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A Diamine-Oriented Biorefinery Concept Using Ammonia and Raney Ni as a Multifaceted Catalyst

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Supporting Information
available online

Diamines are important industrial chemicals. In this paper we outline the feasibility of lignocellulose as a source of diol-containing molecules. We also illustrate the possibility of turning these diols into their diamines in good to excellent yields. Central to these transformations is the use of commercially available Raney Ni. For diol formation, the Raney Ni engages in hydrogenation and often also demethoxylation, that way funneling multiple components to one single molecule. For diamine formation, Raney Ni catalyzes hydrogen-borrowing mediated diamination in the presence of NH₃.

Keywords: Amine, Catalysis, Cellulose, Lignin

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1 Introduction

Primary diamines hold vast industrial importance as prime building blocks for the polymer and pharmaceutical industry [1–4]. More specifically, they are widely used as monomers for the synthesis of amides (e.g., Nylon) [5, 6], polyurethanes [7–9], polyimides [10, 11], or as crosslinkers, curing agents, and hardeners in the synthesis of epoxy resins [12, 13], and polybenzoxazines [14, 15]. Following suitable reductive alkylation, diamines can also serve as valuable intermediates for the pharmaceutical industry [16], switchable solvents [17], and as precursors to (hetero)gemini surfactants [18].

Various methods have been described to the formation of primary amines, many of which are in principle also applicable to the synthesis of diamines. Commonly industrial processes to the manufacturing of primary amines follow a) N-introduction via -CN or -NO₂ groups, followed by hydrogenation [19, 20], b) reductive amination starting from ketones/aldehydes [21], c) alkene hydroformylation followed by amination and hydrogenation [22], d) direct alkene amination [21], e) Buchwald-Hartwig amination with aryl halides (Fig. 1A). With most synthetic amination methodologies involving petroleum-derived substrates, and featuring multistep synthetic routes, a high demand exists for the development of efficient catalytic methodologies that use renewable resources [23–27]. Due to the abundant presence of hydroxy groups in biomass-derived compounds, catalytic amination by the hydrogen-borrowing (HB) methodology offers a great way to the introduction of nitrogen. More specifically, the HB amination methodology com-

prises the dehydrogenation of an alcohol functionality, followed by intermediate imine formation, and final imine hydrogenation towards the target amines [28–30]. Notably, primary amines are obtained when ammonia is used as a coupling partner to the alcohols, this transformation being particularly challenging as outlined below [31–33]. Key benefits to the HB amination methodology are the non-requirement of pressurized H₂ gas and the fact that water is the only by-product (Fig. 1B). Over recent years the HB amination field has seen significant progression with the development of a range of homogeneous [28] and heterogeneous [29] catalytic systems. Notable examples to the heterogeneous catalytic amination of alcohols to primary amines via HB are: Ni/ θ -Al₂O₃ (or Ni/ γ -Al₂O₃) [34], Ni/Al₂O₃-SiO₂ [35], Ni/CaSiO₃ [36], Raney Ni [37], NiAl/HT [38], Pd/CeO₂ [39], and PtCo/CeO₂ [40].

A major challenge to HB-mediated amination with ammonia is the undesired formation of secondary and tertiary amines, suppression of which typically requires higher ammonia excesses [37]. In the gas phase this equals to the use of very high ammonia pressures (>300 bar), therewith explaining its current industrial redundancy [41]. Catalyst

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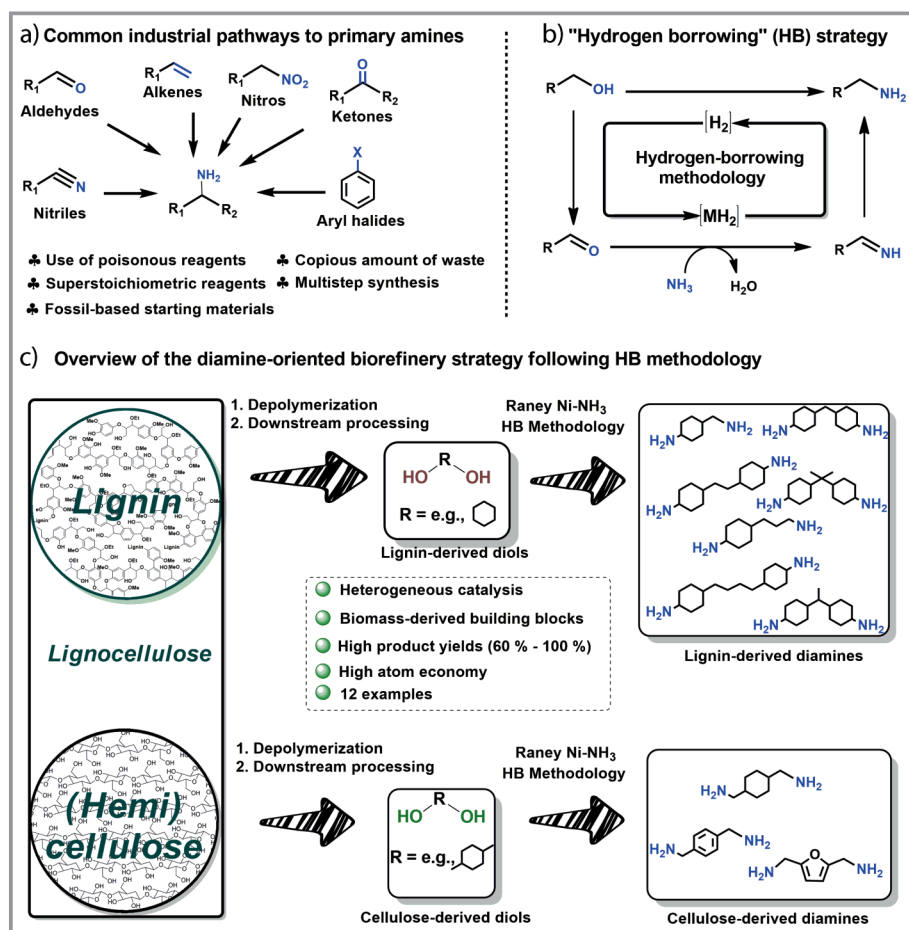


Figure 1. Overview of the "diamine-oriented biorefinery" concept. A) Common industrial pathways to primary amines; B) general reaction mechanism of the HB strategy for the conversion of diols to diamines; C) general overview of a comprehensive downstream catalytic processing methodology converting lignocellulose-derived diols to diamines.

deactivation has also been observed and this especially with non-noble metal catalysts [42]. For example, it was found that NH_3 preferably reacts with Ni to form catalytically inactive Ni_3N for the reductive amination of phenol to cyclohexylamine [42]. It is equally noteworthy that HB amination of (primary) diols tends to lead to incomplete amination (i.e., a mixture of amino alcohols) thus posing severe separation challenges [43,44].

Irrespective the exact amination mechanism, a limited number of heterogeneous catalytic procedures for diol-diamination have been reported. Moreover, these concern quasi always single substrates and almost all developed methodologies employ a positive H_2 pressure as to suppress undesired dehydrogenation. Exemplary heterogeneous catalytic systems to the diol-to-diamine transformation are:

- The Ru/MgO- TiO_2 catalyzed amination of 2,5-bis(hydroxymethyl)furan into 2,5-bis(aminomethyl)-furan in 86 % yield through an HB strategy [45].
- The conversion of isomannide to a mixture of mono- and diamines using Ru/C in respectively 40 and 10 % yield using more than 10 bar of H_2 [41]. Through this

methodology biogenic diols (e.g., isosorbide, isomannide) were generally observed to form predominately amino alcohols over diamines, which was attributed to the preferential adsorption of formed diamines on the active sites, therewith blocking these [41].

- The catalytic amination of 1,3-propanediol to 1,3-propanediamine in supercritical NH_3 using a CoFe alloy in 32.2 % yield, in the presence of a small amount of H_2 [46].
- The direct amination of 1,4-butanediol over a Cu, Ni, Ti, Zr, Sn, Co, Mn/zeolite catalyst to afford 1,4-butane-diamine in 70 % yield using an NH_3/H_2 mixture with a respective 3:1 ratio [47, 48].
- The Raney Ni catalyzed diamination of benzenedimethanols to xylylene-diamines (para yield: 63 %; meta yield: 50 %), as reported by our group [37]. This methodology was recently extended to the quantitative conversion of 4,4-methylene-biscyclohexanol into its corresponding diamine [44].

In this paper we present a range of strategies for the development of a potential diamine-oriented biorefinery, thereby considering various cutting-edge lignin depolymerization strategies as well as the valorization of the cellulose platform. Naturally, the proposed strategies could in the future be combined with other established biorefinery schemes that may already focus on different product classes such as biofuels or materials. In our current discussion, neither routes to fuels nor the manufacturing of complex specialty chemicals were considered, but rather, full focus was devoted to the synthesis of diamines. To this purpose this paper first highlights potential routes towards suitable diols from key lignin and cellulose-derived platform chemicals focusing on the use of Raney Ni as an industrially relevant catalyst, and this in line with two previous topical papers by our group [37, 44]. Interestingly, especially for the lignin platform, Raney Ni is responsible for key hydrogenation and demethoxylation steps to afford a single diol, even from more complex bio-oil mixtures. This builds further on a topical diamination paper recently published by our group [37]. The current paper exemplifies the broad applicability of this methodology, and the high achievable

isolated diamine yields over a wide range of compounds (Fig. 1C).

2 Results and Discussion

2.1 Catalytic Strategies to Access Well-Defined Lignin-Derived Diols

Due to the parent monolignols from which lignin biosynthesis occurs, guaiacyl (G) and syringyl (S) units are the dominant structural moieties in lignin and this consequently also in the platform chemicals obtained by various depolymerization methods. These structures feature neighboring aromatic alcohol and methoxy groups and offer vast potential for the transformation into (aliphatic) alcohols. This is not only achievable by the creation of 1,2-diol motifs following demethylation/(hydrogenation) of guaiacyl units [49,50] but also by consecutive demethoxylation and hydrogenation of G- and S-containing aromatic moieties into their corresponding aliphatic alcohols [51]. In line with previous investigations by our group, the use of such tandem defunctionalization/hydrogenation steps is one of the main foci of this paper.

Key aspects to consider when aiming for efficient catalytic conversion strategies from lignin to diols are: 1) the lignin depolymerization method; 2) the structural nature and reactivity of the lignin-derived platform chemicals and 3) suitable downstream processing strategies. Herein we detail a range of specific strategies (Strategy 1–5), taking our own findings, and the ones of other groups, as suitable starting points. Reductive catalytic fractionation (RCF) is a central method for the efficient conversion of native lignin into aromatic platform chemicals. RCF typically entails the use of H₂ or an (in)organic H-donor and a heterogeneous transition metal catalyst, which is introduced during the fractionation process. The process conditions, type of lignocellulose and type of catalyst have significant impact on the product outcome. For example, when Cu₂OPMO is used for RCF of lignocellulosic biomass, monomeric dihydroconyferyl alcohol (1G) and/or dihydrosynapyl alcohol (1S) are obtained as the main products [52]. Conversely, the use of noble metals, and this typically at higher operational temperatures (≥ 250 °C), results in the formation of 4-propyl guaiacol/syringol [53]. Accordingly, several specific strategies can be developed for obtaining diols based on the RCF methodology (Strategy 1–4):

Strategy 1: Cu₂OPMO-created 1G and 1S can be subjected to demethoxylation and hydrogenation to yield diol L-1 over Raney Ni catalyst at 150 °C (Fig. 2). This procedure is particularly interesting as it concerns funneling catalysis whereby both guaiacyl and syringyl units are converted into the L-1 compound [51].

Strategy 2 concerns the valorization of isoeugenol, a compound which can be obtained by Pd-catalyzed transfer hydrogenolysis of pine wood lignin using EtOH/water at

195 °C [54]. Self-metathesis of isoeugenol to β -1 bisphenol [55], followed by demethoxylation and hydrogenation with Raney Ni at 180 °C, yields diol L-2 [44].

Strategy 3 entails the catalytic transfer hydrogenolysis (Ru/C) of ionic liquid processed biorefinery lignin in the presence of isopropanol – an economically viable way to eugenol [56,57]. Solvent-free self-metathesis of eugenol (over a Grubbs catalyst) and hydrogenation (Pd/C) leads to the formation of β - β bisphenol [58], a compound which can be further demethoxylated and hydrogenated with Raney Ni at 180 °C to L-3 [44].

Strategy 4 constitutes a three-step catalytic methodology to lignin-derived phenol in 20 wt % yield as developed by the Sels group: 1) Ru/C catalyzed reductive lignin depolymerization, 2) Ni/SiO₂-mediated selective removal of the methoxy groups therewith generating 4-alkylphenols and 3) dealkylation by zeolite Z140-H to phenol [59]. Then, condensation of two molecules of phenol with respectively acetone and acetaldehyde, in the presence of a strong solid acidic catalyst [60] or simply HCl [61], gives bisphenol-A and bisphenol-E (Fig. 2). In spite of the latter being a homogeneous acid, it is noteworthy that it is inexpensive, widely used industrially, and recyclable [62]. Next to bisphenols, phenol can also be dimerized into 4,4'-biphenol over a solid acid catalyst (≥ 225 °C) [63]. Alternatively, it was also recently shown that 1 wt % Au/TiO₂ can catalyze the dimerization of phenol to biphenol at 150 °C in the presence of 12 bar O₂, potentially opening the door to a fully sustainable process [64]. The subsequent hydrogenation of the aromatic ring in bisphenols and biphenol can be achieved by our Raney Ni or Ru/C methodology at 90–150 °C [65], yielding diols L-4, L-5 and L-6.

In addition to diols obtained from the RCF pathway, the oxidative depolymerization of lignin, a methodology which tends to yield larger amounts of vanillin, can also be used to create diols. For example, **Strategy 5** describes the formation of diol L-7 (34 % yield) from vanillin over vanillyl alcohol over Raney Ni catalyst at 90 °C – the route also holding for the syringyl equivalents of the latter two compounds. Even though the direct chemical vanillin production from lignin has been in stark decline – the Borregaard company being the last industrial manufacturer following that route [66,67] – it must be noted that the main worldly vanillin production method does still start from guaiacol, a compound relatively easily derivable from lignin [68,69]. Over the last two decades though, also a range of biotechnological routes to vanillin have become commercial realities, the starting materials being lignin, ferulic acid, curcumin (turmeric), and eugenol/isoegenol [70]. Of particular note is also the fact that the waste streams of the paper and pulp industry are excellent resources to the making of benzaldehydes, among which vanillin. Another possibility to derive diols from vanillin is by reducing vanillin (or its syringyl equivalent) to its corresponding benzylic alcohol, which upon dehydration react readily with phenol following an electrophilic aromatic substitution [44]. The so resulting

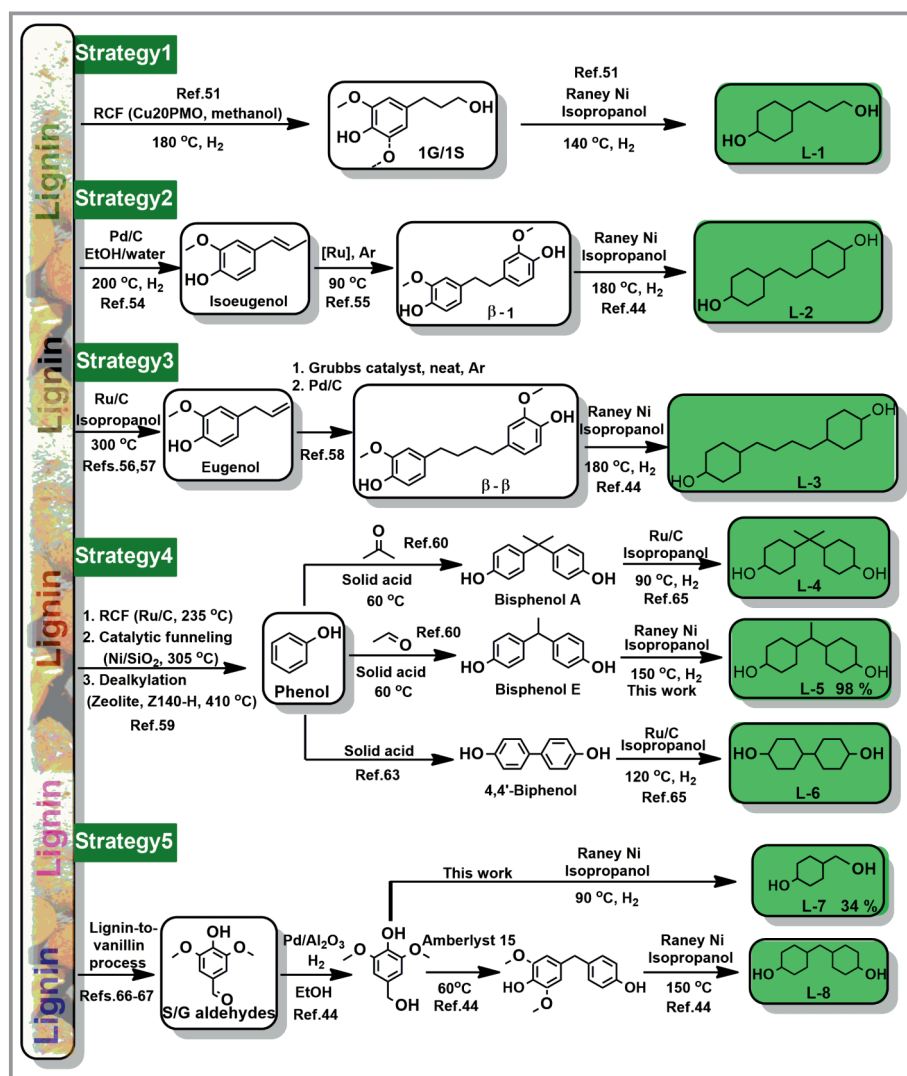


Figure 2. Overview of a range of catalytic strategies to turn lignin-derived platform chemicals into cyclic aliphatic diols.

diaromatic products can be demethoxylated/hydrogenated by Raney Ni to L-8 [44] (Fig. 2).

2.2 Catalytic Strategies to Well-Defined Cellulose-Derived Diols

A long-time central platform molecule from cellulose is 5-hydroxymethylfurfural (HMF) – many cellulose-based methods to which have been developed [71–73]. Three main strategies exist to convert HMF to diols:

Strategy A consists of the controlled reduction of HMF to C1 [74–82], a transformation to which many catalytic methods have been reported. We have previously reported on the use of a Cu-Zn alloy nanopowder catalyst in ethanol at 120 °C and 70 bar H₂ [81] and a Cu₂PMO catalyst in ethanol at 120 °C and 50 bar H₂ [82]. Other notable exam-

ples include the use of Pt/MCM-41 [83], Pt/CeO₂-ZrO₂ [84], PtSn/Al₂O₃ [85] and Ir-ReOx/SiO₂ [86] at mild reaction conditions [87].

Strategy B involves the transformation of HMF to dimethylfuran (DMF) and further on, via Diels-Alder reaction with ethylene and subsequent acid-catalyzed ring opening/dehydration, to *p*-xylene [88–91]. To this end Tao et al. proposed a most interesting one-pot procedure to produce DMF from HMF, based on a Pd-Au/ZrO₂ catalyst and the use of formic acid as the H-donor [91]. The conversion of *p*-xylene to C2 can be achieved at very mild temperature (10 °C) using photo-bromination to 1,4-bis(bromomethyl)benzene (BBMB), followed by a substitution reaction with an alkali base/carboxylate compound [92]. Alternatively, *p*-xylene can undergo direct oxidation into *p*-terephthalic acid (TPA) via the Amoco process, the currently industrially practiced way. More specifically, the Amoco process concerns the oxidation of 25% *p*-xylene in glacial acid at 175–225 °C and 15–30 bar air in the presence of manganese and cobalt salts as catalysts, and a bromide salt as a promotor, and this over a total reaction time of 1 h [93]. In turn TPA can be

hydrogenated to compound C2 using Ru/Sn/B supported on Al₂O₃ (230 °C, 100 bar H₂) [94]. The subsequent hydrogenation of C2 into C3 can be achieved in 91.2% yield using a Ru/Al₂O₃ catalyst in water (100 °C, 80 bar H₂) [95]. A 2014 patent reports the (rare) direct hydrogenation of TPA to C-3 in 42% yield using a Ru/Sn-Re catalyst at 250 °C and 150 bar H₂ [94].

Strategy C: Several pathways were also reviewed to produce TPA from cellulose-derived platform compounds [96]. One important way is the transformation of HMF into furan-2,5-dicarboxylic acid (FDCA), a process which is most commonly performed using heterogeneous catalysts in the presence of an excess of O₂ or air [97,98]. Very recently though it was shown that a homogeneous ruthenium pincer catalyst could perform this oxidation using alkaline water as the formal oxidant and producing H₂ in the process [99]. With though two electron-withdrawing

substituents on the furan, FDCA is poorly reactive in the Diels-Alder reaction with ethylene to TPA [89]. The currently most performing catalytic methods to this transformation are: 1) the use of an aluminum-pillared montmorillonite at 250 °C and 60 bar ethylene (50 % TPA yield) and 2) silica-supported heteropolyacid at 225 °C and 30 bar ethylene (60 % TPA yield) [89]. The obtained TPA can be further converted to diols **C2** and **C3** as described above.

In addition to diols obtained from HMF, other cellulose-derived platform chemicals can also serve as suitable starting materials for diols (Fig. 3), exemplary being:

Strategy D proposes the production of **C3** starting from CMF, a more stable analogue/alternative of HMF, which can be synthesized from cellulose using aqueous HCl in a biphasic reaction in between 80–120 °C [100]. The direct

synthesis of 5-methyl-2-furanoate (MFU) from CMF can be achieved via a redox-neutral N-heterocyclic carbene catalyst in the presence of base [100]. Then TPA can be obtained through a Diels-Alder reaction with ethylene (35 bar) in the presence of Lewis acidic zeolites (e.g., Sn-Beta, Zr-beta) as the catalyst at 190 °C [89], followed by the Amoco process (see before). Interestingly, CMF can also be directly converted to 5-HMF in water at 100 °C [101].

Strategy E details the conversion of muconic acid to TPA. Muconic acid can be obtained from saccharides through mainly (engineered) biotechnological routes [102, 103]. In contrast to FDCA, the absence of aromaticity in muconic acid makes that it engages easier in Diels-Alder reactions. Alike to the FDCA case, the muconic acid Diels-Alder reaction is preferentially run from the muconic acid diester.

Diels-Alder reaction between (esterified) muconic acid and ethylene (high pressure) leads to the formation of the diesters of cyclohex-2-ene-1,4-dicarboxylic acid and cyclohex-1-ene-1,4-dicarboxylic acid, both of which can be converted to diethyl terephthalate (DET) in 80.6 % yield when using silicotungstic acid for the Diels-Alder step (99 % yield) and Pd for the dehydrogenation reaction [104]. TPA can be obtained by hydrogenolysis of DET in a yield of 96 % using polyphosphoric acid [105]. It is noteworthy that muconic acid can also be obtained from lignin-derived catechol (and by extension guaiacol and phenol) through chemical and biotechnological routes [103].

Strategy F yields **C3** via an unusual, yet highly interesting, pathway as published by the groups of Wang and Li [106]. It concerns the formal [3+1+2] proline-catalyzed condensation of crotonaldehyde (CRA), formaldehyde (FA) and ethyl acrylate (EA) to ethyl 4-formylcyclohex-3-enecarboxylate, which is then converted to **C3** in 83 % yield (240 °C, 40 bar H₂) using a commercial Cu/Zn/Al catalyst [106].

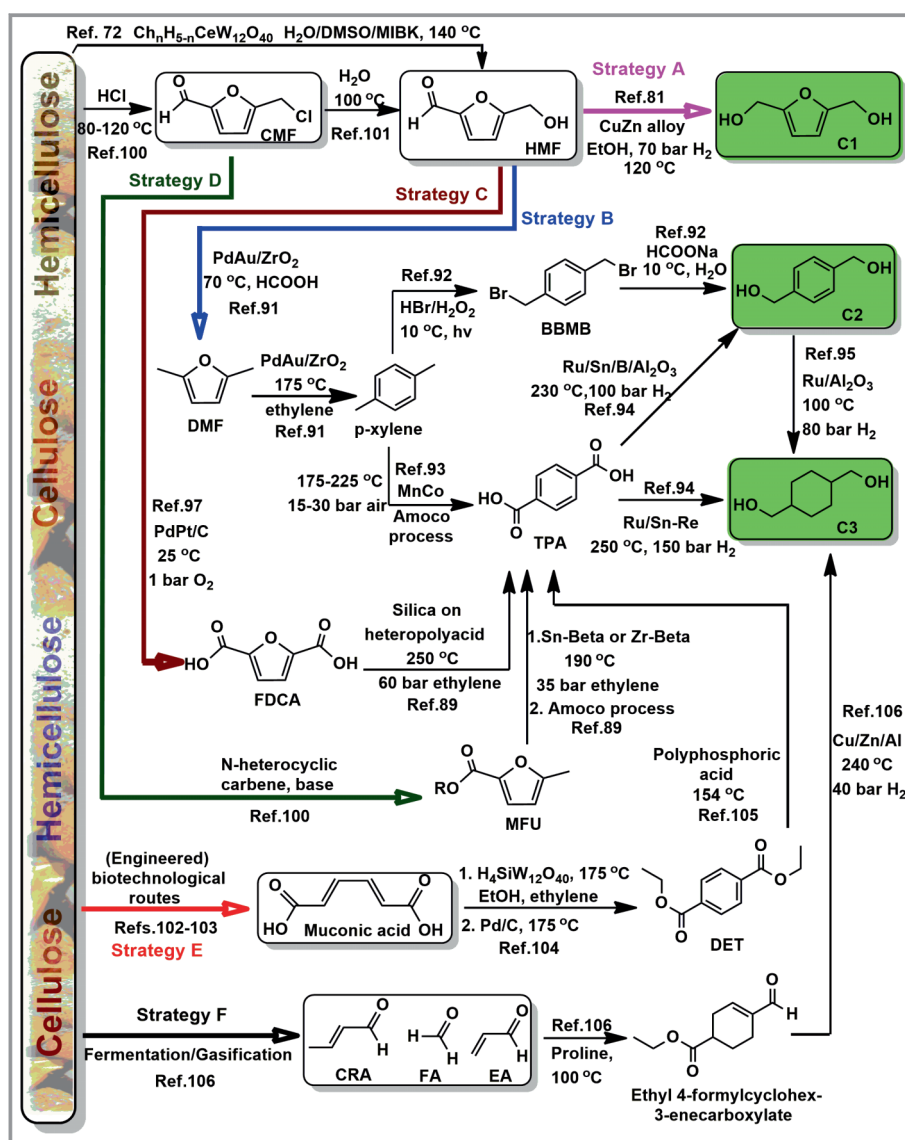


Figure 3. Overview of a range of catalytic strategies to turn (hemi)cellulose-derived platform chemicals into cyclic aliphatic/aromatic diols.

2.3 Catalytic Strategies to Well-Defined Lignocellulose-Derived Diamines

Within this work we set out for the identification of a suitable catalytic amination strategy that can convert a wide variety of lignin- and cellulose-derivable diols (Figs. 2 and 3) directly into diamines, and this preferentially using ammonia as the N-donor and following the HB methodology. However, such a direct catalytic transformation of diols to diamines is generally significantly challenging with the achievable catalytic efficiency being low and the final purification protocol being tedious. To achieve this goal, we evaluated the use of Raney Nickel, a catalyst which our group has previously shown to be very efficient to the transformation of the industrially relevant diol **L-8** into **L-DA8** (96 % yield) and this using ammonia and an HB methodology. Using optimized reaction conditions [44], this technology proved to be applicable to all the above-mentioned diol-containing substrates therewith underscoring the power of this method for the development of diamine oriented biorefinery concepts (Fig. 4).

With **L-1** and **L-7** featuring both an aliphatic primary alcohol and a secondary alcohol, the possibility existed that these non-equal alcohol functions would show a different catalytic coupling reactivity with ammonia. In this area, pioneering work by Shimizu and co-workers has shown that cyclic aliphatic secondary alcohols are more prone to amination than are aromatic/aliphatic primary alcohols [34]. When subjecting diol **L-1** and **L-7** to the optimized Raney

Ni catalyzed diamination methodology, it is observed that all cyclic secondary alcohol moieties undergo fast dehydrogenation/amination/hydrogenation to primary amine while the primary alcohol groups convert much slower. It is exactly the latter observation that lays at the basis of the lower yield of **LDA-1** and **LDA-7**, 76.8 % and 61.2 %, respectively. In line with this observation diols **L-2**, **L-3**, **L-4**, **L-5**, **L-6** and **L-8**, which each bear two cyclic secondary alcohol groups, displayed a very high diamination reactivity, delivering the corresponding diamines (**LDA-2**, **LDA-3**, **LDA-4**, **LDA-5**, **LDA-6** and **LDA-8**) in 95.7–98 % isolated yield. Importantly, the latter diamines are all highly important monomers to the production of high-performing polymers such as polybenzoxazine [44] and epoxy vitrimer [107].

As to the cellulose-derivable diamines it is noteworthy that **CDA-1** holds great potential to the construction of novel biopolymers. Recent reports on its synthesis have focused predominately on the heterogeneous/homogeneous catalytic reductive amination of 5-HMF [108,109], 2,5-diformylfuran (DFF) [110], 5-(chloromethyl)furfural (CMF) [111], 5-(hydroxymethyl)furfurylamine [112,113], 2,5-dihydroxymethylfuran (**C1**) [45] or 2,5-diformylfuran dioxime [114]. For each of these approaches ammonia was used as the N-donor and **CDA-1** diamine was obtained in good to high yield. Applying our optimized Raney Ni/NH₃ catalyzed diol amination method, **CDA-1** could be obtained in 75.5 % overall yield, a most encouraging result.

CDA-2 is an industrially important diamine, widely used in the making of thermally stable polyamide fibers (e.g., Kevlar®) [37]. In a previous study it was found possible to convert **C2** into **CDA-2** at 180 °C using Raney Ni and aqueous NH₃ in 61 % overall yield [34]. Gratifyingly, the here employed Raney Ni methodology, which uses *t*-amyl alcohol as the solvent and NH₃ gas, and operates at a lower temperature 160 °C, increased the attainable yield to 83.7 %. Lastly, the deamination of diol **C3** was found to run smoothly, yielding **CDA-3** in 84.6 % yield.

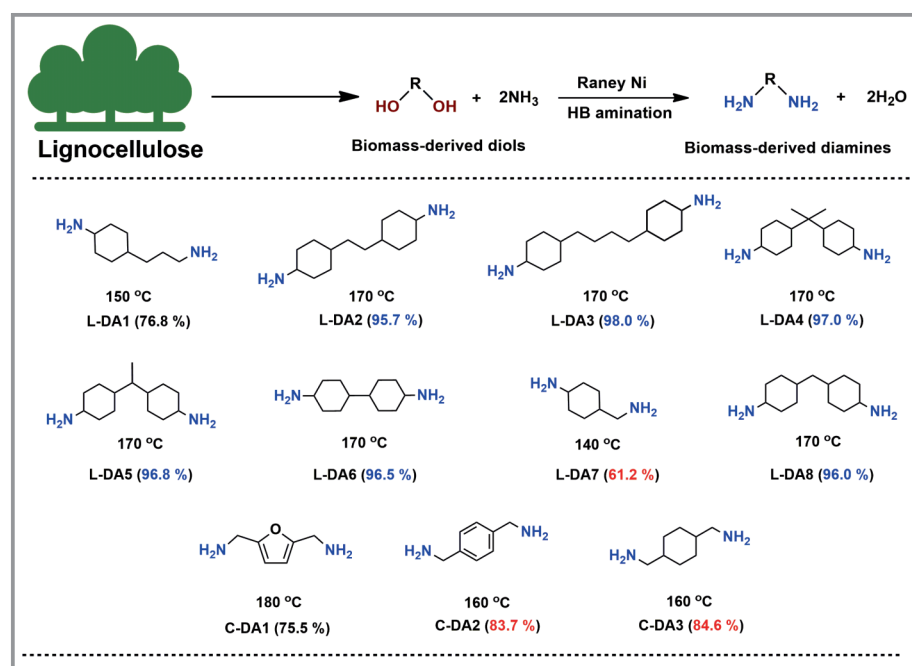


Figure 4. Diamination scope of lignocellulose-derived diols. Reaction conditions: 0.5 mmol diols, 50 mg catalysts, 2.5 mL *t*-amyl alcohol, 140–180 °C, 18 h, 10 mg dodecane as the internal standard; GC-FID determined yields by means of an internal standard are shown in black; yields determined by means of a calibration curve are depicted red; Isolated yields are shown in blue.

3 Conclusion

In this paper we have described in detail a potential diamine oriented biorefinery concept. Firstly, we considered high-yielding pathways toward platform chemicals from lignin as well as cellulose that are suitable and ideally set up for further downstream processing to diols. Next,

a straightforward atom-economical methodology was described to convert these diols into their diamine equivalents. Central to these transformations stands the capability of Raney Ni to act as a hydrogenation, demethoxylation and hydrogen-borrowing amination catalyst. The wide commercial availability of Raney Ni, as well as its vast industrial use, adds strongly to the potential viability of such a diamine-oriented biorefinery concept. This is further underscored by the excellent diamine (isolated) yields, often exceeding 95 %.

4 Experimental

4.1 Materials and reagents

Chemicals were used as received, unless otherwise specified. Raney Ni was purchased from Sigma Aldrich.

The catalytic direct amination of diols into diamines was performed in a 10-mL high pressure autoclave equipped with a magnetic stirring bar. Typically, a 4-mL vial was charged with 50 mg Raney Ni catalyst, 0.5 mmol diol, 2.5 mL *t*-amyl alcohol, 10 mg dodecane as an internal standard. Then the vial was put inside an autoclave and pressurized with 7 bar NH₃. The reactor was heated and stirred at 400 rpm for 18 h. After completion of the reaction, the reactor was cooled down to room temperature. Then, 0.1 mL solution was collected through a syringe and injected in a GC-MS or GC-FID after filtration through a PTFE filter (0.45 μm).

4.2 Characterizations

NMR spectroscopy: At the University of Groningen, ¹H, ¹³C NMR and 2D NMR spectra were recorded on a Varian Mercury Plus 400, Agilent MR 400 and a Bruker Avance NEO 600 (600 and 151 MHz, respectively); At the University of Graz: ¹H, and ¹³C NMR spectra were recorded on a Bruker Avance III 300MHz and 2D NMR spectra were recorded on a Bruker Avance III 700MHz equipped with a 5 mm Triple-Resonance cryoprobe.

Supporting Information

Supporting Information for this article can be found under DOI: <https://doi.org/10.1002/cite.202200091>.

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Abbreviations

L-1	4-(3-hydroxypropyl)cyclohexanol
L-2	4,4'-(ethane-1,2-diyl)dicyclohexanol
L-3	4,4'-(butane-1,4-diyl)dicyclohexanol
L-4	4,4'-(propane-2,2-diyl)dicyclohexanol
L-5	4,4'-(ethane-1,1-diyl)dicyclohexanol
L-6	[1,1'-bi(cyclohexane)]-4,4'-diol
L-7	4-(hydroxymethyl)cyclohexanol
L-8	4,4'-methylenedicyclohexanol
C1	2,5-bis(hydroxymethyl)furan
C2	1,4-benzenedimethanol
C3	1,4-cyclohexanedimethanol
LDA-1	4-(3-aminopropyl)cyclohexanamine
LDA-2	4,4'-(ethane-1,2-diyl)dicyclohexanamine
LDA-3	4,4'-(butane-1,4-diyl)dicyclohexanamine
LDA-4	4,4'-(propane-2,2-diyl)dicyclohexanamine
LDA-5	4,4'-(ethane-1,1-diyl)dicyclohexanamine
LDA-6	[1,1'-bi(cyclohexane)]-4,4'-diamine
LDA-7	4-(aminomethyl)cyclohexanamine
LDA-8	4,4'-methylenedicyclohexanamine
CDA-1	2,5-bis(aminomethyl)furan
CDA-2	1,4-benzenedimethanamine
CDA-3	1,4-bis(aminomethyl)cyclohexane
β-1	4,4'-(ethane-1,2-diyl) bis(2-methoxyphenol)
β-β	4,4'-(butane-1,4-diyl) bis(2-methoxyphenol)

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