ISGC 2022

N°232 / OC
TOPIC(s) : Clean reactions / Alternative solvents

Sustainable production of sugar alcohols by catalytic hydrogen transfer over Raney Ni catalyst

AUTHORS

Beatriz GARCIA / UNIVERSIDAD REY JUAN CARLOS, C / TULIPAN S/N, MOSTOLES
Jovita MORENO / UNIVERSIDAD REY JUAN CARLOS, C / TULIPAN S/N, MOSTOLES
Corresponding author : Jose IGLESIAS / jose.iglesias@urjc.es

PURPOSE OF THE ABSTRACT

Lignocellulose biomass is a plentiful renewable source of carbon offering a solution to cope with some environmental challenges and break down the dependence on fossil feedstocks. Lignocellulose biomass is the main source of monosaccharides, a raw material to produce sugar alcohols like sorbitol or xylitol, both included in the ?Top 10? list of biomass-derived building blocks. [1] Sugar alcohols are versatile precursors to high-value products, including drop-ins like plastics or fuels, and find a large number of applications themselves in food, cosmetic, pharmaceutical, and industrial sectors. [2] This versatility has made sorbitol the largest-volume sugar alcohol worldwide produced accounting for more than 60% of the market.

Sugar alcohols are conventionally produced by catalytic hydrogenation over Raney Nickel catalysts. These processes require high-pressures and make use of aqueous phase reaction media, thus leading to extensive metal leaching from the catalysts, [3] so that expensive purification steps and catalyst replacement are required.

This work focuses on the use of an alternative reaction pathway to sugar alcohols by using biomass-derived hydrogen donors and a catalytic hydrogen transfer route to replace the conventional hydrogenation pathway. The absence of molecular hydrogen allows operating under mild pressure condition and the use biomass derived hydrogen donors drive out leaching problems. The reaction has been studied for monosaccharides and more complex sugars, evidencing the high potential of diols as hydrogen donors using commercial low-priced nickel catalysts.

Catalytic tests were carried out under batch conditions in a 100 mL stain-steel reactor fitted with a temperature controller and mechanical stirrer. In a typical assay, a 90 mM sugar solution in alcohol/diol was treated with the appropriate amount of Raney Nickel for a total period of 6h.

Short-chain monoalcohols (C1-C4) used as hydrogen donors pointed to ethanol as the best candidate for hydrogen transfer, producing 58.2% sorbitol yield at 130ºC after 6h reaction when treating glucose. C4 alkyl diols, revealed as more efficient hydrogen donors, have also been tested in the transfer hydrogenation. Different butanediol regioisomers, showing primary or secondary hydroxyl groups (Figure 1) were used. 1,2-diol displayed a good performance as hydrogen donor but slower substrate conversion than 2,3-diol, as the dehydrogenation preferentially occurs on the secondary hydroxyl group. Nevertheless, the presence of two terminal hydroxyl groups (1,4-butanediol) led to a higher selectivity to the desired sugar alcohol, providing 98% sorbitol at 90ºC after 6h reaction (Figure 2).

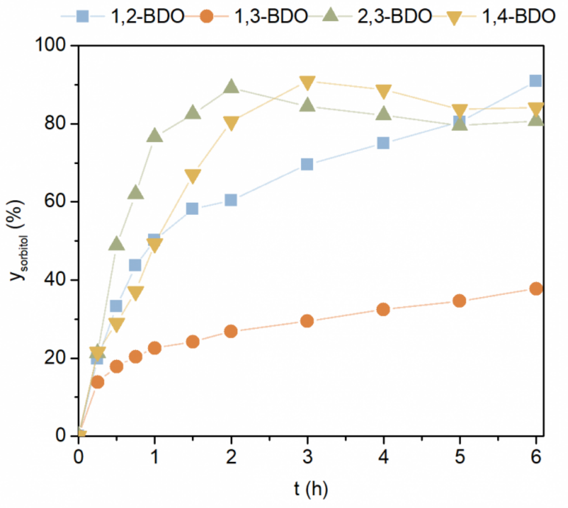
Treating other sugar substrates under the same conditions, using 1,4-butanediol, provided very successful results, achieving sugar yields above 90% when treating pentoses such as xylose, and arabinose. Treating fructose was also quite efficient, though in this case, almost equimolar amounts of sorbitol and mannitol were achieved, due to the lack of enantioselectivity in the hydrogen transfer. This reaction procedure resulted also suitable for the transformation of more complex substrates, such as dimers like cellobiose and maltose, providing the corresponding reduced sugars with product yields exceeding 60%.

This study demonstrates the feasibility of using biomass derived diols as hydrogen donors in catalytic transfer hydrogenation of a wide variety of sugar monosaccharides and disaccharides, evidencing the excellent

performance of a readily available conventional catalytic systems as Raney Nickel. Finally, the required mild conditions to drive the transformation is also an important feature of the CTH route as compared to conventional hydrogenation, offering important economic and sustainable advantages to produce sugar alcohols.

This research was funded by the Spanish Ministry of Science, Innovation, and Universities (project RTI2018-094918-B-C42).

FIGURES



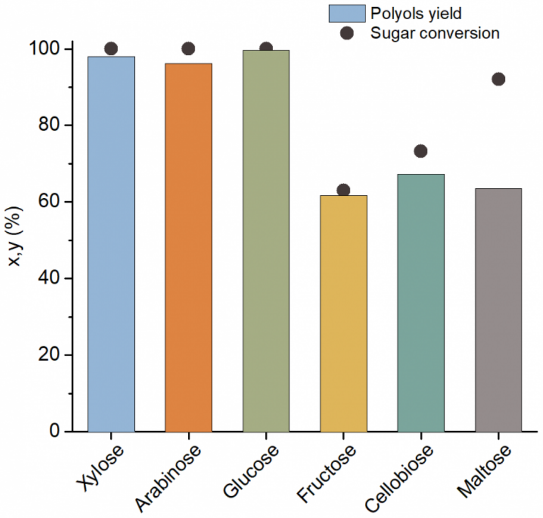


FIGURE 1

Kinetic profile obtained for sorbitol yield in the catalytic transfer hydrogenation of glucose in the presence of different butanediol regioisomers.

Reaction conditions: reaction volume = 100 mL; [glucose] = 90 mM; catalyst to substrate weight ratio = 1:1; reaction temperature = 130 °C.

FIGURE 2

Results achieved in the catalytic transfer hydrogenation of glucose in the presence of 1,4-BDO.

Reaction conditions: reaction volume = 100 mL; substrate loading = 1.65 g; catalyst to substrate weight ratio = 1:1; reaction temperature = 90 °C.

KEYWORDS

Catalytic transfer hydrogenation | Raney nickel | Sugar alcohols | Sorbitol

---

BIBLIOGRAPHY

[1] J.J. Bozell, G.R. Petersen, Green Chemistry, 12 (2010) 539-554.
[2] F.H. Isikgor, C.R. Becer, Polymer Chemistry, 6 (2015) 4497-4559.
[3] B.W. Hoffer, E. Crezee, F. Devred, P.R.M. Mooijman, W.G. Sloof, P.J. Kooyman, A.D. van Langeveld, F. Kapteijn, J.A. Moulijn, Applied Catalysis A: General, 253 (2003) 437-452.