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Environmental Significance Statement

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

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COMMUNICATION

Green Valorisation of Bio-wastes – Electrochemical "One-pot" Reductive Amination of Furfural on Graphite Electrode in Water

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Abstract **New way of reductive amination of furfural (extracted from lignocellulosic bio-wastes) is presented, using electrochemical approach, where in situ formed imines are directly reduced on carbon electrode in basic buffers to (furyl)-substituted vicinal diamines identified by NMR spectroscopy. "One-pot" process, avoiding isolation of intermediates, without organic solvents and metal catalysts.**

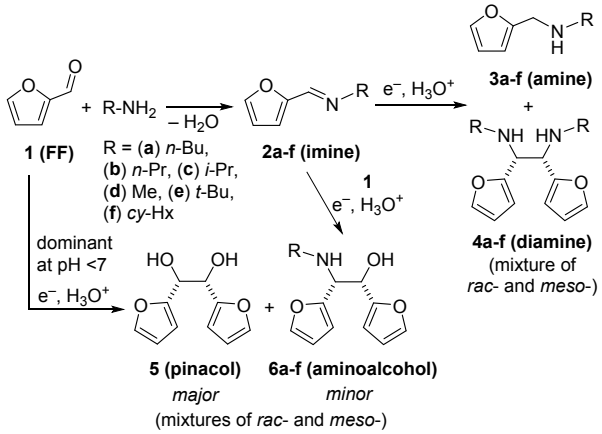
One of the general tasks of the today fundamental research is to decelerate the global warming and to utilize renewable sources in order to substitute some petroleum (oil) products. One of these cheap resources are lignocellulosic bio-wastes generated in agriculture. Instead of their burning, their transformation 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-hydroxymethyl furfural (HMF) and others) [1-4]. This topic is of special interest namely in Africa.

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

One of the desired type of products are various furfurylamines used for synthesis of bio-plastics, agrochemicals, but mainly for food additives and pharmaceuticals like furosemide, anti-hepatitis B, anti-hypertensives, furtrethonium, etc [5-7]. Amination of furfural derivatives is therefore in the focus of synthetic chemists. The basic mechanism consists in condensation of FF with a primary amine resulting in an imine which could be reduced to an amine. The problem is 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 procedures are costly and harmful to the environment. The only process of reduction of imines in aqueous solution is based on the use of zinc powder [15].

The aim of this project is to look for an alternative way (method) of reductive amination, which would be cheap and viable at room temperature, without presence 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 application of electrochemistry.



Scheme 1 Expected reaction pathway of the electroreductive amination of FF.

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

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In the published literature, only 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 obtaining 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 stabilizing imines. Phosphate buffer-based electrolyte was used (avoiding amine ones) to be able to study independently (and stoichiometrically) 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 intermediate imine. The continuous selective consumption of imines should shift the reaction equilibria (condensation as well as imine hydrolysis) in favour of imines increasing thus the total yield of electroreductive amination.

In the previous paper [18] we tested the suitable conditions for condensation of FF and HMF with five primary amines and two diamines and checked the electrochemical properties of the expected substances present in the mixture in order 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 mercury electrode occurs around -1,4V vs. SCE in pH 11, the reduction of all formed imines is at least by 200 mV less negative enabling their selective reduction. After condensation reaction various types of imines were identified by NMR [18]. Finally, a testing electrolysis of the mixture FF and *n*-propylamine was performed at mercury pool electrode. According to expectation based on analogy in the literature, the cathodic electrolysis results in a mixture of the amine **3** and the coupling product **4** – see Scheme 1.

Encouraged by the previous positive results, in this pilot study the attention is focused to replacement of mercury electrode by cheaper and more environmentally friendly graphite-carbon rod, to perform reductive amination with more types of amines and to the search for optimal conditions (pH, potential, duration) of the electrosynthetic process (including identification of products and their proportions). The aim is to present generally applicable one-pot truly green electroreductive amination process based on the precedent condensation of FF and an amine, where the organic solvents are replaced by aqueous buffers and the reduction occurs electrochemically at 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 (supplied by Aldrich Company) and immediate subsequent electrolysis under various pH, various potential and various duration of the electrolysis. The composition of the final reaction mixture was analyzed by ^{1}H NMR at room temperature in $CDCl_3$ with a Bruker Avance NEO 500 spectrometer.

The checking voltammetric experiments were performed at GC- disc electrode ∅ 3mm, 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 saturated calomel electrode (SCE) as reference electrode and a platinum foil as the auxiliary one. 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.L^{-1} FF and, 1.5×10^{-3} mol.L^{-1}amine, i.e. FF:amine ratio 1:1.5), in pH 11.

The preparative electrolysis was carried out potentiostatically (Autolab PGSTAT204, Nova 1.11 software) in the same setup using undivided electrochemical cell. A graphite-carbon rod ∅ 1cm, immersed 2 cm in the solution (surface area approx. 6 cm^2) was used as the working electrode and a magnesium rod of the similar size served as a sacrificial anode. For preparative electrolyses, furfural was dissolved in 10 mL of the 0.1 M phosphate buffer (pH 6-11), deaerated and after addition of the due 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, the amount of amine varied between 4.4–20 $\times10^{-2}$ 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 carbon electrode for the same purpose, voltammetry at GC-RDE as well as at the carbon rod used for electrolysis confirmed the same ***i*** vs. ***E*** pattern like on 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.

The influence of the working potential on the product distribution was tested for slight excess of the amine (FF : *n*-$BuNH_2$ 1 : 1.1) at two pH: 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 took place, only starting FF **1** and condensation product, imine **2a**, was detected. Starting

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from potential of -1.4 V, increasing amount of reduction products of imine is found, where coupling product, diamine **4a** (analogy to pinacol) strongly dominates over the amine **3a**. It is evident that using graphite electrode, potential of electrolysis has no influence on selectivity of reductive amination (diamine **4a** vs. amine **3a**).

Because the parent FF itself is reduced by appr. 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** appears also among 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.

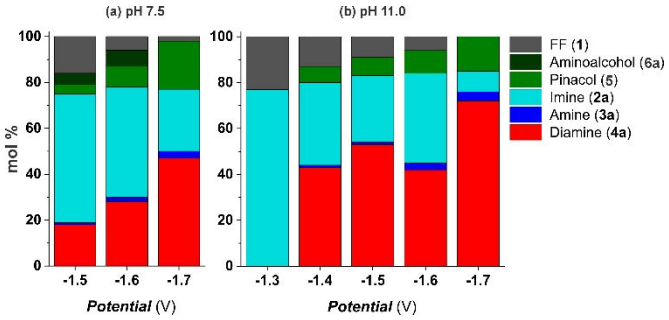

Figure 1. Influence of the working potential on the product distribution in the DCM extract after electrolyses at pH 7.5 (a) and 11.0 (b). Graphite rod working electrode, Mg-sacrificial auxiliary electrode, SCE, FF:*n*-$BuNH_2$ 1:1.1; 0.1M phosphate buffer-based electrolyte, pH 11, electrolysis 3 h.

Selection of this working potential has also another aspect: In case of carbon rod electrode for preparative electrolysis, its shape and larger surface together with the real geometry of electrodes in the cell does not ensure the precise setting of the applied working potential all around the electrode surface. Consequently, a part of the surface will have the applied potential, but the rest will have its potential less negative. Therefore, for effective electrolysis the potential should be set (in relation to the GC-RDE data) a bit more negatively (to -1.7V). However, at this potential part 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 demonstrated 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, in brackets is pH of the buffer used for the condensation reaction. The highest proportion of the coupling product **4a** (72 %) was found at pH 11, the mixture also contained unreacted imine **2a** (9 %) and pinacol **5** (15 %) but only small amount of the amine **3a** (4 %). Formation of aminoalcohol **6a** was also detected 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, at least 70 % of **4a** was 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.

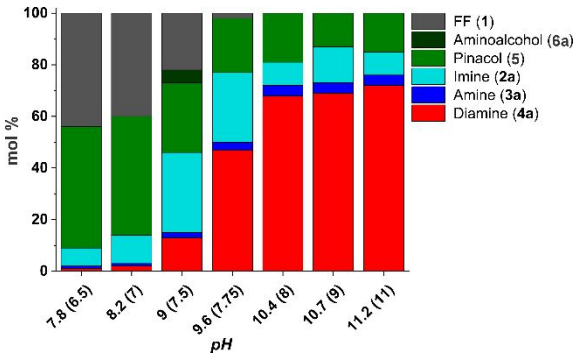

Figure 2. Composition of products in the DCM extract after electrolyses – pH dependence. Graphite rod working electrode, Mg-sacrificial auxiliary electrode, FF:*n*-$BuNH_2$ 1:1.1; phosphate electrolyte, measured data pH 6.5–11 (in brackets - pH of original electrolyte used), -1.7 V (SCE), 3 h of electrolysis.

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, potential -1.7 V, FF : amine ratio 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. Since the desired products were amines **3** and diamine **4,** in **Fig. 3** the amines are ordered according to their efficiency to form the respective target compounds – amines **3** and diamines **4.** Because of the relatively negative working potential (-1.7V) when direct pinacolization occurs simultaneously with the imine reduction, the differences in product proportions reflect different rates of the above mentioned concurrent reactions which are influenced by the type/structure of amines.

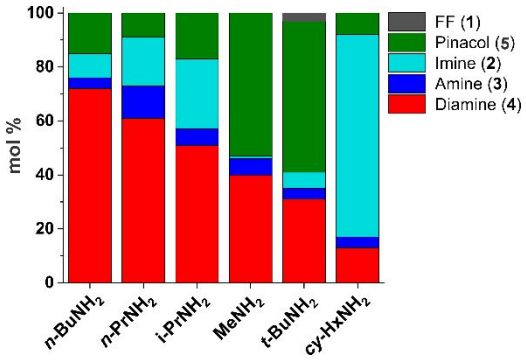

Figure 3. Product distribution in the DCM extract for electroreductive amination of FF using different amines. Graphite rod working electrode, Mg-sacrificial auxiliary electrode, SCE, phosphate buffer-based electrolyte pH 11, FF : amine 1 : 1.1, -1.7 V, electrolysis 3 h.

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It is evident that the selectivity and efficiency is influenced by many factors which is difficult to decipher. In our previous contribution dealing with condensation reaction [18], we used the same series of amines like in this manuscript. We found that the reduction potential of the formed imines was always nearly the same (around -1.2V vs. SCE), thus the observed differences in product yield cannot be caused by reduction potential of imines. On the other hand, we several times proved, that the equilibrium proportion of formed imine vs. starting compounds differed substantially. These differences definitely do not correlate with pKa (which are within the amine series 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 the 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 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 electrochemical approach at mild conditions in buffered aqueous solution. Graphite rod was used as working electrode, and magnesium rod as an auxiliary sacrificial electrode for the electrolysis. The Mg sacrificial anode is generally used as an auxiliary electrode inert towards organic substrates and often precipitating as an insoluble salt or hydroxide. During our electrolysis a precipitation was noted, but after replacing Mg by a Pt sheet, only negligible impact on pH and no impact on the percentage of formed diamines was observed. In this way metal catalysts, noble metals and organic solvents were avoided, the process was designed as a "one-pot" type without any isolation of intermediates. For amination five aliphatic and one alicyclic amines were successfully used. The model compound *n*-BuNH$_2$ was chosen for the tests of the experimental conditions and exhibited highest yield of the diamine product. On the other hand, 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 product, amines **3**, is obtained only negligibly. To prepare more selectively furyl amines, different electrode material should be used – theme of the next investigation.

The presented communication proves viability of the "one-pot" reductive amination of furfural in aqueous solutions with the aim of cheaper and environmentally friendly valorization of furfural derivatives obtained from biowastes. The optimization of processes, the way, how to increase the amount of the furfurylamines **3,** involvement of other types of primary (di)amines and amination of other derivatives of furfural (HMF and others) is the task for ongoing research. As for potential industrial scalability, alternative anode should be found, e.g. cheaper Al which is also being used as 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.

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Data availability statement

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