An Industrial Approach for the Synthesis of functionalized-Xylose via Direct Transacetalization

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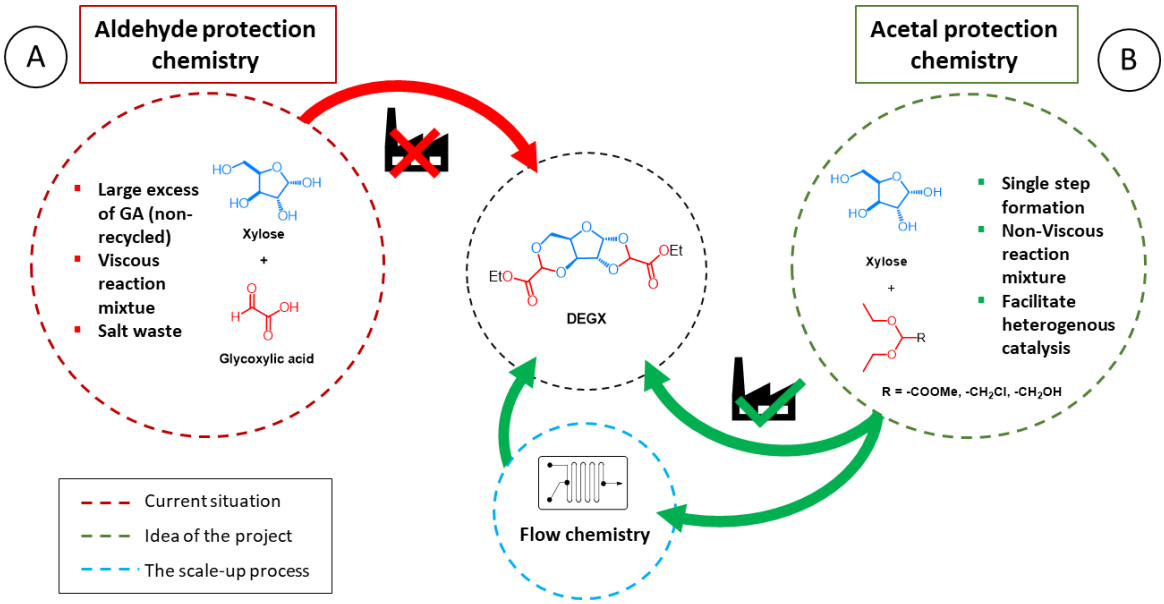
The development of bio-based monomers is crucial for reducing the environmental impact of fossil-based plastics. However, existing methods[1], like dimethyldiglyoxylate xylose (DMGX) synthesis using aldehyde protection chemistry, often require harsh conditions and complex purification.



Here, we present a novel synthetic process for producing a xylose-derived monomer (acetal protection), diethyldiglyoxylate xylose (DEGX), via an trans acetalization reaction using ethyl diethoxyacetate (EDEA) as both a solvent and a reactant. This process was optimized using heterogeneous (Amberlyst-15) and lewis acid ($FeCl_3$) catalysis and achieve yields of up to 80%. The purification of DEGX was achieved through hydrolysis to diglyoxylic acid xylose (DGAX), followed by salt formation, yielding 50% of purified DGAX from xylose. Compared to the reference process based on glyoxylic acid and xylose (aldehyde protection), this approach avoids the use of non-recyclable aldehydes and hazardous acids, while enabling the recyclability of EDEA, which was recovered at 80% for reuse in subsequent batches. The final product shows high purity (92-97% determined by NMR), and its simplified purification steps improve industrial feasibility. Additionally, a preliminary exploration of flow chemistry was conducted, demonstrating its potential but highlighting challenges in ethanol removal and catalyst regeneration. This work establishes a scalable and sustainable alternative for bio-based monomer production.

(1) Manker, L. P.; Dick, G. R.; Demongeot, A.; Hedou, M. A.; Rayroud, C.; Rambert, T.; Jones, M. J.; Sulaeva, I.; Vieli, M.; Leterrier, Y.; Potthast, A.; Maréchal, F.; Michaud, V.; Klok, H.-A.; Luterbacher, J. S. Sustainable Polyesters via Direct Functionalization of Lignocellulosic Sugars. *Nat. Chem.* **2022**, *14* (9), 976–984. https://doi.org/10.1038/s41557-022-00974-5.