Toward a green synthesis of Levoglucosenone (LGO) derivatives: an example of lignocellulosic biomass valorization

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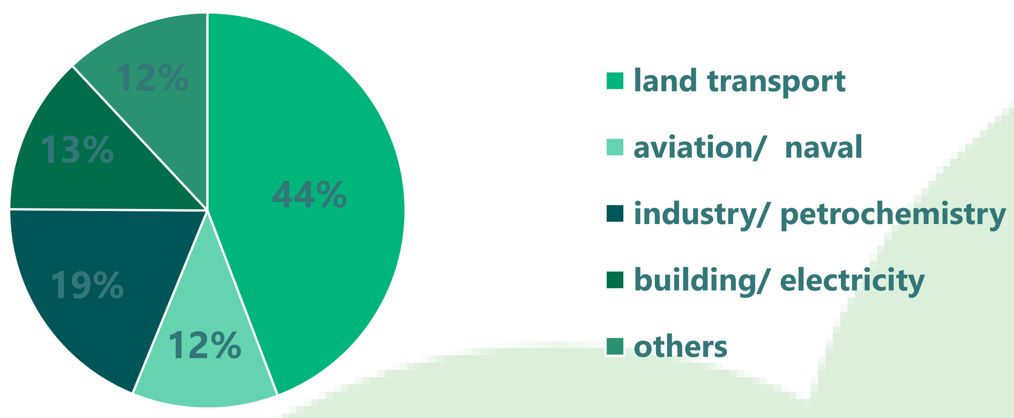
Context

Our planet has a limited amount of fossil fuel, which has been massively used in different ways in our civilization for more than a century. To anticipate its depletion, a sustainable solution is to switch from petrochemistry to a biomass-derived chemistry. Multiple fields of research would be impacted by the biorefinery (Chart). The usage of biomass as raw material for chemical industries will have a global impact in our ecosystem and will reduce the climate changes due to fossil energies.

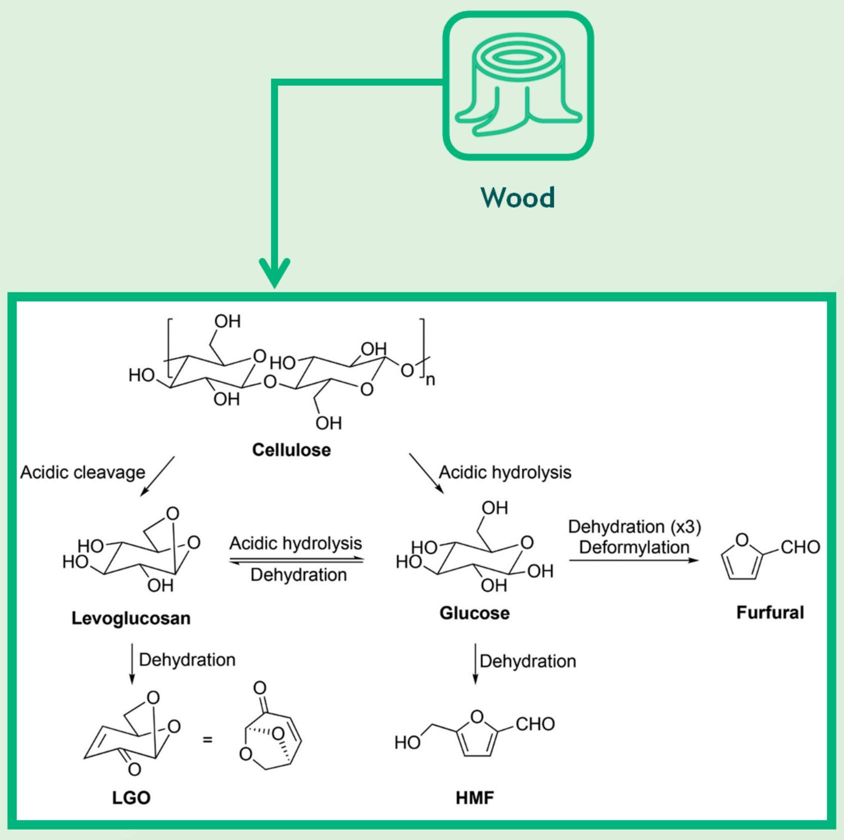
Distribution by activity sectors of worldwide petrol consumption in 2017[1]



Biomass and valorization

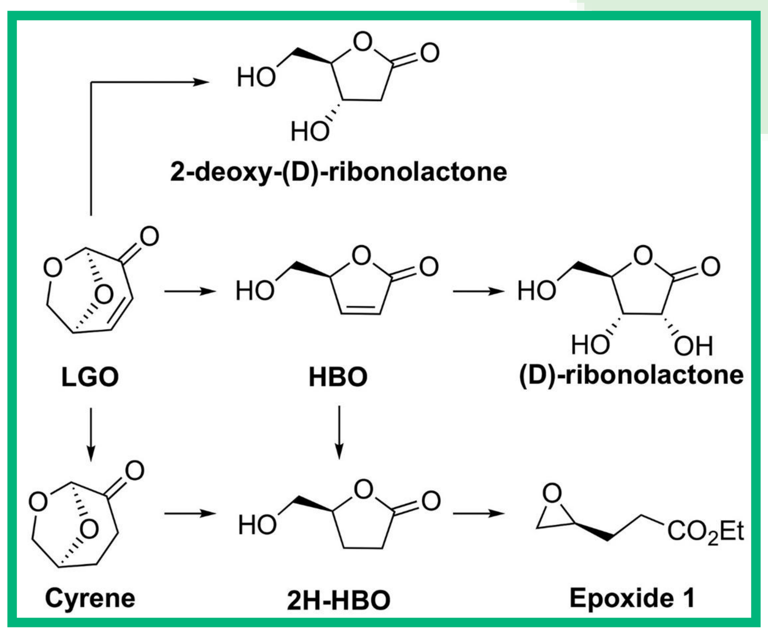
- The biomass is a source of energy and carbon present in vegetal organic matter. 35-50% of the biomass is composed by cellulose, an homopolymer of D-glucose, primer component of cell wall. Cellulose is the main component of wood and represents 2/3 of plant biomass, making it the most abundant biopolymer on Earth[2].

- Cellulose, due to its high functionalization and the presence of lot of chiral centers, offers a good source of building blocks that show great advantages compared to fossil hydrocarbons. Different methods exist to obtain small molecules called "building blocks" from cellulose, depending on the conditions of its deconstruction. The usage of selective processes allow the transformation of cellulose into Levoglucosenone (LGO), a chiral α,β-unsaturated bicyclic ketone with an internal ketal moiety (Scheme 1).



Scheme 1: Production of LGO, Levoglucosan, furfural, and HMF from the acidic degradation of cellulose/D-glucose extracted from wood

- LGO has been studied for more than 50 years now. Mild reducing conditions have been optimized recently to produce Cyrene™, a green solvent that proved to be a sustainable alternative to toxic polar solvents (*e.g.*, DMSO, ACN, pyridine). A couple of sustainable processes (*i.e.*, organic solvent- and catalyst-free Baeyer-Villiger oxidations) allow to transform LGO and/or Cyrene™ into 4(*S*)-γ-hydroxymethyl-α,β-butenolide (HBO) and (*S*)-γ-hydroxymethyl-γ-butyrolactone (2H-HBO), respectively[3]. From HBO, three other valuable building blocks have been synthesized: chiral epoxide 1, (D)-ribonolactone and 2-deoxy-(D)-ribonolactone (Scheme 2).

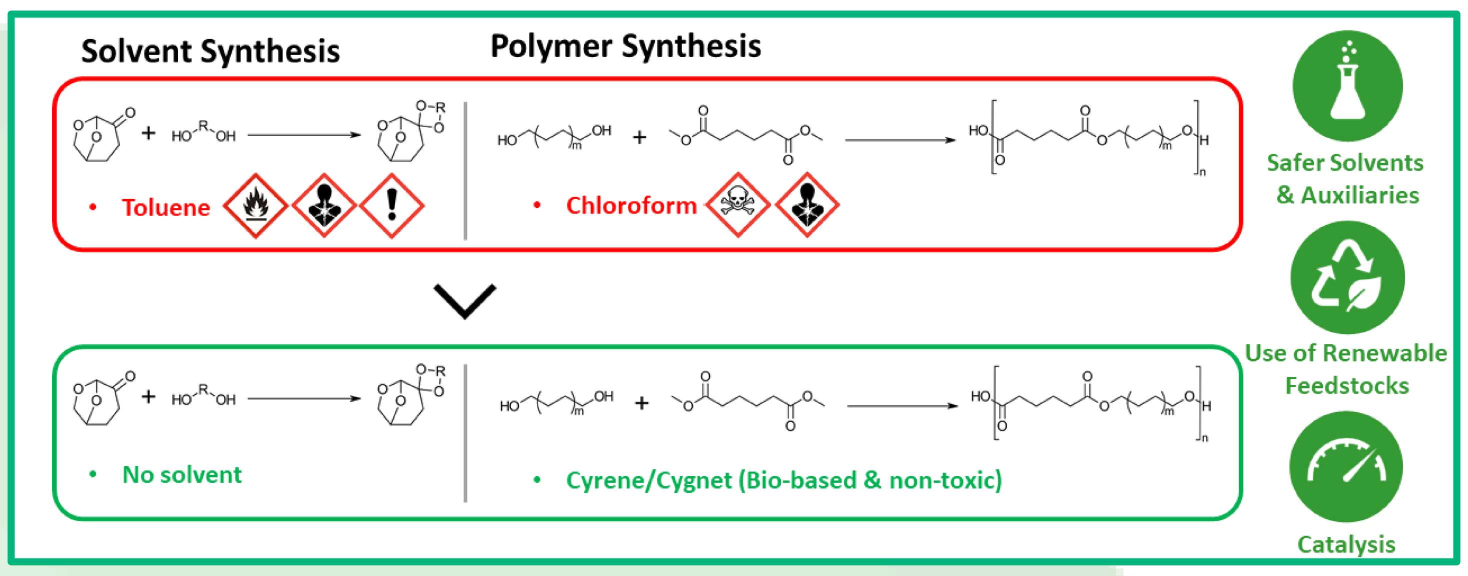


Scheme 2: Transforming LGO into high-value chiral building blocks and Cyrene™

Green Chemistry

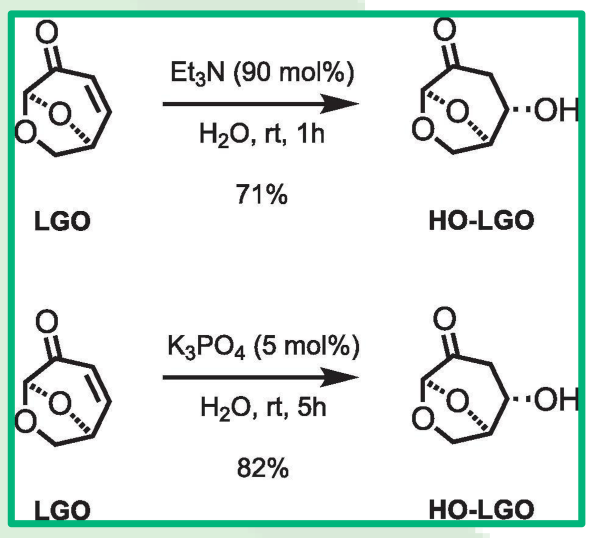
- Green chemistry is important to offer sustainable synthetic methods. It relies on 12 fundamental principles such as atom economy, usage of safer and greener solvent, … In that design, they are multiple examples of applications for HBO and LGO.

- Cyrene™ has been useful to replace hazardous solvents in different chemical procedures (*e.g.*, L/L extraction, enzymatic reduction of α-ketoesters). Very recently, Sami Fadlallah *et al.* have developed novel Cyrene™- and Cygnet-based sustainable polymerization reactions[4] (Scheme 3).

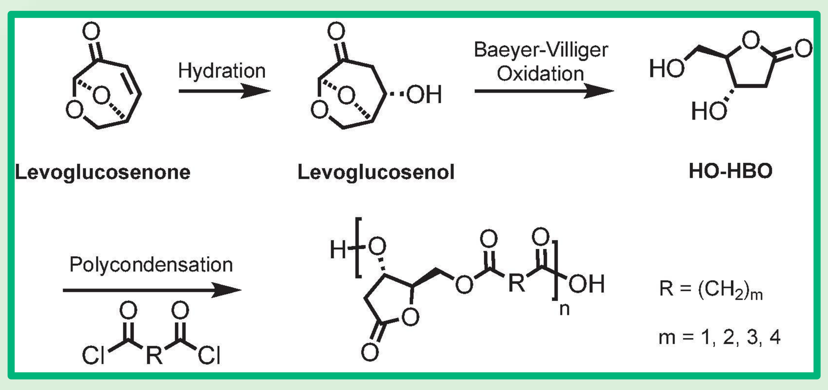


Scheme 3: Levoglucosenone-derived synthesis of bio-based solvents and polyesters

- In the synthesis of OH-LGO (or Levoglucosenol), green chemistry strategies have resulted in a better yield and greener conditions for Michael Addition[5] (Scheme 4).



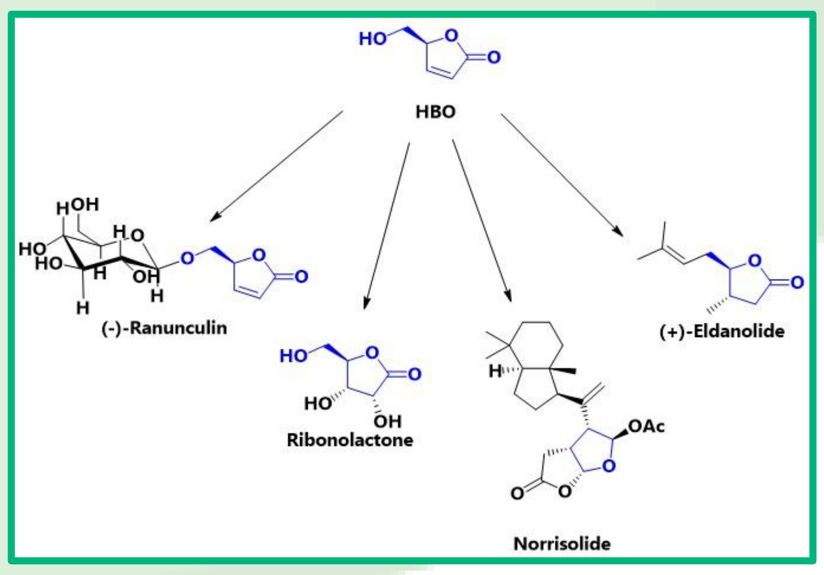
Scheme 4: Optimization of the Michael addition of H_2O



Scheme 5: Usage of LGO in the synthesis of bio-sourced polymers.

- HO-HBO could be used in many syntheses of polymers that could potentially lead to a new type of bio-sourced plastics that cand degrade in the environment[5] (Scheme 5).

- HBO is a very interesting starting material for a lot of natural products synthesis. From pheromones to complex sugars, HBO could open new opportunities in different fields of research to introduce greener procedures (Scheme 6). In conclusion, the many applications and possibilities of bio-based LGO-derived compounds are yet to be discovered, and represent a huge step in lignocellulosic biomass valorization.



Scheme 6: Natural products that could be synthesized from HBO

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