Efficient Conversion of L-Rhamnose into 5-Methylfurfural Combining Performance of Ionic Liquids and Zeolites

Martina SILACO, Salvatore MARULLO, Francesca D'ANNA^{1,*}

¹Università degli Studi di Palermo, Dipartimento STEBICEF, Palermo, Italy *Corresponding author: francesca.danna@unipa.it

Most carbon-based products that our society uses daily, derive from petroleum, and therefore require the exploitation of fossil fuels; this leads to a consequent increase in carbon dioxide emissions and global warming.¹ For this reason, interest in alternative and renewable energy sources has grown in recent years. Biomass resources including carbohydrates are an ideal petroleum alternative to produce fuels, chemicals, and materials. 5-Methylfurfural (5-MF) is an important intermediate widely used in pharmaceuticals, cosmetics, pesticides, and other applications. Thanks to the presence of several functional groups, 5-MF can be used to produce value-added product, such as 2,5-Dimethylfuran and 2,5-Furandicarboxilic acid. On the other hand, the industrial production of 5-MF involves 2-

Methylfuran, phosgene and *N*,*N*-dimethylformamide, resulting in high production cost. However, 5MF can be obtained from biomass-derived carbohydrates.² L-Rhamnose is a deoxyhexose carbohydrate, and it is the cheapest deoxy sugar. The conversion to 5-MF involves two steps, in particular the isomerization gives L-rhamnulose and the following dehydration form 5-MF.³ In this study, we worked on the direct conversion of L-Rhamnose to 5-MF using Ionic Liquids (ILs) as solvents (Figure 1) and b zeolite as catalyst.

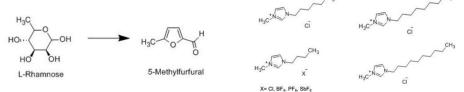


Figure 1. Synthesis of 5-MF from L-Rhamnose and structures of ILs tested.

Reaction conditions such as temperature, the amount of L-Rhamnose and catalyst loading were optimized. To illustrate the effect of solvent, ILs different for both anion and cation were tested, along with mixtures of ILs. Finally, using the best operating conditions, thanks to a biphasic system, we evaluated the possibility of extracting 5-MF and reusing the solvent-catalyst system.

References

- (1) Raud, M.; Kikas, T.; Sippula, O.; Shurpali, N. J. Potentials and Challenges in Lignocellulosic Biofuel Production Technology. *Renewable Sustainable Energy Rev.* **2019**, *111*, 44–56.
- (2) Peng, Y.; Li, X.; Gao, T.; Li, T.; Yang, W. Preparation of 5-Methylfurfural from Starch in One Step by Iodide Mediated Metal-Free Hydrogenolysis. *Green Chem.* **2019**, *21* (15), 4169–4177.
- (3) Tuteja, J.; Nishimura, S.; Ebitani, K. One-Pot Synthesis of Furans from Various Saccharides Using a Combination of Solid Acid and Base Catalysts. *Bull. Chem. Soc. Jpn.* **2012**, *85* (3), 275–281.

ACKNOWLEDGEMENTS

This study was carried out within the MICS (Made in Italy – Circular and Sustainable) Extended Partnership and received funding from the European Union Next-GenerationEU (PIANO NAZIONALE DI RIPRESA E RESILIENZA (PNRR) – MISSIONE 4 COMPONENTE 2, INVESTIMENTO 1.3 – D.D. 1551.11-10-2022, PE00000004). This manuscript reflects only the authors' views and opinions, neither the European Union nor the European Commission can be considered responsible for them.