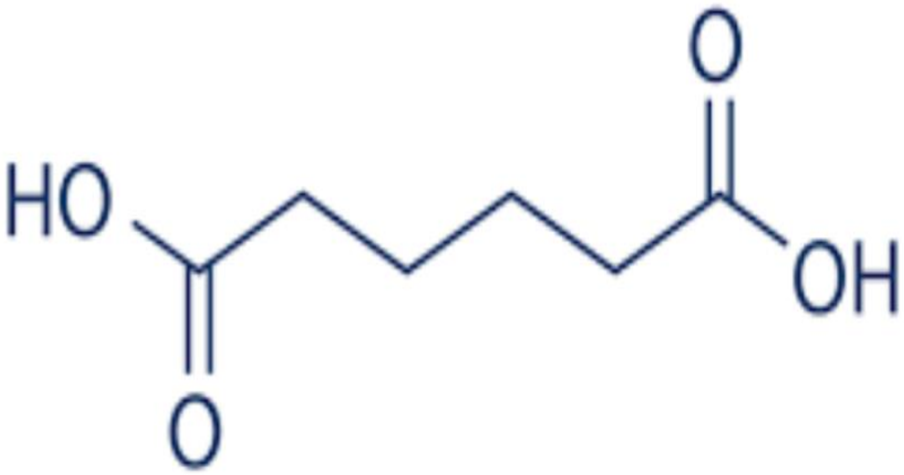

GREEN SYNTHESIS OF ADIPIC ACID

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GREEN SYNTHESIS OF ADIPIC ACID

A literature review submitted in partial fulfilment of the requirements for the degree of **Master of Science in Chemistry (Organic Chemistry)**.

BY

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APRIL 2022

DECLARATION

I declare that the literature review titled “**Green synthesis of Adipic Acid**’’ has been carried out by me in the Chemistry Department, School of Chemical Sciences, Goa University. The information derived from the literature has been duly acknowledged in the text and a list of references is provided.

CERTIFICATE

This is to certify that the literature review entitled: "**Green synthesis of Adipic Acid**" submitted by the student is the record of research work carried out by the candidate during the academic year 2021-2022 under my supervision in the partial fulfilment of the requirements for the degree of Master of Science in Chemistry.

Dr. Kashinath Dhumaskar	**Dr. Vidhyadatta Verenkar**
(Project Guide)	(Dean of SCS, Goa, University)

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There is no good work done which comes without efforts; but those efforts cannot be obtained without proper guidance. So in these few humble lines I take this opportunity to express my profound gratitude to the people who have made invaluable contribution during the course of completion of the literature review in time.

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No acknowledgments would be complete without giving thanks to our Family and friends. Finally with silent words we thank God for the energy, health and life so far and in future.

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I] ABSTRACT

Adipic acid is an organic diacid intermediate used in nylon manufacturing. It is commercially produced by an industrial process that forms nitrous oxide as a by product. Nitrous oxide has a 300-fold higher global warming potential than carbon dioxide, and an estimated 10% of its annual global emissions are a result of adipic acid production. These concerns have led to significant efforts for the development of nitrous oxide abatement technologies as well as more environmentally friendly routes for adipic acid production. New processes include both advanced chemical and biotechnological routes. In this review, we discuss developments in mitigation as well as new technologies.

II] INTRODUCTION

Adipic acid (ADP), a six carbon diacid, and used in the production of nylon 6,6 (about 75%), it is also used as a starting material for polyurethanes and plasticizers that is used to make polyvinyl chloride, the world's third-most widely produced synthetic plastic polymer.[1] The annual global production of ADP exceeds 3 million tonnes, growing at a rate of 3–5% annually, with a 10 years average price of \$1.60 ± 0.26 per kg.[1,2] The global market for ADP is expected to exceed \$8 billion USD by 2025.[2] However, a major concern of ADP manufacturing is its negative environmental impact. In 2016, U.S. petrochemical production released 37.3 million metric tonnes (MMT) of CO_2 equivalents (CO_2, CH_4 and NO_2).[3] The production of adipic acid, due to release of nitrous oxide (NOx), was responsible for nearly 20% of these emissions.[3] In addition, the ADP manufacturing chain has been responsible for other environmentally hazardous wastes.[3] Benzene, the primary feedstock for ADP, is a non-renewable petroleum based feedstock as well a volatile carcinogen.[4] Given the rising demand for ADP and the need to reduce its negative environmental impact, significant effort has been made for the development of a more sustainable process.[5] Work with petroleum-based feedstocks has focused on NOx abatement strategies and alternative routes to ADP that do not produce NOx. Additionally, both the chemical and biological conversion of renewable feedstocks (such as glucose, glycerol or lignocellulosic sugars) have been evaluated. To date, current alternative routes to ADP are not competitive with the traditional chemistry.[6] Previous reviews have been dedicated to new catalytic processes,[7] or biotechnology based approaches to manufacture ADP,[1,6]Additionally, recent technoeconomic analyses have reported the potential of newer greener processes to reach competitive selling prices.[6,8] This review is focused on providing an overview of alternative new competing routes to ADP synthesis. Specifically, we discuss the routes which are less harmful to the environment and less polluting than the commercial route.

ADP is primarily manufactured via the Nitric Oxidation (NO) process; a two-step oxidation of cyclohexanone and cyclohexanol mixture (KA) catalyzed by nitric acid.[1,7,9] This reaction was developed in the late 1930s. ADP is typically produced in a one pot reaction starting with benzene as the initial feedstock.[2,10,11] After reduction of benzene to cyclohexane, at high temperature and pressure, cobalt aerobically oxidizes this intermediate to form KA oil.[10,12] KA oil oxidizes more readily than cyclohexane, thus, limited oxidation is necessary to prevent undesired byproducts.[13] This results in the need to recycle 90% of unreacted cyclohexane. Finally, KA oil is oxidized with excess HNO_3 to produce ADP with a conversion yield of ∼95%.3

A variant of the NO process, namely the two-step hydration/oxidation of cyclohexene via cyclohexanol is a second process currently used for ADP production.[13]The major drawback of this route, like the NO process, remains the requirement for nitric acid for the final oxidation of cyclohexanol to ADP, and the subsequent generation of NOx. NOx is well known for its negative environmental impacts like ozone layer damage, acid rain causation, and global warming. It is estimated that a complete replacement of the NO process could reduce 7.9 million tonnes of CO_2 equivalents per year. Therefore, there is a need of different route for the synthesis of adipic acid which is more environment friendly and less toxic.

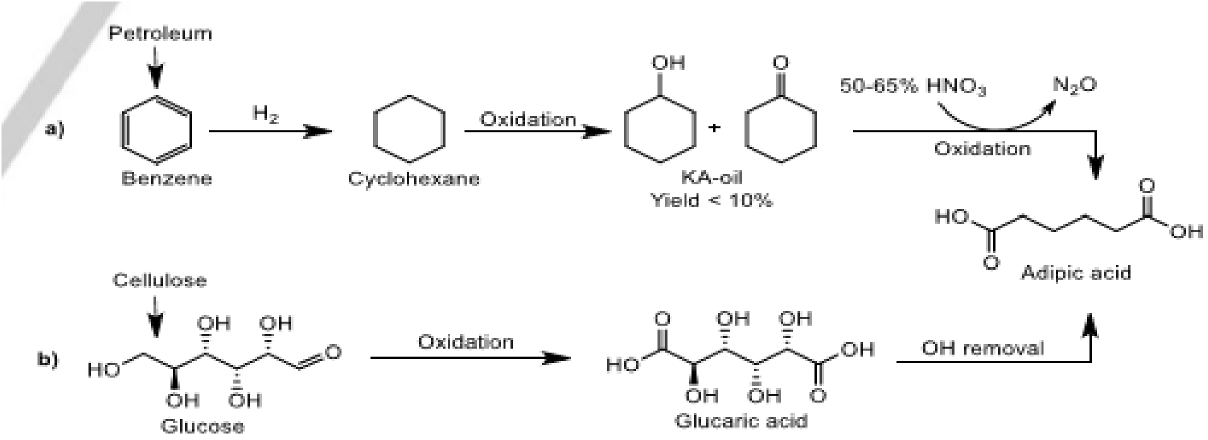
III] LITERATURE REVIEW

Adipic acid is one of the most important platform industrial chemicals, and is still being manufactured with an unsustainable, inefficient multistep process involving a toxic oxidant (HNO_3) and generating large amounts of nitrous oxide ga. This has raised many concerns. The use of NOx free routes to ADP has garnered significant effort. Not only will it greatly reduce the burden of controlling greenhouse gas emissions, but it also will have the potential to reduce the capital cost investments associated with the installation of abatement systems in situ. To address this, various petrochemical feedstocks, and oxidants have been evaluated in the development of new or improved NOx free and more sustainable chemical routes to ADP. These routes are discussed below.

Synthesis of Adipic Acid from Biomass:

Weiping Deng et al reported a reaction on the development of efficient catalysts for a two-step chemo-catalytic route for the conversion of glucose to adipic acid via glucaric acid.[14] In the first step, both the aldehyde and terminal hydroxyl group are oxidized to carboxylic groups. In the second step, the four hydroxyl groups in glucaric acid is removed. Successful strategies to remove multiple hydroxyl groups simultaneously are very few. A study disclosed that the addition of HBr or HI could promote the cleavage of C–OH bonds in glucaric acid in an acid solvent in the presence of a supported noble metal catalyst under H_2. The use of corrosive halogen and acid solvent, however, increases the complexity and cost in reactor design and product separation, and makes the process less green. Deoxydehydration (DODH), an emerging strategy to remove two vicinal hydroxyl groups in diols. Most DODH catalysts, such as rhenium oxide, can only catalyze the conversion of cis-diols to olefins. However, in addition to a pair of cis-diols, glucaric acid also contains one pair of trans-diols, which is difficult to be removed by the DODH catalyst. In this it reported a combination of heterogeneous catalysts for the synthesis of adipic acid from glucose via glucaric acid which gave an overall yield of 81%.[14] Carbon nanotube-supported platinum nanoparticles (Pt/CNT) are found to catalyze the selective oxidation of glucose to glucaric acid. In this it demonstrated that a bifunctional catalyst composed of rhenium oxide and palladium on activated carbon (Pd−ReOx/AC) is very efficient for the removal of hydroxyl groups in a variety of biomass-derived carboxylic acids and offered adipic acid with a yield of 99% in the conversion of glucaric acid.

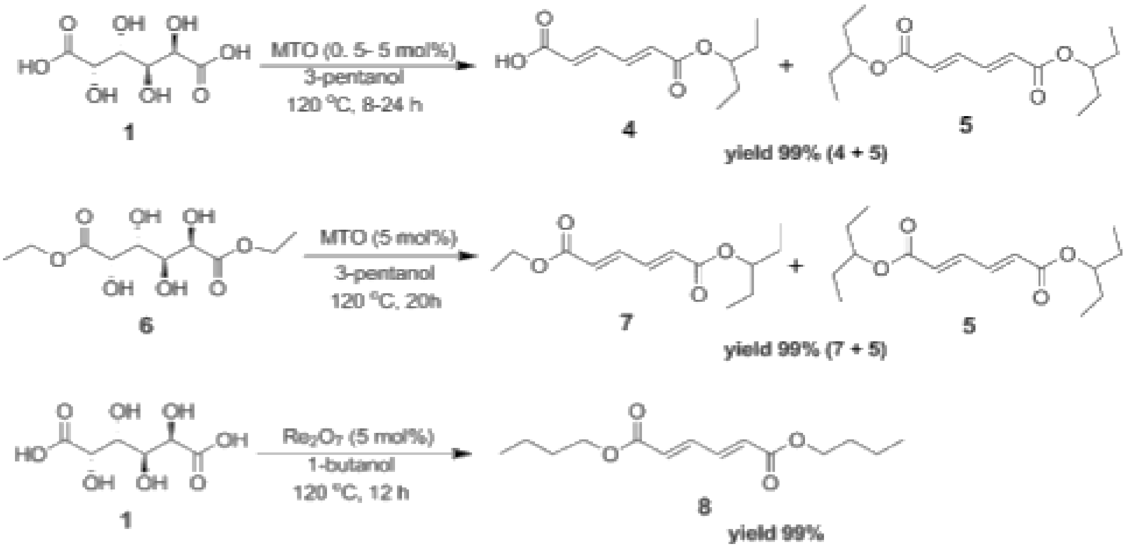
The pH value of the reaction medium determined the product selectivity. By increasing the initial pH value of the reaction medium with a base (e.g., KOH), the formation of glucaric acid was remarkably enhanced.



Scheme: Conversion of Glucose to Adipic Acid.[14]

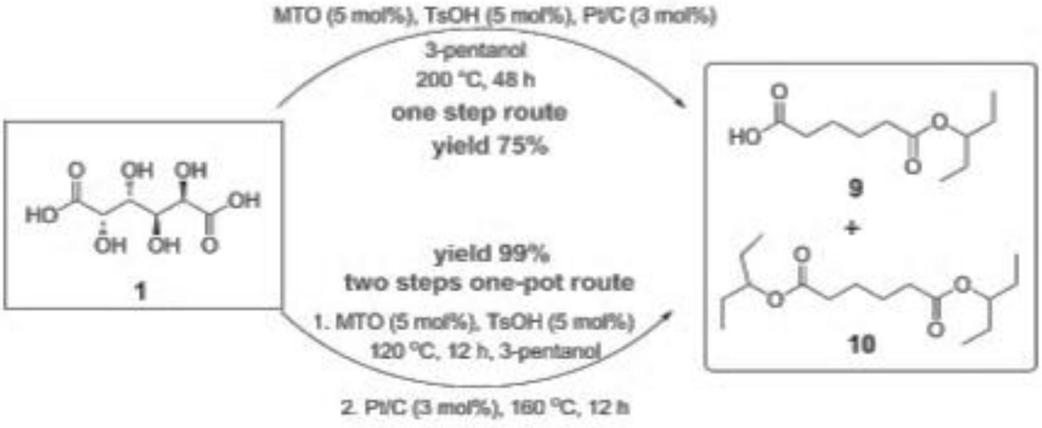
Xiukai Li et al tested Mucic Acid under typical DODH reaction conditions with methyltrioxorhenium (MTO) as a catalyst.[15] Initially Mucic Acid was heated in 3-octanol at 180°C for 2 hours. The reaction went very slowly and the selectivity was low. The majority of mucic acid remained insoluble throughout the reaction. With 3-pentanol as the solvent at 120°C, the reaction was still slow in the initial stage, because of low solubility, but showed excellent selectivity. Kinetic studies showed that mucic acid was gradually converted into monoester and diester in boiling 3-pentanol (120°C) with 5 mol% MTO. The yield of monoester increased continuously and reached the maximum at 24 hours, and then decreased. Whereas, the yield of diester kept increasing even after 24 hours. This showed that mucic acid was first converted inti monoester and then into diester. To accelerate the reaction, Brønsted acids were added as cocatalysts to promote the esterification step and enhance the solubility of the starting material. Various Re catalysts have also been tested for the reaction. However, [$Re_2(CO)_{10}$] is inactive for the DODH reaction of mucic acid, probably because of the poor tolerance of [$Re_2(CO)_{10}$] to the carboxylic acid group.[15] Using bioderived 1-

butanol showed that the reaction efficiency is similar to that of 3-pentanol, and quantitative conversion of mucic acid into muconate was achieved in 12 hours with Re_2O_7 as the catalyst.



Scheme: DODH of Mucic Acid and its Diethyl ester to muconates.[15]

A subsequent transfer-hydrogenation reaction was demonstrated for the conversion of Muconates to adipic acid or its esters in 3-pentanol at 200°C in 12 to 24 hours with different catalysts (Ru/C, Pd/C, or Pt/C). The reaction was highly selective and no other by product was observed. Since both the DODH and transfer hydrogenation reaction could be conducted in 3-pentanol, the reaction was carried out in a closed reaction system with MTO, TsOH, and Pt/C catalysts, mucic acid was converted into adipic acid esters in 75% yield within 48 hour at 200°C. But when the reaction was carried out in a one-pot, two step manner, run at 120°C a 99% yield of the adipic acid esters (96% isolated yield) was achieved directly from mucic acid.[15] The adipic acid esters could be further hydrolyzed to give free adipic acid in 94% yield upon isolation.

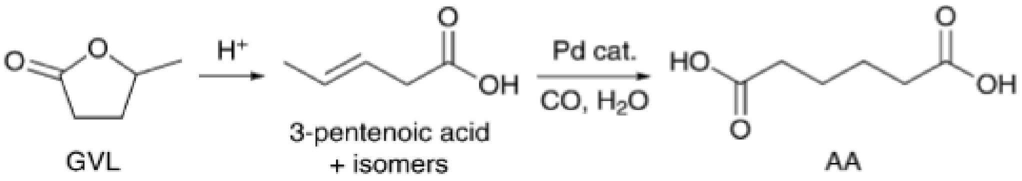


Scheme: Conversion of Mucic Acid into Adipic Acid esters by a DODH/ transfer-hydrogenation process in one pot.[15]

Nara Shina et al developed a recyclable Re-catalyzed deoxydehydration (DODH) reaction with an ionic liquid (IL) as a reaction medium for an efficient synthesis of adipic acid, from biomass galactaric acid.[16] The solubility of ILs allowed a homogeneous DODH reaction to produce muconate in excellent yields. Use of the IL also enabled an efficient separation of the DODH product from the reaction mixture by simple decantation.[16]

Stijn Van de Vyver and Yuriy Roma ´n-Leshkov reported a three-step catalytic process for adipic acid production,[12] comprising: (i)reactive distillation of gamma-valerolactone (GVL) in the presence of an acid catalyst such as SiO_2–Al_2O_3 to produce a mixture of pentenoic acid isomers, (ii) carbonylation of the pentenoic acids to adipic acid with an in situ prepared palladium catalyst, and

(iii) precipitation of adipic acid and recycling of the catalyst together with the unreacted pentenoic acid isomers.



Scheme: Catalytic conversion of GVL to adipic acid via pentenoic acid.[12]

Adipic acid was the only compound formed. After collection of crude Adipic Acid fractions by, crystallisation, filtration, washing with ethyl acetate and drying under vacuum yields of 22–48% were obtained.

The selective formation of Adipic Acid was attributed to the rapid equilibrium between the pentenoic acid isomers and the difference in carbonylation rate depending on the position of the C=C double bond.

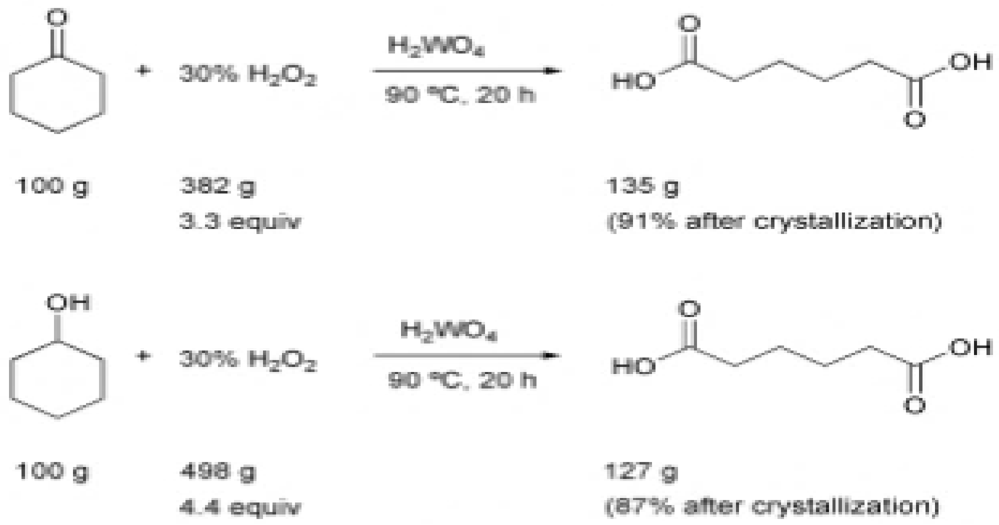
The relatively high yield of Adipic Acid from sugars, enabling cost structures in line with petrochemical processes, makes Adipic Acid a good candidate for bioproduction. The non-renewable petroleum feedstock in the commercial production is replaced by carbohydrates which are environment friendly renewable source. Also there is no use of HNO_3 as in commercial production and hence no production of nitrous oxide which is considered toxic.

Alternative oxidants:

Hydrogen peroxide is an ideal oxidant because it has a high oxygen content, and water is the sole theoretical co-product. This oxidant has become very inexpensive, and in fact is produced in quantities of ca. 2.4 million metric tons year^{-1} for use, mainly as a bleach. H_2O_2 can be a clean oxidant only if it is used in a controlled manner without organic solvents and other toxic compounds.[17]

Yoko Usui and Kazuhiko Sato reported the practical procedures for adipic acid synthesis from the oxidation of cyclohexanone and cyclohexanol with aqueous 30% H_2O_2.[18] These synthetic procedures satisfied the following conditions: (1) they are organic solvent and halide-free systems; (2) they give a high yield; and (3) they are simple and involve safe manipulation.

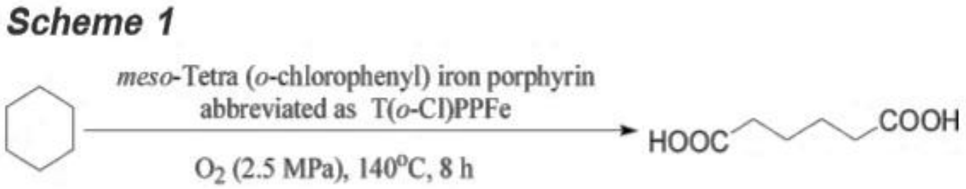
Reaction of Cyclohexanone, 30% H_2O_2, and H_2WO_4 in open air at 90 °C gave adipic acid in >99% yield. The collection of the crystalline product by filtration followed by drying in air produced a colourless, analytically pure adipic acid in 91% yield. The aqueous phase of the reaction mixture was reused with 60% H_2O_2 and gave adipic acid in 71% yield. The oxidation of cyclohexanol also produced crystalline adipic acid in 87% yield.[18]



Scheme: Catalytic conversion of Cyclohexanone and Cyclohexanol to Adipic acid.[18]

Although the reaction utilizes H_2WO_4 as the precatalyst, it is readily oxidized with H_2O_2 to form $H_2[WO(O_2)_2(OH)_2]$, which is soluble in water. When Na_2WO_4 was used instead of H_2WO_4, the oxidation of cyclohexanone and cyclohexanol did not proceed. Since Na2WO4 is also readily oxidized with H_2O_2 to form $Na_2[WO(O_2)_2(OH)_2]$, the acidic nature of the catalyst is crucial for the reaction.

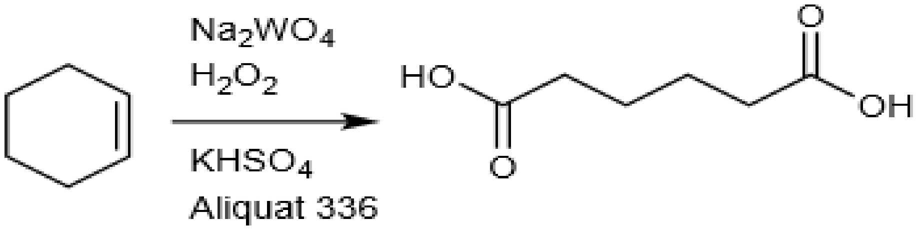
A one-pot oxidation from cyclohexane to adipic acid has been developed, catalyzed by Fe-porphyrin in the presence of molecular oxygen without any additives.[19] Ying Yuan et al performed a reaction of cyclohexane and T(o-Cl)PPFe catalyst. After flushing several times with O_2, 2.5 MPa of O_2 was charged. The reaction was performed at 140 °C for 8 h. The oxidation products were a mixture of solids and liquids. The solid products were separated from the resulting mixtures by vacuum distillation, followed by recrystallization. The obtained product gave 2.503 g of pure adipic acid (21.4%). Identifications of the different products were carried out with melting-point testing device and IR and HPLC analysis. [19]



Scheme: Conversion of Cyclohexane to Adipic Acid.[19]

G. Lapisardi et al prepared a catalyst Ti–AlSBA15 used for the synthesis of adipic acid from cyclohexene and organic hydroperoxides.[20] The incorporation of aluminium into the framework of mesostructured SBA15 silica either by direct synthesis or by post-synthesis followed by titanium grafting using titanium tetrachloride as Ti precursor leads to bifunctional Ti–AlSBA15 catalysts very active in the ‘‘one-pot’’ synthesis of adipic acid. Depending on the mode of preparation, the reaction between cyclohexene and tert-butyl hydroperoxide (TBHP), under mild, stoichiometric conditions, can lead to an adipic acid yield better than 80%.[20]

Scott M. Reed and James E. Hutchison reported a process for adipic acid synthesis that uses sodium tungstate–catalyzed oxidation of cyclohexene by hydrogen peroxide in water.[21] This process substitutes an environmentally benign oxidizing agent for a hazardous one, uses water as the solvent. Because the sodium tungstate and the phase-transfer reagents are not consumed in the reaction, it is possible to recycle the aqueous reaction mixture. It is only necessary to add fresh cyclohexene and hydrogen peroxide to the recycled catalyst solution to repeat the reaction.



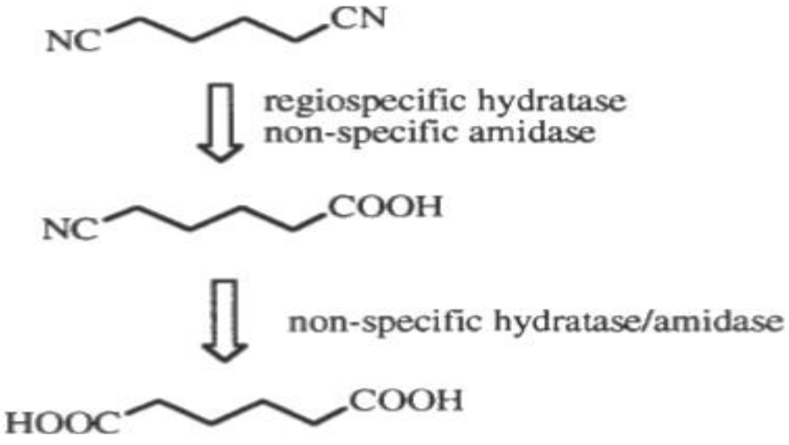
Scheme: Catalytical conversion of cyclohexene to Adipic Acid using Hydrogen peroxide.[21]

Using alternative oxidants avoids the production of nitrous oxide which causes greenhouse effect acid rain and much more, as a result of which the production of Adipic Acid is much more greener, less toxic and environment friendly.

Biological conversion of substrates to adipic acid:

Adipic Acid occurs in nature as a metabolic intermediate in the n-alkyl cyclohexane degradation pathways of several bacteria including Pseudomonas, Acinetobacter and Nocardia. However, the initial heterologous expression of these pathways in E. coli resulted in only trace production, too low for industrial production. As a result, numerous biotechnological routes to Adipic Acid have been investigated. These routes either directly produce Adipic Acid from various carbon sources or produce Adipic Acid via the biosynthesis of a precursor which then is converted to Adipic Acid through traditional chemical catalysis.

Donald A. Cowan et al reported the synthesis of adipic acid from Adiponitrile by nitrile metabolizing enzymes.[22] Comamonas testosteroni nitrilase was reported to have a specific activity for conversion of adiponitrile to adipic acid.

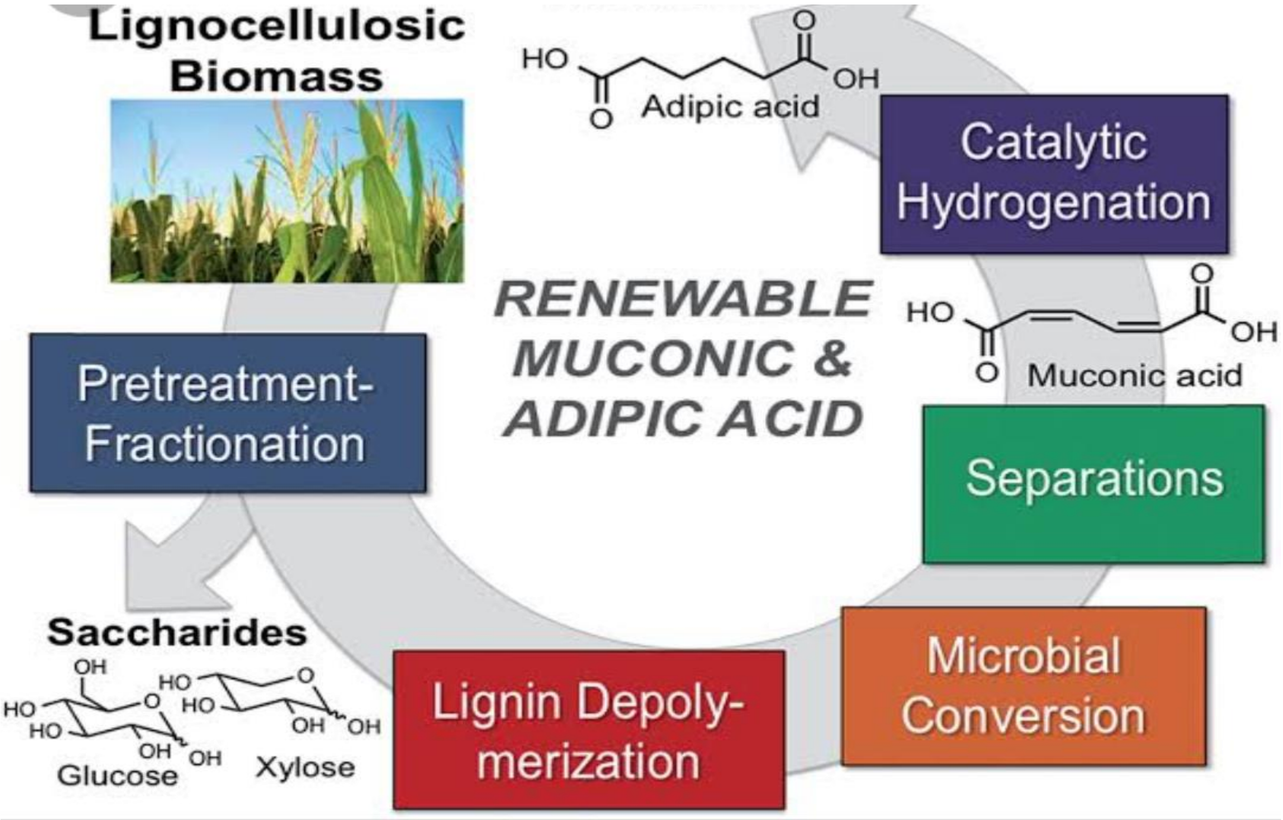


Scheme: Conversion of Adiponitrile to Adipic Acid.[22]

Yu Deng Yin Mao et al reported a reaction where in adipic acid could be synthesized by engineering yeast strains through α- and/or ω-oxidation of long chain substance such as n-alkanes or fatty acid. The long-chain fatty acid entered ω-oxidation by hexanoate synthase (HexS).[10] The first step of the ω-oxidation pathway in Candida tropicalis, was to produce 6-hydroxycaproic acid. The cytochrome P450 hydroxylase complex, was responsible for this reaction, consisting of the NADPH cytochrome P450 reductase (CYP) and NADPH cytochrome P450 reductase (CRP). Then, 6-oxohexanoic acid was prepared from 6-hydroxycaproic acid by fatty alcohol dehydrogenase (ADH) or fatty alcohol oxidase (FAO). 6-oxohexanoic acid was converted to adipic acid by fatty aldehyde dehydrogenase (Ald DH). It over-expressed HexS, CPR, CYP450, ADH, FAO and Ald DH genes in C. tropicalis and modified other genes to channel more carbon to adipic acid. After 6 days of cultivation, more than 4 g/L of adipic acid was produced by Candida tropicalis sAA580 on coconut oil.[10]

Currently, the yield of adipic acid is very low. The unbalanced expressions of the genes encoding the adipate synthesis enzymes made the host cells over-accumulate the metabolic intermediates, reducing the adipate yield and the cell growth. This has been one of the major problems.

The consolidated bioprocessing (CBP) is the process biologically converting lignocellulosic biomass to the desired products without pre-treatment or adding enzymes to hydrolyze lignocellulosic biomass. Using a CBP scheme for adipic acid was a promising route for industrial production specifically because, it does not use food source as the carbon source but rather a waste product. Additionally, the lignocellulosic biomass could be procured for manufacturing at a cheap starting price, which further lowered the production cost of adipic acid, making it more economically competitive than other production platforms.[10]



Scheme: Conversion of Lignocellulosic biomass to Adipic Acid.

Adipic acid was found to be produced in a cellulolytic actinobacterium Thermobifida fusca. In an effort to produce 1-propanol, T. fusca was transformed by using a celR-kan-adhe2 plasmid to produce a mutant strain called T. fuscaB6. This strain was able to produce small amounts of 1-propanol and adipic acid. The native-occurring adipate pathway in T. fuscaB6 was identified to be the reverse adipate degradation pathway including 5 steps: β-ketothiolase (Tfu_0875), 3-hydroxyacyl-CoA dehydrogenase (Tfu_2399), 3-hydroxyadipyl-CoA dehydrogenase (Tfu_0067), 5Carboxy-2-pentenoyl-CoA reductase (Tfu_1647) and succinyl-CoA synthetase (Tfu_2576, Tfu_2577). Tfu_1647 was the limiting step regulating the production of adipic acid. 2.23 g/L from 50 g/L glucose with 0.045 g/g-glucose yield was the highest titer of adipic acid. The B6 strain was then grown on ~20 g/L milled corncob, and 0.22 g/L adipic acid was produced. It was the first example of directly producing adipic acid from untreated lignocellulosic biomass by fermentation.

The furan derivative, 5-hydroxymethylfurfural (5-HMF), was converted to adipic acid by chemical and biological processes. The four steps involved were:

1) Acid-catalyzed dehydration of cellulose to 5-HMF in the solution of H_2SO_4, 2) Hydrogenation of 5-HMF to 2,5-di-hydroxymethyltetrahydrofuran (DHMTHF), 3) hydrogenolysis of DHMTHF to 1,6-hexanediol catalyzed by a copper chromite, 4) biological conversion of 1,6-hexanediol to adipic acid by Pseudomonadaceae spp.

There was a new discovery demonstrating that adipic acid could be converted from 5-HMF via 2,5-furandicarboxylic acid (FDCA) by a two-step process.

Production of adipic acid biologically is strongly preferable than the commercial production as it is environment friendly as HNO_3 is replaced by microorganisms and enzymes, and there are no chances of NOx production, which has negative environmental impacts.

But there are some issues with biological production such as:

1) pH of fermentation
2) Tolerance to adipic acid

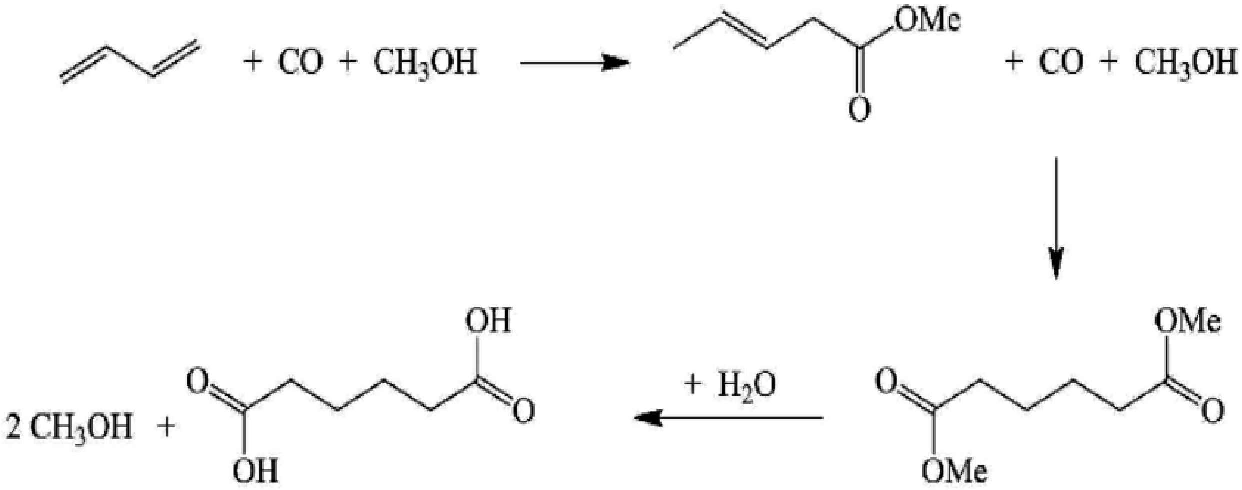
These can be resolved in future.

Alternative feedstock:

Along with the exploration of alternative oxidants, alternative carbon feed stocks have also been studied. The investigation of various feedstocks including cyclohexene, phenol, butadiene or adiponitrile have been done most of which are also produced from benzene, leading to a similar cost structure. Phenol was seen as an interesting alternative feedstock, due to its very high conversion rate to cyclohexanol (99%) favouring Adipic Acid formation with limited amount of side product generation. However, its higher selling price compared to benzene has favoured the 2-steps oxidation of cyclohexane, consequently removing it from the list of cost competitive options. Additionally, phenol based processes still generate NOx.

Jeovanna Rios et al reported a reaction where in Butadiene (1,3-butadiene) was used as an alternative feedstock for Adipic acid production. Butadiene was converted to ADP via a 2 step homogenous carbonylation, first described in the 1970’s. This route requiring methanol and carbon monoxide showed relatively high conversion yields of 72% and produced dimethyl-adipate which was then converted to adipic acid. This route did not produce NOx. Converting butadiene (\$0.79 per kg) and syngas (CO, ~\$0.10 per g) to ADP would have estimated costs for feedstocks of only \$0.34 per kg of ADP at 100% conversion yields. Current estimated yields of only 65–70% would lead to estimated operating costs in the range of ~\$0.60–0.74 per kg of ADP, again assuming feedstock costs are from

70–80% of the total operating costs for a mature petrochemical process. This cost structure makes the route through butadiene competitive with the NO process.



Scheme: Conversion of Butadiene to Adipic Acid

IV] CONCLUSION

The traditional industrial route involves oxidation of a mixture of cyclohexanol and cyclohexanone with nitric acid, but many new substrates has emerged as promising resources for the future production of adipic acid.

Important accomplishments in the research area have been achieved by the implementation of advanced process and catalyst design principles.

The production of adipic acid from renewable resources, offers a more sustainable option. Use of greener reagents avoids the production of toxic by products.

But they are not yet implemented in the industrial market as these strategies are not competitive to the commercial strategy as the overall cost of these strategies are more than the commercial one.

The preparation of adipic acid from biomass uses food stock which makes it an expensive process.

The yields of some of the new processes are very low, making it less feasible than the commercial one.

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