



Mini-review

Toward biotechnological production of adipic acid and precursors from biorenewables

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ABSTRACT

Adipic acid is the most important commercial aliphatic dicarboxylic acid in the chemical industry and is primarily used for the production of nylon-6,6 polyamide. The current adipic acid market volume is about 2.6 million tons/y and the average annual demand growth rate forecast to stay at 3–3.5% worldwide. Hitherto, the industrial production of adipic acid is carried out by petroleum-based chemo-catalytic processes from non-renewable fossil fuels. However, in the past years, efforts were made to find alternative routes for adipic acid production from renewable carbon sources by biotechnological processes. Here we review the approaches and the progress made toward bio-based production of adipic acid.

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1. Introduction

Adipic acid or hexanedioic acid ($C_6H_{10}O_4$, M_r 146.14) is the most important commercial aliphatic dicarboxylic acid. It is isolated as colorless, odorless crystals having an acidic taste (Musser, 2005). The primary application of adipic acid is in the chemical production of nylon-6,6 polyamide, which was established in the early 1930s by W.H. Carothers of DuPont (Luedeke, 1977). The global production of adipic acid has been estimated to be at 2.6 million tons/y in 2010 and is expected to reach 3.3 million tons/y in 2016 (Merchant Research & Consulting Ltd., 2011). The adipic acid used in nylon-6,6 fibers and some resins accounts for about 65% of the total output (Merchant Research & Consulting Ltd., 2011). Adipic acid is also used to produce polyurethanes, as a reactant to form plasticizers, lubricant components and polyester polyols (Merchant Research & Consulting Ltd., 2011; Musser, 2005). Other outlets are as a food ingredient (E355) in gelatins, desserts and other foods that require acidulation (Merchant Research & Consulting Ltd., 2011; Musser, 2005).

In the industry large-scale chemical processes have been established to produce adipic acid (Merchant Research & Consulting Ltd., 2011). Almost all of the commercial adipic acid is obtained from

benzene, which is first reduced to cyclohexane. Cyclohexane is then converted to a mixture of cyclohexanone and cyclohexanol by two successive oxidation steps. This mixture is further reacted to adipic acid with nitric acid and air using copper or vanadium as catalyst (Fig. 1). Adipic acid is also made by the hydrocyanation of butadiene, followed by hydroisomerization to adiponitrile, which then is hydrolyzed. These and further chemical synthesis routes to adipic acid have been reviewed, e.g. by Musser (2005).

During the oxidation processes with nitric acid and air, N_2 , NO , NO_2 and N_2O are formed, with nitrous oxide as main byproduct. These NO_x emissions are a major environmental concern. The chemically active gas nitrous oxide contributes to global warming and ozone depletion. It is estimated that about 10% of the worldwide anthropogenic N_2O emission originates from the production of adipic acid (Alini et al., 2007). The development of an environmentally friendly chemical production of adipic acid needs a strong reduction of nitrous oxide emission, for example by N_2O -decomposition in industrial conditions (Alini et al., 2007; Shimizu et al., 2000). An alternative “green” route to the generation of adipic acid with nitric acid by direct oxidation of cyclohexene with aqueous 30% hydrogen peroxide in organic solvent- and halide-free conditions could provide a solution to this serious problem (Blach et al., 2010; Sato et al., 1998). However, the starting materials of chemical adipic acid syntheses are derived from limited non-renewable fossil fuels and have harmful properties in common, whereas adipic acid itself has very low acute toxicity (Kennedy,

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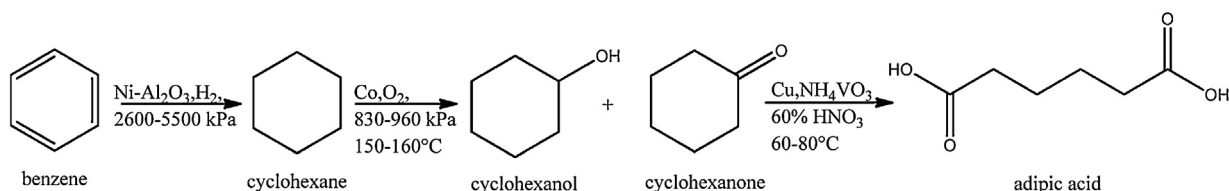


Fig. 1. Chemical route of adipic acid synthesis from benzene (Niu et al., 2002).

2002). Benzene is a volatile carcinogen and acute myeloid leukemia, a malignant hematopoietic disease, has been clearly linked to benzene exposure (Galbraith et al., 2010).

Currently and in the future, industrial biotechnology and clean technologies are keys for economic developments. It includes the production of chemicals of high purity in an environmentally acceptable, energy-efficient manner from biorenewables (Cooke, 2008; Kircher, 2006). In this field, the provision of biorenewables by green biotechnology and their processing by white biotechnology have built up two markets (Kircher, 2006). However, oil-based chemistry is so far winning the economical competition, since ecological benefits of white biotechnology are only honored by the markets if they go with cost advantages (Kircher, 2006). In the case of adipic acid, commercial production based on renewable carbon sources was announced by the companies Rennovia and Verdezyne for 2013/2014 and 2014/2015, respectively, and depending on the feedstock used, the cost advantage was estimated to be around 20–30% in the long run compared to petrochemical-based adipic acid (De Guzman, 2010).

Several attempts to produce adipic acid, or more often, precursors of adipic acid, by fermentation using selected or engineered microbial strains have been published. Here we review attempts and progress made toward the biotechnological production of adipic acid.

2. Adipic acid in cellular metabolism

In nature adipic acid has been found in juice of sugar beet and beet red. In cellular metabolism, adipic acid is an intermediate in the degradation pathways of cyclohexane, cyclohexanol or cyclohexanone, and of ϵ -caprolactam (KEGG map00930), which can be utilized for example by some *Pseudomonas* strains (Cheng et al., 2002; Steffensen and Alexander, 1995). The degradation of these compounds results in the common intermediate adipate semialdehyde, which is then further oxidized to adipic acid by 6-oxohexanoate dehydrogenase (ChnE, EC 1.2.1.63). This enzyme was found to use NADP⁺ as coenzyme in *Acinetobacter* sp. (Iwaki et al., 1999). Alternatively, the oxidation could be catalyzed by NADP⁺-dependent aldehyde dehydrogenases (EC 1.2.1.4) which catalyze the oxidation of long-chain aliphatic aldehydes to the corresponding acids (Ahvazi et al., 2000). Subsequently, adipic acid is activated to adipyl-CoA and degraded to succinyl-CoA and acetyl-CoA via β -oxidation that might employ a different set of enzymes or regulatory machinery for dicarboxylic acids as for fatty acids (Ahvazi et al., 2000; Chapman and Duggleby, 1967; Cheng et al., 2000). Moreover, various carboxylic acids including adipic acid were found to be formed by the degradation of longer aliphatic dicarboxylic acids in the mammalian liver (Cerdan et al., 1988), and by the degradation of *n*-alkylcyclohexanes with an even number of carbon atoms in the side chain as found in *Micrococcus* sp. (Yoshizako et al., 1989). Adipic acid was also found to be formed by aliphatic nitrilases from adiponitrile, which belongs to the group of nitrile compounds synthesized on large scale for applications in solvents, plastics, synthetic rubber, pharmaceuticals or herbicides (Levy-Schil et al., 1995). Since nitriles are toxic, their degradation is an important environmental concern. However, known nitrilases

exhibit low activity on adiponitrile and industrial exploitation for production of adipic acid requires higher nitrilase activity (Bayer et al., 2011; Levy-Schil et al., 1995). Fig. 2 schematically summarizes the basic mode of access to bio-based adipic acid including the chemo-catalytical conversions of glucose and *cis, cis*-muconic acid which are mentioned below.

The degradation pathway of cyclohexanol and cyclohexanone has been under investigation for decades (see, for example, Cheng et al., 2002; Donoghue and Trudgill, 1975; Norris and Trudgill, 1971). Several screenings for relevant metabolic genes from various species revealed gene clusters and enzymes including cyclohexanol dehydrogenases, monooxygenases, ϵ -caprolactone hydrolase, and 6-hydroxyhexanoate dehydrogenases, which were characterized and tested for activity (see, for example, Brzostowicz et al., 2000, 2002, 2003, 2005; Cheng et al., 2000). When distinct gene clusters from *Acinetobacter* sp., *Arthrobacter* sp. or *Rhodococcus* sp. were expressed in *Escherichia coli*, traces of adipic acid could be detected, demonstrating the specific degradation of cyclohexanol and cyclohexanone (Brzostowicz et al., 2003; Cheng et al., 2000). For example, adipic acid was accumulated at a higher level in the heterologous *E. coli* host than in the native *Acinetobacter* sp., possibly due to the inability of *E. coli* to further metabolize adipic acid. However, the conversion rates and adipic acid levels were much too low for production and the petroleum-based substrates (cyclohexanol, cyclohexanone) would not follow the idea of a sustainable production process from renewable carbon sources.

3. Bio-based production of the adipic acid precursors *cis, cis*-muconic acid and glucaric acid

In contrast to the degradation pathways leading to adipic acid as an intermediate, metabolic pathways for adipic acid biosynthesis which start from intermediates of the central carbon metabolism have not been described in the literature or in the pathway databases listed on www.pathguide.org. However, adipic acid can be obtained by chemo-catalytic conversion of the bio-based precursors *cis, cis*-muconic acid or glucaric acid in a hydrogenation process using Pt on carbon or nanoparticles of Ru₁₀Pt₂ as catalysts (De Guzman, 2010; Niu et al., 2002; Thomas et al., 2003).

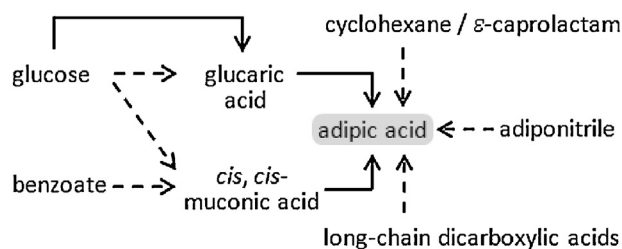


Fig. 2. Basic mode of access to bio-based adipic acid. The precursors glucaric acid and *cis, cis*-muconic acid can be produced by fermentation (---) from glucose and benzoate and chemo-catalytically converted (\rightarrow) to adipic acid. Furthermore, adipic acid is generated as intermediate in the degradation pathways of cyclohexane and even-numbered *n*-alkyl derivatives thereof, ϵ -caprolactam and long-chain aliphatic dicarboxylic acids or aldehydes, and is formed from adiponitrile by aliphatic nitrilases.

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