DOE

MARKET RESEARCH STUDY

ADIPIC ACID AND NYLON 66

August 2023

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Table of Contents

1.0 Introduction

In 2023, the Bioenergy Technology Office (BETO) released its Multi-Year Program Plan. One of its strategic goals is to decarbonize the industrial sector through research, development, and demonstration (RD&D) to produce cost-effective and sustainable chemicals, materials and processes that utilize biomass and waste resources. Biomass is classified as a renewable carbon resource (RCR) that is capable of displacing finite or non-renewable carbon resources such as petroleum, natural gas, and coal. RCR can be used in producing gasoline, plastics and industrial chemicals and is a substitute for the materials and methods used today.

A specific BETO Performance Goal for 2030 is to enable "commercial production of >10 renewable chemicals and materials with > 70% GHG reduction relative to relevant petroleum-derived counterparts, supporting >1 million metric tons/year CO2 emissions reductions.[1] Conversion technologies can produce intermediates such as sugar and lignin from low-temperature deconstruction which can then be recombined using various techniques to produce renewable chemicals and materials such as nylon 66.

The purpose of this report is to explore biomass feedstocks and those companies that to date have advanced goals that align with the BETO's Performance Goals. As commercialization is the ultimate goal of research in this area, various markets are introduced in which nylon made from biomass could have an impact including markets for automotive components, textiles and the markets for adipic acid. The report concludes with a brief look at research activities globally aimed at making this conversion a reality.

2.0 Muconic Acid Background

In the chemical industry, there is a major push to develop sustainable processes for creating renewable chemicals, many of which are currently made using petroleum.[2] One of these chemicals is muconic acid which is a platform chemical that is used in the synthesis of products like adipic acid, terephthalic acid, and caprolactam, which are used in nylon and thermoplastic polymer products.[3] A key strategy to develop a more renewable process is engineering bacteria that can convert sugar and lignin from biomass to biochemicals and biofuels. Producing muconic acid from sugars has been successful, however the engineering of bacterial strains is not yet commercially viable.

Current research is focusing on glucose and xylose in the soil bacterium Pseudomonas putida to produce muconic acid. The Agile BioFoundry which is a consortium of Department of Energy national laboratories, has been at the forefront of leading these research efforts and have identified an efficient and sustainable strategy for converting sugars into muconic acid.[4]

The chemical industry currently uses processes to extract fossil carbon to be refined into products, which has a significant impact on the environment in terms of the plastics and other chemicals from the manufacturing process that accumulate in the atmosphere. The benefit of a circular bioeconomy includes the repurposing of waste carbon from renewable sources to create high value products without the negative environmental impact. A coordinated effort is needed to explore and utilize the opportunities of future feedstocks and realize their potential for the circular bioeconomy. The Department of Energy has identified the following feedstocks as potentials for replacing the 162 million tons of petroleum, natural gas, and coal used each year for **non-energy purposes**.[5]

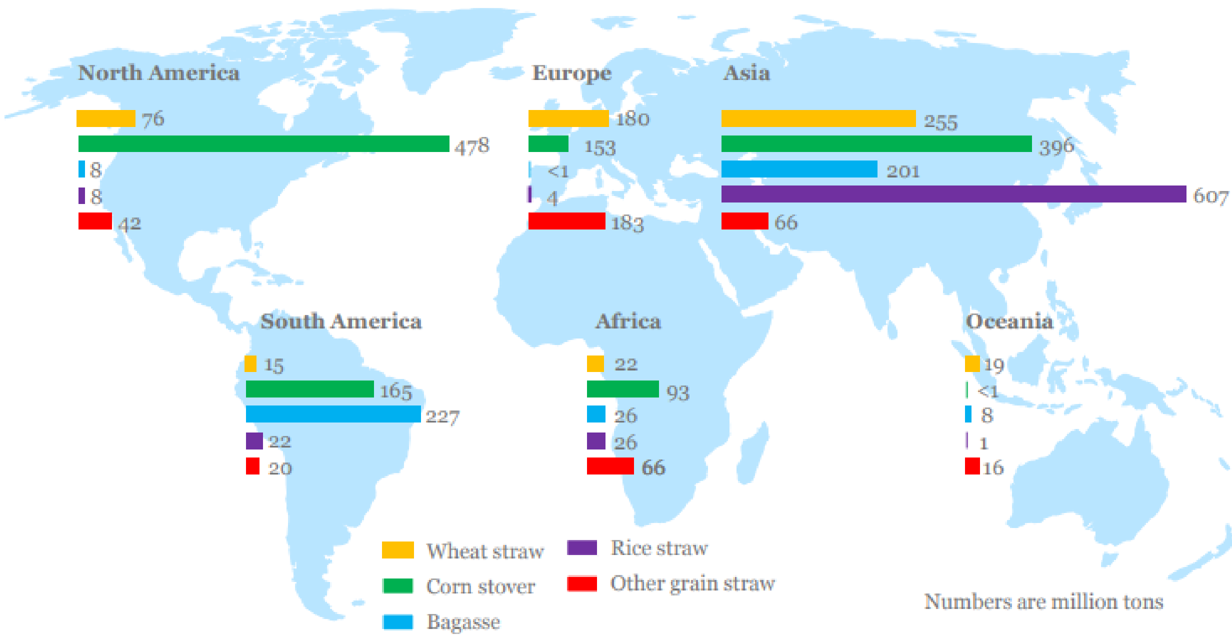
Corn Stover is the largest feedstock source of lignocellulosic material in North America, which can be used to produce muconic acid.

- 100 million dry tons of crop residues, mainly corn stover from the Midwest - $60/ton
- 18 million dry tons of manure
- 5 million dry tons of orchard trimmings
- Forestry residues
- 63 million tons of food waste
- 67 million tons of paper and paperboard

Sugars and plant lignin are the two main sources for producing bioprivileged molecules like muconic acid.[6]

2.1. Feedstock Sources

As seen in the graphic below, corn stover is the largest feedstock source of lignocellulosic material in North America. This is the most popular source in North America for conversion to sugar and lignin which is then converted to muconic acid.



Redrawn from KTN (2016). From Shale Gas to Biomass: the Future of Chemical Feedstocks. KTN, UK

Figure 1: Main Sources of Lignocellulosic Material Around the World
Source: OECD, 2018[7]

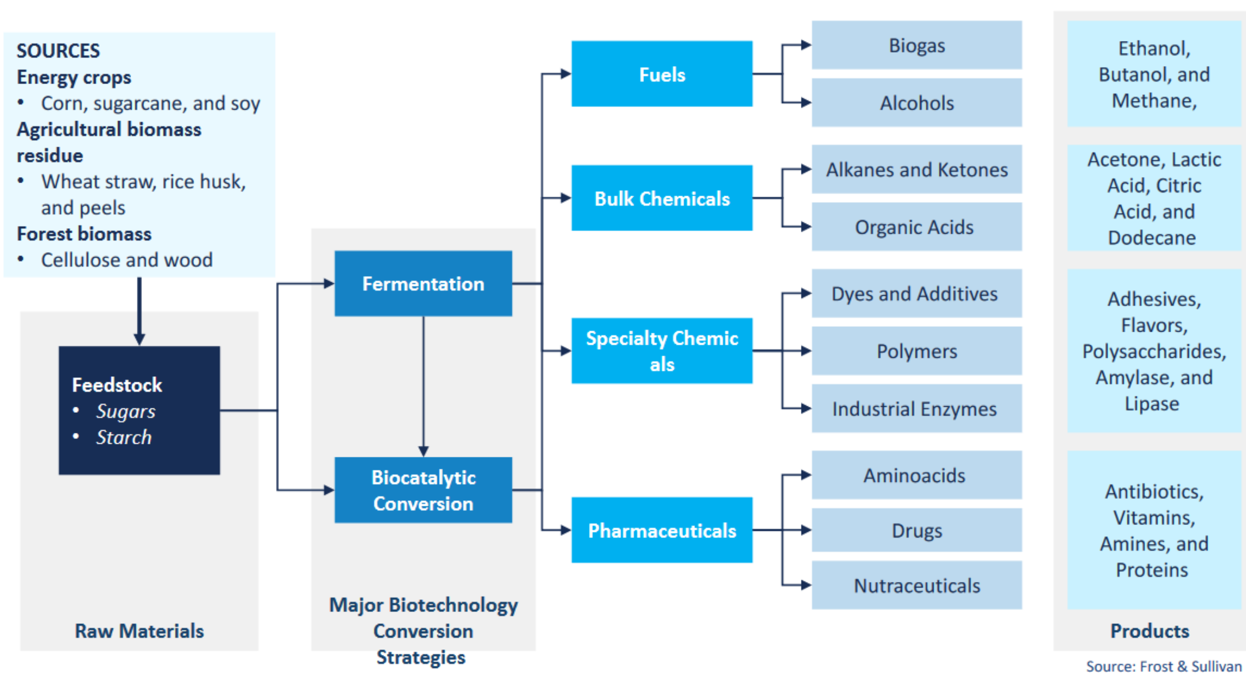


Figure 2: Process of Chemical Transformations of Substrates into Products and Sources of Biomass
Source: Frost & Sullivan, 2022[8]

2.1.1 Major Feedstocks for Biorefineries

The major feedstocks for biorefinery platforms for renewable chemicals include starch crops (wheat and maize), sugar crops (beet and cane), perennial grasses and legumes (ryegrass and alfalfa), lignocellulosic crops (managed forest, short rotation coppice, switchgrass), lignocellulosic residues (forest, stover and straw), oil crops (palm and oilseed), aquatic biomass (algae and seaweed), and organic residues (industrial, commercial, and postconsumer waste).[9]

Lignin

"Currently most lignin on the market is a by-product from the pulp and paper industry in the form of lignosulfonates and Kraft lignin. It is estimated that 50-70 million tonnes of lignin is produced annually, but more than 95% is used internally at pulp mills for energy generation. In addition, lignin is also produced concurrently with sugars during the biochemical conversion of lignocellulosic biomasses and therefore closely linked to the sugar platform. It is foreseen that large amounts of lignin will be available when industrial scale production of bioethanol for transportation from lignocellulosics is realized. The global lignin market size was estimated at USD 733 million in 2015 of which lignosulfonates was by far the biggest segment."[10]

Figure 3: Lignin Materials
Source: Click here to see video

The following figure shows the different products that can be produced using lignin.

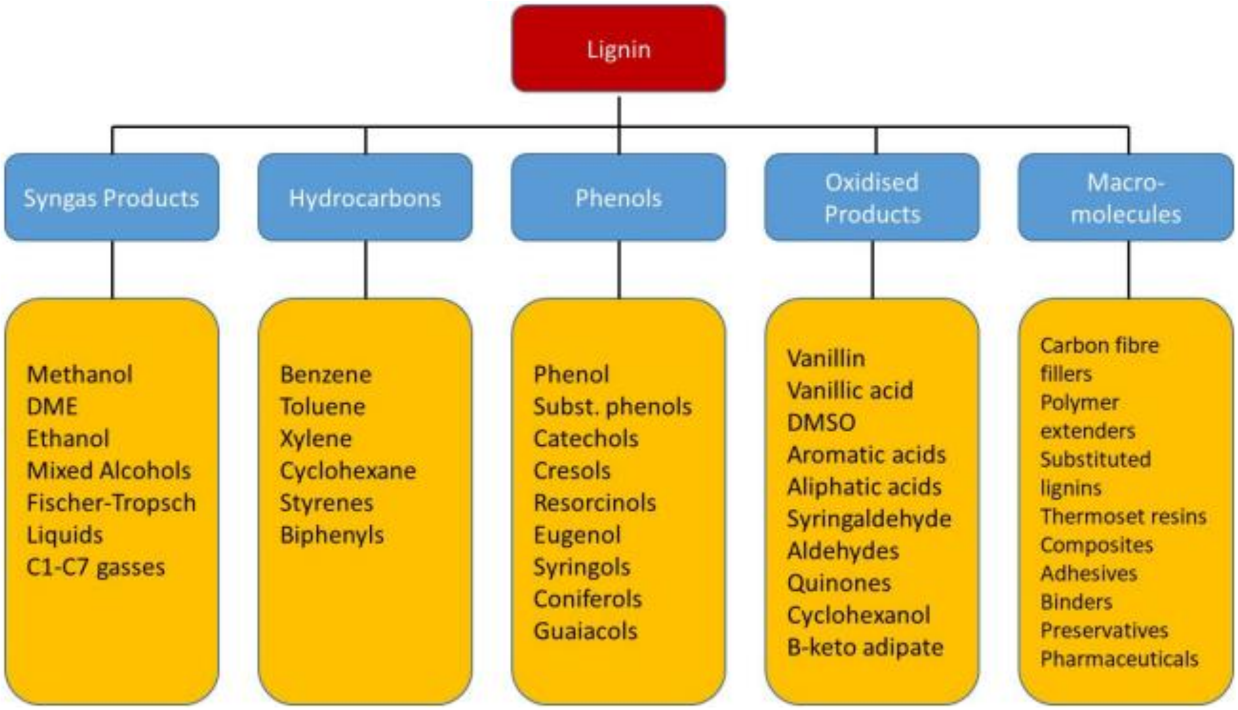


Figure 4: Potential Products From Lignin
Source: IEA Bioenergy, 2020[11]

2.1. Agile BioFoundry – Commercial Viability of Adipic Acid via Muconic Acid

The Agile BioFoundry is a consortium of national laboratories partnering with the biomanufacturing industry to develop new processes for bioproducts. One of their areas of research is adipic acid production via muconic acid fermentation from mixed sugars using Pseudomonas putida. Their research has the market price for adipic acid at $1.89/kg AA and the minimum selling price (MSP) is driven by productivity below 0.3 g/L.h and starts to plateau at productivities higher than 0.3-0.5 g/L.h. Some strategies for further reducing the MSP include aiming to lower the feedstock costs, increasing biorefinery scale, using lower-cost separation strategy, and adding value to lignin.[12]

Furthering the process to commercial viability of this technology, a research group as part of the consortium identified a sustainable strategy for converting glucose and xylose to muconic acid using the bacterial strain Pseudomonas putida KT2440. Research done by a multi-institutional team of scientists used metabolic engineering to improve strain performance. The researchers were able to produce 33.9 grams per liter of muconic acid at a rate of 0.18 grams per liter per hour and a 46% molar yield which is 92% of the maximum theoretical yield.[13]

2.1.1 FY23-FY25 Milestones

The Agile Biofoundry's milestones for Muconate for the next few years include pursuing the commercial interest of muconic acid from hydrolysate sugars, engineering arabinose into muconic-acid producing strains of P. putida and demonstration of improved productivity for muconic acid production, and media optimized for muconic acid producing P. putida strain with the ART tool. The milestone for FY24 is a scale up of muconic acid production to 100 L. The milestones for FY25 include transferring the muconic acid producing strains and bioprocesses to industry to produce direct replacement and performance chemicals, and a clear path to commercialization for muconic acid by 2030.[14]

2.2. Alternative Carbon Feedstocks for Adipic Acid

Alternative carbon feedstocks being explored for the creation of adipic acid include cyclohexene, phenol, butadiene, or adiponitrile, most of which are also produced from benzene. Butadiene is an attractive feedstock because the route for conversion to adipic acid produces no nitrous oxide.

> "Converting butadiene ($0.79/kg) and syngas (CO, ~$0.10/g) to adipic acid would have estimated costs for feedstocks of only $0.34/kg of adipic acid 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/kg of adipic acid, again assuming feedstock costs are from 70-80% of the total operating costs for a mature petrochemical process."[15]

Biotechnological Routes include developing adipic acid from glucose with a current estimated feedstock cost of $0.531/kg of adipic acid at a 100% conversion yield which is competitive with the nitrous oxide process. At maturity, feedstock costs may account for up to 80% of operating costs in direct chemical conversions, with non-feedstocks, the costs are larger in fermentation-based processes, accounting for 40-60% of overall costs.[16]

> "Lignin and its derivative offer another potential feedstock for cis, cis-muconic acid, and although best case technoeconomic models have been published, these assume a low end cost for this feedstock. Lignin, depending on assumptions and purity has been estimated in the best case to have a $0.04/kg cost, to costing upwards of $0.50/kg ($500/ton) for purified streams. In the event that lignin feedstock prices as low as $0.04/kg can be realized at scale, the route to ADP through cis, cis-muconic acid has potential as an attractive alternative to the incumbent process with operating costs estimated between $0.15/kg and $0.28/kg. Of course this is a best case scenario, and likely some level of lignin purification or upgrading will be needed if only to provide a consistent input to a large scale process from an agricultural feedstock."[17]

Toray Industries Feedstock Example

Different companies and universities are developing technologies for adipic acid production using a variety of biomass sources. Toray Industries which is based in Tokyo, Japan, has developed a 100% bio-based adipic acid derived from **sugars from crop residues and other inedible plant resources**. The process uses the company's microbial fermentation technology and chemical purification technology that uses separation membranes. Toray is working on scaling up their technology and will test polymerization of nylon 66 to **commercialize applications for the adipic acid by around 2030**.[18]

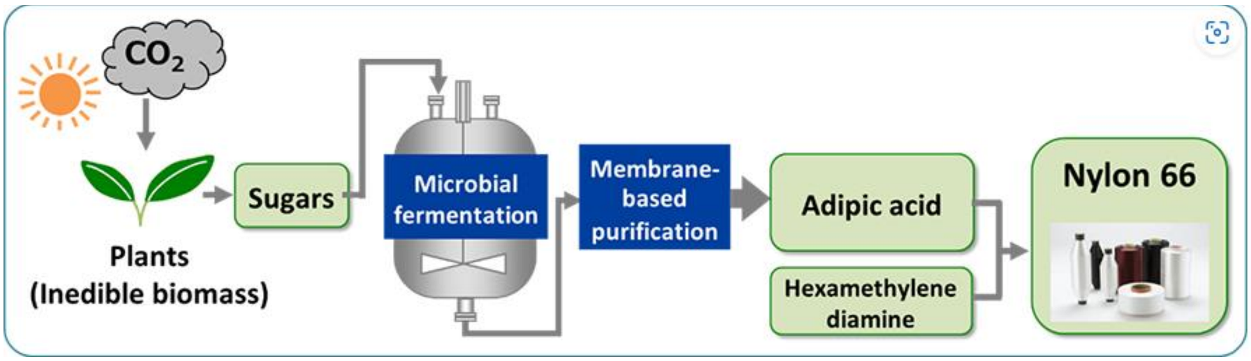


Figure 5: Overview of Toray Process
Source: Toray Industries, 2022[19]

As of 2023, Toray announced a partnership with Mitsui DM Sugar Co. that jointly demonstrated a basic technology to manufacture sugar derived from inedible biomass. Toray verified a process to separate, purify, and concentrate cellulose-derived sugars in inedible biomass and undertook this effort at a facility in Thailand as part of a project that the New Energy and Industrial Technology Development Organization (NEDO) supported. Toray is currently looking to establish an integrated technology to manufacture fiber and resin from agricultural residue to avoid competition with the food chain.[20] Toray plans to supply cellulosic sugar in collaboration with Thai sugar refineries and starch manufacturers and other companies using biomass. Toray will upscale its technology from their effort under development to produce adipic acid from cellulosic sugar. Toray's goal of providing cellulosic sugars to chemical companies will help to develop a circular economy by replacing petroleum-based chemicals.[21]

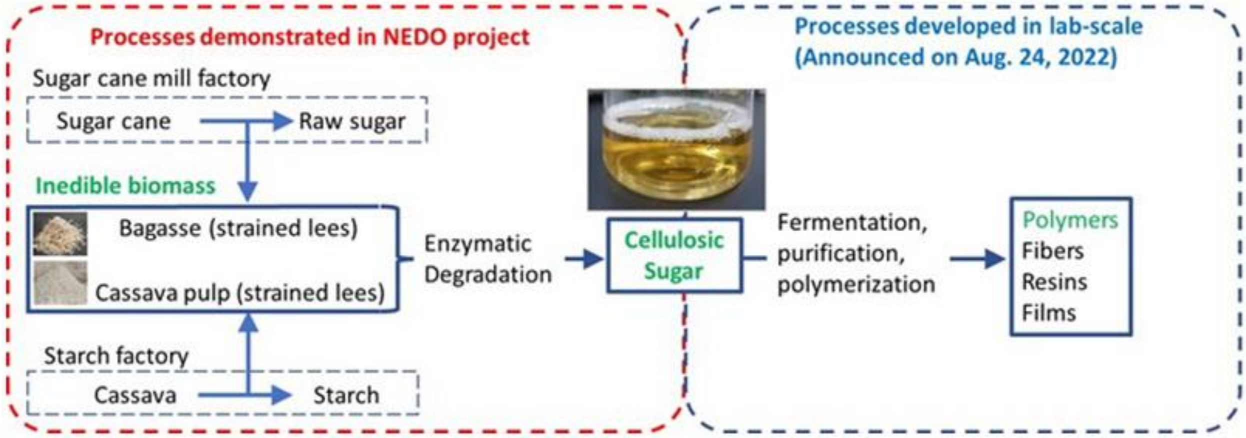


Figure 6: Concept for Transforming Inedible Plants Into Chemical Raw Materials
Source: Toray Industries, 2023[22]

3.0 Feedstock/Biomass Infrastructure

Biomass sources for producing sustainable chemicals come from sugars and lignin from sources like corn stover and gas fermentation from municipal solid waste. Other sources include cane sugar or beet sugar. There is a concern that there won't be enough of the feedstock sources to create the needed amount of chemicals. This section includes research being done on the infrastructure for feedstocks and their availability for use in the chemical industry.

3.1. Feedstock Challenges

One of the main challenges of using feedstocks for chemical production is the complexity and variability of the feedstocks which can disrupt biological processes, deactivate catalysts, and compromise product quality. Another challenge is that carbon in feedstocks such as cellulose, hemicellulose, and lignin, is not as easily biologically accessible as the carbon in starches, sugars, and oils that were successful early on in the development of a bioeconomy. The additional challenge of transporting feedstocks comes from the fact that many cannot be pipelined like petroleum or other liquids.[23] There is a need for efficient biomass feedstock collection and aggregation systems. Although the cost of many feedstocks are initially low, the cost of transportation can be excessively high. Regional networks could be established, such as the one in California's North San Joaquin Valley, where a non-profit is facilitating local feedstock aggregation for a bioindustrial hub. Farmer co-ops could also aggregate feedstocks and help to lower transportation costs.[24]

Feedstock challenges include complexity and variability, seasonality, supply, and storage.

Feedstock supply is another concern, as bio-based feedstocks will need to completely substitute for oil-based supplies. Chemical players are partnering with industry and waste management partners to secure sufficient feedstock. Chemical companies will need to redesign their feedstock supply chains. This includes creating transparency for the risk profile and mitigation needs for the main oil-based feedstock suppliers, creating back-up plans for unexpected feedstock chain loss, building cross-industry partnerships with waste management companies to build circular supply chains, and integrating all of these into a supply chain strategy with flexible setups.[25]

Challenges associated with scaling up processes in the circular bioeconomy include the difficulty of demonstrating processes at scale before building large scale infrastructure. Many startup companies need to prove they can make products at scale to attract investment to scale-up production. Companies are using test-bed sites that can be adapted to validate and limit the risk of the processes.[26]

Below are challenges and opportunities that have been identified for the different potential feedstocks and their use in the chemical industry.

Table 1: Future Feedstock Challenges and Opportunities

Challenges	Opportunities
Lignocellulosic Waste Broadly (e.g., hulls, soybean residue, corn fiber, bran)	
• Only available during part of the year. • Short duration before spoiling if untreated. • Inconsistent quality of raw materials. • Biodegradation is difficult. • Insufficient supply to provide economies of scale for niche products.	• Already collected and aggregated in many situations. • Conversion to methane may be a realistic intermediate.
Almond hulls and shells	
• Wet, needs to be processed quickly. • Only available half the year. • Niche. Is there enough volume?	• Already used to produce platform chemicals and large integrated facilities exist for large-volume processing.
Sugarcane bagasse	
• Wet, needs to be processed quickly. • Only available half the year.	• Already used to produce platform chemicals and large integrated facilities exist for large-volume processing.
Forest residuals	
• Often located far from processing facilities.	• Currently being paid (approximately $30/ton) for harvesting and disposal.
Methane and biogas	
• Need large digesters due to slow production rates. • Need to transport inputs to locations where the methane or biogas can be used. • Compete with low-cost natural gas. • Often flared or wasted.	• Can be common intermediates. • Climate benefit to using them. • Low-cost input for aviation fuel. • Solve a waste problem for dairy.
Municipal solid waste	
• Highly heterogeneous.	• Already collected in cities. • Available year-round.
Food waste	
• High moisture content (approximately 75%). • Highly heterogeneous.	• Readily degradable. • Available year-round.
Sweet sorghum	
• Only available part of the year. • Needs to be processed right away.	• Create both sugar stream and high yield of biomass. • Suited to a range of growing conditions.

Challenges	Opportunities
Cotton seed hulls	
• Niche and has questionable scalability.	• Not generally used for other applications like animal feed.
Carbon dioxide gas	
• Electrocatalysis and hydrogen gas are needed as inputs to utilize.	• Use could yield carbon credits. • More products could be developed from fermentation where carbon dioxide is a coproduct. • Forthcoming hydrogen hubs could provide the hydrogen needed to reduce carbon dioxide.
Starch reallocation	
• Need to transition animal feed to lignocellulosic materials to free up the starch supply.	• There is existing infrastructure for handling and processing. • Quickly degradable to an array of products. • Readily available.
Lipids and oils from plants	
• Expensive. • Often utilized in the food chain.	• Known conversion pathways.

Source: Foundation for Food and Agriculture Research, 2023[27]

3.2. Biomass Storage for Preserving Feedstocks

Research is being done on the use of storage for biomass feedstocks in order to allow biorefineries to run year-round despite the variability and seasonality of feedstocks. Seasonal variation is a challenge for most agricultural products and necessitates storage for access to product year-round. Corn stover is typically available during a 1–2-month period and dependent on the harvest of the primary product (corn). Energy crops are harvested seasonally but have more flexibility in their harvest windows because it is the primary product not the residue left over. Storage systems offer the opportunity to minimize the challenges of seasonal crops and availability and allow biorefineries to have a consistent year-round feedstock supply. Another benefit is that long term storage allows the biorefinery to be developed at an appropriate scale, leading to minimized down-time and reducing capital expenditures.[28]

Figure 7: Corn Stalk Harvesting in Ontario
Source: Click here to see video

3.2.1 Dry Storage

Dry storage involves bale stacks for field-side storage of agricultural residues, which are often covered with tarps to reduce moisture. Bale-based storage can be effective in preserving biomass but conditions much be managed carefully. A study was done that suggested that only an average of 36% of corn stover harvested in the U.S. is capable of being stored long term. Moisture content of 20% or less is recommended for corn stover baled in long term storage because significant loss has been reported in field-side storage that exceeds this moisture threshold due to microbial degradation. Microbial degradation is caused by bacteria, yeast, and fungi that consumes valuable carbohydrates and produces CO2 as a byproduct.[29]

3.2.2 Wet Storage

Wet storage systems have demonstrated biomass preservation in long term storage for livestock feed and forage. Wet storage has been suggested for corn stover to address the loss of corn stover bales from fire. The wet systems are based on forage chopping herbaceous biomass in the field at moisture contents between 40-65%, transporting the biomass, and utilizing anaerobic storage systems to limit oxygen and preserve the biomass. Benefits of long-term wet storage include stabilization of the biomass and providing an environment to begin depolymerization of components such as lignin and hemicellulose, which can help to lower the conversion costs for high moisture feedstocks. A challenge of wet storage systems is the higher cost compared to dry storage systems. Transportation costs for wet storage corn stover are higher because of the larger bulk density.[30]

3.3. Muconic Acid from Plants

Plants, which produce organic carbon skeletons by harvesting carbon dioxide and energy from the sun, can serve as green factories for bio-manufacturing muconic acid. The process for developing muconic acid from plants is explained from a research study that explored this pathway.

> "We engineered Arabidopsis to demonstrate that plants can serve as green factories for the bio-manufacturing of MA. In particular, dual expression of plastid-targeted bacterial salicylate hydroxylase (NahG) and catechol 1,2-dioxygenase (CatA) resulted in the conversion of the endogenous salicylic acid (SA) pool into MA via catechol. Sequential increase of SA derived from the shikimate pathway was achieved by expressing plastid-targeted versions of bacterial salicylate synthase (Irp9) and feedback-resistant 3-deoxy-D-arabino-heptulosonate synthase (AroG). Introducing this SA over-producing strategy into engineered plants that co-express NahG and CatA resulted in a 50-fold increase in MA titers. Considering that MA was easily recovered from senesced plant biomass after harvest, we envision the phytoproduction of MA as a beneficial option to add value to bioenergy crops."[31]

3.4. Cost Analysis

There has been a variety of research done in the area of cost analyses and cost competitive sustainable processes. One of the areas of focus include in planta and microbial routes for production of bioproducts, and the viability of these routes for muconic acid. One study conducted a technoeconomic analysis with the in planta route and conversion to ethanol, and the other route was microbial production of the product using glucose as a feedstock. Relevant excerpts that demonstrate the accumulation rate of each bioproduct studied are included below.

> "In the plant system, the mass accumulation rate (dwt%) of each bioproduct in biomass sorghum (a proxy bioenergy feedstock crop) is based on the highest reported yield in the literature (3.2 dwt% 4-HBA, 3.0 dwt% PDC, 0.06 dwt% muconic acid, and 0.045 dwt% catechol). This represents the average mass accumulation rate in all of the harvestable sorghum biomass, including both stems and leaves. Once the biomass is delivered to the biorefinery, bioproducts are extracted by solvents. The remaining biomass is routed for downstream conversion to ethanol, consisting of processes including one-pot high-gravity ionic liquid (IL) pretreatment, enzymatic hydrolysis, fermentation, ethanol recovery and purification, wastewater treatment, and onsite energy generation."[32]

In terms of pricing, revenue, and cost for the in planta bioproducts extracted prior to the conversion of biomass to ethanol, the ethanol selling prices are based on three scenarios. The first is a base case price of $1.44/LGE as a base case for the ethanol biorefinery model. The second is a target fuel price of \$0.66/LGE or \$2.50/gasoline gallon equivalent based on targets set by DOE. The third is a historical average gasoline price of \$0.40/LGE or \$1.53/gal of gasoline based on average U.S. gasoline prices from 1940-2020. Based on the base case scenario of ethanol selling price, muconic acid can be sold at a minimum price of \$18.9/kg which is about four times the achievable minimum selling price (MSP) if muconic acid is produced microbially from glucose. In order to make this process more cost competitive, the in-planta production of muconic acid needs to be increased.[33]

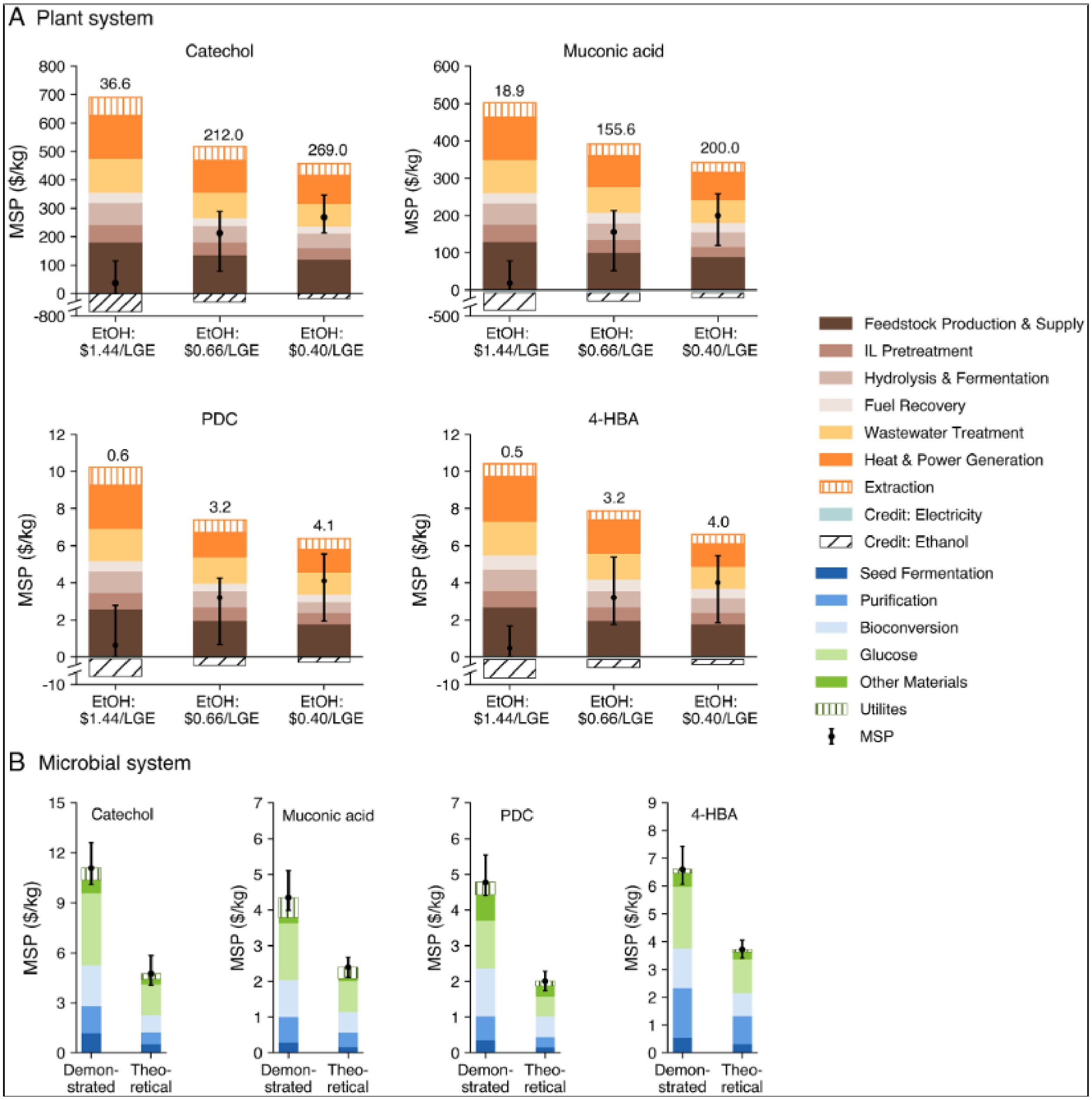


Figure 8: Cost Scenarios
Source: Proceedings of the National Academy of Sciences, 2022[34]

Muconic acid has demonstrated a higher yield via microbial conversion of glucose at 0.378 mol muconic acid/mol glucose, or 0.298 g or muconic acid/g glucose and achieves a lower MSP of $4.4/kg. The price of glucose, $0.59/kg, is the largest cost contributor for this process.[35]

Cost Between Plant and Microbial Systems

To compare the costs of bioproducts for both processes, researchers modeled feedstock input amounts of 2,000 dry tonnes of biomass sorghum per day for the plant systems and a bioethanol selling price of $1.44/LGE. For microbial systems, the glucose input is 1,000 dry tonnes and the production yields were varied to determine final MSPs for the bioproducts. The breakeven accumulation rate for plant systems to be able to compete with microbial production ranges from 0.1 to 0.3 dwt% of plant tissue in a bioenergy crop. Production of muconic acid is more advantageous in microbes compared to accumulation in plants. The current highest reported microbial yield of muconic acid is 0.378 mol/mol glucose which corresponds to 50% of theoretical yield. The highest reported yield of muconic acid in engineered plants is lower than the needed thresholds at 0.06 dwt%.[36]

4.0 Company/Partnership Landscape

Companies and partnerships in the sustainable chemical industry working on muconic acid and companies who work with nylon 66 and are looking for sustainable processes are explored in this section. Of particular interest are those companies which are working on or interested in scaling up sustainable processes for producing muconic acid, buyers of adipic acid, venture capital investments, and companies making nylon.

4.1. Spero Renewables converts biomass lignin into polymers and plastics

Spero Renewables, located in Santa Barbara, California, received an award from EERE to scale up and commercialize their SPERLU technology which converts biomass lignin into polymers and plastics. The company was founded in 2018 and is located near the University of California, Santa Barbara. Today it has a 3,725 square foot facility used for advanced synthesis, chemistry, and biotech research. and develops sustainable, plant-based alternatives to products that are manufactured with petrochemicals. [37]

The SPERLU technology converts lignin into biophenols which can be used to make replacements for petroleum-based bisphenol A (BPA) in the synthesis of epoxies and thermoset plastics. Along with the funding from the EERE, the U.S. Department of Agriculture and National Science Foundation have also helped to fund the development of the SPERLU technology. Spero Renewables have a mini-pilot and are planning another pilot unit to process one ton of biomass per day, which will prepare for commercial deployment. [38]

4.2. Genomatica Develops a Plant-Based Nylon

Founded in 2000, Genomatica, based in San Diego, California, is working to replace fossil fuel sources for sustainable materials with plant sources. Genomatica's technology uses microorganisms and industrial processes to ferment plant sugars into materials and ingredients.[39] The company is developing a plant-based nylon by converting renewable carbon (sugar from plants) to the precursor to nylon with a 100% renewable carbon-based nylon-6. Genomatica is partnering with Lululemon, Asahi Kasei, Aquafil, Unilever, Kao, and L'Oreal to provide plant-based nylon products.[40] The video below discusses Genomatica's development of sustainable nylon products.

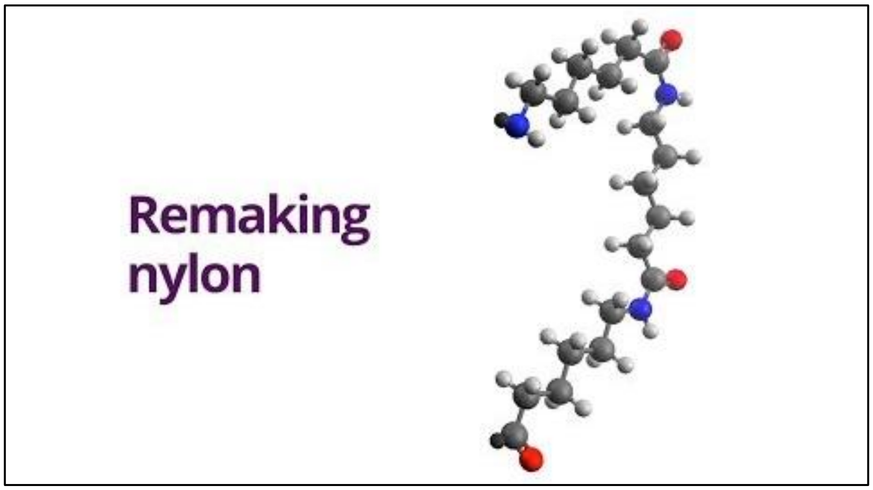


Figure 9: Genomatica Remaking Nylon
Source: Click here to see video

Genomatica's business model is to partner with a variety of companies In 2022 Genomatica partnered with Japan-based Asahi Kasei to commercialize renewably produced nylon 6,6 made from Genomatica's bio-based HMD (hexamethylenediamine) building block. Asahi Kasei is looking to bring the sustainable version of nylon 6,6 for applications in the automotive and electronics industries. Asahi Kasei intends to apply Genomatica's HMD process technology to make more sustainable materials for use in products in high-temperature automotive parts and electronics and plans to license the HMD process to commercialize its own nylon 6,6.[41]

4.3. Ascend Performance Materials is a Leading Producer of Adipic Acid

Ascend Performance Materials, based in Houston, Texas was formed in 2009 when SK Capital Partners purchased Solutia's integrated nylon business. The company has 2,300 employees with regional offices in Shanghai, Brussels, and Detroit. The company is the world's leading producer of adipic acid and the only large-scale producer of Food Grade

Adipic Acid in the world[42] Ascend also manufactures a variety of different grades of Vydyne PA66 and PA6 resins and compounds used in a variety of products.[43]

Through its Bioserve platform, Ascend is committed to reducing the environmental footprint with its bio-derived, renewably sourced materials. The Bioserve products are drop-in replacements which use existing processes to scale up production of sustainable materials more quickly. A figure of the Bioserve process is illustrated below.

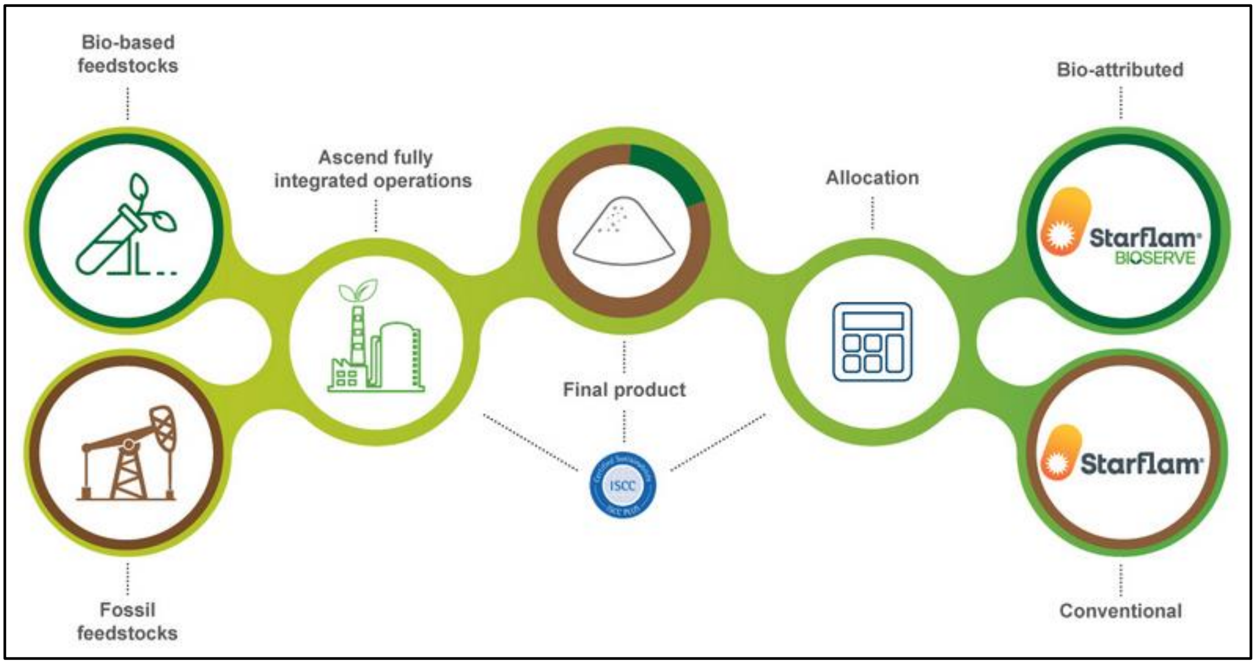


Figure 10: Bioserve Process
Source: Ascend Performance Materials, 2023[44]

According to [Ascend's 2022 Sustainability report](), the company's 2030 vision focuses on creating sustainable practices and working with suppliers to assess their sustainable practices as well. One of the areas of sustainability that Ascend is focusing on is reducing emissions. One of their current projects is to reduce nitric acid (N2O) emissions, by using a catalyst to convert the nitric acid to nitrogen and oxygen. The project is slated to remove approximately 300,000 metric tons of CO2 equivalent emissions annually. Ascend has also been able to make operations at their seven compounding sites in North America, Europe, and Asia carbon neutral.[45]

4.4. Sumatra Biorenewables

[Sumatra Biorenewables]() is a startup company based in Ames, Iowa that produces trans-3-hexenedioic acid, a novel biobased monomer manufactured from biologically produced muconic acid. The company is in the process of scaling up production of the first hydrophobic nylon 6,6.[46]

"Conventional nylon 6,6, made of two monomers: adipic acid and hexamethylenediamine, has many desirable properties like high strength and chemical resistance, however when exposed to water these physical properties are diminished. Sumatra makes use of 3-hexenedioic acid, HDA, a monomer derived from the fermentation of sugars and only differs to adipic acid by having a double bond in the middle of the carbon chain. This bond allows the functionalization of the nylon 6,6, to add new properties to the end material. For instance, the new Bio-Advantaged Nylon can be made hydrophobic, anti-static, anti-microbial, or have tuned mechanical strength to meet customer specifications. The conversion technology is inexpensive, robust, unaffected by feedstock impurities, and can produce HDA being cost competitive when compared to adipic acid."[47]

4.5. Companies That Have Received Funding From DOE

This section provides a cursory overview of companies in the sustainable nylon, sustainable muconic acid/adipic acid space that have received SBIR funding from DOE.

4.5.1 ZymoChem Inc.

ZymoChem, a small California based company, is developing solutions to create high-value materials from renewable feedstocks. They are developing a novel biosynthetic pathway for the production of adipic acid from renewable sources such as biomass-derived sugars. The project involved the identification of enzymes catalysts for the adipic acid pathway and in vivo pathway validation. The goal is to produce industrial adipic acid that is significantly less expensive than the current petroleum-based processes.[48]

The company is also developing a carbon conserving platform to increase the maximum product yield by up to 50% of biological feedstocks. The focus of the project is to develop a novel biosynthetic pathway for producing caprolactam from metabolic intermediates made from microbes using the carbon conserving technology. ZymoChem's carbon conserving technology to biologically synthesize chemicals can substantially reduce production costs and supplant petroleum-based processes. Caprolactam is used in the production of bio-based nylon 6.[49]

4.5.2 Technology Holding, LLC

Technology Holding LLC is a small R&D company located in Utah, focused on a variety of sustainable solutions including novel processes for developing fuels and chemicals. They have received funding to develop a novel method to produce adipic acid (BKA), which when used in nylon production can reduce water permeability by 20% and has a 70 degrees Celsius higher glass transition temperature. The company's prior work has involved the production of BKA from glucose using genetically engineered P. putida.[50]

4.6. Companies That Have Closed Operations

There are some companies that invested in adipic acid production from sustainable sources that have closed down their operations over the last 5 years. Some of the reasons for closing operations include a decline in demand for adipic acid and an oversupplied global market.[51] In 2011, renewable chemistry company, BioAmber entered an exclusive licensing agreement with CELEXION to accelerate the development of bio-based adipic acid. However BioAmber closed its operations in 2018 because of bankruptcy. Celexion was acquired by Agenus in 2015.

Companies that have closed their adipic acid production facilities include BioAmber, Verdezyne, and Rennovia.

4.6.1 Verdezyne

Verdezyne closed its operations in 2018. The low oil prices caused investors to rethink the need for alternative technologies to create renewable chemicals. Verdezyne was in its' prime in 2011 with a group of investors including BP Ventures, DSM Venturing B.V., OVP Venture Partners, Monitor Ventures, and Sime Darby. Verdezyne was looking to build pilot plants to produce both ethanol and adipic acid from cellulosic feedstocks in their Carlsbad location.[52]

4.6.2 Rennovia

Rennovia has a similar story to Verdezyne in that it closed its operations in 2018 because it couldn't raise sufficient funding for its pilot scale technology. Rennovia was a company based out of California that had developed a transformative catalyst and process technology for a bio-based nylon 6,6, made from Rennovia's renewable adipic acid and hexamethylenediamine. In 2014, Archer Daniels Midland Company (ADM) committed $25 million in Rennovia because of their promising technology and initial results. However, when oil prices started to decline rapidly, the risks of the new technology outweighed the financial benefits of the carbon reduction. In 2015, Rennovia had started up a mini-plant for production of glucaric acid from glucose, in 2017, ADM did sign a license agreement to provide the support they had originally promised for the technology for bio-based glucaric acid. But when the level of investment did not meet the needs of the company, Rennovia was not able to keep its doors open.[53]

4.6.3. Invista

Invista is a subsidiary of Koch Industries based Wichita, Kansas, and a leading producer of chemical intermediates for nylon and polypropylene value chains and companies.[54] Invista's Adi-pure adipic acid is high purity and is produced in the company's Victoria, Texas facility. The product is a crystalline, white powder with typical carboxylic acid chemistry and is used in the following applications:

- “as a monomer in nylon, paper additives, copolyamides, terpolymers and unsaturated polyester resins
- in polymer additives for epoxy curing agents and plasticizers
- as a chemical intermediate in the synthesis of polyesters/diesters, polyester polyols, adiponitrile, cyclopentanone, 1,6-hexanediol and dimethyl sebacate
- in solvents, lubricants, electronics, soil conditioners, glass protection agents, briquetting agents, leather tanning agents, flue gas desulfurization scrubbers and cleaning aids”[55]

In 2015, Invista announced it was shutting down its adipic acid plant in Orange, Texas. One of the main reasons for shutting down the plant was the lower demand for adipic acid in North America and increases in the supply in the global market. The company continues production of adipic acid at the Victoria, Texas site.[56]

5.0 Nylon 66 and the Hexamethylenediamine Market

Hexamethylenediamine is a chemical compound used in the production of polymers, mainly nylon 66 and polyurethanes. Nylon 66 (polyhexamethylene diamine adipamide) is a polyamide made from adipic acid and hexamethylenediamine by polycondensation. This section provides an overview of the hexamethylenediamine market size, the drivers and constraints and key players. In the market research report released by MarketsandMarkets in 2022 on the Hexamethylenediamine market, increased R&D focused on the development of a replacement for hexamethylenediamine during the manufacturing of nylon 66 is recognized as a major market constraint.

> “Due to the general increased demand for bio-based nylon resins, companies are focusing on developing a bio-based production technology for the production of hexamethylenediamine and adipic acid (the other component used in the manufacturing of nylon 66 along with hexamethylenediamine). The primary differences between conventional and bio-based hexamethylenediamine are cost-effectiveness, raw material prices, and the manufacturing process. Another significant trend observed in the global hexamethylenediamine market is that major manufacturers are focusing on increasing their production capacity to gain

> a competitive advantage. Many manufacturers have increased their presence in the emerging markets of China, India, and other Asian countries."[57]

The hexamethylenediamine market by application clearly shows nylon synthesis as the primary application.

Table 2: Global Hexamethylenediamine Market Size, by Application, 2022 vs 2027 (USD M)

Application	2020	2021	2022	2023	2024	2025	2026	2027	CAGR (2022-2027)
Nylon Synthesis	6,673.4	7,030.1	7,441.3	7,834.2	8,231.9	8,674.9	9,176.9	9,691.0	5.4%
Curing Agents	306.8	323.2	345.3	363.0	380.9	400.8	423.5	446.4	5.3%
Lubricants	280.5	295.4	320.2	334.9	349.6	366.0	384.7	403.3	4.7%
Biocides	249.7	262.9	270.8	283.4	295.9	309.9	325.8	341.7	4.8%
Intermediate for Coatings	163.9	172.6	176.1	186.9	197.9	210.2	224.1	238.4	6.2%
Adhesives	141.4	148.9	151.0	160.1	169.4	179.7	191.4	203.3	6.1%
Water Treatment Chemicals	82.9	87.4	97.4	102.6	107.9	113.8	120.5	127.3	5.5%
Others	93.3	98.3	101.1	105.5	109.8	114.6	120.0	125.5	4.4%
Total	**7,991.9**	**8,418.8**	**8,903.2**	**9,370.5**	**9,843.3**	**10,370.0**	**10,966.9**	**11,577.0**	**5.4%**

Source: Reprinted with permission of MarketsandMarkets[58]

The following table shows the volume by application, year, and kiloton; followed by the market size for nylon synthesis by geographic region.

Table 3: Global Hexamethylenediamine Market Size, by Application, 2022 vs 2027 (kiliton)

Application	2020	2021	2022	2023	2024	2025	2026	2027	CAGR (2022-2027)
Nylon Synthesis	1,508.2	1,565.6	1,632.8	1,693.7	1,753.5	1,820.7	1,897.7	1,974.4	3.9%
Curing Agents	69.1	71.7	75.4	78.2	80.8	83.8	87.2	90.6	3.7%
Lubricants	63.1	65.5	69.9	72.0	74.1	76.4	79.1	81.7	3.2%
Biocides	56.0	58.1	59.0	60.8	62.6	64.6	66.9	69.1	3.2%
Intermediate for Coatings	37.0	38.4	38.6	40.3	42.1	44.0	46.2	48.5	4.7%
Adhesives	31.8	33.0	32.9	34.4	35.9	37.5	39.3	41.1	4.5%
Water Treatment Chemicals	18.7	19.5	21.3	22.2	23.0	23.9	24.9	25.9	4.0%
Others	21.2	22.0	22.3	22.9	23.5	24.2	25.0	25.7	2.9%
Total	**1,805.0**	**1,873.6**	**1,952.3**	**2,024.5**	**2,095.4**	**2,175.0**	**2,266.3**	**2,357.0**	**3.8%**

Source: Reprinted with permission of MarketsandMarkets[59]

Table 4: Nylon Synthesis: Hexamethylenediamine Market Size, by Region, 2020-2027 (USD million)

Region	2020	2021	2022	2023	2024	2025	2026	2027	CAGR (2022–2027)
Asia Pacific	1,366.7	1,446.7	1,537.2	1,624.5	1,713.4	1,812.5	1,924.6	2,058.4	6.0%
Europe	1,696.8	1,794.5	1,907.1	2,007.8	2,109.8	2,223.3	2,352.0	2,455.4	5.2%
North America	2,966.7	3,130.8	3,322.7	3,499.8	3,679.3	3,879.1	4,105.6	4,337.0	5.5%
South America	257.6	248.0	240.1	244.9	249.1	253.7	259.2	293.1	4.1%
Middle East & Africa	385.5	410.1	434.2	457.1	480.3	506.2	535.5	547.1	4.7%
Total	**6,673.4**	**7,030.1**	**7,441.3**	**7,834.2**	**8,231.9**	**8,674.9**	**9,176.9**	**9,691.0**	**5.4%**

Source: Reprinted with permission of MarketsandMarkets[60]

In North America hexamethylenediamine is primarily consumed in the production of nylon, much of which is used in the automotive industry.

> "Hexamethylenediamine is majorly used in the synthesis of nylon 66, widely used in the automotive end-use industry for making various products and components such as connectors & housing, under-the-hood components, wheel well, and lighting components, including headlamp structural housings, headlamps & fog lamps, and reflectors & lighting sockets. Nylon-based products and components are used in all classes of vehicles, from high-performance track cars to five-door sedans and trucks. The demand for hexamethylenediamine from the automotive industry is expected to increase substantially as the industry is currently moving toward vehicle weight reduction and improved fuel efficiency, majorly driven by governmental norms and regulations."[61]

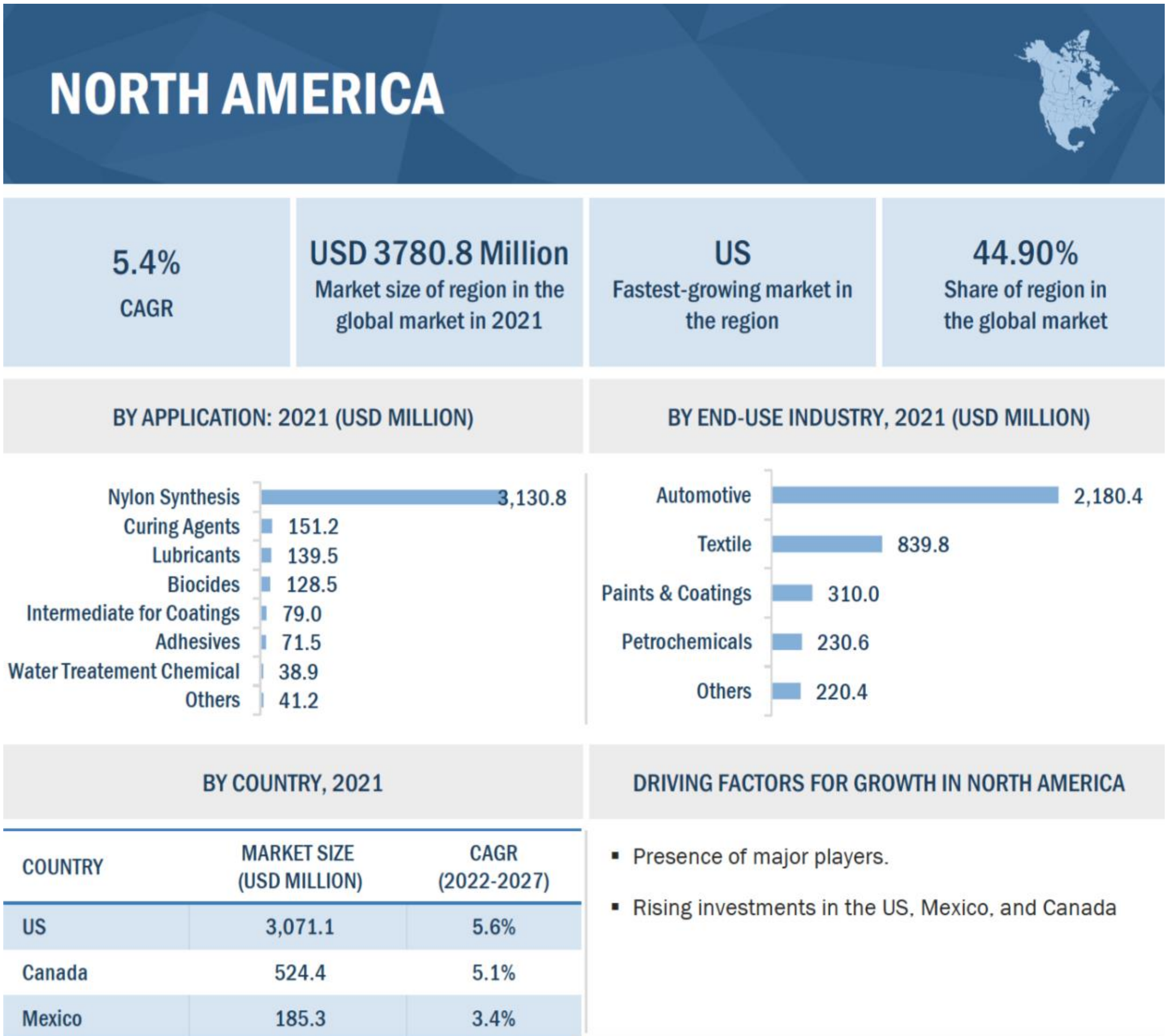


Figure 11: North America: Hexamethylenediamine Market Snapshot
Source: Reprinted with permission of MarketsandMarkets[62]

Prominent North American players are DuPont, Invista, Ascend Performance Materials, Ashland Global Holdings Inc., Genomatica, and Rennovia. **The five largest players globally jointly account for 40% of the hexamethylenediamine market and include BASF SE (10.4% share), Merck KGaA (8.1%), Toray Industries (7.5%), Evonik (6.1%) and DuPont de Nemours, Inc (6%).**

The following is a listing of recent articles that indicate if the major players in the hexamethylenediamine market are beginning to consider biomass applications.

BASF SE

- BASF, "BASF's biomass balance approach," *BASF,* last accessed October 8, 2023

TORAY INDUSTRIES

- Toray, "Ajinomoto and Toray to Conduct Joint Research on Biobased nylon," *Toray*, February 13, 2012
- Renewable Carbon News, "Toray succeeds in production of bio-based PBT and part samples," *Renewable Carbon News*, April 25, 2013
- Biomass Magazine, "Toray Produces Biobased Adipic Acid from Inedible Biomass," *Biomass Magazine*, August 28, 2022
- ISSUU, "Sustainable nylon 66 Breakthrough," *Issue* 2, 2023
- NonWovens Industry, "Toray Ups Stake in Cellulose Biomass Technology," *NonWovens Industry,* September 4, 2023

EVONIK

- Evonik, "Certified bio-based: high-performance plastics from Evonik," *Evonik,* March 23, 2012
- Evonik, "VESTAMID Terra: Because we care," *Evonik,* Accessed October 8, 2023

DuPont de Nemours, Inc.

- DuPont, "Innovating with Renewables," DuPont, Accessed on October 8, 2023

5.1. Automotive Applications of Nylon 66

Nylon 66 was developed in 1935 by Wallace Hume Carothers at DuPont's research facility and officially introduced into one market in 1938: Ladies' hosiery. However, with the advent of World War II the use of nylon was redirected to military applications where it was used in parachutes, tire cords, aircraft fuel tanks, hammocks and numerous other applications. According to "Nylon: A Revolution in Textiles," as soon as the War was over,

> "DuPont jumped back into consumer nylon production almost as soon as the war ended, with the first pairs of stockings returning to stores in September 1945. Everywhere the stockings appeared, newspapers reported on "nylon riots" in which hundreds, sometimes thousands, of women lined up to compete for a limited supply of hosiery. Perhaps the most extreme instance occurred in Pittsburgh in June 1946, when 40,000 people lined up for over a mile to compete for 13,000 pairs of nylon stockings."

Perhaps because of this history, there is the tendency to still think of nylon primarily with respect to the fashion industry. However, as noted in the previous section, the biggest application of nylon 66 is in the automotive industry where it is used in engine covers, air intake manifolds, airbag containers, rocker valve covers and numerous other parts. In most instances nylon has been substituted for metal, thus reducing vehicle weight, as well as production costs.

In 2018 there were supply chain issues with nylon 66 – the primary constraint being the availability of the key precursor adiponitrile (ADN). Four major suppliers were relied upon to provide the 3.8 billion pounds required to meet the demand including: Ascend Performance Materials and Invista in the U.S.; Butachemie – a joint venture between Invista and Solvay in Germany and Asahi Kasei in Japan. The constraint was initiated by a fire in 2015 which had destroyed a plant in China that had previously accounted for 18% of global demand.

A 2018 article in Plastics Technology[63] indicated that although the supply chain issues had precipitated looking for alternatives, little headway had been made as switching is not easy "Switching from nylon 66 to an alternative material is generally not as easy as just dropping a new resin into the machine. Oftentimes, potential impacts on dimensions, part features or the performance of the part need to be considered. Choosing a supplier that can provide technical and application development support should be part of the decision as well."

5.2. Textile Applications of Nylon 66

The abrasion resistance of nylon 66 makes is ideal for use in carpets, upholstery, fishing nets and conveyor belts. A detailed overview of the preparation and properties of Nylon 66 as well as the applications are available in a report prepared by Mufaddal Bagwala. Since the 1950's when DuPont developed a method to impart "loft" to nylon it has been used extensively in carpets. Today the commercial carpet market is dominated by nylon with the key players being Invista, Asahi Kasei and DuPont (which is now part of Invista).[64] Although nylon is also prevalent in residential carpets, it appears that its presence there has decreased as the need for its use in the automotive industry has increased.

Nylon carpets can be recycled, and some companies are decreasing their carbon footprint by doing just that. Ascend Performance Materials, a leading player in the hexamethylenediamine market recently announced its partnership with Circular Polymers.

Figure 12: Ascend Acquires Majority Stake in Circular Polymers

Source: Click here to see video

Today, Ascend Performance Materials not only makes the nylon 66 that is used in airbag fibers, but also uses polymers from recycled carpets in its Cerene line, a sustainable feedstock that can be used in molding and compounding.

Another item being recycled is nylon fishing nets or ghost fishing nets as they are often called which are said to account for hundreds of millions of marine animals killed or injured annually.[65] Efforts are being made to retrieve and recycle the fishing nets, transforming them into carpets and other textiles.

Figure 13: Interface | Net-Works: Turning Waste Nets Into Carpets
Source: Click here to see video

6.0 The Price for Sustainable Clothing

Whether you call it ethical fashion, sustainable apparel, or sustainable clothing, a question that arises often is are consumers willing to pay more for it. A survey done by Blue Yonder found that 69% of respondents said they were willing to pay more for sustainable products, although only 4% expressed a willingness to pay more than 20%. Inflation is a top concern for consumers, with 58% reporting that price is the most important factor determining a sustainable purchase, with apparel being one of the categories that consumers were most willing to pay a premium for sustainable products.[66]

A McKinsey report explored the role of sustainability in consumers' spending habits. A 2020 McKinsey U.S. consumer survey found that more than 60% of respondents said they would pay more for a product with sustainable packaging. A study by NielsenIQ found that 78% of respondents say a sustainable lifestyle is important to them. However, many companies report challenges in generating a consumer demand for these products.

McKinsey analyzed five years of U.S. sales data, from 2017-2022 and examined the rate of sales growth for individual products by category. The analysis compared the different growth rates for products with and without ESG-related claims. Environmental social and governance (ESG) related products accounted for 56% of all growth in product sales which is 18% more than would be expected with their standing at the beginning of the five years. Some demographic groups are more likely to buy products with ESG-related claims, such as higher-income households, urban and suburban residents, and households with children. However, a wide range of consumers across demographic groups have been shown to be environmentally and socially conscious buyers.

According to the results of the survey, McKinsey offers suggestions to companies to advance their ESG commitment and differentiate their products.

- ESG claims should support an overall ESG strategy with meaningful environmental impact across the product portfolio.
- Product design process should embrace the ESG related claims and cost engineering.
- Invest in ESG through existing brands and innovative products.
- Understand the dynamics of sustainability in each category and brand.
- Create products that address multiple environmental concerns.[67]

An article published by the National Retail Federation examined a variety of surveys and found that for consumers between the ages of 18 and 34, 80% of them say they are willing to pay more for sustainable products. However other research has shown that 53% of U.S. consumers think sustainable products cost too much. Inflation is large determiner of consumers spending habits. Consumer concerns about the quality of sustainable products is also a trend and rose 8 percent from 2020-2022. Another trend is that consumers have trouble identifying sustainable products, with 78% wanting to buy from environmentally friendly companies but don't know how to identify them.[68]

7.0 Related Global Research

Numerous companies, universities, or organizations outside the U.S. are also working in the sustainable chemical industry. A number of these organizations are explored in more detail in this section with abstracts from their research papers highlighted.

7.1.1 Leipzig University – Helmholtz Centre for Environmental Research

Researchers from the Helmholtz Centre for Environmental Research and Leipzig University have developed a process that produces adipic acid from phenol using an electrochemical synthesis using microorganisms. The original process involves converting phenol to cyclohexanol which can then be converted to adipic acid. This process requires high temperatures, high gas pressure, and organic solvents, and release nitrous oxide and carbon dioxide. The new process can convert phenol to cyclohexanol with an electrochemical process which needs a catalyst, such as carbon-based rhodium. The researchers have also discovered the bacterium Pseudomonas taiwanensis can convert cyclohexanol into adipic acid. In order to develop an environmentally friendly nylon product, the researchers used monomers such as syringol, catechol, and guaiacol, produced from the degradation of lignin.[69]

Though the scientists working on this project have achieved a yield of 57% through a 22-hour process, there is still a way to go before this process is ready for market. This yield is based on laboratory tests and only at the milliliter scale. To scale up this process, there needs to be a better understanding of the entire process and the use of real lignin instead of models and improvements needed to make to the electrochemical reactors.[70]

7.1.2 The Novo Nordisk Foundation Center for Biosustainability – Technical University of Denmark

Researchers at the Technical University of Denmark developed an integrated process for manufacturing muconic acid from glucose using yeast fermentation. The yeast strains used in the research included those derived from CEN.PK113-7D. The research team engineered Saccharomyces cerevisiae strain which produces muconic acid from glucose. The engineered strain accumulated less biomass but produced 1.4 g/L muconic acid in microplate assay, which is 71% more than previous engineered strains.[71]

> "Some microbial strains, such as *Pseudomonas putida* KT2440, *Corynebacterium glutamicum*, and *Amycolatopsis* sp. ATCC 39116 can degrade lignin-based aromatic compounds such as catechol, phenol, guaiacol, and *p*-coumaric acid, with CCM as the degradation product. The CCM titers reported in yeasts are lower than in *E. coli*, but yeast fermentation presents several advantages that make it attractive to develop a yeast-based process. Yeast fermentation can be carried out at acidic rather than neutral pH, which reduces the risk of contamination, and yeasts are phage-resistant. The CCM production in yeasts was improved in different studies by optimizing the 3-DHS-to-CCM pathway, boosting 3-DHS supply from PEP and E4P, tailoring the pentose phosphate pathway, biosensor-aided genome engineering, transporter engineering, and by fermentation optimization."
>
> "The highest CCM titer (20.8 g/L) was achieved in a CEN.PK background strain with a yield of 66.3 mg/g glucose and productivity of 139 mg/L/h, as reported in our previous publication. The titer, productivity, and yield of the yeast cell factory still need further improvement to achieve a commercially viable CCM production. Moreover, the engineered strains should be tested at a pilot scale to evaluate the strains' robustness and validate the absence of scale-dependent discrepancies."[72]

7.1.1 Saarland University, Saarbrücken, Germany

Jozef B.J.H van Duuren et al, "Limited Life Cycle and Cost Assessment for the Bioconversion of Lignin-Derived Aromatics Into Adipic Acid," *Biotechnology and Bioengineering*, February 5, 2020.

> "We applied a fast-pyrolysis process using softwood lignin resulting in a two-phase bio-oil containing monomeric and oligomeric aromatics without syringol. We demonstrated that an additional hydrodeoxygenation step within the process leads to an enhanced thermochemical conversion of guaiacol into catechol and phenol. After steam bath distillation, Pseudomonas putida KT2440-BN6 achieved a percent yield of cis, cis-muconic acid of up to 95 mol% from catechol derived from the aqueous phase."

7.1.2 Lund University, Lund Sweden

Sang-Hyun Pyo et al, "A Facile Process for Adipic Acid Production in High Yield by Oxidation of 1,6-hexanediol Using the Resting Cells of Cluconobacter Oxydans," *Microbial Cell Factories,* 21, 2022

> "The present report involves a study on the effect of different parameters on the microbial transformation of 1,6-hexanediol to adipic acid, and subsequently testing the process on a larger lab scale for achieving maximal conversion and yield. Comparison of three wild-type strains of G. oxydans DSM50049, DSM2003, and DSM2343 for the whole-cell biotransformation of 10 g/L 1,6-hexanediol to adipic acid in batch mode at pH 7 and 30 °C led to the selection of G. oxydans DSM50049, which showed 100% conversion of the substrate with over 99% yield of adipic acid in 30 h. An increase in the concentrations of the substrate decreased the degree of conversion, while the product up to 25 g/L in batch and 40 g/L in fed-batch showed no inhibition on the conversion. Moreover, controlling the pH of the reaction at 5–5.5 was required for the cascade oxidation reactions to work. Cell recycling for the biotransformation resulted in a significant decrease in activity during the third cycle. Meanwhile, the fed-batch mode of transformation by intermittent addition of 1,6-hexanediol (30 g in total) in 1 L scale resulted in complete conversion with over 99% yield of adipic acid (approximately 37 g/L). The product was recovered in a pure form using downstream steps without the use of any solvent."

7.1.1 University of Insubria, Varese, Italy

Fillipo Molinari et al, "Whole-Cell Bioconversion of Renewable Biomasses-Related Aromatics to cis-cis-Muconic Acid," *ACS Sustainable Chem Eng*, February 1, 2023

> "Lignin and wheat bran represent renewable feedstocks for generation of useful and value-added compounds such as vanillin (a popular flavoring agent) and cis,cis-muconic acid (ccMA, a building block for the synthesis of plastic materials). In the present work, we report on the setup of an efficient and green process for producing such valuable compounds based on (a) the optimization of the extraction procedures for vanillin from lignin and ferulic acid from wheat bran and (b) the genetic engineering of an Escherichia coli strain with up to three plasmids differing in copy numbers to modulate the expression of up to seven recombinant enzymes."

7.1.2 Università degli Studi di Milano, Milan, Italy

Allesandro Rosengart et al, "Hydrogenation of Trans, Trans-Muconic Acid to Bio-Adipic Acid: Mechanism Identification and Kinetic Modelling," Processes, 2020

> "Intensive biotechnological research has identified a number of genetically engineered strains able to produce cis,cis-muconic acid (ccMA) in quantitatively significant amounts from different feedstock. Some engineered strains have achieved the best conversions to date, in particular, strains of Escherichia coli starting from glucose and of Pseudomonas putida from aromatics. The feedstock flexibility is particularly relevant as both the cellulosic and lignin fractions of the biomass could be employed as cheap and abundant raw materials, opening the door to second generation biorefinery applications for fully sustainable adipic acid production. Additionally, Saccharomyces cerevisiae was proved effective in converting sugars to MA, paving the way to future low-cost industrial fermentations."

7.1.3 Ain Shams University, Cairo, Egypt

Selim Ashoor et al, "Bioupgrading of the Aqueous Phase of Pyrolysis Oil from Lignocellulosic Biomass: A Platform for Renewable Chemicals and Fuels From the Whole Fraction of Biomass," *Bioresources and Bioprocessing*, 2023.

> "Versatile chemicals, such as lipids, ethanol, and organic acids, could be produced through microbial assimilation of anhydrous sugars, organic acids, aldehydes, and phenolics in the hydrophilic fractions. The presence of various toxic compounds and the complex composition of the aqueous phase are the main challenges. In this review, the potential of bioconversion routes for upgrading the aqueous phase of pyrolysis oil is investigated with critical challenges and perspectives."

7.1.4 Institute of Chemical Technology, Mumbai, India

Amol Narendra Joshi, "Agricultural Biomass to Adipic Acid – An Industrially Important Chemical," *European Journal of Sustainable Development Research,* 2022, 6(2)

> "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."

7.1.5 Laboratory of Molecular Cell Biology, Institute of Botany and Microbiology, KU Leuven, Leuven-Heverlee, Belgium

Thomas Nicolai et al, "In-Situ Muconic Acid Extraction Reveals Sugar Consumption Bottleneck in a Xylose-Utilizing Saccharomyces Cerevisiae Strain," *Microbial Cell Factories*, 2021

> "We have constructed a yeast cell factory converting glucose and xylose into muconic acid without formation of ethanol. We consecutively eliminated feedback inhibition in the shikimate pathway, inserted the heterologous pathway for muconic acid biosynthesis from 3-dehydroshikimate (DHS) by co-expression of DHS dehydratase from P. anserina, protocatechuic acid (PCA) decarboxylase (PCAD) from K. pneumoniae and oxygen-consuming catechol 1,2-dioxygenase (CDO) from C. albicans, eliminated ethanol production by deletion of the three PDC genes and minimized PCA production by enhancing PCAD overexpression and production of its co-factor. Maximal titers of 4 g/L, 4.5 g/L and 3.8 g/L muconic acid were reached with glucose, xylose, and a mixture, respectively. The use of an elevated initial sugar level, resulting in muconic acid titers above 2.5 g/L, caused stuck fermentations with incomplete utilization of the sugar. Application of polypropylene glycol 4000 (PPG) as solvent for in situ product removal during the fermentation shows that this is not due to toxicity by the muconic acid produced."

8.0 Summary and Conclusions

To reduce green-house gas emissions in the chemical industry, research and development is being conducted to replace non-renewable carbon with renewable carbon resources (RCR). The example explored in this report is the substitution of renewable carbon resources for hexamethylenediamine, a precursor used in the production of Nylon 66. This report introduces numerous challenges associated with this transition including the use of corn stover as the feedstock source for lignocellulosic material in the U.S. Challenges include the seasonality and variability of the supply, as well as its preservation and storage. Various methods were introduced for turning these challenges into opportunities.

The scalability of solutions is the next challenge. This requires both significant investment from the public and private sector and partnerships. Examples are provided of various companies that are at various points on their commercialization journey. Genomatica is an example of a firm, whose business model, implemented over two decades is having an impact on this transition. As the shift from non-renewable carbon sources to RCR is a significant undertaking, examples are also included of companies that have closed operations.

The global and domestic market for hexamethylenediamine, used in the production of nylon and various other products is introduced. In the U.S. the dominant use of hexamethylenediamine is in nylon synthesis, much of which is used in the automotive industry as a substitute for metals in a wide variety of components. These include engine covers, air intake manifolds, airbag containers, rocker valve covers and numerous other parts. This substitution makes cars lighter and the process less expensive. Various supply chain issues of important precursors have arisen during the past several years. Although this led major suppliers to start considering substitutions (not from RCR), it is cautioned that this is not easy to do. Other applications for hexamethylenediamine are in textiles, with a large volume being used in carpets.

Many companies in the chemical industry are reducing their GHG footprint by recycling, as opposed to using non-renewable sources of carbon.

Endnotes

1 U.S. Department of Energy, "Bioenergy Technologies Office Multi Year Program Plan 2023," *U.S. Department of Energy*, 2023

2 The Royal Society of Victoria, "Reinventing the Chemical Industry with Green Chemistry," Click here to see Video.

3 Aymerick Eudes et al., "Production of Muconic Acid in Plants," *Metabolic Engineering*, vol. 46, 2018.

4 Environmental Molecular Sciences Laboratory, "Biologically Produced Muconic Acid Can Replace Petroleum-Based Products," *Office of Science Biological & Environmental Research*, January 31, 2023

5 R. RedCorn et al., "Feedstocks of the Future for a Circular U.S. Bioeconomy: A Summary From a Stakeholder Convening," *Foundation for Food & Agriculture Research and Schmidt Futures*, June 2023.

6 R. RedCorn et al., "Feedstocks of the Future for a Circular U.S. Bioeconomy: A Summary From a Stakeholder Convening," *Foundation for Food & Agriculture Research and Schmidt Futures*, June 2023.

7 Jim Philp, "A Roundup of Bioeconomy Work at DSTI," *OECD*, 2018

8 Frost & Sullivan, "Biotechnology Advancements That Enable Sustainability in the Chemicals Industry: Technology Growth Opportunities," *Frost & Sullivan*, July 2022.

9 Ed de Jong et al., "Bio-Based Chemicals: A 2020 Update," *IEA Bioenergy*, February 2020.

10 Ed de Jong et al., "Bio-Based Chemicals: A 2020 Update," *IEA Bioenergy*, February 2020.

11 Ed de Jong et al., "Bio-Based Chemicals: A 2020 Update," *IEA Bioenergy*, February 2020.

12 P. Thathiana Benavides et al., "Economic and Environmental Assessment of Biological Conversions of Agile BioFoundry (ABF) Bio-Derived Chemicals," *Agile BioFoundry*, October 15, 2020.

13 "Biologically Produced Muconic Acid Can Replace Petroleum-Based Products," *Environmental Molecular Sciences Laboratory*, January 31, 2023.

14 Nathan J. Hillson et al., "ABF Future Strategy – Implementation Plan," *Agile BioFoundry*, April 4, 2023.

15 Jeovanna Rios et al., "A Critical Review on the Progress and Challenges to a More Sustainable, Cost Competitive Synthesis of Adipic Acid," *Green Chemistry*, 2021

16 Jeovanna Rios et al., "A Critical Review on the Progress and Challenges to a More Sustainable, Cost Competitive Synthesis of Adipic Acid," *Green Chemistry*, 2021

17 Jeovanna Rios et al., "A Critical Review on the Progress and Challenges to a More Sustainable, Cost Competitive Synthesis of Adipic Acid," *Green Chemistry*, 2021

18 Toray Industries, "Toray Invents 100% Bio-Based Adipic Acid from Sugars Derived from Inedible Biomass, Scaling Up for Application to Eco-Friendly Nylon 66," *Toray*, August 24, 2022.

19 Toray Industries, "Toray Invents 100% Bio-Based Adipic Acid from Sugars Derived from Inedible Biomass, Scaling Up for Application to Eco-Friendly Nylon 66," *Toray,* August 24, 2022.

20 Toray Industries, "Toray and Partner Demonstrate Inedible Biomass-Based Sugar Manufacturing Technology That Could Pave Way to Sustainable Fibers, Resins, and Films," *Toray Industries,* April 17, 2023.

21 Toray Industries, "Toray and Partner Demonstrate Inedible Biomass-Based Sugar Manufacturing Technology That Could Pave Way to Sustainable Fibers, Resins, and Films," *Toray Industries,* April 17, 2023.

22 Toray Industries, "Toray and Partner Demonstrate Inedible Biomass-Based Sugar Manufacturing Technology That Could Pave Way to Sustainable Fibers, Resins, and Films," *Toray Industries,* April 17, 2023.

23 R. RedCorn et al., "Feedstocks of the Future for a Circular U.S. Bioeconomy: A Summary From a Stakeholder Convening," *Foundation for Food & Agriculture Research and Schmidt Futures*, June 2023.

24 R. RedCorn et al., "Feedstocks of the Future for a Circular U.S. Bioeconomy: A Summary From a Stakeholder Convening," *Foundation for Food & Agriculture Research and Schmidt Futures*, June 2023.

25 Ingo Schroeter et al., "The Path to Net Zero in Chemicals: Rethinking the Whole Supply Chain," *Kearney,* October 6, 2022.

26 R. RedCorn et al., "Feedstocks of the Future for a Circular U.S. Bioeconomy: A Summary From a Stakeholder Convening," *Foundation for Food & Agriculture Research and Schmidt Futures*, June 2023.

27 R. RedCorn et al., "Feedstocks of the Future for a Circular U.S. Bioeconomy: A Summary From a Stakeholder Convening," *Foundation for Food & Agriculture Research and Schmidt Futures*, June 2023.

28 Lynn M. Wendt et al., "Review on Bioenergy Storage Systems for Preserving and Improving Feedstock Value," *Frontiers in Bioengineering and Biotechnology,* Vol. 8, 2020.

29 Lynn M. Wendt et al., "Review on Bioenergy Storage Systems for Preserving and Improving Feedstock Value," *Frontiers in Bioengineering and Biotechnology,* Vol. 8, 2020.

30 Lynn M. Wendt et al., "Review on Bioenergy Storage Systems for Preserving and Improving Feedstock Value," *Frontiers in Bioengineering and Biotechnology,* Vol. 8, 2020.

31 Aymerick Eudes et al., "Production of Muconic Acid in Plants," *Metabolic Engineering*, vol. 46, 2018.

32 Minliang Yang et al., "Comparing In Planta Accumulation With Microbial Routes to Set Targets for a Cost-Competitive Bioeconomy," *Proceedings of the National Academy of Sciences,* vol.119, no. 30, 2022.

33 Minliang Yang et al., "Comparing In Planta Accumulation With Microbial Routes to Set Targets for a Cost-Competitive Bioeconomy," *Proceedings of the National Academy of Sciences,* vol.119, no. 30, 2022.

34 Minliang Yang et al., "Comparing In Planta Accumulation With Microbial Routes to Set Targets for a Cost-Competitive Bioeconomy," *Proceedings of the National Academy of Sciences,* vol.119, no. 30, 2022.
35 Minliang Yang et al., "Comparing In Planta Accumulation With Microbial Routes to Set Targets for a Cost-Competitive Bioeconomy," *Proceedings of the National Academy of Sciences,* vol.119, no. 30, 2022.
36 Minliang Yang et al., "Comparing In Planta Accumulation With Microbial Routes to Set Targets for a Cost-Competitive Bioeconomy," *Proceedings of the National Academy of Sciences,* vol.119, no. 30, 2022.
37 Spero Renewables, "About Spero Renewables," *Spero Renewables*, Accessed July 11, 2023.
38 Spero Renewables, "SPERLU Turns Waste Into Plastics
39 "Our Products," *Genomatica*, Accessed July 17, 2023.
40 "Geno's Nylon," *Genomatica,* Accessed July 17, 2023.
41 "Genomatica and Asahi Kasei Partner on Renewably-Sourced Nylon 6,6 for Automotive," *Green Car Congress*, March 16, 2022.
42 "Adipic Acid Product Stewardship Summary," *Ascend Performance Materials*, April 12, 2017.
43 "Vydyne," *Ascend Performance Materials,* Accessed July 17, 2023.
44 "Bioserve," *Ascend Performance Materials,* Accessed July 17, 2023.
45 "2022 Sustainability Report," *Ascend Performance Materials,* 2022.
46 Sumatra Biorenewables, "Sumatra Biorenewables," *Sumatra Biorenewables*, Accessed August 25, 2023.
47 Sumatra Biorenewables, "Sumatra Biorenewables," *Sumatra Biorenewables*, Accessed August 25, 2023.
48 SBIR, "Novel Adipic Acid Synthesis Pathway from Biomass-Derived Sugars and Intermediates," *DOE*, February 17, 2015.
49 SBIR, "Carbon Conserving Microbial Pathway for the Production of Caprolactam from Renewable Feedstocks," *DOE,* February 21, 2017.
50 SBIR, "Novel Syn Bio Method to Produce Performance Advantaged Polymers," *DOE*, February 22, 2021.
51 CHEManager International, "Invista Closing Texas Adipic Acid Unit," *CHEManager International*, October 13, 2015.
52 Jim Lane, "Verdezyne, Ave Atque Vale," *The Digest*, May 15, 2018
53 Jim Lane, "Rennovia's Demise, The Triple Rule, and The Pursuit of Sustainable Nylon in a World of Low Oil Prices," *The Digest*, March 9, 2018.
54 "A Part of Your Everyday Life," *Invista,* Accessed July 17, 2023.
55 "High-Purity Adipic Acid and N2O Abatement Technology Licensing," *Invista,* Accessed July 17, 2023.
56 Tracy Dang, "US Invista to Close Adipic Acid Plant in Texas," *Independent Commodity Intelligence Services*, October 6, 2015.
57 MarketsandMarkets, "Hexamethylenediamine Market: Global Forecast to 2027," *MarketsandMarkets,* 2022

58 MarketsandMarkets, “Hexamethylenediamine Market: Global Forecast to 2027,” *MarketsandMarkets,* Page 40, 2022
59 MarketsandMarkets, “Hexamethylenediamine Market: Global Forecast to 2027,” *MarketsandMarkets,* Page 40, 2022
60 MarketsandMarkets, “Hexamethylenediamine Market: Global Forecast to 2027,” *MarketsandMarkets,* Page 41, 2022
61 MarketsandMarkets, “Hexamethylenediamine Market: Global Forecast to 2027,” *MarketsandMarkets,* Page 51, 2022
62 MarketsandMarkets, “Hexamethylenediamine Market: Global Forecast to 2027,” *MarketsandMarkets,* Page 61, 2022
63 Lilli Manolis Sherman, “ Nylon 66: Pricing & Supply Issues Spur Processors to Consider Alternatives,” Plastics Technology, November 30, 2018.
64 QR Research, “Market Size 2023-2030 Global Industrial Analysis, Key Geographical Regions, Market Share, Top Key Players, Product Types,” QR Research, October 5, 2023
65 Plastic Soup Foundation, “Ghost Nets,” Plastic Soup Foundation, Accessed October 10, 2023
66 Fibre2Fashion, “69% US Consumers Willing to Pay More For Sustainable Products,” *Fashion Network*, March 31, 2023.
67 Jordan Bar Am et al., “Consumers Care About Sustainability – And Back it Up With Their Wallets,” *McKinsey & Company,* February 6, 2023.
68 Scot Case, “Consumers Care About Sustainability – But Will They Pay More?,” *National Retail Federation*, April 10, 2023.
69 UFZ, “Leipzig Research Team Develops Process for Bio-Based Nylon,” *Helmholtz Centre for Environmental Research Press Release*, July 4, 2023.
70 UFZ, “Leipzig Research Team Develops Process for Bio-Based Nylon,” *Helmholtz Centre for Environmental Research Press Release*, July 4, 2023.
71 Guokun Wang, “An Integrated Yeast-Based Process for cis,cis-Muconic Acid Production,” *Biotechnology and Bioengineering*, vol. 119, no. 2, 2022.
72 Guokun Wang, “An Integrated Yeast-Based Process for cis,cis-Muconic Acid Production,” *Biotechnology and Bioengineering*, vol. 119, no. 2, 2022.