Transfer Hydrogenation of Furfural Under Continuous Flow Conditions by Shvo Catalyst

Maitê CAMPOS[1], Luís ADRIANO SANTOS DO NASCIMENTO[1], Emilia PAONE[2], Giulia BRUFANI[2,3], Chiara LENZI[4], Andrea PIAZZI[4], Rita MAZZONI[4], Luigi VACCARO[3], Francesco MAURIELLO[*,2]

[1]Universidade Federal do Pará UFPA, Department of Biotechnology, Augusto Corrêa Street, Belém, Brazil.

[2] Dipartimento DICEAM, Università degli Studi Mediterranea di Reggio Calabria, Via Zehender, Reggio di Calabria, Italy.

[3] Dipartimento di Chimica Biologia e Biotecnologie, Università degli Studi di Perugia, Via Elce di Sotto 8, Perugia

[4] Dipartimento di Chimica Industriale, Università degli Studi Alma Mater Studiorum di Bologna, Viale Risorgimento 4, Bologna, Italy.

** francesco.mauriello@unirc.it*

Significance and Relevance

This study introduces the first-ever application of the Shvo catalyst in continuous-flow conditions for the transfer hydrogenation of furfural to furfuryl alcohol. Achieving a conversion rate of 94.1%, this method represents a substantial improvement in safety, efficiency, and sustainability over traditional batch processes.

Preferred and 2nd choice for the topic: "Green chemistry and biomass transformation, renewable resources conversion"

Preferred presentation: Oral only

Introduction and Motivations

Furfural is a cornerstone biomass-derived platform chemical with numerous industrial applications [1-2]. Traditional hydrogenation techniques, employing molecular hydrogen in batch reactors, face several limitations, including high pressure requirements and harsh reaction conditions. Addressing these challenges, our research utilizes the Shvo catalyst [3], a renowned ruthenium-based complex, in a continuous-flow system for the catalytic transfer hydrogenation (CTH) of furfural [4]. This approach not only circumvents the drawbacks of batch processing but also enhances reaction efficiency and safety. Significantly, this study represents the first implementation of the Shvo catalyst in continuous-flow conditions in the reduction of furfural, promoting an efficient, safer and more sustainable approach for transfer hydrogenation process of biomass derived molecules.

Results and Discussion

Our study successfully implemented the Shvo catalyst in a continuous-flow system for the transfer hydrogenation of furfural to furfuryl alcohol, achieving a high conversion rate of 94.1% under optimized conditions (150°C, a flow rate of 250 µL/min, and 1.5 equivalents of 2-propanol). These conditions were meticulously fine-tuned to balance efficiency, sustainability, and cost-effectiveness. The use of 2-methyloxolane (MeOx) as a co-solvent played a pivotal role in enhancing the solubility of the Shvo catalyst, facilitating its applicability under continuous flow conditions. The exceptional selectivity of the Shvo catalyst in the transfer hydrogenation of furfural into furfuryl alcohol was highlighted by the absence of etherification, acetalization, or other unwanted pathways, even under varied experimental conditions. While 2-propanol provided the highest conversion rates, experiments with ethanol and methanol showcased lower efficiencies, underscoring the importance of selecting an appropriate hydrogen donor for maximizing yield and selectivity.

Varying the equivalents of 2-propanol demonstrated a clear trend: higher equivalents generally improved the conversion efficiency. At 90°C, increasing the isopropanol from 1.0 to 1.5 equivalents resulted in an increase from 80.1% to 85.2% in furfural conversion. This trend was consistent across all tested temperatures, peaking at 97.4% conversion at 150°C with 1.5 equivalents of isopropanol (Figure 1). These results illustrate the importance of hydrogen donor availability in optimizing the catalytic process, highlighting a crucial factor in the design of continuous-flow chemical reactions.

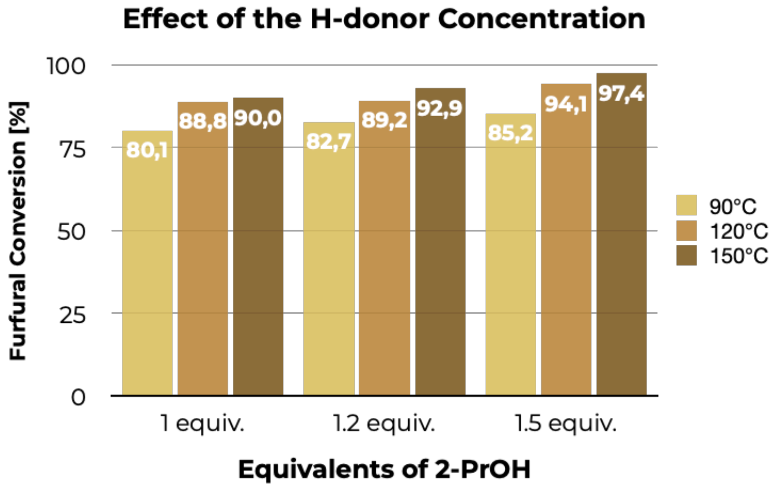

Figure 1 Effect of Hydrogen Donor Concentration (1.0, 1.2, and 1.5 equivalents of 2-PrOH) on the Conversion Efficiency of Furfural at Temperatures of 90°C, 120°C, and 150°C.

After completing the transfer hydrogenation reaction, the Shvo catalyst can be easily recovered by a simple process of precipitation into hexane. This method effectively separates the catalyst from the reaction mixture, allowing it to be collected and reused after a proper regenerative process. Our studies have demonstrated that the Shvo catalyst maintains a high level of activity even after five cycles of reuse, with minimal degradation in performance.
The study also focused on green chemistry metrics to evaluate the environmental impact of the reaction system. The atom economy (AE) was calculated at 0.63, indicating moderate efficiency in using reactant atoms towards the desired product. The reaction mass efficiency (RME) stood at 0.34, reflecting the challenge of balancing reactant use with desired output but also highlighting areas for process improvement. The E-factor, which measures waste production relative to the product, was 1.9, demonstrating a relatively low level of waste generation. These metrics underscore the sustainable nature of the process, suggesting that while there is room for improvement, the system offers significant environmental benefits compared to traditional batch methods.
Finally, in order to extend the substrate scope, transfer hydrogenations of other aldehydes and ketones were also tested, confirming the applicability of this process to a broad range of substrates.
In conclusion, this research not only confirms the viability of the Shvo catalyst for continuous-flow applications but also emphasizes its potential for industrial-scale sustainable chemical synthesis, marking a significant advancement in the field of green chemistry.

References

1. M. Besson, P. Gallezot, C. Pinel, *Chem. Rev*. **2014**, *114*, 1827–1870.
2. C. Xu, E. Paone, D. Rodríguez-Padrón, R. Luque, F. Mauriello, *Chem. Soc. Rev*. **2020**, *49*, 4273–4306.
3. B. L. Conley, M. K. Pennington-Boggio, E. Boz, T. J. Williams, *Chem. Rev*. **2010**, *110*, 2294–2312.
4. M. J. Gilkey, B. Xu, *ACS Catal*. **2016**, *6*, 1420–1436.

Acknowledgements
This work has been funded by the European Union – NextGenerationEU under the Italian Ministry of University and Research (MUR) within PNNR MUR - M4C2 - Investimento 1.5 - "Ecosistemi dell'Innovazione”. In particular, authors thanks projects “Ecosistema TECH4YOU”, “Ecostistema ECOSISTER” and “Ecosistema VINITALY”.