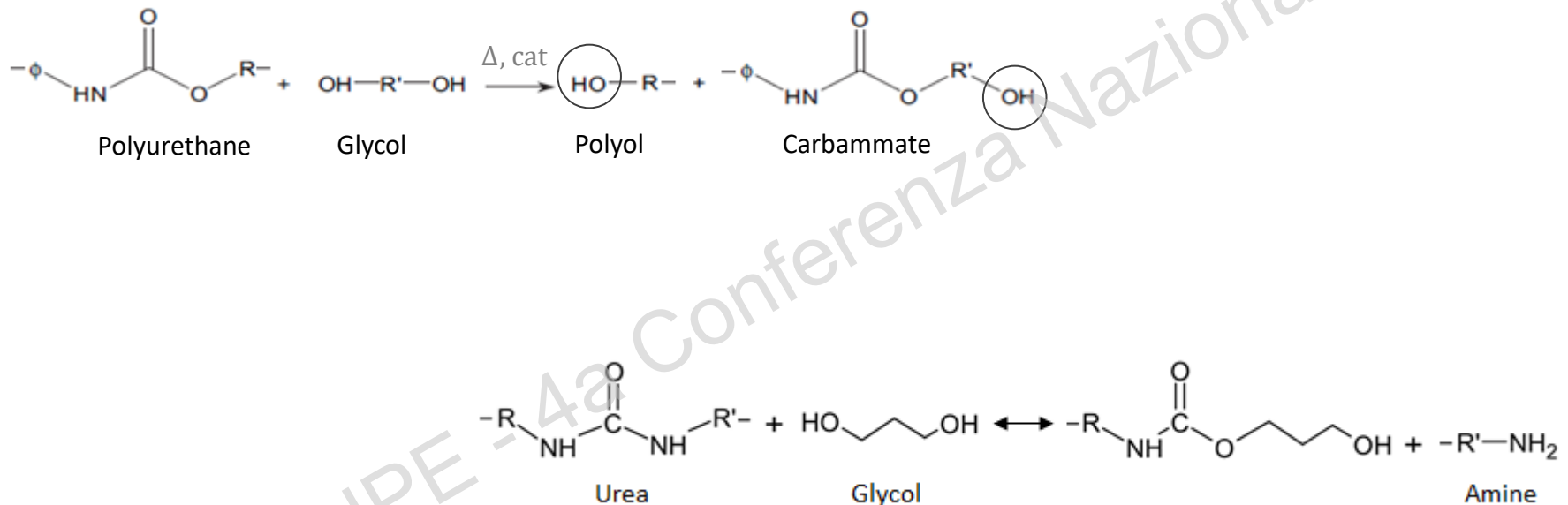
RECYCLING AND DISPOSAL OF POLYURETHANES





MAIN REACTIONS:

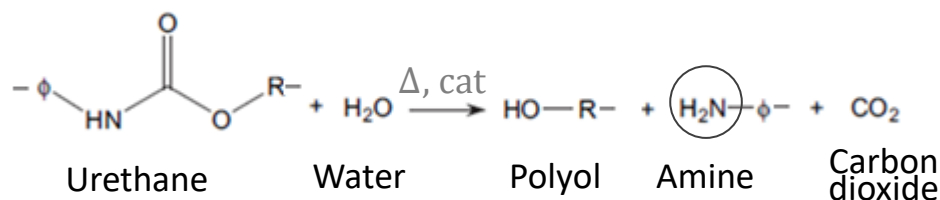
TRANSESTERIFICATION through a glycol



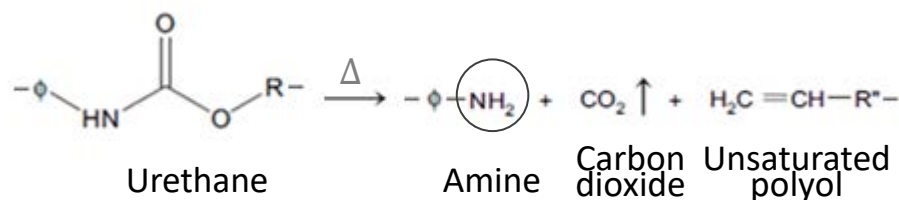
All these reactions lead to the formation of products with end groups reactive with isocyanate

SIDE REACTIONS:

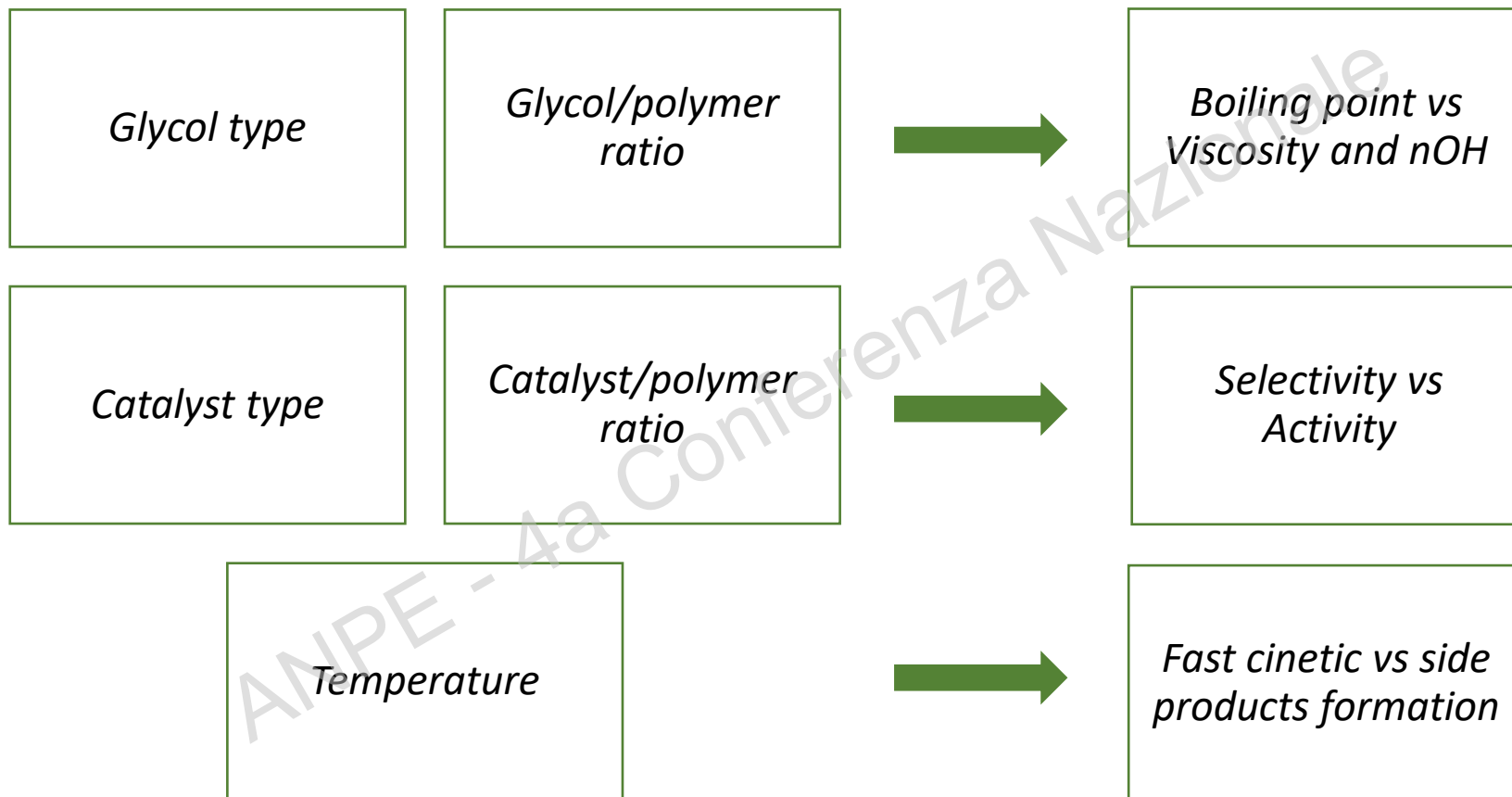
HYDROLYSIS



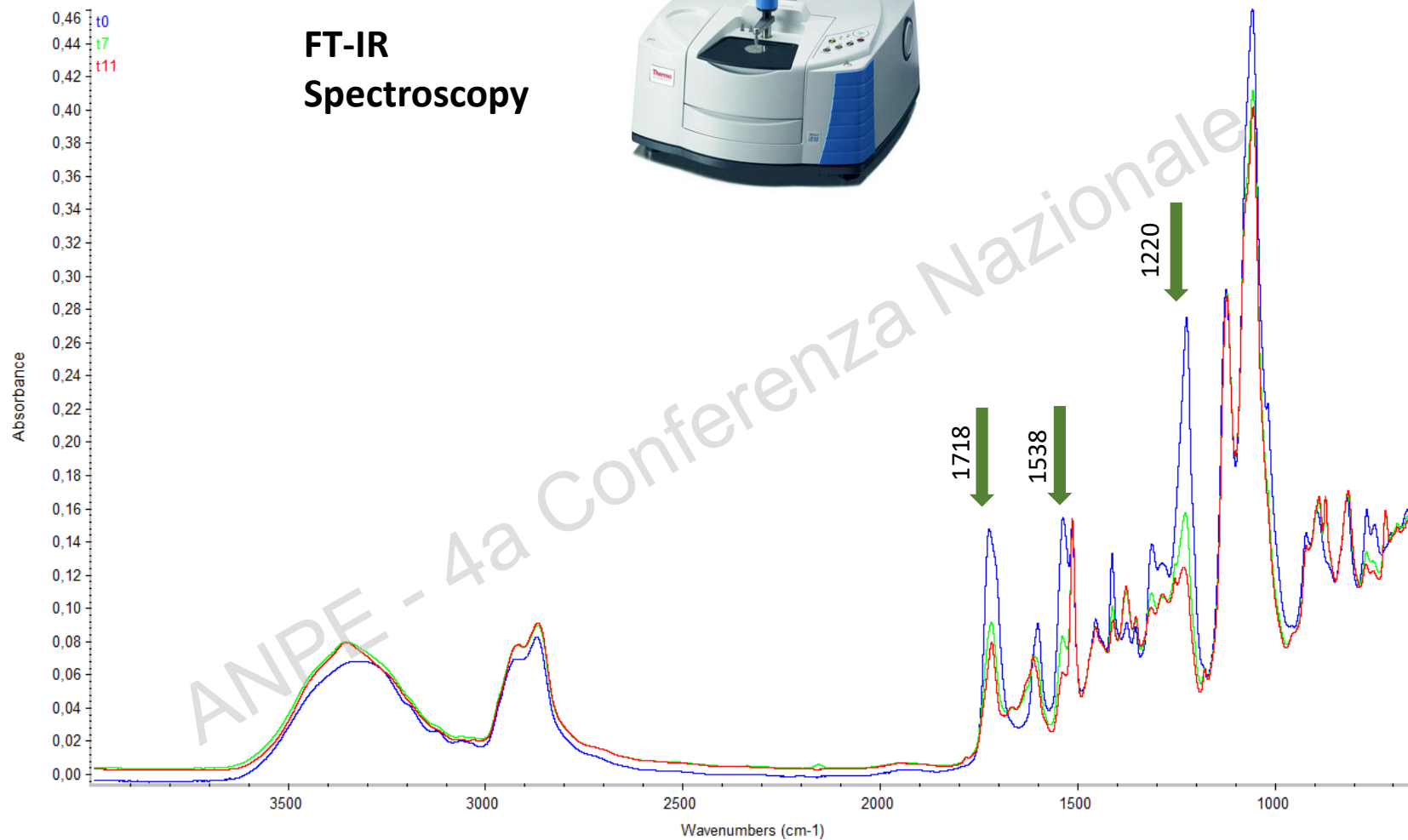
PYROLYSIS



All these reactions lead to the formation of products with end groups reactive with isocyanate



FT-IR Spectroscopy



Glycolysis can be extended to **different classes of polyurethanes** or materials:

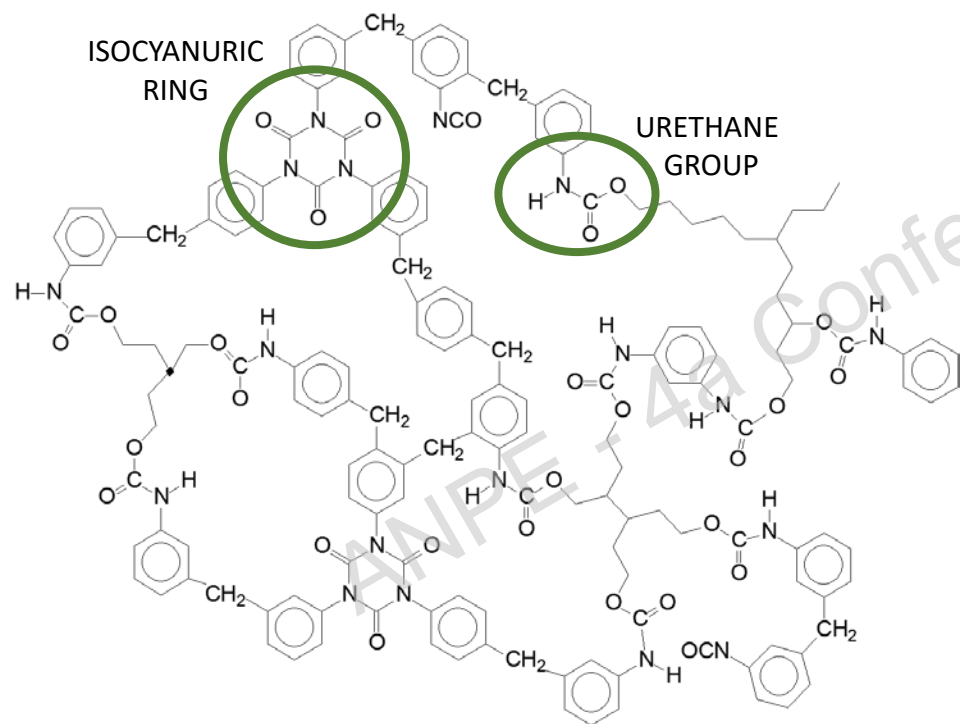
Polyurethane rigid foams



Polyurethane rigid blocks



Polyisocyanurate rigid foams



The **highly cross-linked structure** of the rigid polyisocyanurate foams lead to a liquid glycolysis product with highly **branched oligomers**.

Reinforced injection molding (RIM) polyurethane or polyurea

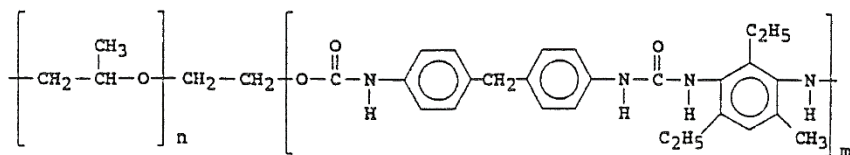


Flexible foams



Reinforced injection molding (RIM) polyurethane or polyurea

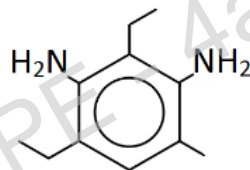
Polyurea basic molecular structure:



+ Glycol

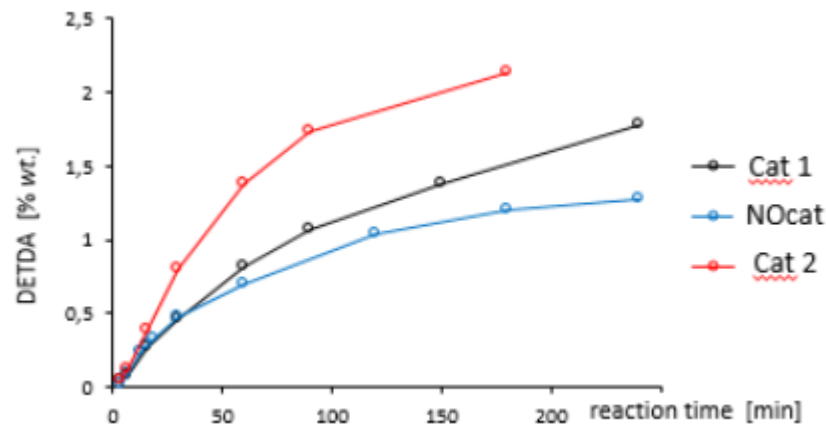
Oligomers

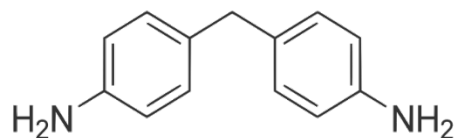
+



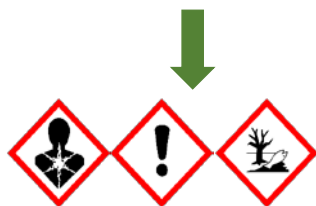
diethyl toluene diamine (DETDA)

Glycol/RIM	Viscosity [cP]	nOH [mgKOH/g]
60/40	650	520
50/50	1448	446
40/60	3557	404





4,4'-methylene dianiline (**MDA**)



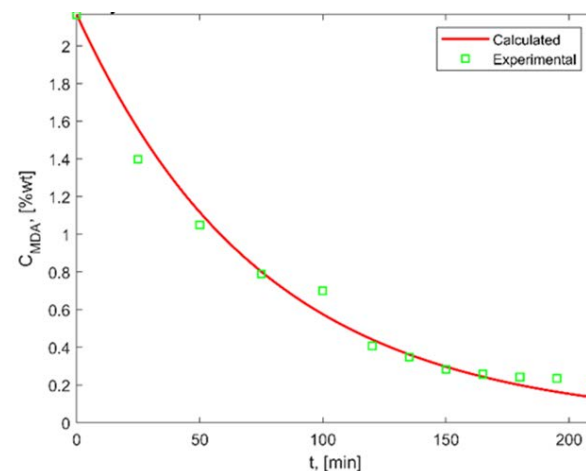
considered suspected
carcinogen by NIOSH and
ECHA

SOLUTIONS:

- **Prevent MDA formation**
 - Use a more selective catalyst towards glycolysis;
 - Optimize the catalyst concentration;
 - Dehydrate the reactants before glycolysis.
- **Abate MDA through a deaminating agent**

CONSEQUENCES:

- Can cause **skin irritation** and **liver damages**;
- **Labelling costs** for the handling and transport;
- Amines catalyse *PU* synthesis, so **bad reaction control**.





Viscosity (μ)

*Hydroxyl number
(nOH)*



Amine content (HPLC)

*Molecular weight
(GPC)*



The **liquid product** obtained by glycolysis can be used in the production of **new rigid foams**.



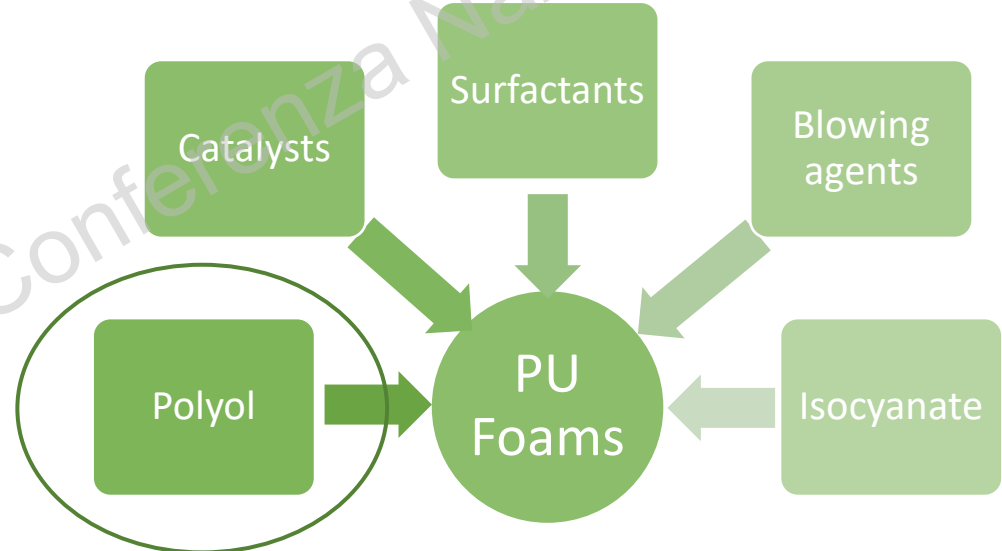
Virgin polyol



Recycled polyol

Ratio recycled/virgin polyol:

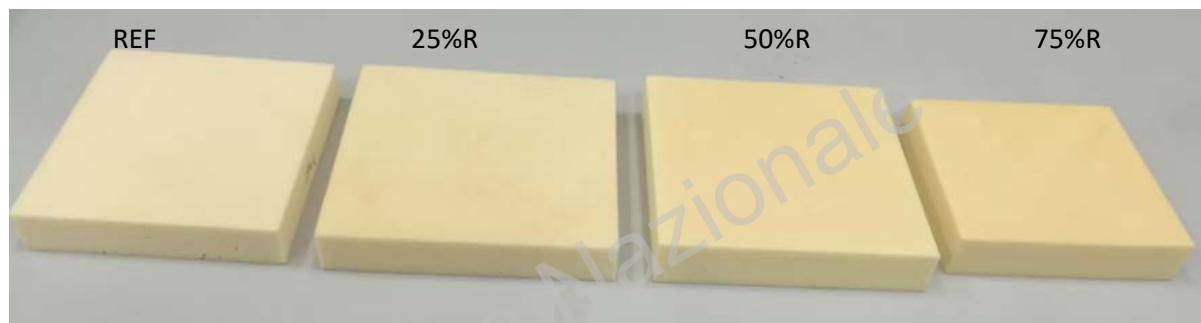
0/100	75/25
25/75	100/0
50/50	



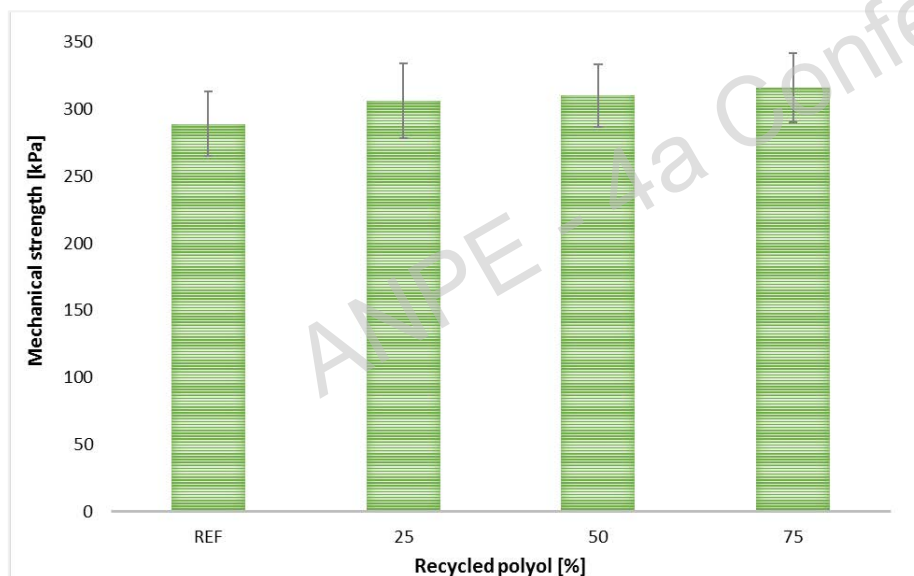
Glycolysis product from polyurethane rigid blocks

Glycol/PU	Viscosity [cP]	nOH [mgKOH/g]
40/60	2500	560

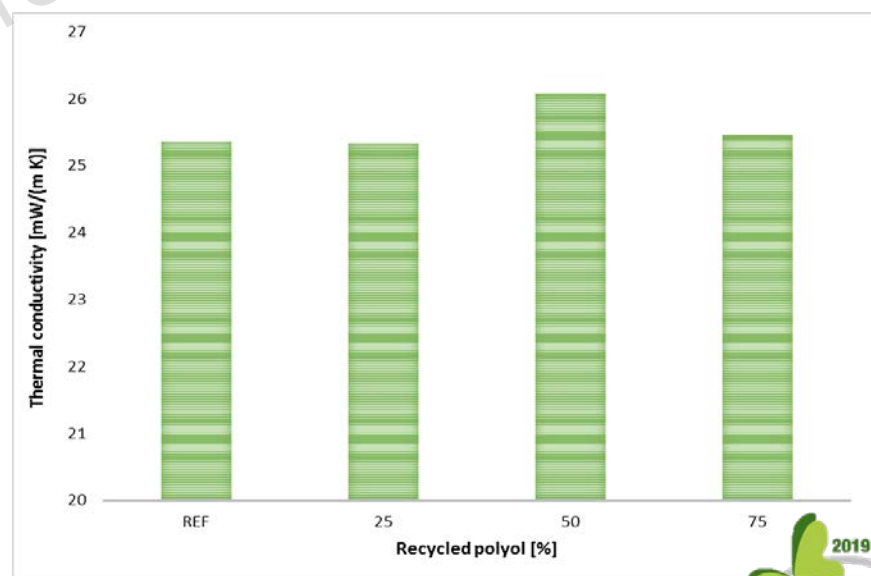
Density 46 kg/m³



Mechanical properties



Thermal properties



Glycolysis product from reinforced injection molding (RIM) polyurethane or polyurea

Glycol/PU	Viscosity [cP]	nOH [mgKOH/g]
60/40	650	520

Density 38 kg/m³



REF

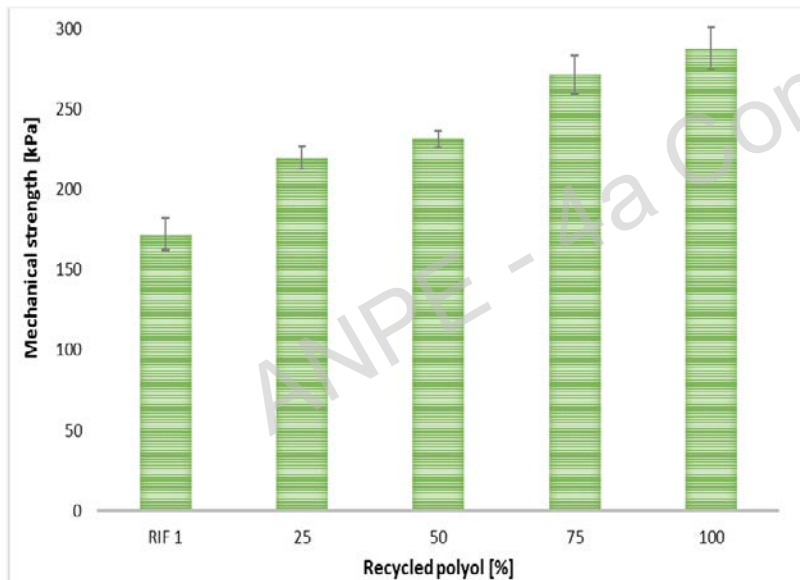
25%R

50%R

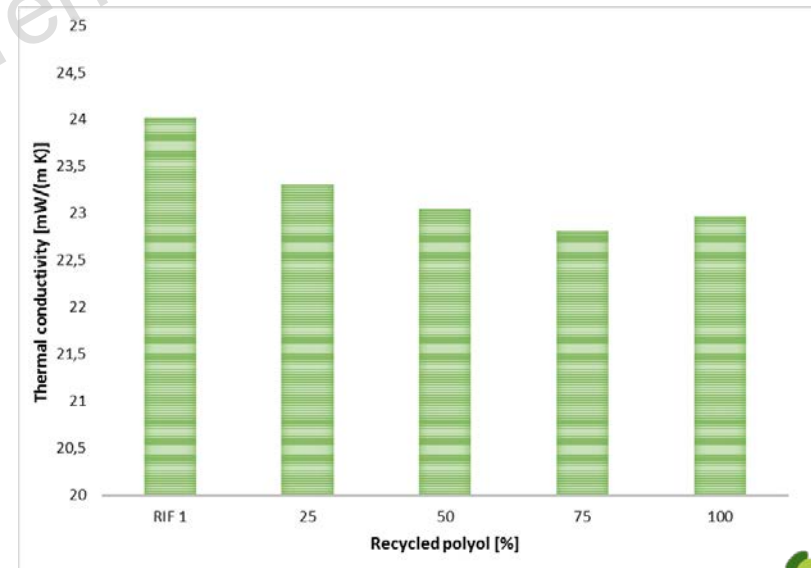
75%R

100%R

Mechanical properties



Thermal properties





Thank you for your attention



ANPE - 4a Conferenza Nazionale