Review Article

VERITAS

Agricultural Biomass to Adipic Acid–An Industrially Important Chemical

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ABSTRACT

Adipic acid is widely used in the production of nylon, plasticizers, polyurethane resins, adhesives, lubricants, etc. and hence the compound annual growth rate of adipic acid is expected to be 4.4% with a market size of over USD 7,000 million. At present adipic acid is commercially manufactured using petrochemical feedstock like benzene, hexane, hexene, hexanone, etc. using nitric acid as the catalyst. The research community is exploring newer methodologies to synthesize adipic acid and other industrially valuable chemicals using renewable feedstock one of them being biomass. There are mainly two routes of synthesizing adipic acid from biomass–chemocatalytic and biological. Within these routes, there are a variety of processes like deoxydehydrogenation (DODH), hydrodeoxygenation, direct synthesis via oxidation-hydrogenation that help convert biomass to adipic acid. With heterogeneous catalysis as a developing domain, researchers have developed a variety of catalysts like zeolites, silica-based catalysts, biological catalysts, deep utectic solvents as catalysts and a variety of other heterogeneous catalysts that convert that biomass containing cellulose, hemicellulose, lignin, other sugars to adipic acid efficiently. The paper reviews all the methodologies, catalysts for conversion and market demand of adipic acid.

Keywords: adipic acid, biomass, deoxydehydrogenation, heterogenous catalysts, hydrodeoxygenation

INTRODUCTION

Biomass refers to the mass of living organisms including plants, animals, microorganisms. Considering biochemical perspective, biomass contains lignin, cellulose, fats, proteins, sugars, etc. Biomass is generally reported in mass per unit area (gm/m^2) dry weight without water and has 50% carbon (dry basis) (Houghton, 2008). Biomass is a valuable source of energy in the energy crisis that we are facing today as the plants capture carbon dioxide, have solar capturing efficiencies similar to the solar panels and store this energy (Fekete, 2013). In the coming future, biomass would have the potential to provide a cost-effective and sustainable supply of energy and help countries meet their greenhouse gas reduction targets (Demirbas, 2004). The development of newer biomass technologies, leading to more efficient biomass conversion to valuable materials is one of the best options for the use of biomass.

In an agricultural country like India where a huge amount of biomass is generated, effective and efficient use of biomass would surely lead to the development of the country and provide solutions to the energy crisis. India has already met the biomass energy target but the lack of commercial-level production facilities has made it difficult to grow. West Bengal, Uttar Pradesh, and Punjab are the top three agricultural states in India and hence proper utilization of biomass and agricultural wastes from these states would surely lead to a green economy and sustainability. As per the latest report of the Ministry of New and Renewable Energy, Government of India, about 32% of total primary energy in the country is derived from biomass and numerous steps under the 'Biomass Power and Cogeneration Programme' have been taken by the ministry to extract power from biomass that has led to total 10,145 MW capacity biomass power generation (Ministry of New and Renewable Energy, n. d.).

As an abundant, source of carbon, biomass can be considered as a promising renewable alternative to fossil fuels that can be transformed into a variety of value-added chemicals, solvents, and high-energy-density fuels by various chemical and biological means by the destruction of the structure (Luque, 2014). The US Department of Energy has reported 12 molecules that can be converted to HMF, levulinic acid (Chodimella, 2020), adipic acid, furfural, furfuryl alcohol, etc. that are industrially important chemicals. Global annual production of biomass is expected to be greater than 10 billion tonnes on a dry basis which is more than 10% of the global energy supply (Sudarsanam et al., 2018). Wood, paper that is made up of biomass has a heating value of about 4,300 kcal/kg (Biron, 2020). Dry and wet torrefaction techniques are also
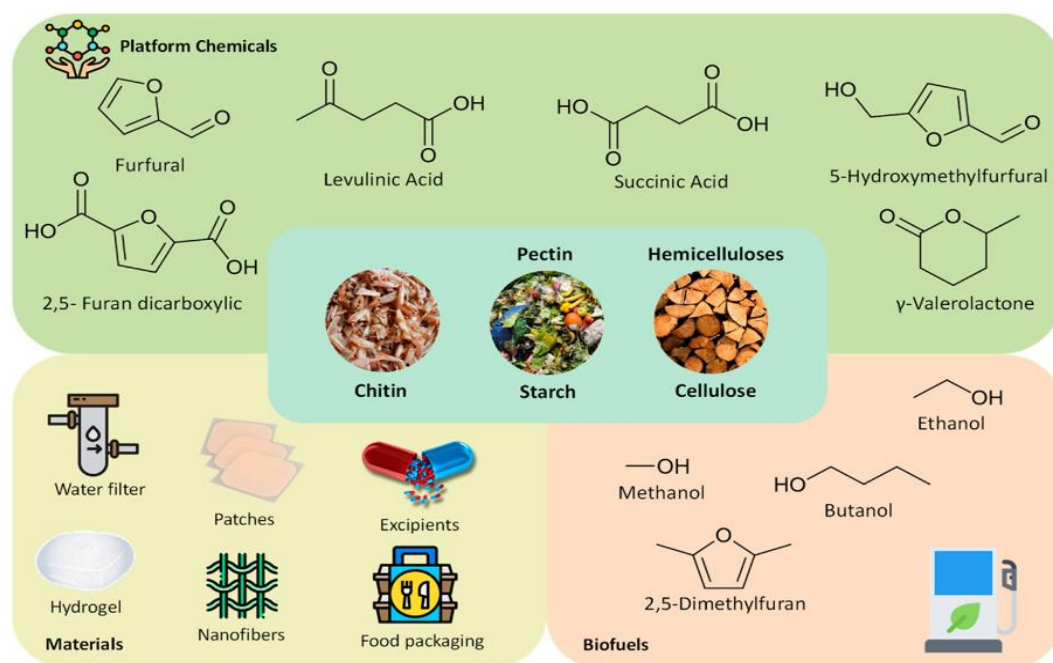
Figure 1. Various value-added chemicals and materials from biomass (Morais et al., 2020)

used to remove oxygen from the biomass and convert it into carbon-rich compounds (Itoh et al., 2018) that can be further converted into other materials via various chemical processes.

Most of the current industrial processes use carcinogenic and environmentally hazardous chemicals for the synthesis of adipic acid, levulinic acid, etc. Biomass provides a good source for the synthesis of such valuable chemicals but there is a dearth of literature on such topics and commercial production of these chemicals needs further advancements in the process. The following paper reviews various catalysts and different processes by which adipic acid can be synthesized from biomass.

BIOMASS TO VALUABLE CHEMICALS–A BRIEF OVERVIEW

Today the reserves of fossil fuels are decreasing and we are bound to depend upon renewable resources like biomass. Numerous studies have been on the way to developing newer materials from biomass and attaining a green economy approach. The term 'valorization' means to increase or enhance the value of something. Thus, biomass valorization typically means utilizing waste biomass and converting it into valuable chemicals and other biobased materials, enhancing the value of the waste. Biomass is a carbon-neutral source of producing energy and other valuables as the biomass during its growth absorbs CO_2 and upon combustion, it releases CO_2; thus, becoming carbon neutral and this helps achieve a 100% reduction in greenhouse gas emissions compared to fossil fuels (Perea-Moreno et al., 2019) and petrochemicals. But the burning of agricultural biomass is not an efficient process when compared to chemolytic processing as the former can produce fine soot particles that cause environmental pollution as reported by Ahmed et al. (2020).

Hatzis et al. (1996) performed a detailed material balance for the conversion of biomass to ethanol considering simultaneous saccharification and fermentation of various components like glucose, mannose, galactose (hexose sugars), arabinose, xylose (pentose sugars), lignin, acetic acid, furfural, and HMF products that are produced by sugar degradation, levulinic acid that is present in the biomass. Chemocatalytic conversion of biomass into valuable chemicals has several advantages like high recyclability, high catalytic activity, sustainable and green synthesis to name a few. Zeolites, silica-based catalysts, biological catalysts, deep utectic solvents as catalysts, and a variety of heterogeneous catalysts are used for converting cellulose, hemicellulose, lignin, etc into chemicals of industrial importance (Chodimella, 2020; Kalhor and Ghandi, 2021; Singhvi and Kim, 2020; Yu et al., 2020). This biomass as a feedstock and biological agents like E. coli helps synthesize cis-muconic acid from glucose and further hydrogenation yields adipic acid. Here the numerous reaction and separation steps are less as compared to that in the synthesis of adipic acid from benzene in presence of Ni-Al$_2$O$_3$ catalyst via cyclohexane, cyclohexanol, and cyclohexanone (Doble and Kruthiventi, 2007). Cellulose is the most abundant natural polymer occurring in the biomass accounting for about 35-55% followed by hemicellulose 20-35% followed by lignin 10-30% (Zhou et al., 2016). The large and complex chemical structure of biomass is an important factor to consider when processing biomass. Biomass is broken down into simpler fractions by a series of pre-treatment steps that reduce complexity in the structure. Thus, the individual sugar units produced by destruction of huge molecules of biomass can be further used a renewable feedstock for production of green hydrogen, furfurals, levulinic acid, biofuels that can be distilled into gasoline and diesel range fractions (Alonso et al., 2010). **Figure 1** shows different chemicals that can be synthesized from biomass and agricultural waste.
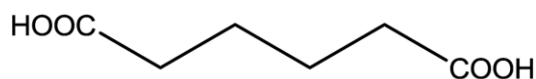
Figure 2. Structure of adipic acid (Fun et al., 2014)

BIOMASS TO ADIPIC ACID

Adipic acid is used widely for the production of nylon, polyurethanes, and other commercial products as well. The industrial synthesis of adipic acid uses nitric acid oxidation of cyclohexanone and cyclohexanol typically called KA oil (ketone and alcohol oil) (Isac-García et al., 2016) via a ring-opening mechanism. This reaction generates nitrous oxide adding to the greenhouse gas emissions thereby depleting the ozone layer. Adipic acid being commercially an important chemical needs to be developed by some other sustainable means to decrease greenhouse gas emissions. Various researchers have been studying the synthesis of adipic acid from biomass–a green synthesis route complying with the 12 principles of green chemistry. The application of heterogeneous solid catalysts in biomass valorization is of great interest because of their versatile physicochemical characteristics. The heterogeneous catalysis field contributes to about 90% of chemical production processes and more than 20% of all industrial products just because of some notable features of these catalysts like particle size, porosity, and shape (Sudarsanam et al., 2019).

Adipic acid is one of the most important chemicals from the industrial point of view. Globally every year three million tonnes of adipic acid having a value of around USD six billion is produced. Mostly it is used by the nylon industry but the food and pharmaceutical industry also have applications of adipic acid in flavouring, controlled release of acidic and basic drugs, etc. Adipic acid is a dicarboxylic acid having molecular formula COOH-(CH2)4-COOH generally obtained from petrochemical feedstock like benzene, hexene, hexanone, etc. IUPAC name of adipic acid is butane-1,4-dicarboxylic acid. It is slightly soluble in water and soluble in acetone and alcohols. Apart from petroleum feedstock, adipic acid can be synthesized from biomass sources. The following section reviews various methods and catalysts used for the synthesis of adipic acid from biomass. **Figure 2** shows the chemical structure of adipic acid.

Deoxydehydration and Hydrodeoxygenation Process for the Adipic Acid Synthesis

Deoxydehydration is a chemical reaction that involves the removal of two adjacent hydroxyl groups from a diol producing an alkene. Shin et al. (2017) used ionic liquids as a reaction medium for galactaric acid to a muconate in presence of methyltrioxorhenium catalyst (MeReO$_3$) and rhenium oxide (Re$_2$O$_7$) catalyst that on further hydrogenation with Pd/H$_2$ gave adipic acid. Dibutyl ester of galactaric acid was used as the reactant and 0.05 equivalents of para toluene sulphonic acid were also used along with 0.05 equivalents of catalyst. Ionic liquids used were [BMIm]OTf, [BMIm]PF$_6$, [BMIm]OAc, [BMIm]TFSI, [OMIm]OTf, [EMIm]OTf, and [HMIm]Otf. Bis(trifluoromethane) sulphonimide [BMIm]TFSI gave 93% muconate yield with 1g ionic liquid and 30 ml butanol as the

solvent in inert argon medium for 12 hours. Re$_2$O$_7$ catalyst showed better efficiency than MeReO$_3$ even after three runs. Dibutyl muconate when hydrogenated gave dibutyl adipate that on hydrolysis that concentrated hydrochloric acid gave adipic acid that when recrystallized in acetonitrile gave more than 91% yield of adipic acid.

Li et al. (2014) studied methyltrioxorhenium (MTO) catalyst for conversion of mucic acid to corresponding esters and then into adipic acid in presence of 3-pentanol and 5% catalyst at 120°C for 24 hours. Mucic acid is a six-carbon sugar obtained from galactose. With bronsted acid catalyst para toluene sulphonic acid (TsOH), MTO loading was decreased to 0.5 mole percent. It was reported that with Re$_2$O$_7$ catalyst, mucic acid got converted into muconate in 12 hours. These muconates were used for transfer hydrogenation reaction to get esters of adipic acid that when hydrolyzed gave adipic acid. It was observed that when all the catalysts and reactants (MTO, TsOH, Pt/C, mucic acid) were put together in a closed system, mucic acid gave 75% yield of adipic acid and with step by step reaction involving mucic acid to muconates to esters followed by hydrolysis 99% yield of adipic acid was obtained.

Zhang et al. (2016) came up with a process to get adipic acid from sugar beet residue using DODH reaction using NH$_4$ReO$_4$ catalyst followed by hydrogenation using Pt/C catalyst. Sugar beet residue contains typically contains 24% pectin, 24% cellulose, and 21% arabinan. Initially, the residue was hydrolyzed using the combination of cellulase, pectinase, and viscozyme L in 50 mM citrate buffer to give 22% glucose, 17.4% L-arabinose, and 16.5% D-galaturonic acid. Further D-galacturonic acid was converted into mucic acid and 86% conversion was achieved. This product then underwent DODH reaction for 8 hours followed by hydrogenation that gave 83% yield of adipic acid. The overall yield of adipic acid based on the sugar beet residue was found to be 8.4%.

Shi et al. (2020) developed derivatives of adipic acid from D-glucaric acid by hydrodeoxygenation reaction using HI-Rh/C catalyst. 5 weight percent of Rh/C was used under 28 bar H$_2$ pressure. 67.2% yield of 3-iodoaipic acid was obtained under optimum conditions of 130°C and 4-hour reaction time. It was observed that with no HI used, the reaction rate dropped sharply. 3-iodoadipic acid that was obtained as the product can be further converted into 3-hydroxyadipic acid (HAA) by alkaline hydrolysis using NaOH at 80°C and 3 hours to get 91.6% yield of HAA and into adipic acid using Pd/C catalyst at 160°C and 28 bar H$_2$ pressure to get 80.4% yield of adipic acid. Jenkins (2017) reported a process of producing adipic acid from glucose via hydrodeoxygenation reaction. The process proceeds as follows–first glucose is oxidized to glucaric acid that is then dissolved in acetic acid and heated that undergoes hydrodeoxygenation reaction that yields adipic acid, acetic acid, and water that is sent to a crystallizer that yields crude adipic acid that is again dissolved in water and recrystallized, filtered and dried to obtain crystals of adipic acid.

Chemocatalytic Conversion of Biomass to Adipic Acid

A variety of catalysts like bimetallic catalysts, zeolite-based catalysts, supported catalysts, noble metal catalysts have been investigated by researchers for the conversion of biomass into adipic acid. Lin et al. (2019) developed zirconia supported rhenium oxide catalyst and Pd/C catalyst for

Table 1. Optimum catalyst composition for glucose to glucaric acid and glucaric acid to adipic acid (Boussie et al., 2016)

Reaction	Catalyst composition	Yield
Glucose to glucaric acid	4% Pt on silica	66% glucaric acid
Glucaric acid to adipic acid	(a) 1.65% Rh & 4.7% Pt on silica (b) 0.5% Ru & 5% Pd on silica	(a) 89% adipic acid (b) 77% adipic acid

conversion of D-glucaric acid-1,4-lactone to dibutylhexa-2,4-dienedioate and 5 membered lactones that on hydrogenation gave dibutyl adipate. At 393 K and 24-hour reaction time, D-glucaric acid-1,4 -lactone that is a stable structure of glucaric acid was converted into dibutylhexa-2,4-dienedioate and 5 membered lactones. Post reaction, ReO_x/ZrO_2 was removed by simple filtration, and Pd/C (5 weight percent) was added with H_2 at 393 K for 4 hours. The products included dibutyl adipate and one byproduct that had unreacted reactants. The byproduct was again treated with ReO_x/ZrO_2 followed by filtration followed by treatment with Pd/C. The subsequent reaction gave 82% yield of dibutyl adipate. The OH removal was attributed to the high reducibility of ReO_x due to weak interaction with ZrO_2. Thomas et al. (2003) studied various bimetallic catalysts including Ru_6Sn, Ru_6Pd_6, $Ru_{12}Cu_4$, Ru_5Pt, $Ru_{10}Pt_2$, $Ru_{12}Ag_4$, $Ru_{10}Ag_3$, and Pt_3Cu for the conversion of cis, cis-muconic acid, or trans, trans-muconic acid (obtained from D-glucose) to adipic acid via hydrogenation reaction. All the catalysts were nanoparticles on a silica support. Ru_6Pd_6 gave 100% conversion of muconic acid and nearly 65% yield of adipic acid. $Ru_{10}Pt_2$ was found to be superior amongst all giving 90% yield of adipic acid and 90% conversion of muconic acid. Settle et al. (2019) reported supported metal catalysts synthesized by atomic layer deposition (ALD) used for the development of biobased adipic acid and overall biomass conversion. 1% by weight Pd/TiO_2 was found to be a superior catalyst techno-economically and was scalable in a fluidized bed to increase the number of layers in ALD. Boussie et al. (2016) patented metal catalysts supported silica for the oxidation of glucose to glucaric acid and bimetallic catalysts for conversion of glucaric acid to adipic acid. The optimum composition of catalysts is given in **Table 1**.

Wei et al. (2019) successfully converted furandicarboxylic acid (FDCA) to adipic acid using niobic acid-supported platinum nanoparticles ($Pt/Nb_2O_5.xH_2O$). Platinum was used for activation and dissociation of H_2 to H. Nb_2O_5 has Lewis acid site and xH_2O was used for adsorption and activation of C-O-C bond in furan. The mean size of Pt nanoparticles used was 4.2 nm. The reaction was carried out at 433 K for 4 hours and it was found that with 3.8 nm size highest yield of adipic acid was obtained. FDCA first undergoes hydrogenation over C=C bond over Pt nanoparticles forming tetrahydrofurandicarboxylic acid (THFDCA) followed by C-O-C bond cleavage to give 2-hydroxyadipic acid (HAA) followed by adipic acid by removal of hydroxyl group. It was observed that with higher pressure, the selectivity of adipic acid increased but at low pressure selectivity of THFDCA and HAA increased. At 473 K 38% yield of adipic acid was obtained. Similar work of converting THFDCA to adipic acid was reported by Gilkey et al. (2020) using various zeolite catalysts namely H/Y, H/BEA, H/ZSM-5, H/FER, H/SSZ-13 where zeolites act as proton source and reaction proceeds via ion exchange mechanism. H/BEA exhibited the highest reaction rate of 15.8 mol L^{-1} h^{-1} $site^{-1}$. THFDCA in propionic acid was used for the reaction. Post reaction the zeolite was filtered and sodium iodide was added to the supernatant solution to conduct the reaction for 4 hours at 140°C and 35 bar H_2 pressure. Zeolites being stable no aluminium leaching was observed after the reaction and the catalysts were recovered by reverse ion exchange reaction using NH_4NO_3 followed by calcination at 550°C. Gilkey et al. (2018) used a combination of solid acid nafion along with hydroiodic acid (HI) for ring-opening reaction of THFDA to adipic acid. It was firmly stated that metal or metal oxide catalysts overhydrogenate THFDCA and remove carboxylic groups. The combination of HI and nafion gives controlled release of protons and kinetic studies showed the rate law as per **Equation (1)**:

$$rate_{adipic\ acid} = k\ [THFDCA] * [HI]^2 * P_{H_2} \qquad (1)$$

Amberlyst 15 catalyst was not employed as it is thermally not very stable compared to nafion. Spent nafion was regenerated by using 5 M H_2SO_4. More than 85% selectivity of adipic acid was obtained and significant reduction in corrosiveness in the overall reaction was observed. Gilkey et al. (2017) reported similar work of metal free catalytic hydrogenolysis of THFDCA to adipic acid using HI, HBr, and HCl and the yield of adipic acid using HI, HBr, and HCl with THFDCA in propionic acid, 35 bar H_2 pressure, and 2 hours of reaction time was found to be as given in **Equation (2)**.

$$HI\ (89\%) > HBr\ (14\%) > HCl\ (3\%) \qquad (2)$$

HI cleaves the CO bond via SN2 mechanism and iodide is added to the α-Carbon. Hydrogen is added to the molecule via iodide-mediated H_2 activation. Thus the reaction proposes strong acidity and mild hydrogenation by metal-free hydrogenolysis.

Nanotechnology is the enabler and future catalyst of environment, food, agriculture, electronics, and biomedicals applications. A variety of researchers focus on nanocatalysts since they provide a larger area of application and efficient catalytic activity. Deng et al. (2020) used platinum nanoparticles on carbon nanotube support for selective oxidation of glucose to glucaric acid followed by the use of Pd-ReO_x on activated carbon as a catalyst for the removal of hydroxyl groups from glucaric acid to yield adipic acid. The carbon nanotube support promotes the oxidation of alcoholic and aldehydic groups present in glucose. At 333 K and 10 bar O_2 pressure, 67% yield of glucaric acid (mainly potassium glucarate) was obtained with platinum nanoparticles in the size range of 2.3-6 nm. The bifunctional catalyst Pd-ReO_x on activated carbon had 0.5 weight percent Pd and 5 weight percent Re. This catalyst was recyclable 25 times when the reaction was carried out for 6 hours. Post oxidation of glucose mainly potassium glucarate was obtained that on undergoing DODH reaction gave 99% yield of adipic acid. Other studies on nanocatalysts for the oxidation of glucose to glucaric acid that is a part of the synthesis of adipic acid is reported by Solmi et al. (2017) wherein Au/Carbon and AuBi/activated carbon gave 31% glucaric acid from glucose.

Han (2016) presented a green process for the synthesis of adipic acid from cellulose and hemicellulose via γ-
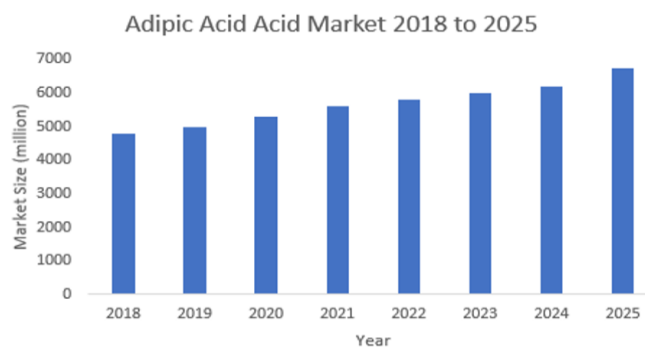
Figure 3. Global growth of adipic acid market (2018-2025)

valerolactone (GVL). Corn stover was shredded and put into a packed bed reactor in presence of Pt_3Sn/SiO_2 catalyst to get furfural (FF) and furfuryl alcohol (FFA) about 90% yield at 373 K and 35 bar H_2 pressure. In the second reactor, furfuryl alcohol was converted into levulinic acid (LA) in presence of Amberlyst 70 catalyst to get 70% yield at 398 K. LA in presence of GVL water gave 99% molar yield of GVL in presence of RuSN/C (Ru:Sn=1:4) catalyst and 35 bar H_2 pressure. Further, this GVL was converted to adipic acid at 378 K, 60 bar pressure with palladium acetate catalyst in presence of CO and H_2O to get about 48% molar yield of adipic acid. As per the energy and economic analysis performed by Han (2016) total heat requirement for this process was 93 MW and the minimum selling price of this bio-based adipic acid was determined to be $633 per metric tonnes adipic acid.

APPLICATIONS AND GLOBAL GROWTH OF ADIPIC ACID

Adipic acid is widely used in the production of nylon 6,6 and commercial production of adipic acid uses petrochemical feedstock that generates about 10% of global nitrogen oxide emissions (Kruyer et al., 2020). Thus, it is high time now that we shift to the renewable and green synthesis of adipic acid-one of that is biomass.

Once the adipic acid is synthesized, 90% of it is used for nylon production and also for the production of plasticizers and lubricants. Apart from that, adipic acid has applications in engineering plastics, automotive, electrical appliances, film coatings, footwear applications to name a few. Even if in a particular process, adipic acid is not completely synthesized, the intermediates like furfuryl alcohol, THFDCA, FDCA have numerous applications like bio-renewable plastics, spandex-a synthetic fiber from furfural (Anthonia and Philip, 2015), other polyurethane-based resins, etc. Even though it is expected that the commercial adipic acid market would rise to USD 2 billion by 2023, biobased adipic acid is still in a developing stage with very few companies like Verdezyne, DSM, BioAmeber, Ameris, Aemethis, Genomatica, and Rennovia that have developed a process for commercial production of bio-based adipic acid but that is yet to commercialize in the upcoming years. On average, adipic acid market demand and production is increasing by around 5-6% globally with its market price being $1500-1700 per metric ton. Adipic acid is considered to be the most important dicarboxylic acid and an important platform chemical for bio-based production by the International Energy

Agency (IEA) since the worldwide production of adipic acid is around three million tonnes (Skoog et al., 2018). As per the report of valuates reports, the adipic acid global market size will increase to USD 6,730 million by 2025 with a compound annual growth rate of 4.4% between 2018 and 2025 as depicted by **Figure 3** (Valuates Reports, 2019).

CONCLUSION AND FUTURE ASPECTS

Thus, the chemocatalytic conversion of biomass to adipic acid would commercialize in near future. The development of newer active catalysts for biomass conversion and achieving maximum recyclability of the catalysts remains a major challenge. The majority of catalysts used are Rh, Pt, Au, Pd, Re, etc. that are rare elements and are expensive making the overall process not very economical. Also, recovery of these catalysts post-reaction poses an issue as many times some regents or biomass components leach and adsorb on the surface of the catalyst decreasing its activity. Many researchers have utilized butanol and other alcohols as solvents for biomass valorization that are toxic and also cause environmental hazards after disposal. Thus, the use of green solvents that are not toxic and cause no harm to the environment should be used. The use of solvents derived from biomass should be preferred compared to petrochemical solvents. Simple burning of biomass to dispose of the waste releases a huge amount of greenhouse gases that cause ozone layer depletion and hence catalytic route is the most preferred one as it is carbon neutral and also helps get valuable products out of biomass.

Even though the synthesis of adipic acid from biomass that contains cellulose, hemicellulose, lignin, etc. has been successfully carried out on a laboratory scale, process development for commercial production of bio-based adipic acid needs a push and further process improvements. Most of the literature mentions some processes that are a part of adipic acid synthesis from biomass and do not report and perform complete reaction of biomass to adipic acid. Many times, the complete process involves harsh reaction conditions like very high pressure that may cause the sintering of the catalysts. Thus, the development of a reaction process that has mild reaction conditions and goes according to the green chemistry principles needs to be developed. Although the development of a green and economical process for the synthesis of adipic acid from biomass is a challenging task, once successful would surely make significant contributions to the bio-based economy. This study would surely provide the research community a comprehensive analysis of adipic acid synthesis from biomass and would help them provide solutions to the existing problems in the process and propose newer processes that are green and sustainable.

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