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Selective transfer hydrogenation of furfural under continuous flow conditions promoted by the recoverable homogeneous Shvo's catalyst†

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The continuous-flow application of the homogeneous Shvo's catalyst for the selective transfer hydrogenation of furfural to furfuryl alcohol, utilizing biobased 2-methyltetrahydrofuran as the reaction medium and 2-propanol as a stoichiometric hydrogen donor is reported for the first time. The homogeneous catalyst demonstrated excellent recyclability, maintaining high performance over at least five consecutive reaction cycles. This process represents an efficient and waste-minimized strategy for the reductive catalytic valorization of biomass-derived furfural under continuous-flow conditions, as validated by a comprehensive green metrics assessment.

Furfural (FUR), which is derived from pentosan-rich biomass, is a key platform chemical for producing high-value compounds such as furfuryl alcohol, tetrahydrofurfuryl alcohol, and levulinic acid.[1,2] Among these, furfuryl alcohol (FAL) is essential for manufacturing resins, adhesives, and polymers and serves as an intermediate in pharmaceuticals and agrochemicals.[1,3] Conventional hydrogenation of furfural into furfuryl alcohol with molecular hydrogen (H_2) ensures excellent performance under both batch and flow conditions.[1–3] A wide range of supported noble metals (*e.g.*, Pt, Pd, Ru, Rh) and non-noble metals (*e.g.*, Cu, Ni) have been reported as effective catalysts in these processes.[4–6]

In this context, flow chemistry offers significant advantages for hydrogenation reactions, primarily due to improved gas–liquid contact and the in-line generation of hydrogen, which reduces associated safety risks.[7,8] However, the use of hydrogen gas is often considered undesirable in industrial applications, as it involves specialised and expensive equipment, along with safety risks associated with the handling of high-pressure flammable gases. In addition, at present, commercial hydrogen is predominantly produced from non-renewable fossil resources, raising further environmental and sustainability concerns.[9]

A viable alternative to molecular hydrogen is the application of catalytic transfer hydrogenation (CTH) with a wide range of hydrogen donors, such as hydrazine, formic acid, and simple aliphatic alcohols (*e.g.*, methanol, ethanol, and 2-propanol), to promote reactions under milder conditions.[10–13]

Continuous flow technology enhances safety, improves heat and mass transfer, maximises energy efficiency and intensifies the conditions for maximising yield and throughput. Moreover, it offers significant environmental and safety advantages for the large-scale implementation of CTH.[14,15]

Both homogeneous and heterogeneous metal-based catalysts have been successfully utilized in CTH processes, demonstrating broad applicability and efficiency across a range of substrates.[16–19] Heterogeneous catalysts are often preferred in chemical industries due to their inherent advantages, such as easy separation and recyclability. However, several homogeneous catalysts have been reported to display high activity and excellent selectivity in catalytic transfer hydrogenation (CTH) reactions. Among them, Shvo's catalyst, a commercially available dinuclear ruthenium complex, is widely employed in catalytic transformations due to its exceptional stability as a pre-catalyst for bifunctional hydrogenation and dehydrogenation processes.[20–24] Notably, it demonstrates excellent performance in CTH reactions, efficiently mediating hydrogen transfer from donor molecules to a wide range of aldehyde and ketone substrates.[25,26]

To the best of our knowledge, the use of this highly effective homogeneous catalyst under continuous-flow conditions has not yet been reported, likely due to challenges associated with the limited solubility of Shvo's catalyst at room temperature.

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In this communication, we report the first results on the continuous-flow application of the homogeneous Shvo's catalyst for the selective catalytic transfer hydrogenation (CTH) of furfural to furfuryl alcohol. The adoption of the bio-based solvent 2-methyltetrahydrofuran (2-MeTHF) overcomes solubility limitations, enabling the efficient use of Shvo's catalyst in standard flow equipment without the need for specialised apparatus.

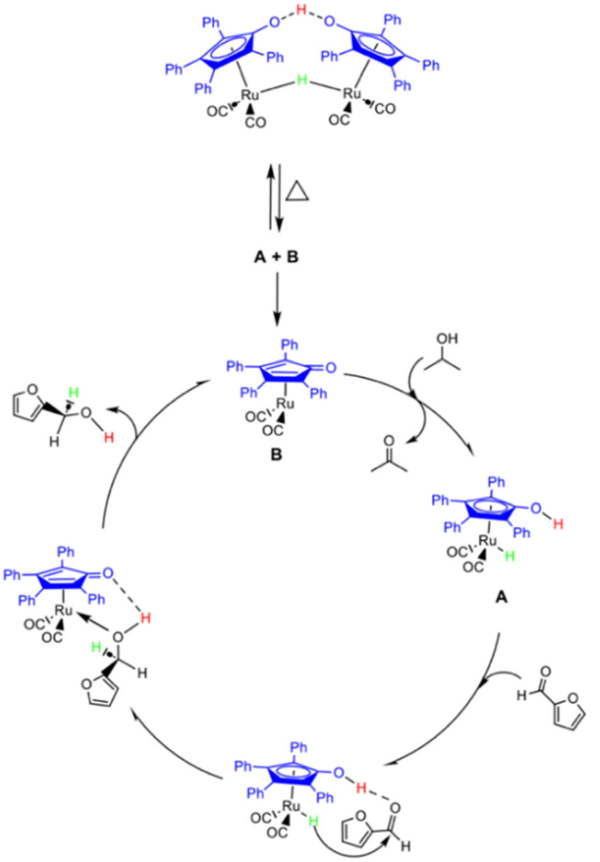
Additionally, 2-MeTHF promotes effective hydrogen transfer from simple aliphatic hydrogen donors, employed in equimolar amounts, which limits the formation of ketone byproducts. Its selection is strategically motivated by both its ability to solubilise the catalyst under flow conditions and its favourable environmental profile as a renewable, resource-derived solvent.[27,28]

With the aim of combining the high catalytic activity and selectivity of homogeneous systems with the recoverability and recyclability typically associated with heterogeneous catalysis, we present early findings on a streamlined continuous-flow protocol that allows efficient recovery and reuse of Shvo's catalyst, maintaining high performance over five consecutive reaction cycles. This communication also includes a screening of key reaction parameters, including temperature, flow rate, and hydrogen donor, with the goal of maximising furfuryl alcohol yield while improving performance across relevant green chemistry metrics.

At the outset of our investigations, a series of batch experiments were conducted to evaluate the efficiency of Shvo's catalyst (1 mol% relative to FUR) in catalysing the CTH of FUR (0.25 mmol l^{-1}) to FAL. 2-Propanol (2-PrOH) was used as the hydrogen donor in equimolar amount with respect to FUR, while 2-MeTHF served as the reaction medium.

The catalytic performance was evaluated by screening a range of temperatures (90 °C, 120 °C and 150 °C) at different times (30 min, 60 min and 90 min) under inert conditions (N_2, 1 atm) in a 15 mL Schlenk bomb. The kinetic test revealed that the reaction progressed rapidly, reaching high conversion within the initial minutes. Higher temperatures progressively enhanced the performance of Shvo's catalyst, with complete conversion achieved at 150 °C within 90 minutes. In terms of productivity, the highest reaction rate was 1.20 mmol h^{-1}, while the space–time yield (SPTY) reached 79.7 at 150 °C after 30 min of reaction time (Table S1†). Conversions were determined by GC analysis using *n*-tetradecane as an internal standard. The analysis confirmed the exclusive formation of FAL, with no detectable byproducts from etherification, acetalization, or aldol condensation (the only remaining material was unreacted FUR). These findings were further validated by the isolated yields of FAL, which closely matched the measured conversions.

Based on previous mechanistic studies on Shvo's catalyst-mediated hydrogen transfer,[21–23] we propose a reaction mechanism for the reduction of FUR to FAL (Scheme 1). Indeed, the Shvo's catalyst facilitates the transfer of hydrogen from 2-PrOH to FUR through a bifunctional mechanism. 2-PrOH donates a hydride to Shvo's catalyst, forming acetone, while the activated catalyst transfers hydrogen to FUR, reducing it to FAL. Further insights into the catalyst's behaviour were obtained through IR spectroscopy (Fig. S2†) and ^{1}H-NMR (Fig. S3†) analysis of the resting state. The spectra revealed the unaltered signature of Shvo's precursor as the sole ruthenium-based species, confirming the recombination of intermediates into the stable dinuclear complex upon completion of the reaction. These findings confirm the catalyst's outstanding stability, efficiency, and selectivity, making it a highly reliable system for the CTH of FUR under the adopted reaction conditions and laying the foundation for its recyclability.



Scheme 1 Proposed mechanism for Shvo's catalysed reduction of furfural to furfuryl alcohol.

Building on the results obtained under batch conditions, we extended our investigation under continuous flow (Table 1). A solution of furfural (2.4 mmol), Shvo's catalyst (0.024 mmol, 1 mol%), and the required amount of H-donor, all dissolved in 10 mL of 2-methyltetrahydrofuran (2-MeTHF), was continuously streamed into a pre-heated stainless-steel tubular reactor (internal volume: 4 mL). To prevent the evaporation of volatile components, a back pressure regulator (BPR) of 10 bar was applied to the system (see ESI† for further details).

Analogously with batch tests, the initial screening of reaction conditions under flow conditions began with the strategic selection of an equimolar amount of H-donor. This approach aimed to maximise the efficiency of reactant utilisation while avoiding the unnecessary excess of

Table 1 Results of the Shvo's catalyst in the transfer hydrogenation of furfural under continuous flow conditions[a]

Entry	Temp. [°C]	H-donor molecule	Flow rate [μL min^{-1}]	Conv.[b] [%]
1	120	2-PrOH	125	76
2	120	2-PrOH	250	89
3	120	2-PrOH	500	70
4	120	2-BuOH	250	87
5	120	1-PrOH	250	80
6	120	EtOH	250	78
7	120	MeOH	250	55

[a] Reaction condition: furfural (200 μL–2.4 mmol), H-donor molecule (1 equiv., 2.4 mmol), Shvo's catalyst (26.4 mg–0.024 mmol), 2-MeTHF (10 mL) under 10 bar of Ar. [b] The conversion was determined *via* gas–liquid chromatography analyses using *n*-tetradecane as internal standard.

2-propanol, and at the same time enabled a direct comparison with the corresponding batch experiments performed under equimolar conditions.

The effect of flow rate on the reaction was primarily investigated at 120 °C, with catalytic experiments being conducted at flow rates of 125, 250, and 500 μL min^{-1}, revealing that the conversion of FUR to FAL increased from 76% to 89% as the flow rate was raised from 125 to 250 μL min^{-1} (entries 1–2). This suggests that shorter residence times may reduce catalyst deactivation and improve mass transfer, ultimately enhancing the overall reaction efficiency. However, further increasing the flow rate to 500 μL min^{-1} reduced the conversion to 70%, likely due to insufficient residence time (entry 3). These results prove a clear trade-off between throughput and reaction efficiency, with 250 μL min^{-1} identified as the optimal flow rate, enabling effective interaction between reactants and the catalyst.

We then examined the effect of the H-donor due to its direct influence on hydrogenation efficiency. In addition to 2-propanol (2-PrOH), we consequently tested 2-butanol (2-BuOH), 1-propanol (1-PrOH), ethanol (EtOH) and methanol (MeOH) under reaction conditions of 120 °C and a flow rate of 250 μL min^{-1} (entries 4–7). The results indicated that 2-PrOH and 2-BuOH were the most effective among the aliphatic alcohols screened, achieving the highest furfural conversion rates (89% for 2-PrOH and 87% for 2-BuOH, respectively). In comparison, the conversion rates of FUR to FAL were 80% with 1-PrOH, 78% with EtOH, and 55% with MeOH. The lower performance of primary alcohols as H-donor molecules is commonly attributed to their reduced H-donor ability compared to secondary alcohols, resulting from (i) a stronger electron-releasing inductive effect and (ii) a lower reduction potential and polarity.[29,30]

The effect of the reaction temperature was investigated in the range of 90–150 °C, while maintaining a flow rate of 250 μL min^{-1}. The results demonstrated a clear temperature-dependent increase in the conversion of FUR to FAL. At 90 °C, the conversion rate was 71%, increasing to 89% at 120 °C and further to 90% at 150 °C (Fig. 1, Table S2†). The progressive improvement in conversion rates with rising temperatures can be attributed to enhanced hydrogen transfer efficiency and increased activity of Shvo's catalyst. Higher temperatures facilitate the formation of active catalytic intermediates, thereby improving the overall reaction kinetics and ensuring a more effective interaction between the H-donor and the FUR. Additionally, elevated temperatures reduce viscosity and enhance mass transfer within the system, further supporting the conversion process.

A comparison of the batch and flow experiments reveals that, although the final conversion achieved in batch mode is slightly higher due to extended reaction times, the flow process offers a clear advantage in terms of productivity and volumetric efficiency. Indeed, at 150 °C, the flow system reached a productivity of 3.24 mmol h^{-1} and a space–time yield (SPTY) of 810.0 mmol h^{-1} L^{-1} (Table S2,† entry 9). In contrast, the batch process achieved a maximum productivity of 1.20 mmol h^{-1} and a SPTY of 79.7 mmol h^{-1} L^{-1} after 30 minutes (Table S1,† entry 7). Extending the batch reaction time to 90 minutes slightly improved the yield (from 96% to 99%) but reduced the SPTY to 28.6 mmol h^{-1} L^{-1} (entry 9), due to the longer reaction time. At 90 and 120 °C, a similar trend is observed. On the other hand, flow conditions consistently deliver higher productivities and SPTY values than batch, even when comparable yields are obtained. In batch mode, longer reaction times at these temperatures result in only modest yield improvements, while significantly reducing throughput.

These results confirm that, under identical stoichiometric conditions, the continuous-flow system provides a more efficient and scalable platform for the transfer hydrogenation of furfural. The combination of short residence times, high yields, and superior space–time productivity strongly supports the advantages of flow over batch processing.

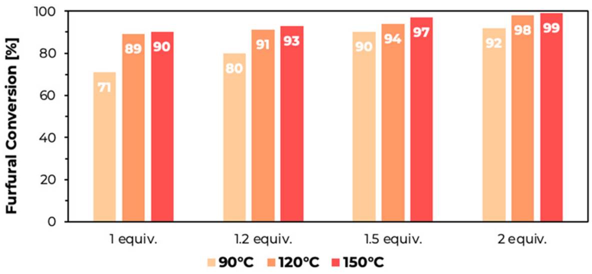


Fig. 1 Effect of the H-donor concentration (1, 1.2, 1.5 and 2 equivalents of 2-PrOH) in the temperature range investigated (90 °C, 120 °C, 150 °C) with a flow rate of 250 μL min^{-1}.

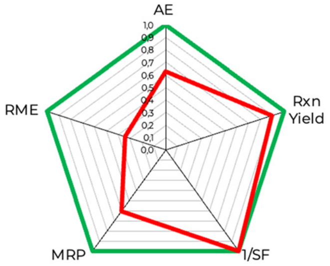
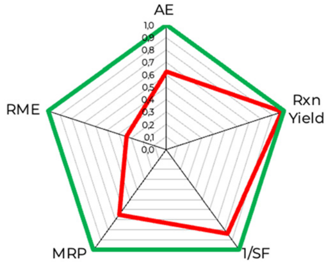
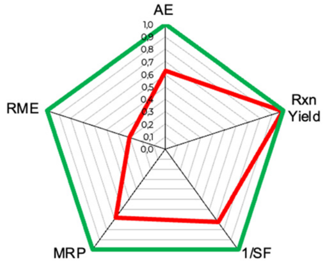
The quantity of H-donor plays a crucial role in determining the efficiency of the CTH process. Experiments were conducted with increasing amounts of 1.2, 1.5, and 2 equiv. of 2-PrOH at a flow rate of 250 μL min^{-1} and the three temperatures under investigation: 90 °C, 120 °C, and 150 °C (Fig. 1, Table S2†). The results demonstrated a trend of increasing conversion rates with higher equivalents of 2-PrOH, emphasising the critical influence of hydrogen availability on reaction efficiency. At 90 °C, the conversion rate increased progressively from 71% with 1.0 equivalent to 92% with 2.0 equivalents. At 120 °C, the conversion rates increase from 89% with 1.0 equivalent to 98% with 2.0 equivalents. This effect was further confirmed at 150 °C, where complete conversion was achieved using 2 equivalents. This highlights the synergistic effect of elevated temperature and increased H-donor concentration, as the higher temperature enhances the activity of the Shvo's catalyst. At the same time, the additional 2-PrOH ensures sufficient hydrogen availability for the reaction. Excess 2-PrOH facilitates complete transfer hydrogenation by providing ample hydrogen, ensuring robust interaction between the donor and furfural. Furthermore, higher equivalents of the donor don't lead to potential side reactions, maintaining excellent selectivity towards FAL.

Under the most effective conditions of 150 °C and 250 μL min^{-1}, the performance of the continuous-flow CTH process was comprehensively evaluated using key green chemistry metrics to construct a five-point radial polygon for three different amounts of 2-PrOH (1.0, 1.5, and 2 equivalents) (Table 2).[31]

The atom economy (AE) indicates a moderate efficiency in incorporating reactant atoms into the final product. The isolated yields reflect the increase in conversion with increasing amounts of 2-PrOH. For instance, yield improves from 90% with 1 equivalent to 97% with 1.5 equivalents and reaches 99% at 2 equivalents, confirming the positive correlation between hydrogen donor excess and reaction performance. By contrast, the reciprocal of the stoichiometric factor (1/SF) reflects the excess of 2-PrOH used, with the maximum value (1.00) obtained at stoichiometric conditions, favouring reduced reagent excess. This parameter progressively decreases to 0.84 and 0.72 for 1.5 and 2 equivalents, respectively, highlighting the trade-off between higher yield and atom economy. Solvent recovery and efficient H-donor utilisation contribute to an *E*-factor of 2, which improves slightly from 2.3 (at 2 equivalents) to 2.0 (at 1.5 equivalents), indicating moderate waste generation relative to product formation (see ESI† for *E*-factor calculation). These findings are further supported by the material recovery parameter (MRP), which reaches 0.61 with 1 equivalent, 0.65 with 1.5 equivalents, and 0.68 at 2 equivalents of 2-PrOH, primarily due to the increase in yield. However, the reaction mass efficiency (RME) highlights opportunities for improving material utilisation, particularly those limited by solvent and reagent inputs. RME shows a slight decline from 0.34 to 0.31 across increasing equivalents, reinforcing the importance of adjusting reagent loadings. Finally, the vector magnitude ratio (VMR), ranging from 0.73 (1 equiv.) to 0.70 (2 equiv.), reflects the overall balance of sustainability indicators and confirms that further increase in 2-PrOH provides diminishing returns from a green chemistry perspective.

While operating with 1 equivalent of 2-propanol ensures maximum stoichiometric efficiency and finest AE-based metrics, it results in only 90% yield. To obtain furfuryl alcohol with purity exceeding 95%, a slight excess of H-donor is required. These results guided our decision to adopt 1.5 equivalents of 2-propanol as the most effective condition. This value provides a balanced compromise between high yield, acceptable reagent excess, and overall material efficiency. Rather than pursuing the marginal improvements in yield offered by 2 equivalents, we identified 1.5 equivalents as a more sustainable and practical choice, aligning well with green chemistry principles and offering a suitable foundation for further scale-up under continuous-flow conditions.

Table 2 Comparison of the key green chemistry metrics in the transfer hydrogenation of furfural under continuous flow, promoted by Shvo's catalyst, with the most effective reaction conditions by varying the amount of 2-PrOH (150 °C, flow rate of 250 μL min^{-1})

1 equiv. of 2-PrOH		1.5 equiv. of 2-PrOH		2 equiv. of 2-PrOH	
					
AE	0.63	AE	0.63	AE	0.63
Yield	0.90	Yield	0.97	Yield	0.99
1/SF	1.00	1/SF	0.84	1/SF	0.72
MRP	0.61	MRP	0.65	MRP	0.68
RME	0.34	RME	0.33	RME	0.31
VMR: 0.73		VMR: 0.72		VMR: 0.70	

The recovery and reuse of catalysts are crucial for enhancing the sustainability and economic feasibility of chemical processes, particularly when working with homogeneous catalysts. Therefore, the reusability of Shvo's catalyst was assessed at 150 °C, 1.5 equivalents of 2-propanol and a flow rate of 250 μL min^{-1} by developing a carefully designed workup protocol to precipitate the catalyst in its active form. After completing the reaction, the flow setup was flushed with 2-MeTHF. Following the distillation of the solvent, the catalyst was precipitated using 2-PrOH, selected as a preferred solvent to ensure complete recovery and preservation of catalytic activity, resulting in a 98% recovered yield. Then, the pure FAL was isolated with a 97% yield by distilling 2-PrOH. The recovered catalyst was reused in 5 consecutive runs under flow without any loss in conversion or selectivity, demonstrating excellent recyclability and efficiency (Fig. S4†). The recovered catalyst was characterised by ^{1}H-NMR, ^{13}C-NMR and FT-IR, confirming its structure was identical to that of the fresh catalyst, further validating its stability and reusability in catalytic processes (Fig. S5–S7†).

This result highlights the notable achievement of successfully recovering and reusing a homogeneous catalyst, Shvo's complex, in a continuous-flow system with a complete recovery and no loss of performance over multiple reaction cycles.

At the same time, to demonstrate the feasibility of a scale-up under flow conditions, the reaction was carried out using 12 mmol and 24 mmol of the reactant at three different temperatures (90 °C, 120 °C, and 150 °C). Excellent conversions were achieved in all cases, with isolated yields of 98% at 150 °C for both 12 mmol and 24 mmol of furfural using 1 mol% of Shvo's catalyst, while maintaining a constant elution volume of 10 mL through the reactor (Fig. 2). Scaling up to 24 mmol allowed for a substantial reduction in the *E*-factor, from 2.0 to 1.1, due to improved material recovery, as reflected by an increase in MRP to 0.92 and RME to 0.48 (Fig. S8;† see ESI† for *E*-factor calculation). Productivity and space–time yield (SPTY) increased markedly under these conditions, with the 24 mmol experiment delivering a tenfold improvement over the small-scale setup, reaching 34.9 mmol h^{-1} and 8730 mmol h^{-1} L^{-1}, respectively. These results clearly highlight the scalability and efficiency advantages of the continuous-flow protocol compared to conventional batch processing (Table S2†).

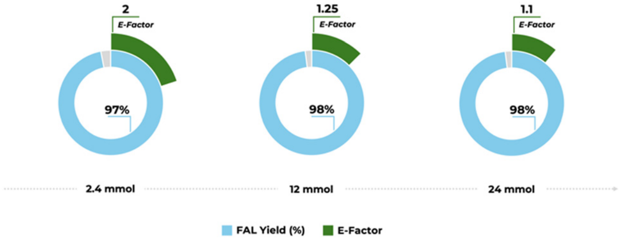


Fig. 2 *E*-Factor assessment for the scaled-up process at 12 mmol and 24 mmol, employing 1.5 equivalents of 2-PrOH, 1 mol% Shvo's catalyst, and 10 mL of reaction mixture, with a flow rate of 250 μL min^{-1}.

Finally, to demonstrate the versatility of the Shvo's catalyst, various biomass-derived molecules were tested under continuous-flow conditions (150 °C, 1.5 equivalents of 2-PrOH, 250 μL min^{-1}). 5-Hydroxymethylfurfural (92%) and benzaldehyde (95%) were converted into their corresponding alcohols in high yields. Cyclohexanone and acetophenone, despite slightly lower conversions of 85% and 58%, respectively, also demonstrated the catalyst's effectiveness. Methyl levulinate was also tested as a substrate for the production of γ-valerolactone (GVL), a key biobased intermediate in modern biorefineries, with a 58% yield. These results highlight the effectiveness of Shvo's catalyst in the reductive upgrading of aldehydes, ketones and esters under flow conditions, further demonstrating its potential for green and sustainable chemical processes.

In conclusion, this communication highlights the efficient catalytic transfer hydrogenation of furfural to furfuryl alcohol under continuous-flow conditions using Shvo's catalyst. The use of bio-based 2-methyltetrahydrofuran (2-MeTHF) as the primary solvent and 2-propanol as the H-donor molecule (1.0–1.5 equivalents) proved critical, ensuring sufficient solubility of all reaction components. Under the best-performing conditions (150 °C, 250 μL min^{-1}, 1.5 equivalents of 2-PrOH), a conversion rate of 97% with 100% selectivity to furfuryl alcohols was achieved, outperforming batch systems in productivity.

The Shvo's catalyst exhibited versatility, enabling the selective hydrogenation of other substrates, including 5-hydroxymethylfurfural and methyl levulinate. Additionally, the catalyst demonstrated exceptional stability, with 98% recovery and reuse over five consecutive cycles, showing no loss in performance. At the same time, the process demonstrated alignment with green chemistry principles, achieving an atom economy of 0.63, a reaction mass efficiency of 0.33 and an *E*-factor of 2, underscoring its sustainability. These results underscore the potential of this continuous-flow system as a scalable, efficient, and sustainable approach for biomass valorisation. Finally, the successful scale-up under continuous-flow conditions, from 12 mmol to 24 mmol of furfural, confirmed the robustness and efficiency of the protocol. Notably, this was achieved without compromising yield or catalyst performance, while significantly improving green metrics and throughput.

Data availability

The data supporting this article have been included as part of the ESI.†

Author contributions

G. B. and M. C. contributed equally. The manuscript was written with contributions from all authors. All authors have approved the final version of the manuscript.

Conflicts of interest

There are no conflicts to declare.

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