Converting wastes into added value products: from glycerol to glycerol carbonate, glycidol and epichlorohydrin using environmentally friendly synthetic routes (P10)

Michele Aresta[1], Angela Dibenedetto [1-3] , Francesco Nocito[3] , Luigi di Bitonto [1,2]

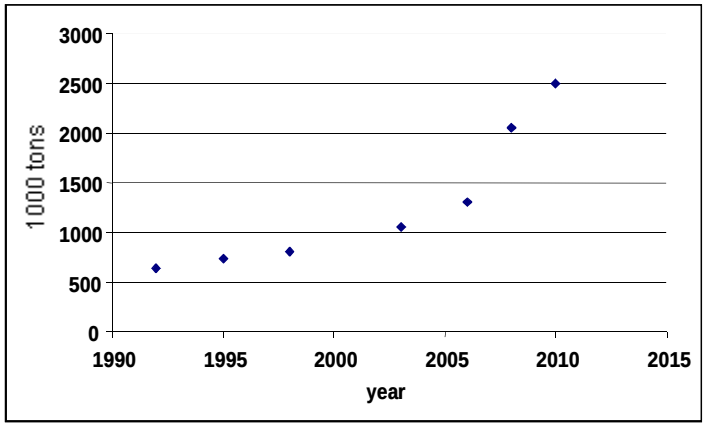
[1] CIRCC, [2] METEA, Department of Chemistry ,University of Bari, Bari, Italy, [3] Valbior Project-Apulia Region

The research leading to these results has received funding from the European Union Seventh Framework Programme (FP7/2007e2013) under grant agreement no 241718 EuroBioRef. One of us (F.N.) thanks the University of Bari, MiUR-PRIN08 and the Apulia Region for a Ph.D.grant

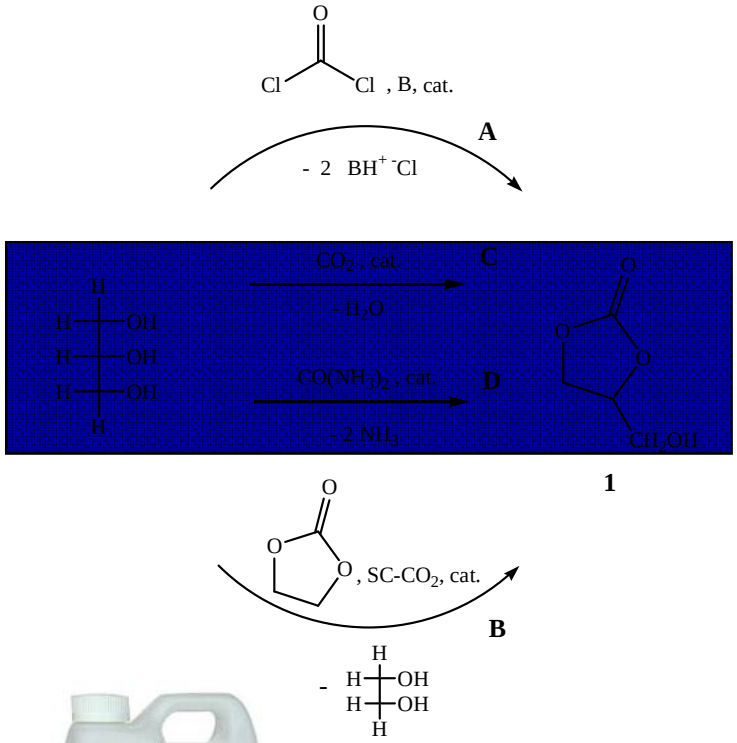
Eurobioref Summer School
Castro (Le), September 18th-24th, 2011

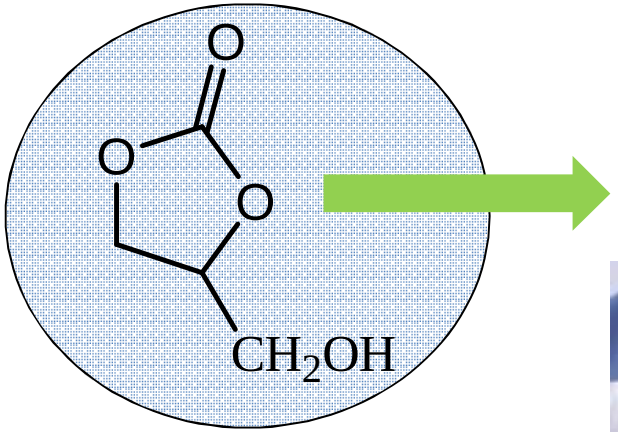
Glycerol: the problem of overproduction and new applications

Glycerol is the by-product with **the largest economic impact in the modern oleochemical industry**, being formed in several processes. The growth of the production of glycerol (mainly due to the expansion of the production of biodiesel), in last years, has speed up the industry and academia research **towards the identification of new initiatives** aimed to identifying new opportunities for using such by-product.

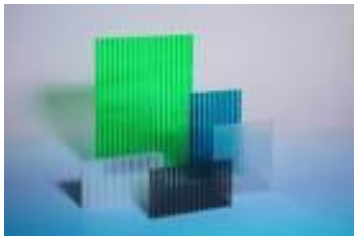


Trend of glycerol production from 1992 to 2010





Glycerol carbonate



polycarbonates

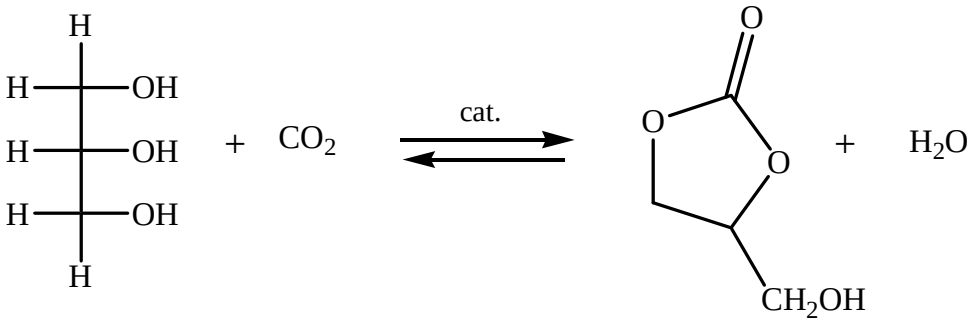
high boiling point solvent

precursor for medical applications

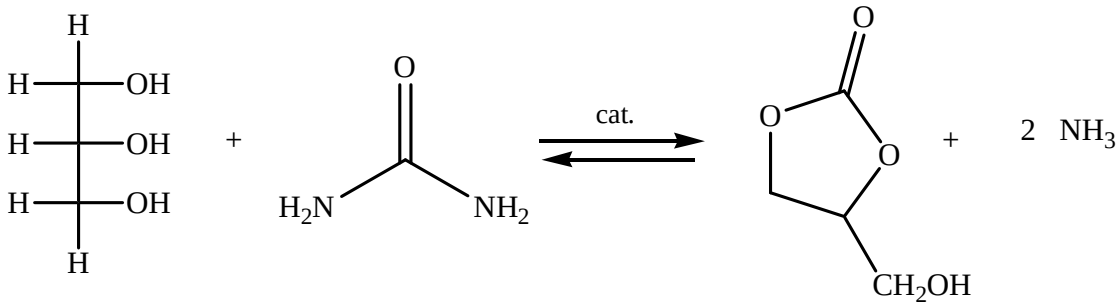
polyurethans

Synthesys of glycerol carbonate

Both the use of two wastes such as glycerol and CO_2 and, in case urea is used, the particularly mild and safe working conditions, coupled to the high yield and selectivity of the processes carried out in presence of heterogeneous catalysts, when necessary, attach environmental value to the synthetic procedures. CeO_2/Al_2O_3 and $[CeO_2/Nb_2O_5]$ were used as catalysts for the direct carboxylation of glycerol in a biphasic system, while TS1 and Zr-γ-P were used in the reaction of glycerol with urea. All the heterogeneous catalysts can be easily recovered and re-used.



T = 453 K, P = 5 MPa, t = 15 h
n cat/gly = 3%
Conversion = 10 % (isolated product) after 3 cycles

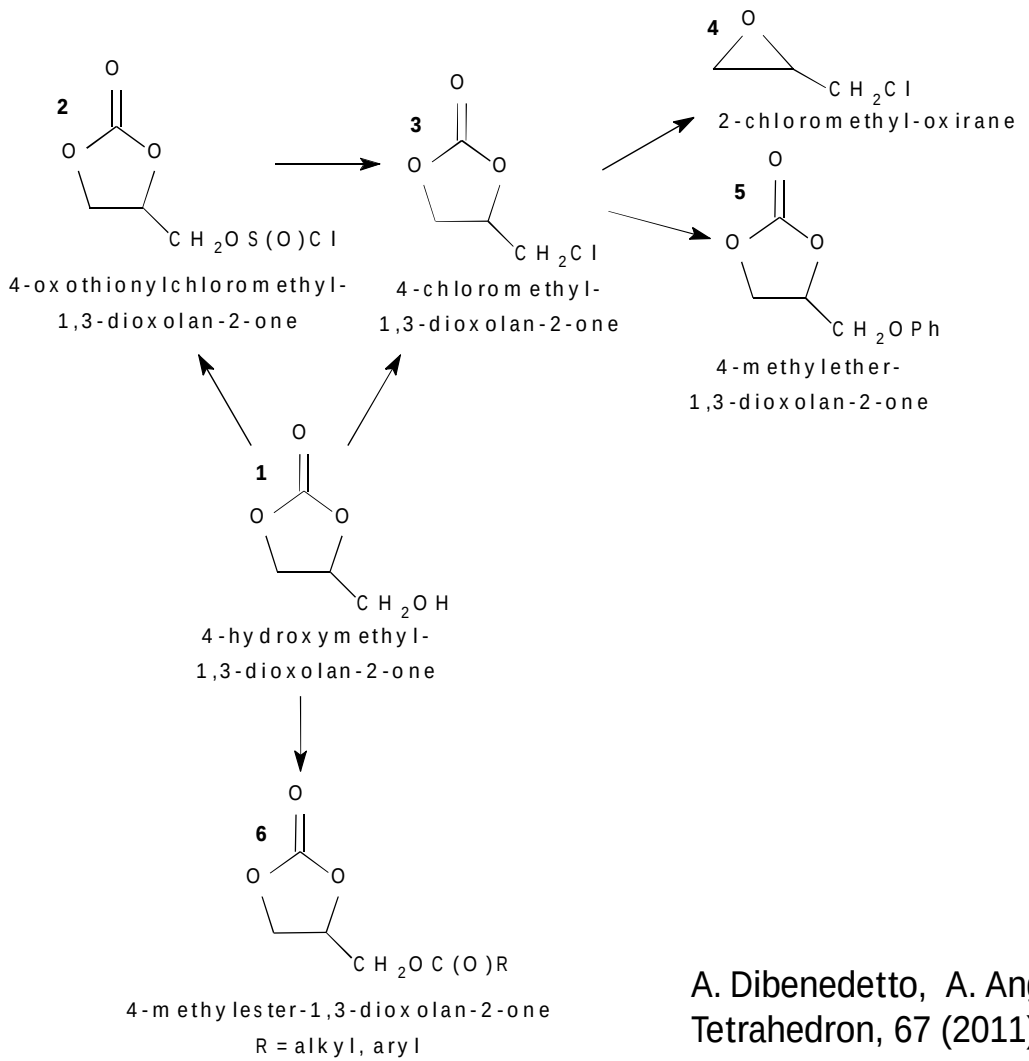


T = 413 K, P = 20 Pa, t = 3 h
w cat/urea = 1 %
n gly/urea = 1
Conversion = 60-80% (isolated product)
Catalysts TS-1 and Zr-γ-P totally recoverable

M. Aresta, A. Dibenedetto, F. Nocito, C. Pastore, Journal of Molecular Catalysis A: Chemical, 257 (2006) 149-153
M. Aresta, A. Dibenedetto, F. Nocito, C. Ferragina, Journal of Catalysis, 268, (2009), 106-114 ;
M. Aresta, J. L. Dubois, A. Dibenedetto, F. Nocito, C. Ferragina, "Process for the synthesis of glycerol carbonate"Filed by ARKEMA (Fr), October 2008, EP 083056531

Functionalization of glycerol carbonate

The hydroxyl functionality of glycerol carbonate allows its derivatization in many different ways, that are cleaner and safer than those on stream, to afford either known or new compounds



2 is a new compound, never described in the literature. It can find several uses including the coupling of the carbonate to N-compounds.

3 is a good intermediate for organic syntheses

4 is a colourless highly reactive compound used in the production of plastics, elastomers and epoxy resins

5 finds application as intermediate for pharmaceuticals

6 finds application in demolding thermoplastic polycarbonates or in urethane coatings

All compounds are prepared under mild conditions (ambient) and with >90% yield and selectivity.

A. Dibenedetto, A. Angelini, M. Aresta, J. Etiraji C. Fragale, F. Nocito, Tetrahedron, 67 (2011) 1308-1313