

INVITED REVIEW PAPER

Catalytic production of hexamethylenediamine from renewable feedstocks

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Abstract—Renewable biomass-derived chemicals have received considerable interest as a potential substitute for petroleum-derived chemicals. Hexamethylenediamine is a key intermediate in manufacturing nylon 66, a synthetic polymer that is broadly used in society. This article reviews the catalytic production of hexamethylenediamine from biomass-derived chemical feedstocks, and specifically the bio-based routes for obtaining hexamethylenediamine. While methods to directly convert biomass to hexamethylenediamine have yet to be commercialized, the use of heterogeneous catalytic systems via combined processes appears to be a promising and emerging chemical pathway to achieve this goal. Current proposed routes for the renewable production of hexamethylenediamine are not yet entirely competitive with petrochemical production techniques, predominantly because of low efficiency and high cost. However, many opportunities exist to advance technologies that exploit renewable and bio-based feedstocks to generate hexamethylenediamine. Thus, the commercialization of biomass-derived nylon monomers appears achievable in the near future.

Keywords: Adiponitrile, Biomass, Biorefinery, Heterogeneous Catalyst, Hydrogenation, Nylon

INTRODUCTION

While more than 90% of industrial organic chemicals originate from crude oil [1], the forecasted depletion of fossil fuels and their environmental impact (e.g., climate change) motivate the production of chemicals from renewable sources, such as biomass. Moreover, growing concern over the environmental impact (e.g., emission of greenhouse gases) of processing petrochemicals have made plastic manufacturers strongly consider replacing fossil fuels with renewable feedstocks like biomass [2-11]. Thus, it is urgent for chemical industries to establish efficient routes to convert biomass into organic chemicals.

Nylon, a thermosoftening plastic, is used in a diverse array of applications, such as in the manufacture of reinforced rubber, electrical equipment parts, car parts, food packaging films, flooring, and apparel [12-14]. Nylon 66 is a type of nylon that is rigid, has high mechanical strength, and exhibits chemical and thermal robustness [15] and, as such, is one of the most common synthetic polymers used in the plastic and textile industries. The global market size of nylon 66 was approximately 5.1 billion USD in 2017 and is projected to grow to 6.7 billion USD by 2026 [16].

Hexamethylenediamine is a monomer in the synthesis of nylon 66 [17,18] and, in industry, is synthesized by the hydrogenation of adiponitrile. Various catalytic systems have been employed to hydrogenate adiponitrile to hexamethylenediamine, including Ziegler-type [19], Raney-type [20-22], amorphous alloy [23,24], supported nickel

(Ni) [25-27], Ni-based bimetallic and trimetallic [28-33], and noble metal-based catalysts [34].

Many studies have reported the use of biomass as a feedstock to yield precursors and monomers for plastic materials [35-40]. While producing hexamethylenediamine from biomass feedstocks is possible [41], such processes have yet to be exploited on industrial scales because they are not technically or economically feasible, as compared to conventional petrochemical-derived synthetic methods.

This review provides an overview of the production of hexamethylenediamine from various biomass feedstocks. The article discusses a variety of processing techniques for converting different bio-based substances into hexamethylenediamine, with a specific technical focus on catalytic routes to determine which has the highest yield. All of the routes described are suggested based on processes available in the literature. Also included is a discussion of the current challenges and future opportunities for hexamethylenediamine production. Heterogeneous catalytic processes are the exclusive focus because processes that employ homogeneous catalysts typically suffer from difficulties in recovering target chemicals from final products [42,43].

PRODUCTION OF HEXAMETHYLENEDIAMINE FROM BIOMASS-DERIVED ADIPONITRILE

Hydrogenation of adiponitrile is the most common synthetic pathway employed to synthesize hexamethylenediamine. This exothermic reaction is performed at high temperature in hydrogen at high pressures [34]. Many patents and scientific papers demonstrate that adiponitrile is hydrogenated to hexamethylenediamine

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by a 6-aminocapronitrile intermediate, as shown in Fig. 1. According to kinetic data for the reaction, it follows the Langmuir-Hinshelwood mechanism [44,45]. Hydrogenation of adiponitrile that is made from biomass feedstocks must be first considered a renewable route to hexamethylenediamine.

1. Production of Adiponitrile from Biomass Feedstocks

1-1. Production of Adiponitrile from Biomass Feedstocks via Heterogeneous Catalysis

Multi-stage hydrocyanation of butadiene is the most extensively

employed method to produce adiponitrile. Fig. 2 illustrates several potentially effective routes that exploit heterogeneous catalysts to generate butadiene from different biomass-derived compounds, such as ethanol, furfural, and 1,4-anhydroerythritol. As shown in Fig. 2(a), butadiene can be synthesized from ethanol. Ethanol derived from sugarcane or corn (i.e., bioethanol) is currently being produced in large volumes as an additive in gasoline [46,47] and as a feedstock of various chemicals [48-50]. The industrial production of butadiene from ethanol exploits the Lebedev process [51-55],

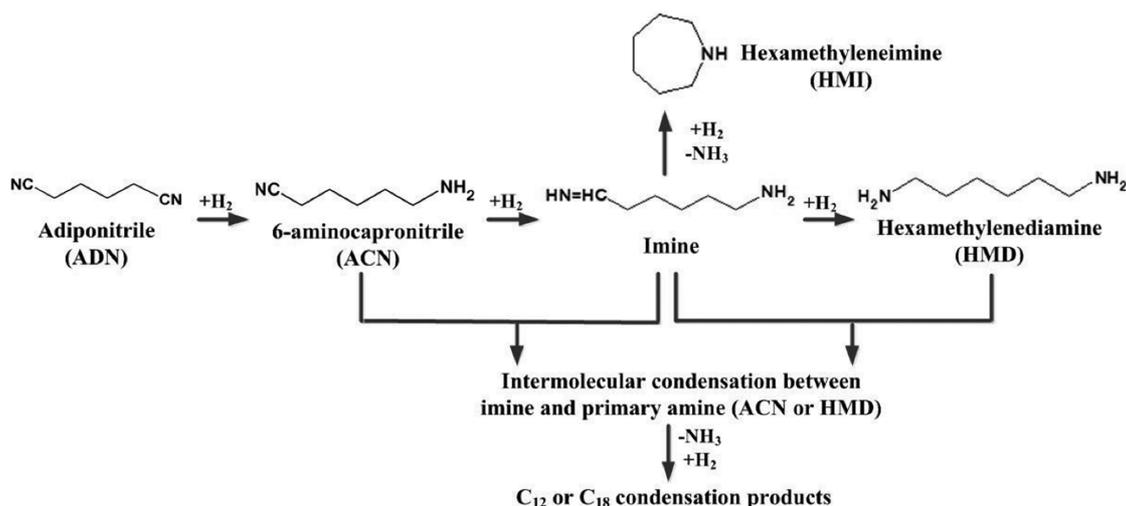


Fig. 1. Reaction pathway for the hydrogenation of adiponitrile to hexamethylenediamine. This figure was reprinted from Wang et al. [27] and is licensed under CC BY 4.0.

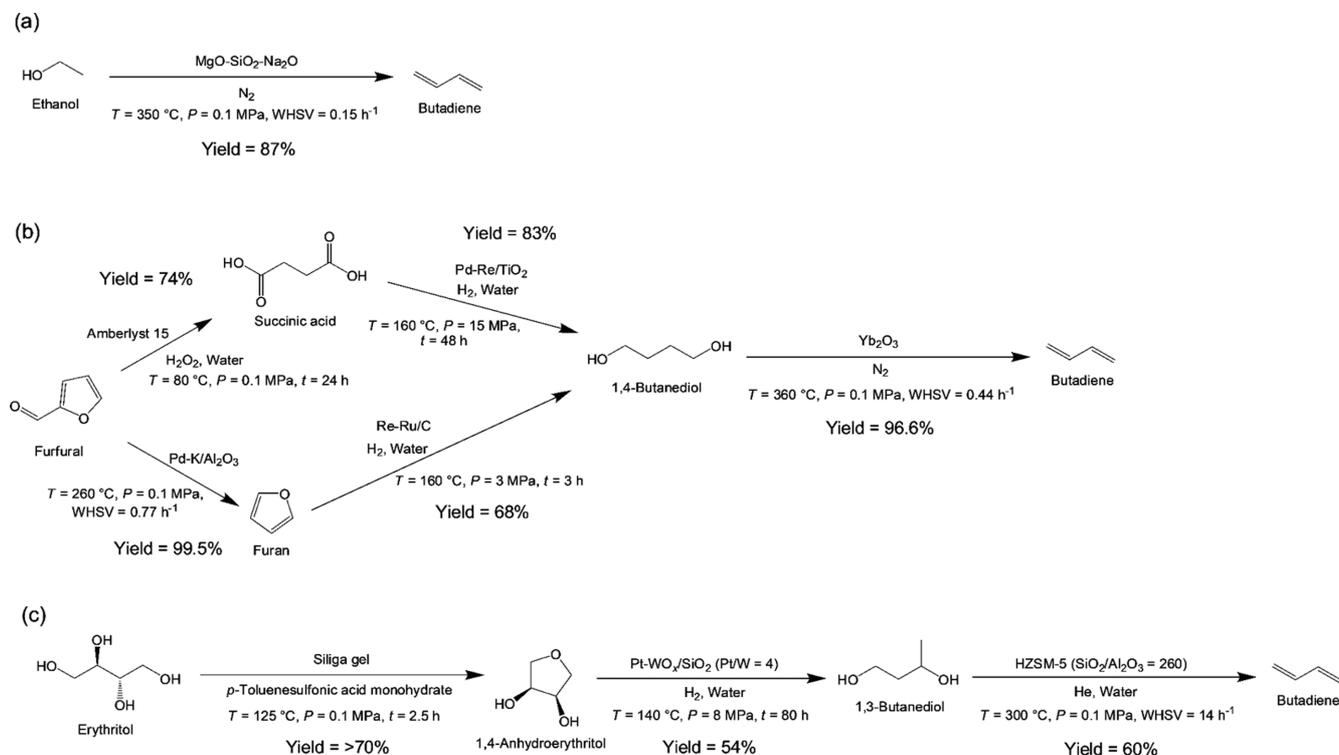


Fig. 2. Potential pathways and reaction conditions for the synthesis of butadiene from biomass-derived feedstocks. The yield indicated at each step reflects the highest yield of each compound reported in the literature.

which is a one-step reaction that occurs between 350 and 450 °C in the presence of a metal oxide-based catalyst, such as MgO-SiO₂, SiO₂-Ta₂O₅, and metal catalysts supported on zeolite. Both dehydrogenation and dehydration reactions occur simultaneously during the Lebedev reaction. An important mechanism of the Lebedev reaction is the conversion of ethanol and crotonaldehyde into butadiene [56].

Fig. 2(b) depicts two possible routes to produce butadiene from furfural at the highest reported yield. Furfural is derived from the hemicellulose in lignocellulosic biomass, which is a potential feedstock for a variety of value-added chemicals [40], and is produced from bagasse at 400,000-500,000 tons per year [37,57,58]. As shown in Fig. 2(b), high-yield production of butadiene from furfural can be achieved via two intermediates: succinic acid or furan. The route that involves succinic acid includes the conversion of furfural to succinic acid [59,60], which is then converted to 1,4-butanediol [61-65]. Oxidation of furfural in the presence of hydrogen peroxide yielded 74% succinic acid in the presence of a solid acid catalyst (e.g., Amberlyst-15) at 80 °C for 24 h [60]. Hydrogenation of succinic acid over a bimetallic Pd-Re/TiO₂ catalyst (Pd: 2 wt%; Re: 3.4 wt%) at 160 °C under 15 MPa H₂ for 48 h resulted in an 83% conversion of succinic acid into 1,4-butanediol [62,64]. For the route that involves furan, decarbonylation of furfural takes place to produce furan. The use of Pd and Pt catalysts produced furan yields of 90% [66-69]. For instance, a Pd/ZrO₂ catalyst led to a 98% yield of furan from furfural when the reaction occurred at 140 °C under atmospheric pressure for 12 h in a batch reaction system [69]. A K-doped Pd/Al₂O₃ catalyst (K: 8 wt%) converted 99.5% of furfural into furan at 260 °C and a weight hourly space velocity (WHSV) of 0.77 h⁻¹ in a fixed bed reactor system [66]. The production of 1,4-butanediol from furan was possible with a bimetallic Ru-Re/C catalyst (Ru: 1 wt%; Re: 5 wt%) at 160 °C under 3 MPa H₂, resulting in a 68% yield of 1,4-butanediol [70]. The 1,4-butanediol derived from furfural via succinic acid or furan intermediates must be further dehydrated to obtain butadiene [71-73]. Wang et al. recently reported a 96.6% yield of butadiene by using a rare earth oxide catalyst such as ytterbium(III) oxide (Yb₂O₃) at 360 °C and a WHSV of 0.44 h⁻¹ [72]. The compound 3-buten-1-ol was found to be an intermediate of butadiene in the dehydration of 1,4-butanediol by the Yb₂O₃ catalyst. In this catalytic system, Yb³⁺ serves as acid sites, and oxygen anion serves as basic sites. For the dehydration of 1,4-butanediol over the Yb₂O₃ catalyst, the formation of 3-buten-1-ol proceeds via acid-base concerted mechanism [74]. The Yb₂O₃ catalyst also hindered side reactions such as the decomposition of 3-buten-1-ol to propylene.

Fig. 2(c) depicts a synthetic route to produce butadiene from erythritol *via* 1,3-butanediol. Erythritol is a common biomass-derived compound manufactured on an industrial scale (60,000 tons per

year) [75]. 1,4-Anhydroerythritol is readily made by the dehydration of erythritol by catalysts with Brønsted acid sites, such as ion-exchange resins [76]. A 70-75% yield of 1,4-anhydroerythritol was achieved in a batch reactor, [76] which could be increased to >90% by using a reactive distillation system that exploits the different boiling points of erythritol and 1,4-anhydroerythritol [75]. Hydrogenolysis of 1,4-anhydroerythritol by a Pt-WO_x/SiO₂ catalyst (Pt: 4 wt%; W: 0.94 wt%) produced 1,3-butanediol; a 54% yield of 1,3-butanediol was achieved at 140 °C under 8 MPa H₂ for 80 h [77]. The carbenium ion with the assistance of Brønsted acid sites is not involved in C-O bond dissociation in 1,3-butanediol. As a final step, the 1,4-anhydroerythritol-derived 1,3-butanediol is converted into butadiene by a direct dehydration reaction on a zeolite catalyst (HZSM-5 with a SiO₂/Al₂O₃ ratio of 260) [78], which yields up to 60% yield of butadiene at 300 °C under atmospheric pressure with a WHSV of 14 h⁻¹ for an 8-h time-on-stream. However, the zeolite catalyst deactivates after a 102-h time-on-stream due to coke formation (confirmed by 36% loss of surface area), decreasing the yield of butadiene [78].

Besides ethanol, furfural, and 1,4-anhydroerythritol, adipic acid can also be used as a feedstock for adiponitrile. For example, ammonization of adipic acid in the gaseous phase at 300 to 350 °C [79] or in the liquid phase at 200 to 300 °C [80] produces adiponitrile. However, the use of adipic acid as an adiponitrile feedstock [39] is not covered in this review. Adipic acid-based processes were formerly the predominant technology for adiponitrile production but are no longer employed by major manufacturers of nylon 66 for economic reasons [81].

1-2. Production of Adiponitrile from Biomass Feedstocks via Electrochemical Process

Electrochemical synthesis of organic chemicals is regarded as more environmentally friendly than conventional chemical synthesis methods by enabling chemical manufacturing processes to use renewable electricity (e.g., photovoltaics and wind power), thus vastly reducing greenhouse gas emission [82]. Dai et al. developed an electrochemical process to synthesize adiponitrile from glutamic acid *via* glutamic acid 5-methyl ester that utilized electrodes made of noble metals such as Pt [83]. Importantly, glutamic acid is designated as a top value-added chemical from biomass by U.S. Department of Energy [84]. Glutamic acid 5-methyl ester can be synthesized at high (>90%) yield by a precipitation method under mild conditions [85]. Electrochemical processing techniques involve an electro-oxidative decarboxylation of glutamic acid 5-methyl ester to 3-cyanopropanoic acid methyl ester. The use of Pt anode and cathode produced an 86% yield in an electrochemical operating at 0 °C with a current density of 80 mA cm⁻² (cell voltage of 5-10 V) in the presence of sodium bromide, methanol, and water. The second step of electrochemical processing is the Kolbe coupling of 3-

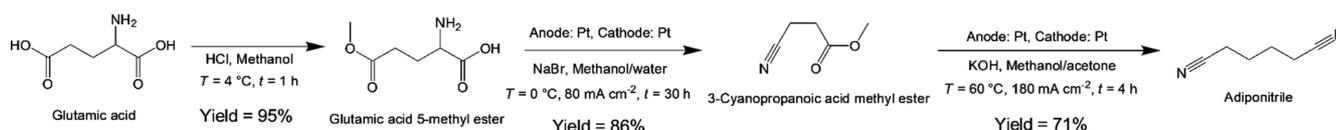


Fig. 3. Synthetic pathways and reaction conditions for the electrochemical synthesis of adiponitrile from glutamic acid. The yield indicated at each step reflects the highest yield of each compound reported in the literature.

Table 1. Heterogeneous catalytic systems that achieve >90% yield of hexamethylenediamine by hydrogenation of adiponitrile. All conditions and results were obtained from the literature

| Entry | Catalyst | Adiponitrile phase | Reaction conditions | Hexamethylenediamine yield (%) | Ref. |
|-------|---|--------------------|---|--------------------------------|----------------------|
| 1 | Raney® Ni 2400 | Liquid | T=100 °C; P _{H₂} =3 MPa; t=2 h; 0.97-3.9 mol/L adiponitrile; NaOH; ethanol/catalyst weight ratio=22.5 | 100 | Alini et al. [34] |
| 2 | Rh/Al ₂ O ₃ (1 wt% Rh) | Liquid | T=90 °C; P _{H₂} =3 MPa; t=4.5 h; 0.97-3.9 mol/L adiponitrile; NaOH; ethanol/catalyst weight ratio=9 | 92 | Alini et al. [34] |
| 3 | Raney® Co 2724 | Liquid | T=75 °C; P _{H₂} =3.4 MPa; t=24 h; adiponitrile/catalyst ratio=37.2; water/hexamethylenediamine/NaOH weight ratio=1/15/0.1 | 99.4 | Sengupta et al. [90] |
| 4 | Ni/MgO (NiO/MgO weight ratio=4 before reduction) | Gas | T=90 °C; P _{H₂} =0.1 MPa; space velocity=21,486 h ⁻¹ ; H ₂ /adiponitrile ratio=6738 | 96 | Serra et al. [94] |
| 5 | Ni-B/SiO ₂ -MgO (Ni: 25.2 wt%; Si/Mg atomic ratio=7) | Gas | T=250 °C; P _{H₂} =0.1 MPa; space velocity=1,700 h ⁻¹ ; H ₂ /adiponitrile molar ratio=37 | 96 | Li et al. [24] |
| 6 | Surface Pd-rich PdAg nanowires (Pd/Ag=1) | Liquid | T=50 °C; adiponitrile/ethanol/formic acid volumetric ratio=1/0.76/0.7 | 98 | Liu et al. [93] |

cyanopropanoic acid methyl ester to produce adiponitrile. Electrochemical cells operating at 60 °C and a current density of 180 mA cm⁻¹ (cell voltage of 7-15 V) converted 71% of 3-cyanopropanoic acid methyl ester fed into adiponitrile when potassium hydroxide, methanol, and acetone were used as an electrolyte. The electrochemical synthesis method of adiponitrile from glutamic acid, described in Fig. 3, produced an overall yield of 58%.

2. Hydrogenation of Adiponitrile to Hexamethylenediamine

As seen in Fig. 1, sequential hydrogenation of 6-aminocapronitrile forms a highly reactive imine intermediate that can undergo intermolecular condensation with primary amines (i.e., 6-aminocapronitrile and hexamethylenediamine) and intramolecular cyclization that leads to the formation of byproducts such as hexamethylenimine (Fig. 1) [27]. Hexamethylenimine, a secondary amine, is formed via nucleophilic addition of the primary amine on one side of adiponitrile chain to aldimino carbon atom on the other side adsorbed by Ni active sites [86]. Unwanted side reactions that form byproducts compete with the hydrogenation reaction that generates hexamethylenediamine. Therefore, byproduct formation must be suppressed to enhance the catalytic performance of adiponitrile hydrogenation.

There are several examples of efforts to hinder the byproduct formation during the hydrogenation of adiponitrile to produce hexamethylenediamine. Ammonia was previously employed to inhibit undesired side reactions that produce secondary and tertiary amines, [87,88], but ammonia is corrosive and a health hazard. Thus, alternative processing techniques that do not require ammonia at lower temperature and pressure are desirable, one example being the use of a Raney Ni catalyst with adiponitrile in a hexamethylenediamine solvent [89]. The addition of water to the adiponitrile hydrogenation reagents controls byproduct formation [90]. Solutions of alkali metal hydroxides (e.g., sodium hydroxide (NaOH) and potassium hydroxide (KOH)) have also been used to impede side reactions that produce undesirable secondary and tertiary amines. Recently,

ionic liquids were used to increase the hexamethylenediamine yield by suppressing byproduct formation. Liu and co-workers employed 1-butyl-3-methylimidazolium hydroxide, a basic ionic liquid, in the hydrogenation of adiponitrile on a Ni catalyst supported on multi-walled carbon nanotubes (MWCNTs), resulting in a 93.2% yield of 6-aminohexanenitrile and hexamethylenediamine [91].

A broad variety of heterogeneous catalysts have been investigated for the conversion of adiponitrile hydrogenation to hexamethylenediamine. Over 90% and even near-complete conversion of adiponitrile into hexamethylenediamine have been achieved with different heterogeneous catalytic systems such as Raney Ni, Raney Co, Rh/Al₂O₃, and metal oxides-supported Ni catalysts, as summarized in Table 1. Hydrogenation of adiponitrile with >90% yield of hexamethylenediamine resulted while using gaseous hydrogen (H₂) with liquid-phase adiponitrile (entries 1, 2, and 3 in Table 1) or gas-phase adiponitrile (entries 4 and 5 in Table 1) as the feedstock. Liquid-phase processes require high H₂ pressures of near 3 MPa. The addition of certain solvents (e.g., water, ethanol, and hexamethylenediamine) and inorganic species (e.g., NaOH) decreased side reaction products, such as secondary and tertiary amines and condensation products. Gas-phase processes could be operated under atmospheric pressures, which is an advantage over liquid-phase processes with respect to process safety. However, gas-phase processes require additional steps to vaporize adiponitrile and condense hexamethylenediamine.

The requirement of molecular H₂ as a hydrogen donor is disadvantageous for hydrogenation processes because H₂ is commonly derived by non-renewable processes, including the steam reforming of coal. Moreover, the use of gaseous H₂ poses problems with respect to transportation, process economy, and safety [92]. To overcome these challenges, Liu et al. used formic acid as a hydrogen donor to reduce adiponitrile to hexamethylenediamine (i.e., catalytic transfer hydrogenation of adiponitrile) in ethanol using PdAg nanowires with Pd-enriched surfaces as a catalyst, which were pre-

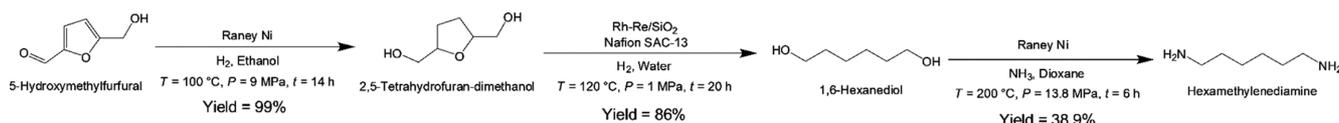


Fig. 4. Synthetic pathways and reaction conditions for the synthesis of hexamethylenediamine from 5-hydroxymethylfurfural. The yield indicated at each step reflects the highest yield of each compound reported in the literature.

pared by seed-mediated growth in polyol solution [93]. This catalytic system produced a high 98% yield of hexamethylenediamine (entry 6 in Table 1). The high activity of the PdAg nanowire catalyst was ascribed to the Pd-rich surfaces, which enabled more efficient electron transfer from Ag to Pd. This study by Liu et al. marks the first investigation into hexamethylenediamine production via catalytic transfer hydrogenation.

PRODUCTION OF HEXAMETHYLENEDIAMINE FROM 5-HYDROXYMETHYLFURFURAL

Besides the hydrogenation of adiponitrile, hexamethylenediamine can also be produced by other synthetic pathways that use biomass-derived compounds such as 5-hydroxymethylfurfural, as depicted in Fig. 4. 5-Hydroxymethylfurfural is a well-known biomass-derived and versatile chemical [95] that is synthesized from glucose via a two-step process: the isomerization of glucose to fructose and then the dehydration of fructose to 5-hydroxymethylfurfural [96-98]. As shown in Fig. 4, 2,5-tetrahydrofuran-dimethanol is a hydrogenation product of 5-hydroxymethylfurfural, which can be obtained at a 99% yield by using a Raney Ni catalyst at 100 °C under 9 MPa H₂ for 14 h [99]. The 2,5-tetrahydrofuran-dimethanol is further hydrogenated to 1,6-hexanediol by a catalytic system comprised of a bimetallic Rh-Re/SiO₂ catalyst (Rh/Re weight ratio of 1.08) and Nafion® SAC-13 (Rh-Re/SiO₂/Nafion® SAC-13 weight ratio of =1.67) [99]. This mixed catalyst system produced an 86% yield of 1,6-hexanediol from 2,5-tetrahydrofuran-dimethanol when operated in water at 120 °C under 1 MPa H₂ with a 20 h reaction time. Subsequent amination of the 1,6-hexanediol led to hexamethylenediamine. This synthetic route is regarded as the most effective for making hexamethylenediamine from biomass feedstocks, such as carbohydrate-containing materials [100]. The amination step should be carried out over Raney Ni catalyst in dioxane and liquid ammonia (dioxane/ammonia/1,6-hexanediol=46/500/174) at 200 °C under 13.8 MPa for 6 h, which produces a 39.9% yield of hexamethylenediamine [101,102]. The overall hexamethylenediamine yield obtained from 5-hydroxymethylfurfural by this route (presented in Fig. 4) was 33.1%.

Dros et al. compared the economic and environmental aspects of the production of hexamethylenediamine from petroleum-derived butadiene and high-fructose corn syrup (i.e., 42 wt% fructose on dry basis) by 5-hydroxymethylfurfural [103]. The overall manufacturing cost using a petroleum-derived butadiene feedstock was estimated to be 1.84 € per kg versus 2 € per kg with a corn syrup feedstock. Biomass-derived hexamethylenediamine would be less expensive than the petroleum-derived product only if the petroleum-derived butadiene price rises above 1.8 € per kg or the price of high-fructose corn syrup price is below 0.3 € per kg [103]. A life

cycle assessment revealed that the biomass-based synthesis route for hexamethylenediamine serves as a carbon sink and thus is more advantageous than the petroleum-based synthetic route with respect to climate change. But the same analysis showed that the bio-based synthesis route also can have a higher environmental impact on terrestrial, marine, and freshwater eutrophication [103].

CONCLUSIONS AND PROSPECTS

This review illustrates the potential for employing biomass-derived chemicals to generate monomeric precursors, i.e., hexamethylenediamine, for nylon 66. Recent research efforts across several groups have made considerable progress in developing versatile and economic platforms to synthesize useful chemicals from renewable resources like biomass. Renewable biomass-derived chemicals can be employed as starting materials for syntheses that yield hexamethylenediamine. Novel and alternative renewable routes with the potential to replace conventional petrochemical synthesis processes to generate hexamethylenediamine were discussed in Sections 2, 3, and 4. Such alternative routes that employ biomass-derived chemicals have not yet become competitive with traditional petrochemical-based routes, principally due to the high prices of intermediate chemicals necessary for biomass-based processed chemicals. This price differential impedes the transition from the current petroleum-based production of hexamethylenediamine.

Processing renewable feedstocks such as biomass can generate residues and byproducts, such as solid leftover, lignin, and spent enzymes. Thaore et al. [104] suggested that such byproducts can be employed as fuels to supply energy to electricity generation. Applications of the residues and byproducts must be more widely investigated for commercialization of the production of nylon monomers from renewable resources.

A survey of the literature revealed that many reactions necessary for biomass-based production of hexamethylenediamine require the addition of organic compounds (alcohols, acetone, dioxane, ionic liquids, etc.) and/or inorganic compounds (potassium hydroxide, sodium hydroxide, sodium bromide, etc.) to achieve high yields. Such additives are not preferable from an economic standpoint, as they necessitate costly downstream separation. Thus, a key objective is to develop processes to synthesize hexamethylenediamine from biomass-derived compounds without the need for organic solvents and inorganic species. Optimization of reaction parameters also offers separate opportunities to improve the biomass-based catalytic routes suggested in this review.

A diverse array of heterogeneous catalysts (e.g., Raney metal, supported metals of both mono- and bimetallic varieties, and solid acid catalysts) are used for hexamethylenediamine production. The studies reviewed here mainly focus on catalytic performance met-

rics, including the conversion of feedstock, selectivity, and yield. Catalytic performance is certainly important, but other performance metrics such as catalyst reusability and stability are also critical factors in the commercialization of catalytic processes [105]. Yet, these performance metrics, including catalyst deactivation [78], reusability, and stability, are rarely interrogated for catalytic reactions in biomass-based synthetic routes that produce hexamethylenediamine. Hence, we recommend that the durability and reusability of candidate heterogeneous catalysts be routinely investigated, for example, by collecting time-on-stream reaction data over extended duration to comprehensively evaluate and facilitate the economic feasibility of the catalytic production of biomass-based hexamethylenediamine.

The use of molecular H₂ for hydrogenation of adiponitrile to hexamethylenediamine has issues in terms of sustainability, process economy, and safety. Although catalytic transfer hydrogenation of adiponitrile is possible, further studies on catalytic transfer reactions for the hexamethylenediamine production may provide opportunity to overcome or circumvent these issues [106]. The electrochemical conversion of adiponitrile into hexamethylenediamine serves as a promising alternative method that avoids the requirement of molecular H₂ [107].

While the catalytic production hexamethylenediamine from biomass-derived intermediates has high potential to replace conventional petrochemical-based pathways, commercialization has yet to be guaranteed. As scale-up from the bench to a pilot plant presents difficulties because of uncertainty in reproducing reaction performance, large-scale process simulation studies should be conducted to elucidate the practicality of renewable hexamethylenediamine synthesis routes.

Societal needs and government legislation are poised to shift the paradigm from petrochemical-based processes to bio-based processes. Nonetheless, this change will be realized when the bio-based processes gain financial advantages in capital, operation, and maintenance costs. Raw biomass collection, catalytic process efficiency, and feedstock processing costs will dictate which synthetic routes will be developed and implemented by polymer manufacturers. Alternative catalytic routes described in this review are currently not competitive with conventional petrochemical routes, yet most of these processes have yet to be fully explored, developed, and optimized.

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REFERENCES

- H. A. Wittcoff, B. G. Reuben and J. S. Plotkin, *Industrial organic chemicals*, John Wiley & Sons, Inc., Hoboken, New Jersey, USA (2013).
- W. Song, S. Wang, D. Xu, Y. Guo, C. Yang, J. Zhang and Y. Li, *Korean J. Chem. Eng.*, **36**, 1604 (2019).
- S. Kim, E. E. Kwon, Y. T. Kim, S. Jung, H. J. Kim, G. W. Huber and J. Lee, *Green Chem.*, **21**, 3715 (2019).
- Z. Wang, Z. Fu, W. Lin, S. Li and W. Song, *Korean J. Chem. Eng.*, **36**, 1235 (2019).
- H. W. Lee, H. Jeong, Y.-M. Ju and S. M. Lee, *Korean J. Chem. Eng.*, **37**, 1174 (2020).
- H. AbdelSalam, H. H. El-Maghrbi, F. Zahran and T. Zaki, *Korean J. Chem. Eng.*, **37**, 670 (2020).
- C. Park and J. Lee, *Green Chem.*, **22**, 2628 (2020).
- H. M. Pham, M. J. Kang, K.-A. Kim, C. G. Im, S. Y. Hwang and H. G. Cha, *Korean J. Chem. Eng.*, **37**, 556 (2020).
- P. K. Dikshit, H.-B. Jun and B. S. Kim, *Korean J. Chem. Eng.*, **37**, 387 (2020).
- A. Purnama, K. Wijaya, I. Tahir, E. A. Suyono and A. Budiman, *Korean J. Chem. Eng.*, **37**, 466 (2020).
- Z. Si, X. Zhang, M. Zuo, T. Wang, Y. Sun, X. Tang, X. Zeng and L. Lin, *Korean J. Chem. Eng.*, **37**, 224 (2020).
- J. Holbery and D. Houston, *JOM*, **58**, 80 (2006).
- E. L. Papadopoulou, F. Pignatelli, S. Marras, L. Marini, A. Davis, A. Athanassiou and I. S. Bayer, *RSC Adv.*, **6**, 6823 (2016).
- G. Pan, Y. Zhao, H. Xu, X. Hou and Y. Yang, *J. Clean. Prod.*, **117**, 212 (2016).
- K. Weissermel and H.-J. Arpe, *Industrial organic chemistry*, Wiley-VCH, Weinheim (2003).
- Maximize Market Research, <https://www.maximizemarketresearch.com/market> (2019).
- E. C. Botelho, N. Scherbakoff, M. C. Rezende, A. M. Kawamoto and J. Sciamareli, *Macromolecules*, **34**, 3367 (2001).
- M. Pelckmans, T. Renders, S. Van de Vyver and B. F. Sels, *Green Chem.*, **19**, 5303 (2017).
- V. Balladur, P. Fouilloux and C. de Bellefon, *Appl. Catal. A: Gen.*, **133**, 367 (1995).
- Y. Lee, S. W. Lee, H. J. Kim, Y. T. Kim, K.-Y. A. Lin and J. Lee, *Appl. Sci.*, **10**, 7506 (2020).
- H. Li, Y. Xu and J.-F. Deng, *New J. Chem.*, **23**, 1059 (1999).
- M. J. Harper, United States Patent, US6156694A (2000).
- X. Yu, H. Li and J.-F. Deng, *Appl. Catal. A: Gen.*, **199**, 191 (2000).
- H. Li, Y. Xu, H. Li and J. F. Deng, *Appl. Catal. A: Gen.*, **216**, 51 (2001).
- F. Medina, P. Salagre, J. E. Sueiras and J. L. G. Fierro, *J. Mol. Catal.*, **81**, 387 (1993).
- Z. Jia, B. Zhen, M. Han and C. Wang, *Catal. Commun.*, **73**, 80 (2016).
- C. Wang, Z. Jia, B. Zhen and M. Han, *Molecules*, **23**, 92 (2018).
- H. Liao, S. Liu, F. Hao, P. Liu, K. You, D. Liu and H. a. Luo, *React. Kinet. Mech. Catal.*, **109**, 475 (2013).
- S. Liu, F. Hao, P. Liu, H. a. Luo and H. Liao, *Res. Chem. Intermed.*, **41**, 5879 (2015).
- Y. Lv, F. Hao, S. Xiong, P. Liu and H. a. Luo, *RSC Adv.*, **6**, 60933 (2016).
- Y. Lv, F. Hao, P. Liu, S. Xiong and H. Luo, *React. Kinet. Mech. Catal.*, **119**, 555 (2016).
- Y. Lv, F. Hao, P. Liu, S. Xiong and H. a. Luo, *J. Mol. Catal. A: Chem.*, **426**, 15 (2017).
- Y. Lv, J. Li, S. Feng, P. Liu, F. Hao, W. Xiong and H. a. Luo, *Chem. Eng. J.*, **346**, 203 (2018).
- S. Alini, A. Bottino, G. Capannelli, R. Carbone, A. Comite and G. Vitulli, *J. Mol. Catal. A: Chem.*, **206**, 363 (2003).

35. K. Wilson, D.J. Adams, G. Rothenberg and J.H. Clark, *J. Mol. Catal. A: Chem.*, **159**, 309 (2000).
36. P. Gallezot, *Chem. Soc. Rev.*, **41**, 1538 (2012).
37. R. A. Sheldon, *Green Chem.*, **16**, 950 (2014).
38. J. J. Pacheco and M. E. Davis, *Proc. Natl. Acad. Sci. USA*, **111**, 8363 (2014).
39. R. Beerthuis, G. Rothenberg and N.R. Shiju, *Green Chem.*, **17**, 1341 (2015).
40. Y. Lee, E. E. Kwon and J. Lee, *Rev. Environ. Sci. Biotechnol.*, **18**, 317 (2019).
41. Y. Lee, K.-Y. A. Lin, E. E. Kwon and J. Lee, *J. Clean. Prod.*, **227**, 624 (2019).
42. D. J. Cole-Hamilton, *Science*, **299**, 1702 (2003).
43. A. Dev, A. K. Srivastava and S. Karmakar, "New generation hybrid nanobiocatalysts: The catalysis redefined", *Handbook of nanomaterials for industrial applications*, Mustansar Hussain, C., ed., Elsevier, 217-231 (2018).
44. C. Matthieu, E. Dietrich, H. Delmas and J. Jenck, *Chem. Eng. Sci.*, **47**, 2289 (1992).
45. C. Joly-Vuillemin, D. Gavroy, G. Cordier, C. De Bellefon and H. Delmas, *Chem. Eng. Sci.*, **49**, 4839 (1994).
46. J. R. Rostrup-Nielsen, *Science*, **308**, 1421 (2005).
47. J. Goldemberg, *Science*, **315**, 808 (2007).
48. M. Zhang and Y. Yu, *Ind. Eng. Chem. Res.*, **52**, 9505 (2013).
49. C. Angelici, B. M. Weckhuysen and P. C. A. Bruijninx, *ChemSusChem*, **6**, 1595 (2013).
50. E. V. Makshina, M. Dusselier, W. Janssens, J. Degrevé, P. A. Jacobs and B. F. Sels, *Chem. Soc. Rev.*, **43**, 7917 (2014).
51. R. Ohnishi, T. Akimoto and K. Tanabe, *J. Chem. Soc., Chem. Commun.*, 1613 (1985).
52. A. Chieragato, J. Velasquez Ochoa, C. Bandinelli, G. Fornasari, F. Cavani and M. Mella, *ChemSusChem*, **8**, 377 (2015).
53. J. V. Ochoa, C. Bandinelli, O. Vozniuk, A. Chieragato, A. Malmusi, C. Recchi and F. Cavani, *Green Chem.*, **18**, 1653 (2016).
54. G. Pomalaza, M. Capron, V. Ordonsky and F. Dumeignil, *Catalysts*, **6**, 203 (2016).
55. P. I. Kyriienko, O. V. Larina, S. O. Soloviev, S. M. Orlyk, C. Calers and S. Dzwigaj, *ACS Sustainable Chem. Eng.*, **5**, 2075 (2017).
56. Z. Wang, "Lebedev process", *Comprehensive organic name reactions and reagents*, Z. Wang, Ed., John Wiley & Sons, Inc., Hoboken, New Jersey, USA, 1728-1730 (2010).
57. K. J. Zeitsch, *The chemistry and technology of furfural and its many by-products*, Elsevier, Amsterdam, The Netherlands (2000).
58. J.-P. Lange, E. van der Heide, J. van Buijtenen and R. Price, *ChemSusChem*, **5**, 150 (2012).
59. H. Choudhary, S. Nishimura and K. Ebitani, *Chem. Lett.*, **41**, 409 (2012).
60. H. Choudhary, S. Nishimura and K. Ebitani, *Appl. Catal. A: Gen.*, **458**, 55 (2013).
61. R. M. Deshpande, V. V. Buwa, C. V. Rode, R. V. Chaudhari and P. L. Mills, *Catal. Commun.*, **3**, 269 (2002).
62. B. K. Ly, D. P. Minh, C. Pinel, M. Besson, B. Tapin, F. Epron and C. Especel, *Top. Catal.*, **55**, 466 (2012).
63. S.-H. Chung, Y.-M. Park, M.-S. Kim and K.-Y. Lee, *Catal. Today*, **185**, 205 (2012).
64. B. K. Ly, B. Tapin, M. Aouine, P. Delichere, F. Epron, C. Pinel, C. Especel and M. Besson, *ChemCatChem*, **7**, 2161 (2015).
65. K. H. Kang, U. G. Hong, Y. Bang, J. H. Choi, J. K. Kim, J. K. Lee, S. J. Han and I. K. Song, *Appl. Catal. A: Gen.*, **490**, 153 (2015).
66. W. Zhang, Y. Zhu, S. Niu and Y. Li, *J. Mol. Catal. A: Chem.*, **335**, 71 (2011).
67. V. V. Pushkarev, N. Musselwhite, K. An, S. Alayoglu and G. A. Somorjai, *Nano Lett.*, **12**, 5196 (2012).
68. K. An, N. Musselwhite, G. Kennedy, V. V. Pushkarev, L. Robert Baker and G. A. Somorjai, *J. Colloid Interface Sci.*, **392**, 122 (2013).
69. T. Ishida, K. Kume, K. Kinjo, T. Honma, K. Nakada, H. Ohashi, T. Yokoyama, A. Hamasaki, H. Murayama, Y. Izawa, M. Utsunomiya and M. Tokunaga, *ChemSusChem*, **9**, 3441 (2016).
70. R. Fischer and R. Pinkos, United States Patent, US5905159A (1999).
71. N. Vecchini, A. Galeotti and A. Pisano, International Patent, WO2016092517A1 (2016).
72. Y. Wang, D. Sun, Y. Yamada and S. Sato, *Appl. Catal. A: Gen.*, **562**, 11 (2018).
73. R. Richard, M. Jacquin, M. Dorato, N. Pacheco and C. Rannoux, United States Patent, US10322978B2 (2019).
74. F. Sato, S. Sato, Y. Yamada, M. Nakamura and A. Shiga, *Catal. Today*, **226**, 124 (2014).
75. Y. Nakagawa, T. Kasumi, J. Ogihara, M. Tamura, T. Arai and K. Tomishige, *ACS Omega*, **5**, 2520 (2020).
76. K. G. Childers, S. D. Dreher, J. Lee and J. M. Williams, *Org. Process Res. Dev.*, **10**, 934 (2006).
77. L. Liu, T. Asano, Y. Nakagawa, M. Tamura and K. Tomishige, *Green Chem.*, **22**, 2375 (2020).
78. F. Jing, B. Katryniok, M. Araque, R. Wojcieszak, M. Capron, S. Paul, M. Daturi, J. M. Clacens, F. De Campo, A. Liebens, F. Dumeignil and M. Pera-Titus, *Catal. Sci. Technol.*, **6**, 5830 (2016).
79. M. Decker, J. Schmidt, H. Hoffmann and H. J. Pistor, United States Patent, US3671566A (1972).
80. J. Shi, X. Zhang, G. Chen, L. Fan, C. Shu, G. Dang, X. Zhan, S. Feng, H. Wang, Z. Cao, Y. Zhang, D. Dong and J. Zhao, China Patent, CN106146345B (2018).
81. M. T. Musser, "Adipic acid", *Ullmann's encyclopedia of industrial chemistry*, Wiley-VCH, Weinheim (2000).
82. D. E. Blanco, A. Z. Dookhith and M. A. Modestino, *React. Chem. Eng.*, **4**, 8 (2019).
83. J.-J. Dai, Y.-B. Huang, C. Fang, Q.-X. Guo and Y. Fu, *ChemSusChem*, **5**, 617 (2012).
84. T. Werpy and G. Petersen, *Top value added chemicals from biomass: Volume 1 - results of screening for potential candidates from sugars and synthetic gas*, U.S. Department of Energy (2004).
85. J. E. Baldwin, M. North, A. Flinn and M. G. Moloney, *Tetrahedron*, **45**, 1453 (1989).
86. C. de Bellefon and P. Fouilloux, *Catal. Rev.-Sci. Eng.*, **36**, 459 (1994).
87. B. W. Howk, United States Patent, US2166151A (1939).
88. R. L. Augustine, *Catal. Rev.-Sci. Eng.*, **13**, 285 (1976).
89. B. D. Herzog and R. A. Smiley, "Hexamethylenediamine", *Ullmann's encyclopedia of industrial chemistry* (2012).
90. S. K. Sengupta, T. A. Koch and K. R. Krause, United States Patent, US5900511A (1999).
91. Y. Lv, H. Cui, P. Liu, F. Hao, W. Xiong and H. a. Luo, *J. Catal.*, **372**, 330 (2019).
92. M. J. Gilkey and B. Xu, *ACS Catal.*, **6**, 1420 (2016).

93. H. Liu, Y. Guo, Y. Yu, W. Yang, M. Shen, X. Liu, S. Geng, J. Li, C. Yu, Z. Yin and H. Li, *J. Mater. Chem. A*, **6**, 17323 (2018).
94. M. Serra, P. Salagre, Y. Cesteros, F. Medina and J.E. Sueiras, *J. Catal.*, **209**, 202 (2002).
95. R.-J. van Putten, J. C. van der Waal, E. de Jong, C. B. Rasrendra, H. J. Heeres and J. G. de Vries, *Chem. Rev.*, **113**, 1499 (2013).
96. E. Nikolla, Y. Román-Leshkov, M. Moliner and M. E. Davis, *ACS Catal.*, **1**, 408 (2011).
97. Y. J. Pagán-Torres, T. Wang, J. M. R. Gallo, B. H. Shanks and J. A. Dumesic, *ACS Catal.*, **2**, 930 (2012).
98. S. Xu, C. Yin, D. Pan, F. Hu, Y. Wu, Y. Miao, L. Gao and G. Xiao, *Sustain. Energy Fuels*, **3**, 390 (2019).
99. T. Buntara, S. Noel, P.H. Phua, I. Melian-Cabrera, J. G. d. Vries and H. J. Heeres, *Angew. Chem. Int. Ed.*, **50**, 7083 (2011).
100. E. L. Dias, J. A. W. Shoemaker, T.R. Boussie and V.J. Murphy, United States Patent, US9518005B2 (2016).
101. T. Horlenko and H. W. Tatum, United States Patent, 3,215,742 (1965).
102. C. Müller, M. Bock, M. D. Silva, R.-H. Fischer, B. Blank, A. Kandler, J.-P. Melder, B. Otto, M. Schelwies and A. Henninger, United States Patent, US20160326092A1 (2016).
103. A. B. Dros, O. Larue, A. Reimond, F. De Campo and M. Peratitus, *Green Chem.*, **17**, 4760 (2015).
104. V. Thaore, D. Chadwick and N. Shah, *Chem. Eng. Res. Des.*, **135**, 140 (2018).
105. S. Kim, Y.F. Tsang, E. E. Kwon, K.-Y. A. Lin and J. Lee, *Korean J. Chem. Eng.*, **36**, 1 (2019).
106. Y.-K. Park, J.-M. Ha, S. Oh and J. Lee, *Chem. Eng. J.*, **404**, 126527 (2021).
107. J. Han, Y. Kim, D. H. K. Jackson, H. Chang, H. W. Kim, J. Lee, J.-R. Kim, Y. Noh, W. B. Kim, K.-Y. Lee and H. J. Kim, *Appl. Catal. B: Environ.*, **273**, 119037 (2020).



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