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Green valorisation of biowastes – electrochemical "one-pot" reductive amination of furfural on a graphite electrode in water

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A new way of reductive amination of furfural (extracted from ligno-cellulosic biowastes) is presented, using an electrochemical approach, where *in situ* formed imines are directly reduced on a carbon electrode in basic buffers to (furyl)-substituted vicinal diamines identified by NMR spectroscopy. This is a "one-pot" process, avoiding isolation of intermediates, without the use of organic solvents and metal catalysts.

One of the general tasks of today's fundamental research is to decelerate global warming and to utilize renewable sources in order to substitute some petroleum (oil) products. One of these low-cost resources is lignocellulosic bio-waste generated in agriculture. Instead of burning them, their transformation to chemical precursors represents an important trend in chemistry. As a result, this biomass is broadly used as a resource of furfural (FF, **1** in Scheme 1) and its derivatives (*e.g.* 5-hydroxymethylfurfural (HMF) and others).[1–4] This topic is of special interest in Africa.

FF, as a reducible aldehyde derived from furan, is typical for its reactivity with nucleophiles (amines, alcohols, thiols, *etc.*) resulting in important starting materials used in the chemical industry. In organic synthesis, FF can replace precursors originating from crude oil or gas.

One desired product type is various furfurylamines, which are used for the synthesis of bio-plastics and agrochemicals, and mainly for food additives and pharmaceuticals like furosemide, anti-hepatitis B, anti-hypertensives, furtrethonium, *etc.*[5–7] Amination of FF derivatives is therefore a focus of synthetic chemists. The basic mechanism consists of the condensation of FF with a primary amine, resulting in an imine, which can be reduced to an amine. The problem is the

Environmental significance

The described process represents the final part of the valorization of biowastes which are renewable resources of furfural, an important precursor for the chemical industry. Amines derived from furfural are desired starting compounds for the pharmaceutical industry. Up to now, amination of furfural has been realized in organic solvents in the presence of various metal catalysts. The presented work is a first attempt to prove the viability of an alternative, environmentally friendly and low-cost method for reductive amination of furfural. To avoid metal catalysts and organic solvents, an electrochemical approach at room temperature in buffered aqueous solution was used with a graphite rod as the working electrode and a magnesium rod as an auxiliary sacrificial electrode. In addition to this, such electrolysis enables a "one-pot" process without any isolation of intermediates.

instability of the imine intermediate. Therefore, aprotic organic solvents are generally used, preventing the hydrolysis of imines.

As for the reduction of imines to amines in organic aprotic solvents, the traditional and often used methods include the use of various metal hydrides,[8,9] complexes[10] or specialized catalysts based on heavy metals.[11–14] Nevertheless, these
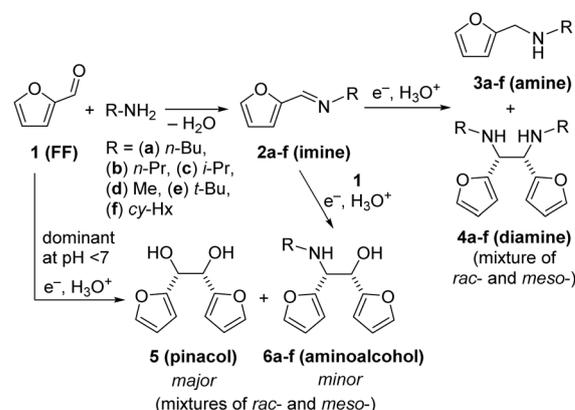
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Scheme 1 Expected reaction pathway of the electroreductive amination of FF.

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procedures are costly and harmful to the environment. The only process for the reduction of imines in aqueous solution is based on the use of zinc powder.[15]

This project aims to explore an alternative method for reductive amination, which would be cheap and viable at room temperature, without the use of heavy metals and organic solvents, and without isolation of intermediates. The electrosynthetic approach was selected because imines are generally more easily reduced than their parent aldehydes, which is a crucial condition for the application of electrochemistry.

Generally, electrochemical reduction of aldehydes results in two types of products: two-electron reduction to alcohols (at lower pH) and a one-electron process yielding the coupling product - pinacol.[16] Because imines formally belong to carbonyl compounds, two analogous reduction products are expected.

In the published literature, Roylance and Choi[17] reported the electrochemical reductive amination of HMF with only aqueous CH_3NH_2 buffer solution and several metal electrodes, which resulted in the selective formation of the corresponding furfurylamine.

Our strategy is to perform condensation of FF (and later HMF) with various primary aliphatic and alicyclic amines in basic aqueous buffers as solvents that stabilize imines. A phosphate buffer-based electrolyte was used (avoiding amine ones) to allow independent and stoichiometric study of reactions with various types of amines. The reaction mixture was then electrolysed selectively at the reduction potential of imine (which is less negative than that of FF) without isolation of the intermediate imine. The continuous selective consumption of imines should shift the reaction equilibria (condensation as well as imine hydrolysis) in favour of imines, thus increasing the total yield of electroreductive amination.

In a previous study,[18] we tested the suitable conditions for condensation of FF and HMF with five primary amines and two diamines and evaluated the electrochemical properties of the expected substances present in the mixture to monitor the progress of condensation and to evaluate the degree of conversion related to pH, stoichiometry and the type of amine. While the reduction of FF and HMF at a mercury electrode occurs around -1.4 V *vs.* SCE at pH 11, the reduction potentials of all formed imines are at least 200 mV less negative, enabling their selective reduction. After the condensation reaction, various types of imines were identified by NMR.[18] Finally, electrolysis of a mixture of FF and *n*-propylamine was performed at a mercury pool electrode. According to expectation based on analogy with the literature, the cathodic electrolysis results in a mixture of the amine **3** and the coupling product **4** (Scheme 1).

Encouraged by the previous positive results, this pilot study focuses on replacing the mercury electrode with a cheaper and more environmentally friendly graphite-carbon rod, performing reductive amination with a wider range of amines and identifying optimal conditions (pH, potential, duration) of the electrosynthetic process (including identification of products and their proportions). The aim is to present a generally applicable, one-pot, truly green electroreductive amination process based on the initial condensation of FF and an amine, where the organic solvents are replaced by aqueous buffers and

the reduction occurs electrochemically at a carbon electrode, under mild conditions, without catalysts and without isolation of imine intermediates.

As a follow-up to the previous study, six primary amines (methylamine, *n*-propylamine, *n*-butylamine, isopropylamine, cyclohexylamine and *tert*-butylamine) – all from commercial resources, used as received – underwent condensation with FF (procured from Sigma-Aldrich) and immediate subsequent electrolysis under various pH, various potentials and various durations of the electrolysis. The composition of the final reaction mixture was analyzed by ^1H NMR at room temperature in $CDCl_3$ with a Bruker Avance NEO 500 spectrometer.

The voltammetric experiments were performed at a GC disc electrode, $\varnothing$ 3 mm, either rotating (1000 rpm, 0.01 V s^{-1} for RDV) or stationary (200 mV s^{-1} for CV) in a three-electrode setup with a saturated calomel electrode (SCE) as the reference electrode and a platinum foil as the auxiliary one. An Autolab potentiostat PGSTAT101 (Metrohm, Switzerland) was driven by Nova 1.11 software. Argon was used to remove oxygen from the studied solutions prepared from 10 mL of phosphate buffer. Sample concentrations were 1×10^{-3} mol per L FF and 1.5×10^{-3} mol per L amine (*i.e.* FF : amine ratio of 1 : 1.5) at pH 11.

The preparative electrolysis was carried out potentiostatically (Autolab PGSTAT204, Nova 1.11 software) in the same setup using an undivided electrochemical cell. A graphite-carbon rod, $\varnothing$ 1 cm, immersed 2 cm in the solution (surface area approx. 6 cm^2) was used as the working electrode, and a magnesium rod of similar size served as a sacrificial anode. For preparative electrolyses, FF was dissolved in 10 mL of 0.1 M phosphate buffer (pH 6–11), deaerated, and, after addition of the required amount of amine, the reaction mixture was stirred for 10 min at room temperature to complete the condensation reaction. The initial concentration of FF was always 4×10^{-2} M, and the amount of amine varied between 4.4 and 20×10^{-2} M (FF : amine ratio from 1 : 1.1 to 1 : 5.5). Then, the reaction mixture was electrolyzed for one or three hours.

After reductive electrolysis, the aqueous mixture was collected from the electrochemical cell, and the cell and electrodes were carefully washed with dichloromethane (DCM). The water/DCM solution was extracted with 3×3 mL of DCM, the extract dried with anhydrous $MgSO_4$, and solvents were removed under reduced pressure to obtain an amber oil. A loss of mass (typically 20–25% *vs.* starting materials) during electrolysis and the following work-up was systematically observed. The products and their distributions in the extracted material were determined by NMR.

To verify the use of the carbon electrode for the same purpose, voltammetry at a GC-RDE as well as at the carbon rod used for electrolysis confirmed the same *i vs. E* pattern as for mercury: even here, imines are reduced about 200 mV less negatively than FF itself; hence, there is also a potential range of approx. 200 mV for preferential reduction of imines. In any case, the reduction potentials on carbon electrodes are slightly shifted to more negative values in comparison with mercury at the same pH. For determination of fundamental conditions and reaction relationships, *n*-BuNH$_2$ was used.
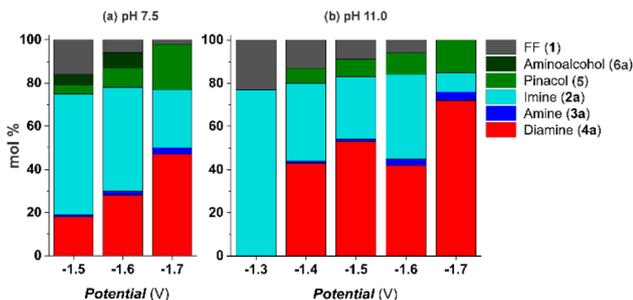
Fig. 1 Influence of the working potential on the product distribution in DCM extract after electrolyses at pH 7.5 (a) and 11.0 (b). Graphite rod working electrode, Mg sacrificial auxiliary electrode, SCE, FF : n-BuNH$_2$ = 1 : 1.1, 0.1 M phosphate buffer-based electrolyte, pH 11, electrolysis for 3 h.
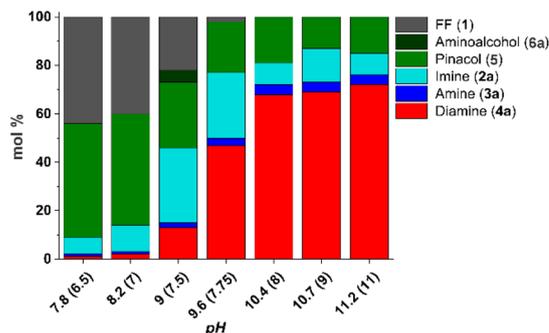

Fig. 2 Composition of products in DCM extract after electrolyses – pH dependence. Graphite rod working electrode, Mg sacrificial auxiliary electrode, FF : n-BuNH$_2$ = 1 : 1.1, phosphate electrolyte, measured data pH 6.5–11 (pH of original electrolyte used in parentheses), −1.7 V (SCE), 3 h of electrolysis.

The influence of the working potential on the product distribution was tested for a slight excess of the amine (FF : n-BuNH$_2$ of 1 : 1.1) at two pH values: 7.5 and 11. Nevertheless, the results did not differ much (Fig. 1). At a potential of −1.3 V, zero current was observed, no reduction occurred, and only starting FF **1** and condensation product, imine **2a**, were detected. Starting from a potential of −1.4 V, an increasing amount of reduction products of imine is found, where the coupling product diamine **4a** (pinacol analogue) strongly dominates over the amine **3a**. It is evident that using a graphite electrode, the potential of electrolysis does not influence the selectivity of reductive amination (diamine **4a** vs. amine **3a**).

Because the parent FF itself is reduced approx. 200 mV more negatively than the imine intermediate, at more negative potentials, direct electrolysis of FF as a side reaction occurs; therefore, pinacol **5** and aminoalcohol **6a** appear also among the products (Fig. 1). The most abundant diamine coupling product **4a** (72%) and also the highest amount of amine **3a** were obtained at a potential of −1.7 V, which was used for further experiments.

Selection of this working potential also has another aspect: in the case of a carbon rod electrode being used for preparative electrolysis, its shape and larger surface together with the real geometry of electrodes in the cell do not ensure the precise setting of the applied working potential all around the electrode surface. Consequently, a part of the surface will be at the applied potential, but the rest will be at a less negative potential. Therefore, for effective electrolysis, the potential should be set slightly more negative, at −1.7 V, based on the GC-RDE data. However, at this potential, a portion of the starting FF will be directly reduced to pinacol, which was also found in the solution after electrolysis (Fig. 1).

The pH dependence was investigated in 0.1 M phosphate buffers in the pH range 6.5–11. The data obtained are shown in Fig. 2, where on the pH axis, the value of the actual pH measured during/after electrolysis (higher value) is presented first, and the pH of the buffer used for the condensation reaction is shown in parentheses. The highest proportion of the coupling product **4a** (72%) was found at pH 11, the mixture also containing unreacted imine **2a** (9%) and pinacol **5** (15%), but

only a small amount of the amine **3a** (4%). Formation of aminoalcohol **6a** was also observed at slightly basic pH, as a coupling product of FF with imine **2a**. Generally, the content of the coupling product diamine **4a** increased with increasing pH, with at least 70% of **4a** being achieved starting from pH 8. At lower pH, direct reduction of the parent FF to pinacol **5** dominates, which is in agreement with the fact that the reduction potential was set to −1.7 V, when not only imine, but also FF itself is reduced.

To test the developed method, electroreduction of imines **2a–f**, products of condensation of FF with six different amines (MeHN$_2$, n-PrNH$_2$, i-PrNH$_2$, n-BuNH$_2$, t-BuNH$_2$, cy-HxNH$_2$), was carried out in phosphate buffer (pH 11), with a potential of −1.7 V, FF : amine ratio of 1 : 1.1, Mg rod as auxiliary electrode, undivided cell and 3-hour electrolysis. The results show that the product distribution differs for different amines. As the desired products were amines **3** and diamines **4**, Fig. 3 shows that the amines are ordered according to their efficiency in forming the respective target compounds. Because of the relatively negative working potential (−1.7 V), when direct pinacolization occurs simultaneously with the imine reduction, the differences in product proportions reflect different rates of the above-
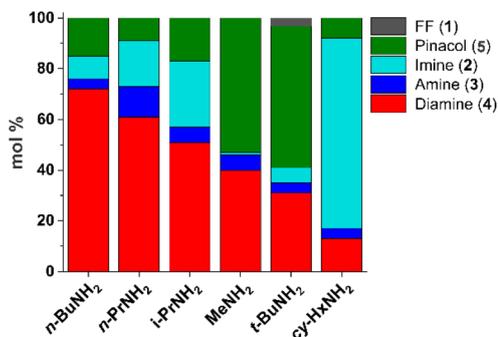

Fig. 3 Product distribution in DCM extract for electroreductive amination of FF using different amines. Graphite rod working electrode, Mg sacrificial auxiliary electrode, SCE, phosphate buffer-based electrolyte (pH 11), FF : amine = 1 : 1.1, −1.7 V, electrolysis for 3 h.

mentioned concurrent reactions, which are influenced by the type/structure of amines.

It is evident that the selectivity and efficiency are influenced by many factors, which are difficult to decipher. In our previous contribution dealing with condensation reactions,[18] we used the same series of amines as that used in the present case. We found that the reduction potential of the formed imines was always nearly the same (around -1.2 V $vs.$ SCE); thus, the observed differences in product yield cannot be caused by the reduction potential of imines. Notably, we repeatedly demonstrated that the equilibrium ratio of formed imine to the starting compounds differed substantially. These differences definitely do not correlate with pK_a (values of which within the amine series are very similar – all around 10.60). Most probably, the degree of conversion is influenced (a) by the shape (bulkiness) of the amine; (b) by the effect of different solubility of formed neutral imines 2 in water (at basic pH) and also solubility of the generated coupled diamine. This can be seen for cy-HxNH$_2$, where the initial imine condensation proceeded smoothly, while the subsequent reduction was much slower, which is reflected by the large amount of remaining unreacted imine 2f.

In the case of 4a, which was obtained in the highest amount of all the diamine products, we demonstrated the possibility to isolate this compound from the reaction mixture as a mixture of rac- and $meso$-diastereomers in a ratio of 1.1 : 1 in 56% yield (see Section 2 of the SI for experimental details).

To summarize, an alternative, environmentally friendly method for reductive amination of FF was designed using an electrochemical approach under mild conditions in a buffered aqueous solution. A graphite rod was used as a working electrode and a magnesium rod as an auxiliary sacrificial electrode for the electrolysis. The Mg sacrificial anode is generally used as an auxiliary electrode that is inert towards organic substrates and often precipitates as an insoluble salt or hydroxide. During our electrolysis, precipitation was noted, but after replacing Mg with a Pt sheet, only a negligible impact on pH and no impact on the percentage of formed diamines were observed. In this way, metal catalysts, noble metals and organic solvents were avoided, the process being designed as a "one-pot" type without any isolation of intermediates. For amination, five aliphatic and one alicyclic amine were successfully used. The model compound n-BuNH$_2$ was chosen for the tests of the experimental conditions and exhibited the highest yield of the diamine product. Conversely, the second expected main products, amines 3, were obtained only in very small yields. It appeared that at the graphite electrode, the electrolysis is selective toward diamines 4 while the other expected products, amines 3, are obtained only negligibly. For a more selective preparation of furylamines, a different electrode material should be used, which is the focus of the next investigation.

The presented communication proves the viability of the "one-pot" reductive amination of FF in aqueous solutions with the aim of cheaper and environmentally friendly valorization of FF derivatives obtained from biowastes. The optimization of processes, how to increase the amount of furfurylamines 3, involvement of other types of primary (di)amines and

amination of other derivatives of FF (HMF and others) are tasks for ongoing research. As for potential industrial scalability, an alternative anode should be found, $e.g.$ cheaper Al, which is also being used as a sacrificial anode.

Author contributions

JDD – concept, experiments, writing; LK – experiments, visualization, data analysis; ML – isolation and NMR identification of products; JL – concept, writing, editing. All authors have read and agreed to the published version of the manuscript.

Conflicts of interest

There are no conflicts to declare.

Data availability

Primary data are handled in agreement with the RDM policy of the J. Heyrovsky Institute (https://www.jh-inst.cas.cz/structure/heyrovskyopen-science-team) to comply with the principle "as open as possible, as closed as necessary" and defines all data management procedures in line with national and European law. HeyRACK (https://data.narodni-repozitar.cz/heyrovsky/datasets/all/), the institutional research data repository, will be used for short- and medium-term data storage and sharing.

Supplementary information (SI) is available. See DOI: https://doi.org/10.1039/d5va00335k.

Acknowledgements

References

1 Y. Shao, Y. Ding, J. Dai, Y. Long and Z. T. Hu, $Green\ Synth.$ $Catal.$, 2021, 2, 187–197.

2 A. Pundir, M. S. Thakur, S. Prakash, N. Kumari, N. Sharma, Z. He, S. Nam, S. Dhumal, K. Sharma, S. Saxena, S. Kumar, S. V. Deshmukh and M. Kumar, $Heliyon$, 2024, 10, e35077.

3 S. Muryanto, F. C. Handita, A. F. Perdana-Harahap, M. Sahlan, H. Hermansyah, M. A. Darmawan, H. Saputra, S. D. Sumbogo-Murti, D. T. Hartanto, A. T. Yuliansyah, M. D. Putra, A. Mirwan, P. Cognet, M. K. Aroua and M. Gozan, $S.\ Afr.\ J.\ Chem.\ Eng.$, 2024, 50, 466.

4 D. Edumujeze, M. C. Fournier-Salaün and S. Leveneur, $Fuel$, 2025, 381, 133423.

5 J. A. T. Caetano and A. C. Fernandes, $Green\ Chem.$, 2018, 20, 2494.

6 A. L. Nuzhdin, M. V. Bukhtiyarova and V. I. Bukhtiyarov, $Molecules$, 2020, 25, 4771.

7 J. He, L. Chen, S. Liu, K. Song, S. Yang and A. Riisager, *Green Chem.*, 2020, **22**, 6714.

8 I. Shibata, T. Moriuchi-Kawakami, D. Tanizawa, T. Suwa, E. Sugiyama, H. Matsuda and A. Baba, *J. Org. Chem.*, 1998, **63**, 383.

9 M. Minato, Y. Fujiwara and T. Ito, *Chem. Lett.*, 1995, **24**, 647.

10 E. Mizushima, M. Yamaguchi and T. Yamagishi, *Chem. Lett.*, 1997, **26**, 237.

11 M. Freifelder, in *Catalytic Hydrogenation in Organic Synthesis Procedures and Commentary*, John Wiley and Sons, Inc., New York, 1978, pp. 65–77.

12 S. Chen, R. Wojcieszak, F. Dumeignil, E. Marceau and S. Royer, *Chem. Rev.*, 2018, **118**, 11023.

13 Y. Wei, Z. Sun, Q. Li, D. Wu, J. Wang, Y. Zhang, C. C. Xu and R. Nie, *Fuel*, 2024, **369**, 131703.

14 X. Du, C. Gao, C. G. C. Jiaxin-Huang, Y. Cui, S. Liu and C. Wang, *ACS Catal.*, 2025, **15**, 4654.

15 T. Tsukinoki, Y. Mitoma, S. Nagashima, T. Kaaji, I. Hashimoto and M. Tashiro, *Tetrahedron Lett.*, 1998, **39**, 8873.

16 J. Ludvík, Reduction of aldehydes, ketones and azomethins, in *Organic Electrochemistry*, ed. O. Hammerich and B. Speiser, CRC Press (Taylor & Francis group), 5th edn, 2016, ch. 31, and references therein.

17 J. J. Roylance and K. S. Choi, *Green Chem.*, 2016, **18**, 5412.

18 J. Donkeng-Dazie, L. Koláčná, M. Lamač, J. Urban, A. Liška, L. Šimková and J. Ludvík, *J. Electroanal. Chem.*, 2024, **966**, 118375A.

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