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CRITICAL REVIEW

Catalytic Routes towards Acrylic Acid, Adipic Acid and ε-Caprolactam starting from Biorenewables

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The majority of bulk chemicals are derived from crude oil, but the move to biorenewable resources is gaining both societal and commercial interest. Reviewing this transition, we first summarise the types of today's biomass sources and their economical relevance. Then, we assess the biobased productions of three important bulk chemicals: acrylic acid, adipic acid and ε-caprolactam. These are the key monomers for high-end polymers (polyacrylates, nylon 6.6 and nylon 6, respectively) and are all produced globally in excess of two million metric tons per year. The biobased routes for each target molecule are analysed separately, comparing the conventional processes with their sustainable alternatives. Some processes have already received extensive scientific attention. Other, more novel routes are also considered. We find several common trends: For all three compounds, there are no commercial methods for direct conversion of biobased feedstocks. However, combinations of biotechnologically produced platform chemicals with subsequent chemical modifications are emerging and showing promising results. We then discuss several distinct strategies to implement biorenewable processes. For each biotechnological and chemocatalytic route, current efficiencies and limitations are presented, but we urge that these routes should be assessed mainly on their potentials and prospects for future application. Today, biorenewable routes cannot yet compete with their petrochemical equivalents. However, given that most are still in the early stages of development, we foresee their commercial implementation in the next two decades.

1. Introduction

Crude oil is currently the feedstock for manufacturing most bulk and fine chemicals. This causes competition over the available resources with the fuels for automotive and power industry, creating fluctuating prices of chemical feedstocks (Fig. 1).[1, 2] Combined with concerns over the environmental impact of petrochemical processing, the chemical industry is considering sustainable and more environmentally-friendly alternatives. The biorenewable production of many chemicals emits less greenhouse gases (GHGs) and employs more environmentally-friendly chemistry.[3, 4] However, the transition faces high technological and economical barriers.

Here, we address this transition for three important bulk chemicals: acrylic acid, adipic acid, and ε-caprolactam. Each of these is produced at over two million metric tons per annum (Mtpa) with current market prices around $1,500 per ton.

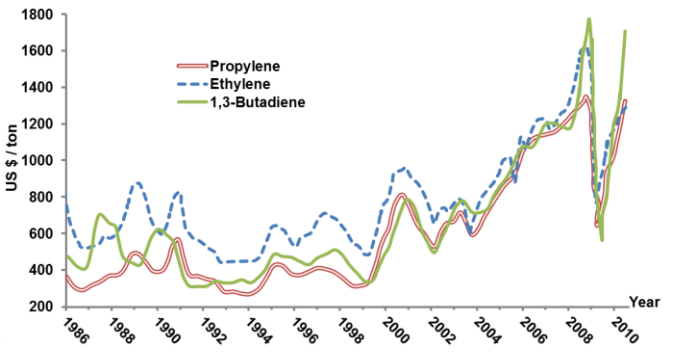

Fig. 1 Annual average prices for ethylene, propylene and 1,3-butadiene in $/ton.[5]

In 2012, more than 60% of all fibres produced worldwide were synthetic materials[6] (Fig. 2, left). Of these synthetic fibres, the largest part was embodied by polyesters and poly-olefins (Fig. 2, right), such as poly(ethylene terephthalate) (PET), polyethylene (PE) and poly-propylene (PP). PET is made from ethylene glycol (EG) and terephthalic acid (TPA). Though biobased EG is commercially available, the non-availability of biobased TPA prevents production of fully biorenewable PET.[7] Braskem produces 200,000 tons of biobased PE in Brazil,[8] using ethylene obtained by dehydrating bioethanol. However,

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biobased PE is currently still more expensive than petrobased PE. An emerging route towards biobased propylene is by producing ethanol and butane from sugars by fermentation, subsequent dehydration and metathesis of ethylene and butene to propylene. However, developing process technology that can economically compete with petrobased PP is a challenge.[9] These monomers are incorporated in a great many chemical and economical value chains. Moreover, their prices are low: below $1,500 per metric ton.[10] Conversely, the bulk chemicals that we will cover here are relatively expensive, ensuring economical margins for innovative alternatives.

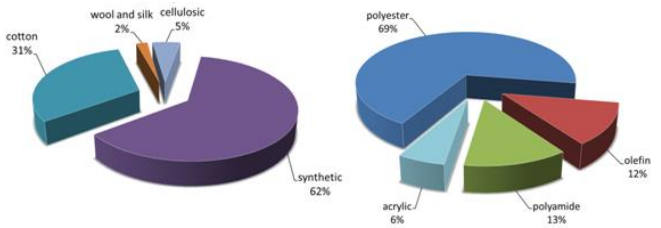


Fig. 2 Overviews by weight percentage. Left: Global fibre market, in 2012. Right: Constituents of synthetic fibres market, by general polymer classes, in 2012.[7]

Acrylic acid is used for making polyacrylic acid and various acrylic esters, known for superabsorbent properties and attractive properties in co-polymerization (Fig. 3). These are used in a range of synthetic products, including diapers, plastics, synthetic rubber, coatings and paint formulations.[11] **Adipic acid** and **ε-caprolactam** are used as monomers for making nylon 6.6 and nylon 6, respectively (Fig. 3). These are the archetypes of polyamides, accounting for 85–90% of the world nylon market. Polyamides are applied chiefly in fibre and textile industry and thus have competitive end-uses, yet dissimilar properties. In terms of performance, nylon 6 has better processability and resistance to wear, while nylon 6.6 has better heat resistance and mechanical properties.[11]

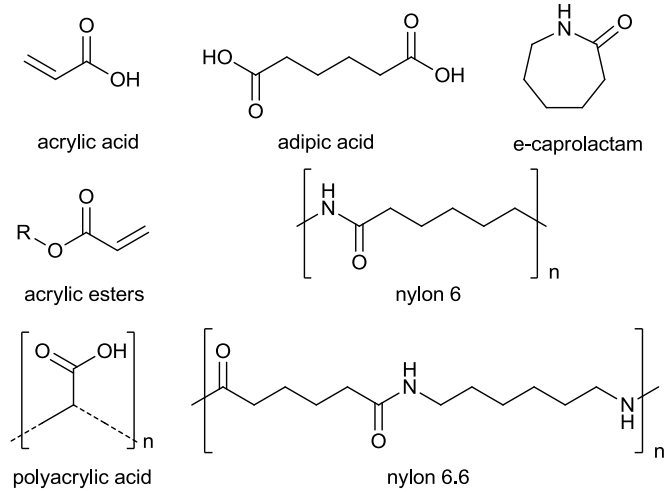


Fig. 3 Structures of acrylic acid, adipic acid, ε-caprolactam and their major end-products.

Over the last decades, much research went into biorenewable chemicals and chemical biomass utilization.[12-20] The growing interest in biorenewables focused mainly on producing platform chemicals, which can be applied in the synthesis for various compounds. It is therefore important to also review the influence of 'white biotechnology' or industrial biorefineries, on manufacturing bulk chemicals. For producing acrylic acid, adipic acid and ε-caprolactam, no commercial biotechnological routes are currently employed. Emerging platform chemicals from biotechnology may present economically viable routes. However, most research deals with specific advancements, rather than giving an overall view.

To assess the current processes and possible advancements made with biorenewable feedstocks, we first analyse the available biomass constituents and biobased feedstock (Table 1). The benchmark prices are averaged across regions and qualities, giving a general impression of availability of biobased feedstocks and their incorporation into chemical value chains.

Table 1 Overview of available biomass feedstocks.

Biobased feedstock	Chemical formula	Global production (Mtpa)[a]	Benchmark price (U.S. $/ton)[a]
starch[21]	glucose polymers	75	500
glucose[1, 22]	H-(C=O)-$(CHOH)_5$-H	175	500
fructose[23]	H-$(CHOH)_4$-(C=O)-(CH_2OH)	7	900
ethanol[2, 24]	CH_3CH_2OH	65	750
virgin oils[1, 25]	various triglycerides	155	1,100
glycerol[26-28]	(CH_2OH)-(CHOH)-(CH_2OH)	1	850
lysine[29, 30]	$C_6H_{14}N_2O_2$	0.85	1,900
glutamic acid[29, 31, 32]	$C_5H_9NO_4$	1.6	1,300

[a] Worldwide production and price indexes for 2012.

Here, we will focus only on the technical analyses of the biorenewable routes and refrain from any economic analyses. Full economical assessments[33-36] are needed for reliable estimations and conclusions. As rough economical estimations are often subjective, we feel that those should be avoided.

The combined results give a critical overview on the transition from petrobased to biorenewable productions of acrylic acid, adipic acid and ε-caprolactam. To understand the developments, we will examine the biobased pathways, and compare these to petrochemical pathways. We use examples of on-purpose reactions towards target molecules, focusing on the most recent and efficient to date.

2. Implementing biorenewable chemicals

There are various incentives for applying biorenewables in the chemical industry. Government regulations are putting pressure on chemical companies to make more environmentally-friendly products. However, these companies can only provide products

that are commercially competitive. The discussion on using biomass for making chemicals is often emotionally charged, giving the biobased industry the added value of the 'bio', 'eco', or 'green' label, which may make up for additional costs for starting up biorenewable processes and products with an environmentally-friendly image.[37]

Biorenewable chemicals are socially attractive. However, their production will only be viable when it can compete economically with the petrobased ones. This is fundamentally possible – biomass is readily available, stable in supply and (depending on type) can be cheap. What's more, biobased chemicals can often be produced under milder conditions and with less toxic reagents and waste, than the petrobased equivalents, being more 'green' with lower processing costs.[38]

However, logistic considerations may determine the choice of companies to produce their chemicals biobased or petrobased. 1,3-Propanediol (1,3-PDO), for instance, is currently manufactured *via* both pathways. At Shell, the hydroformylation of ethylene oxide gives an intermediate, which is subsequently hydrogenated to 1,3-PDO. Conversely, in the DuPont Tate & Lyle BioProducts process, 1,3-PDO is made from corn syrup using modified *E. coli*. DuPont claims the biobased process consumes 40% less energy and reduces GHG emissions by 20%, compared to the petrobased process. Despite this, there is no report on Shell adopting a biobased process. Shell is the largest producer of ethylene oxide, with 40% of the global production, at multiple plants worldwide.[11] Though the biobased process is proven viable and more eco-friendly, economics and logistics dominate.

Platform chemicals vs. chemical modification of biobased feedstock. Unlike crude oil, biomass is typically over-functionalized. Thus, biobased feedstocks must be broken down to provide basic chemical 'building blocks' or platform chemicals.[39] Platform chemicals offer the possibility of synthesizing various end-products. However, biomass feedstocks may also be utilized towards specific end-products with similar chemical structures, by using the already present functionalities.[40]

Top-down vs. bottom-up. Some existing chemical processes may be replaced by competitive biorenewable processes, to produce the same end-product. The production of ethanol, for example, relies both on microbial fermentation of sugars, and hydration of ethylene. Process economics compete, depending on feedstock prices. Such approaches to biorenewability can be seen as 'top-down'.

However, biobased chemicals can also compete on a functional basis. Biobased feedstock and platform chemicals may offer novel compounds that cannot be made on commercial scale by petrochemical processes. These new market products may offer added functionality, such as biodegradability or low/no toxicity. One example of such a 'bottom-up' approach is replacing polyethylene terephthalate (PET) with biodegradable polyethylene furanoate (PEF) made of 2,5-furandicarboxylic acid (FDCA) derived from hemicellulose, for making 'green' bottles. The forerunner in this field is Avantium Technologies, which partnered with Coca-Cola in the YXY project. Avantium's 40 tpa pilot plant is scheduled to open in 2014 in the Netherlands.[41]

Another example is polylactic acid (PLA), produced by NatureWorks under the product name Ingeo. This is the first biopolyester made on an industrial scale (140 ktpa). Commercial application relies on added functionalities of the novel polymer. High efficiency enables competitive economics, with every 2.5 kg corn (15% moisture) yielding 1.0 kg PLA.[42]

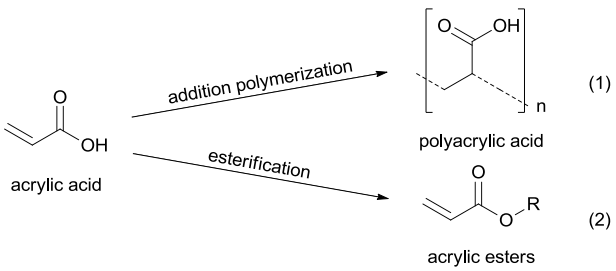
A very recent development from our group is the invention of Glycix – a thermoset resin made from glycerol and citric acid, that is now being commercialized in the Netherlands.[43] In this case, the added value of the biorenewable polymer lies in its biodegradability and strong adhesive properties, that enable the formation of superior composites.[44]

New biorenewable routes vs. intersecting existing chemical value chains. Most novel routes cannot compete with existing technologies, because those are highly optimized. Instead of direct competition, parts of existing process may be adapted. As such, biobased intermediates may support established routes. This combines proven and optimized routes with biorenewable feedstocks. However, many existing 'green' alternatives are ready to be exploited, when environmental restrictions become exceedingly demanding.[45]

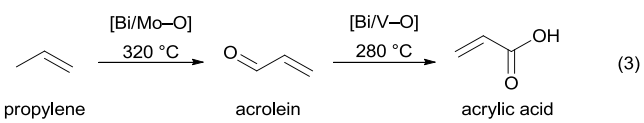
3. Acrylic acid

3.1. Introduction

Acrylic acid is a versatile monomer and intermediate, with major end-uses as acrylic esters for superabsorbent polymers (55%) and plastics and synthetic rubber (30%). The remainder is used in the manufacture of coatings, paint formulations, and leather finishing (eqns (1) – (2)).



In 2012, around 4.5 Mt of acrylic acid was produced worldwide, with a growing demand of 4% per year. The current market price is \$1,600–\$1,800/ton for low-grade and \$1,900–\$2,200/ton for glacial-grade. The Asian-Pacific consumption is about 46%, U.S. 27% and Western Europe 21%. Its major producers are BASF, Dow and Arkema, but several other companies also invest in biobased processes.[46]



Most of the acrylic acid production today follows a two-step energy-intensive gas-phase process. [11, 47] Herein, propylene, a side-product of ethylene and gasoline production, is first oxidized to acrolein using a Bi/Mo–O catalyst at 320 °C. Then the reaction mixture is directly converted to acrylic acid in a second reactor, using a Bi/V–O catalyst at 280 °C (eqn (3)).

3.2. Alternative biorenewable processes

Here, the most recent and noticeable alternative routes towards acrylic acid will be discussed. Some advanced processes include converting glycerol, but also using platform chemicals that are already produced on large scale, such as lactic acid and acrylonitrile. We will also review novel routes, using emerging platform chemicals such as 3-hydroxypropionic acid and 2-acetoxypropionic acid. Fig. 4 gives an overview of the conventional petrobased routes in grey, and the alternative routes based on biorenewable platform chemicals in light blue.

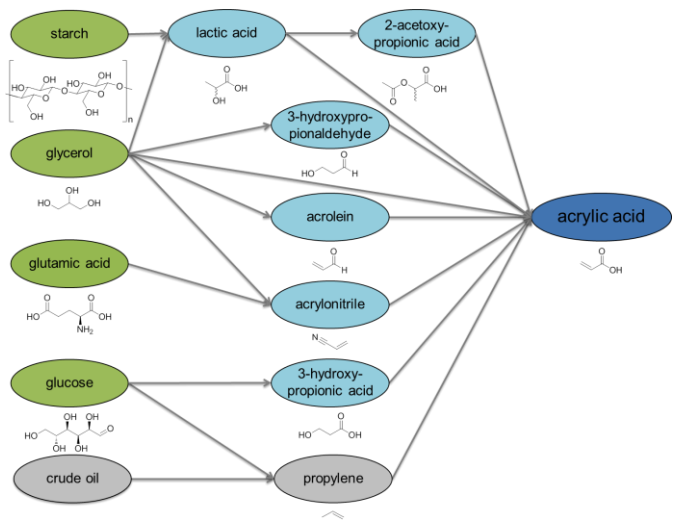


Fig. 4 Production routes to acrylic acid, showing biobased feedstocks (green), biobased platform chemicals (light blue), and existing petrobased routes (grey).

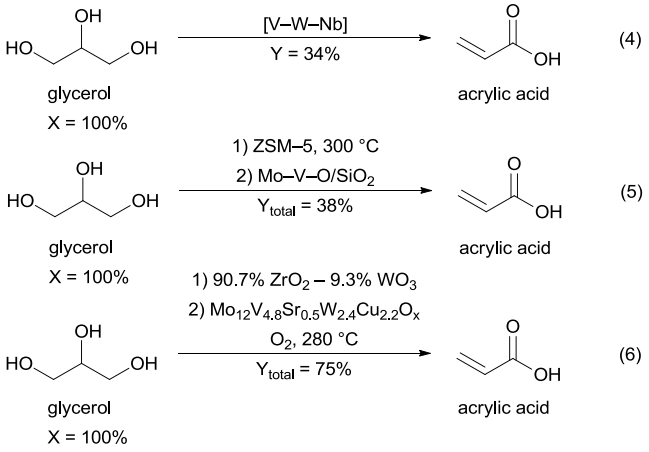
3.2.1. Production of biorenewable propylene

Several companies are investing in the biobased production of propylene. Global Bioenergies, for example, produces isobutene from glucose and is looking to expand their process to propylene.[48] Another pathway to biopropylene is through converting bioethanol. Iwamoto *et al*. reported this route, using a scandium-loaded In_2O_3 catalyst at 500 °C, giving 60% yield.[49]

3.2.2. Glycerol to acrylic acid

Today, glycerol is mainly produced as a biodiesel by-product from the trans-esterification of triglycerides to fatty acid methyl ester (FAME). This process co-generates glycerol by approximately 10% by weight.[26] Its current global production is around 1 Mtpa, with a market price of around $850/ton.[27, 28] The demand for biodiesel is growing, due to governmental fuel regulations. This results in glycerol becoming more available and cheaper, in the coming years. For converting glycerol to acrylic acid, both the direct conversion by a single catalyst, as well as combinations of multiple catalysts are known. The latter may utilize one-pot processes or consecutive reactor beds.

In 2012, Chieregatoa *et al.*[50] showed a robust V–W–Nb-based catalytic system, composed either mainly of vanadium or niobium. Complete conversion was observed with 34% acrylic acid yield and 17% acrolein co-product formation. After 100 h on stream, the acrylic acid yield was reduced from 34% to 31%, while acrolein formation rose from 17% to 21%, retaining 51% overall combined yield of acrylic acid and acrolein (eqn (4)).



In 2011, Witsuthammakul *et al.*[51] described a single reactor using two consecutive reactor beds. First, complete conversion of glycerol with 81% selectivity to acrolein was recorded over a ZSM–5 reactor bed at 300 °C. Subsequently, a V–Mo–O/SiO_2 catalyst bed afforded 48% conversion with 98% selectivity. The combined catalytic system gave 38% overall yield (eqn (5)).

Another patent, from Dubois and co-workers at Arkema,[52] described the conversion of glycerol to acrylic acid using a two-bed oxydehydration reaction, in the presence of molecular oxygen. Optimal results were found, for the first bed with 91% ZrO_2–9% WO_3 and the second bed with a multi-metallic catalyst[53] ($Mo_{12}V_{4.8}Sr_{0.5}W_{2.4}Cu_{2.2}O_x$). Full conversion and 75% overall yield were obtained at 280 °C. These results seem impressive, yet catalyst stability and re-use were not disclosed (eqn (6)).

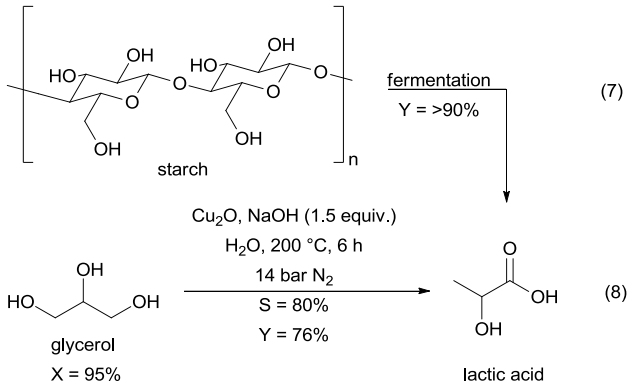
3.2.3. Lactic acid to acrylic acid

In 2012, the global production of lactic acid was estimated at 300–400 ktpa, with existing capacity of over 500 ktpa. The current market prices range from $1,300/ton (50% purity) to $1,600/ton (88% purity). Its major producers are NatureWorks LLC & Cargill, Purac, Galactic, and several Asian companies.[54, 55] The major end-use in 2012 was the production of PLA at nearly 200 ktpa.

Bacterial routes to lactic acid account for > 90% of all lactic acid production, using *Lactobacillus acidophilus* and *Streptococcus thermophiles* bacteria (eqn (7)). Generally, starch is used as feedstock and yields are greater than 90%.

Lactic acid may also be synthesized chemically from other biobased feedstocks, such as glycerol or hexoses *via* triose

derivatives. A recent example is given by Chaudhari *et al.*[56], reacting glycerol in the presence of Cu_2O and 1.5 equivalents of NaOH, in H_2O under 14 bar N_2 at 200 °C. Within 6 h, 95% conversion is reached, with a selectivity of 80% and proven re-usability of the catalyst (eqn (8)).

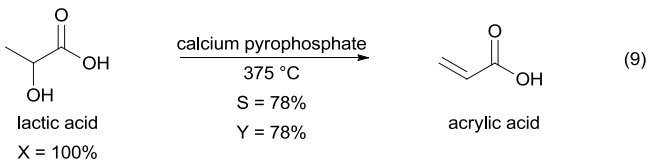


With increased research into utilizing cheaper feedstocks such as molasses and whey waste-streams or crude lignocellulose, the production of lactic acid is expected to grow.[57] For a comprehensive overview of the position of lactic acid, see Dusselier *et al.*[58]

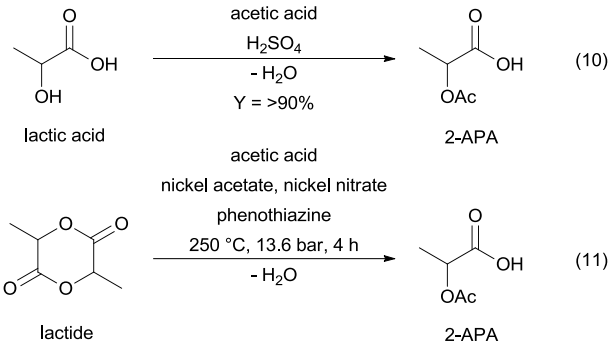
Dehydration of lactic acid to acrylic acid proceeds by abstracting a hydroxyl group and proton, giving the vinyl double bond. The reaction proceeds *via* a carbocation at the carbonyl α-position. This means that decarboxylation ensues readily. At high temperature, this reaction suffers from lactide formation and decomposition to acetaldehyde, CO and water. Furthermore, inhibiting oligomerization is important for maintaining high selectivity.[11]

Experiments in supercritical or near-critical water showed that adding H_2SO_4 increased lactide and acetaldehyde formation, while NaOH increased selectivity to acrylic acid.[59] Moreover, adding Na_2HPO_4 increased acrylic acid yield from 35% to over 58%.[60] Experiments at high temperature (450 °C) and pressure (400–1000 bar) showed that the latter promotes both conversion and selectivity.[61]

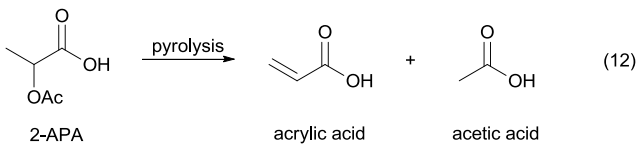
The highest yield was reported by Ghantani and co-workers,[62, 63] who obtained full conversion and 78% yield, converting lactic acid (25 wt% feed) over a calcium pyro-phosphate catalyst at 375 °C, with a WHSV of 3 (eqn (9)). A detailed overview of this reaction is published elsewhere.[64] However, the acrylic yield is lower with feeds containing high concentrations of lactic acid. For commercial application, this has to be improved. Moreover, acrylic acid yield should be high at high space velocities.



Another interesting route to acrylic acid comes from acetoxylation of lactic acid towards 2-acetoxypropionic acid (2-APA) and subsequent pyrolysis. Currently, there are no commercial processes using 2-APA. For this, the traditional acetic anhydride route is unsuitable because lactic acid is mostly available in aqueous solution. To overcome this, inexpensive acetic acid may be used also as solvent. The conversion of lactic acid to 2-APA was reported by Lilga *et al.*, using conc. sulfuric acid in yields over 90% (eqn (10)).[65]



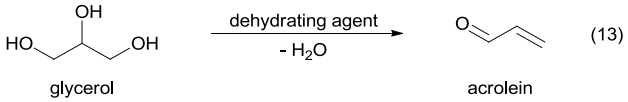
Fruchey *et al.* claim that 2-APA may be produced quantitatively from lactide and acetic acid, using nickel acetate, nickel nitrate and phenothiazine at 250 °C (eqn (11)).[66] Lactide is a common by-product in reactions with lactic acid. Its valorisation is crucial for a cost-effective processes. Under certain conditions, this cyclic dimer shows enhanced activity over the monomer to acrylic acid.[66] On-purpose dimerization is typically done in two steps. First, monomer condensation is achieved by removing water at temperatures above 200 °C. Then, the dimer is cyclized thermally, or by acid catalysis.



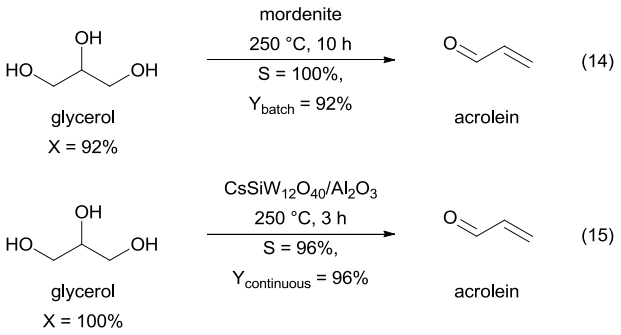
It was suggested that 2-APA readily undergoes pyrolysis at around 95% yield.[47, 66] This reaction is more selective than the direct dehydration of lactic acid, as it does not involve a carbocation (eqn (12)).

3.2.4. Acrolein to acrylic acid

Currently, acrolein is used as a precursor for a range of derivatives, such as acrylates, acrylonitrile and acrylamide. It is usually not isolated, but used as an intermediate and reacted to the desired end-products. Most of the current commercial processes depend on gas-phase oxidation of propylene. These processes generally attain only 20% conversion and 70–85% selectivity and depend on intensive propylene recycling.



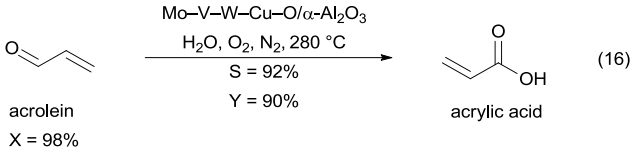
A sustainable alternative for the production of acrolein starts from glycerol (eqn (13)). The dehydration of glycerol can be done in the gas phase, the liquid phase and the (near)supercritical phase,[67] using either homogenous or heterogeneous catalysts.[68, 69] Recently, Liu and co-workers obtained high yields using rare earth metal-pyrophosphates. Their best result, 96% conversion with 83% selectivity, was attaining at pH 6, using a $Nd_4(P_2O_7)_3$ catalyst calcined at 400 °C.[70] Previously, we reported the dehydration of glycerol to acrolein over Nb_2O_5/SiO_2 catalysts, showing that the conversion and selectivity depend on the niobium loading and calcination temperature.[71] Elsewhere, De Oliveira and co-workers[72] investigated liquid-phase glycerol dehydration using various zeolite catalysts. They found that catalytic activity was not directly correlated to Si/Al ratio. However, catalyst structure and porosity, and strength of acid sites were determining factors. Using a mordenite catalyst, they obtained 92% conversion and full selectivity after 10 h at 250 °C (eqn (14)).



The use of heteropoly acids (HPAs) was intensively researched in the last decade.[73-75] Haider *et al.*[76] reported the use of a $CsSiW_{12}O_{40}/Al_2O_3$ catalyst in a continuous flow reaction (eqn (15)). They obtained full conversion and 96% selectivity towards acrolein, after 3 h at 250 °C. HPAs can offer higher Brønsted acidity than mineral acids, but suffer significant limitations due to catalyst instability. Several recent reviews on this topic have been published.[26, 77, 78]

Various catalysts are known for converting acrolein to acrylic acid. Here, we focus on the popular Mo–V–O and Mo–V–M–O (M=W, Cu, Nb, Te) type materials.

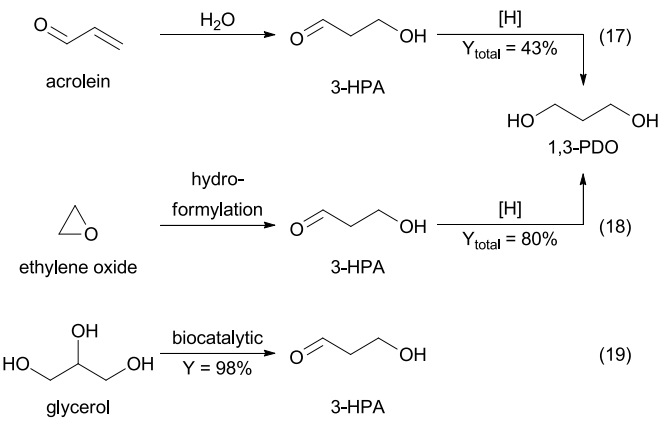
As early as in 1967, Kitahara *et al.* presented the conversion of acrolein to acrylic acid using V–Mo–O catalysts, synthesized from MoO_3, V_2O_5, Al_2O_3 precursors in respective ratio of 8:1:0.4 at 17.8% (by weight) supported on spongy aluminum. Using O_2 and steam at 200 °C, they attained 97% conversion with 86% selectivity to acrylic acid.[79, 80] In 1974, Tichý *et al.* improved the efficiency using a Mo–V–O catalyst supported on SiO_2 aerosil (30% by weight), with a Mo:V ratio of 5:1, in the presence of molecular oxygen and steam at 180 °C. Complete conversion of acrolein was observed with 96% selectivity towards acrylic acid. However, little is known about catalyst stability and re-use.[81] The reaction mechanisms, kinetics, and the effect of promoters are reviewed elsewhere.[82]



Recently, Aoki and co-workers achieved high acrylic acid yields, using a Mo–V–W–Cu–O catalyst supported on α-alumina in a fixed bed reactor. They obtained 98% conversion of acrolein and 90% yield of acrylic acid at 280 °C (eqn (16)).[83]

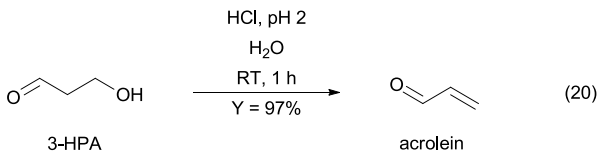
3.2.5. 3-Hydroxypropionaldehyde (3-HPA) to acrylic acid

Another viable route to acrylic acid starts from 3-hydroxypropionaldehyde (3-HPA). Currently, two commercial processes produce 3-HPA as an intermediate for 1,3-PDO.[11] In the Degussa process, propylene is transformed to acrolein, which is hydrated to 3-HPA (eqn (17)). Further reduction yields 1,3-PDO at 43% overall yield, but product separation is costly. Contrarily, the Shell process relies on ethylene oxidation to ethylene oxide, its hydroformylation to 3-HPA under 150 bar and subsequent reduction to 1,3-PDO at 80% overall yield. However, the efficiencies for the intermediate steps are not given (eqn (18)).



The enzymatic conversion of glycerol to 3-HPA was reported in 2008, with yields up to 98% mol/mol. The biorenewable route outperforms petrochemical routes,[84] but is not yet commercialized (eqn (19)). Details on the enzymatic production of 3-HPA can be found elsewhere.[85]

The oxidation of 3-HPA to acrylic acid is an interesting biobased alternative, but no direct (bio)chemical transformations are known at present.[85-87]

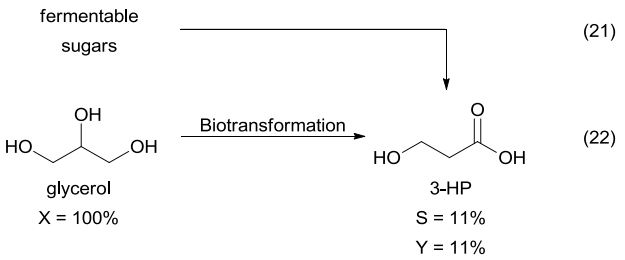


Conversely, 3-HPA may be converted with high efficiency to acrolein. In 2008, Toraya *et al.* reported 97% yield of

acrolein by reacting 0.2M 3-HPA solution with HCl (35%) at pH 2, at room temperature in 1 h (eqn (20)).[84]

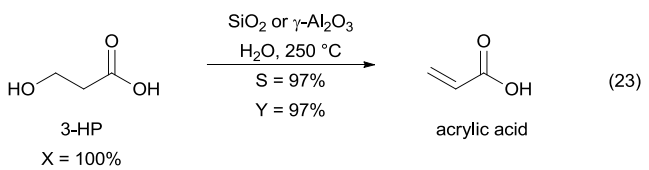
3.2.6. 3-Hydroxypropionic acid (3-HP) to acrylic acid

Another potential platform chemical is 3-hydroxypropionic acid (3-HP), the β-isomer of lactic acid and the carboxylic acid derivative of 3-HPA. Many fermentation routes can produce this compound (eqn (21)).[88] Current yields from glucose are too low for industrial application at high concentration, although coupled fermentation with co-reactions may overcome this problem.[89] The biobased production of 3-HP is currently not commercialized. However, in July 2013, a consortium of BASF, Cargill and Novozymes successfully demonstrated 3-HP production at pilot scale. In September 2014, the same consortium announced the successful conversion of 3-HP to glacial acrylic acid and superabsorbent polymers.[90] Moreover, this process was selected for further scale-up. In 2013, another consortium, of OPX Biotechnologies and Dow Chemical, announced the successful fermentation in 3 thousand litre (kl) capacity *en route* to biobased acrylic acid. The consortium is now scaling up the process to 20–50 kl.[91]



A different biobased approach to 3-HP is *via* fermentation of glycerol (eqn (22)). Recently, Kim *et al.* showed direct biotransformation using *Klebsiella pneumoniae*. Conversion is 100%, but 3-HP selectivity is only 11% mol/mol. The main by-products are 1,3-PDO (47%) and acetic acid (18%).[92]

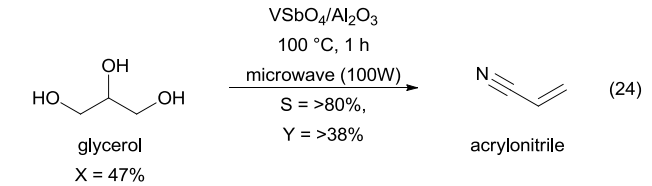
Dehydration of 3-HP to acrylic acid shows high yields for various conditions and catalysts. A recent example was patented by Ciba Specialty Chemicals.[93] The best results were obtained for a 20% aqueous solution over SiO_2 yielding 97%, and 60–80% aqueous solutions over high surface area γ-alumina, also yielding 97–98%. Reactions proceeded at 250 °C, with complete conversion of 3-HP (eqn (23)). The difference in selectivity between lactic acid and 3-HP is attributed to the elimination mechanisms.

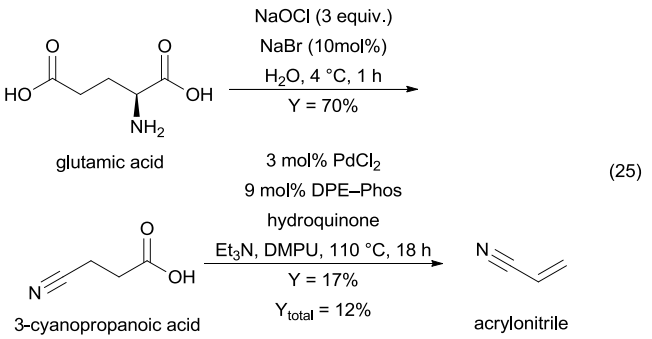


3.2.7. Acrylonitrile to acrylic acid

Acrylonitrile is a highly desired bulk chemical and a potential biorenewable platform chemical. In 2012, production was around 6.0 Mtpa, with a market price of $1,600–$2,000/ton.[94] Currently, it is produced predominantly by the SOHIO process. Herein, propene is converted over a [Bi–Mo–O] catalyst, in the presence of air and ammonia, at 400–500 °C. The direct conversion gives over 70% yield.[7,95-97]

The direct ammoxidation of glycerol to acrylonitrile has only seen few publications. The most noticeable came from Bañares and co-workers[98] in 2008. They used a V–Sb–Nb/Al_2O_3 catalyst, reaching 83% conversion and 58% selectivity, at 400 °C. The same group also reported a solvent-free microwave irradiation reaction at 100 °C, giving 47% conversion with 80% selectivity within 1 h. Although activity is modest, these conditions are mild, solvent-free, and use inexpensive biobased feedstocks (eqn (24)).[99]





Recently, Le Nôtre *et al.* showed that acrylonitrile can be made from glutamic acid, in two steps. Glutamic acid is readily available from biomass and an industrial waste-product *(e.g.* from bioethanol production). However, most glutamic acid is currently produced by fermentation using *Corynebacterium glutamicum*.[31] The first step in converting glutamic acid to acrylonitrile is oxidative decarboxylation to 3-cyanopropanoic acid (70% isolated yield in 1 h). The second step is the decarbonylation/elimination reaction, yielding 17% of acrylonitrile in 18 h (eqn (25)).[100] Even in the presence of the hydroquinone stabilizer, reactant degradation and product polymerization are thought to cause the low overall yield.

Hydrolysis of acrylonitrile to acrylic acid is one of the conventional routes to acrylic acid, adopted by Mitsubishi Petrochemical, Asahi Chemical and others. However, reacting with H_2SO_4 gives stoichiometric NH_4HSO_4 waste. The more recent Mitsui Toatsu process uses only water for conversion over a B_2O_3–based catalyst. Specific details on reaction conditions and yields are not given, but complete conversion and *ca.* 90% selectivity is expected.[11, 101]

The first reports of the biotransformation of acrylonitrile to acrylic acid came in 2010, using *Rhodococcus ruber* bacteria.[102] Under optimal conditions, using purified nitrilase, 92%

mol/mol yield was achieved. Continued research is performed towards optimization and scale-up conditions. Since then, various biotransformations were reported.[103]

3.3. Acrylic acid – summary and analysis

The petrochemical synthesis of acrylic acid depends on processing propylene. The price of propylene has fluctuated greatly in recent years (rising above \$1,300/ton). Substituting petrobased propylene with its biobased equivalent provides a biorenewable pathway to acrylic acid. This approach preserves existing production processes and allows industry to adapt more easily to biorenewability. Propylene may be produced from ethanol (around \$750/ton) at 60% yield. Improving efficiency, this route may soon become commercially competitive.

To obtain platform chemicals *via* fermentation, starch and glucose are typically observed as microbial feedstocks. These are cheap feedstocks (around \$500/ton) and thus provide large economic margins towards acrylic acid (\$1,600–2,200/ton).

The efficient production of 3-hydroxypropionic acid from glucose is emerging rapidly, and commercialization is envisioned in the coming years. Moreover, dehydration of 3-hydroxypropionic acid gives near quantitative yield. With at least two important industrial consortia showing promising results, this route seems to be commercially viable.

Acrylonitrile hydrolysis to acrylic acid was demonstrated at high efficiency (over 90%), in both chemocatalytic and biotechnological processes. Converting glutamic acid shows full conversion, but suffers from selectivity issues (12% overall). Moreover, the current glutamic acid feedstock price (*ca*. \$1,300/ton) makes this route far from economically viable.

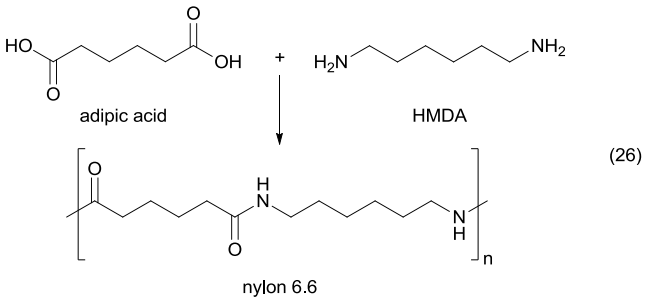
Glycerol is an attractive biobased feedstock for producing acrylic acid. As a by-product from the biodiesel industry, its price (around \$850/ton) is expected to lower in the coming years. Its continuous reaction to acrolein shows high yield (96% yield). Subsequent acrolein conversion to acrylic acid occurs at 90% yield. In the combined process 75% yield was obtained. This provides an economically viable pathway, but has not yet been commercially applied. Another pathway to acrolein is *via* biocatalytic production of 3-hydroxypropionaldehyde from glycerol (98% yield). Subsequent conversion produces acrolein at 97% yield. The theoretical acrylic acid yield is 86%, in three steps. However, the combined process was not yet reported. Most of the studies on glycerol conversion are done with refined feed. Additional studies need to be done, on the catalytic performance and stability, when crude glycerol is used as feed. In general, crude glycerol contains light solvents (water, methanol, and/or ethanol), fatty acid methyl esters, free fatty acids and ash. Since biodiesel production methods vary significantly, the composition of crude glycerol also varies widely.

Compared to glycerol, lactic acid is more expensive (around \$1,600/ton (88% purity). However, bacterial routes to lactic acid show high yields (around 90%). It is expected that expanded production and improved biotechnology will lower lactic acid prices in the coming year. Dehydration of lactic acid shows selectivity issues, due to the instability of the intermediate. A possibility to overcome this problem is using derivative chemicals, such as 2-acetoxypropionic acid. However, this route is still limited to homogeneous catalysis and lacks processing conditions. Nevertheless, this route is worth studying, since pyrolysis of 2-acetoxypropionic acid is reported to lead to acrylic acid efficiently.

4. Adipic acid

4.1. Introduction

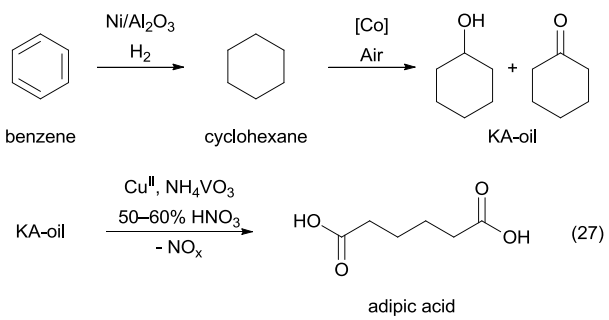
Adipic acid is mainly used for the manufacture of nylon 6.6 (eqn (26)). The polycondensation with hexamethylenediamine (HMDA) towards nylon 6.6 accounts for around 85% of all adipic acid produced, with the remainder used for polyurethanes and adipic esters.[11]



(26)

In 2012, the production of adipic acid was around 2.3 Mt, with a growing demand of 3–5% per year. The current market price is \$1,500–\$1,700/ton, and its major producers are Invista, DuPont, Rhodia, Ascend and BASF.[104] Commercial interest in biorenewable routes to adipic acid is found in plans of both major and start-up chemical companies *i.e.* BioAmber, Ronnavia, Genomatica, DSM, Celexion and Verdezyne.

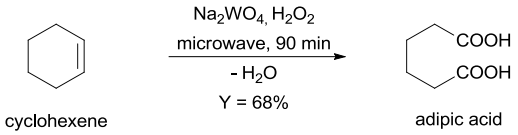
In 2012, more than 90% of the global adipic acid production relied on nitric acid oxidation of cyclohexanol or a mixture of cyclohexanol/cyclohexanone (KA-oil), all derived from petrobased benzene (eqn (27)).[11, 105] This process generates nitrous oxide waste. Consequently, developing less polluting, more 'green' routes has become an important matter and has seen already large improvements. Here we outline the most relevant current routes. A comprehensive overview is published elsewhere.[106]



(27)

In 1975, an alternative route[107, 108] to adipic acid used the hydrocarboxylation of 1,3-butadiene, giving no nitrous oxide

waste. Noyori and co-workers[109] developed in 1989 a halide-free biphasic process for the direct oxidation of cyclohexene to crystalline adipic acid, using a phase-transfer catalyst in the presence of 30% aqueous H_2O_2. This gave adipic acid at 90% yield, albeit after 8 h.



(28)

Freitag *et al.*[110] then improved this biphasic system by using a Na_2WO_4 catalyst and microwave radiation, reducing reaction time to 90 min with 68% yield (eqn (28)). Comparing the routes, the direct oxidations are more eco-friendly, but substrate prices and technical challenges still limit their implementation.

4.2. Alternative biorenewable processes

Here, the most recent and noticeable biorenewable routes towards adipic acid will be discussed. Some advanced routes include pathways *via* muconic acid, glucaric acid and 5-hydroxymethylfurfural, all obtained from sugars. We also include the conversion of levulinic acid and 1,4-butanediol. Fig. 5. summarizes both the conventional petrobased routes towards adipic acid in grey, and the alternative biorenewable routes in light blue.

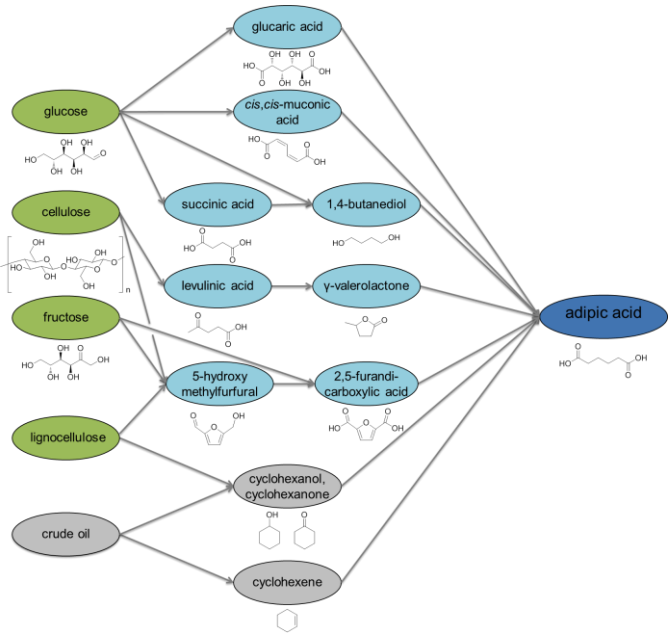
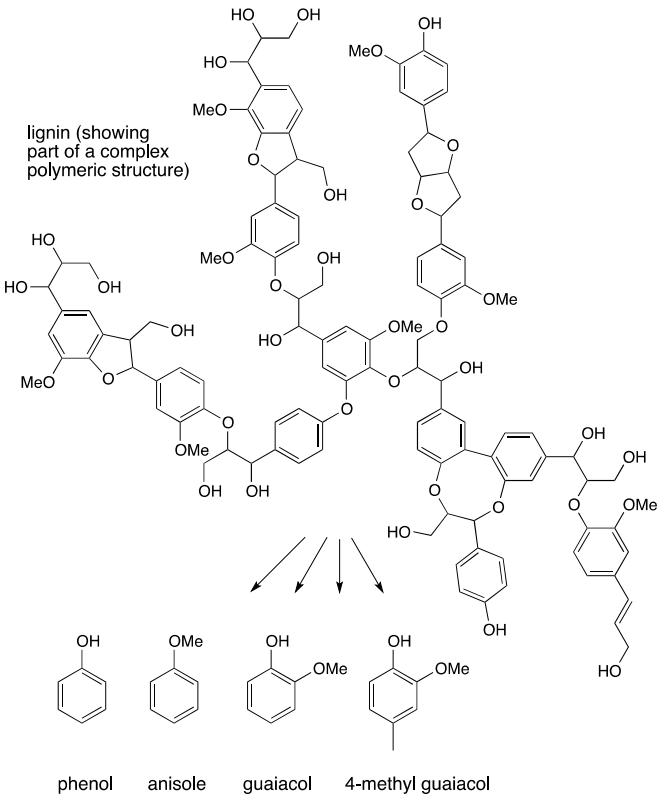


Fig. 5 Outline of the production routes to adipic acid, showing biobased feedstocks (green), biobased platform chemicals (light blue), and existing petrobased routes (grey).

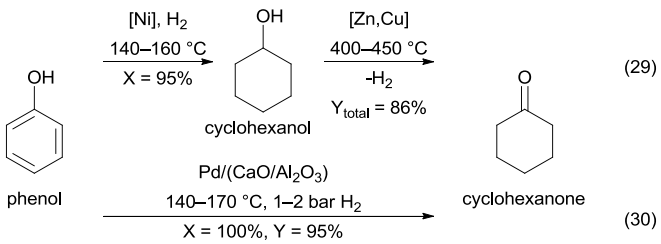
4.2.1. Production of biorenewable KA-oil

Converting lignin to phenols and then to cyclohexanone is an interesting biorenewable pathway to KA-oil.[40] Several approaches for 'cracking' lignin are being pursued, such as hydrogenation, hydrolysis and thermal cracking, to yield a mixture of substituted phenols, (Scheme 1) which can be converted by dehydroxylation and (hydro)de-alkylation to phenol. One promising development is using liquid ammonia, which can dissolve lignin almost instantly.[111] However, yields are too low for industrial application.



Scheme 1 Lignin, the gluey stuff that holds trees together, is a complex biopolymer that can in theory be depolymerised to various phenols via hydrogenation, hydrolysis and thermal cracking. Lignin is the richest natural resource of aromatics, but refining it into building blocks is a tough challenge.[40]

Phenol itself is conventionally converted to cyclohexanone in two steps. First, it is hydrogenated to cyclohexanol using a nickel catalyst under H_2 pressure, at 140–160 °C, then cyclohexanol is catalytically dehydrogenated to cyclohexanone, using a zinc or copper catalyst at 400–450 °C under atmospheric pressure, providing 90% phenol conversion and 95% overall selectivity towards cyclohexanone (eqn (29)).



(29)

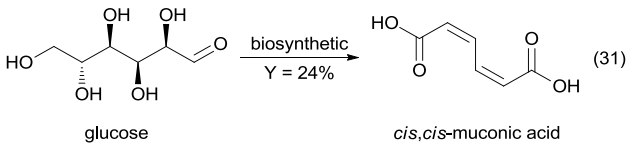
(30)

Recently, Liu *et al.*[112] proposed a single-step hydrogenation of phenol to cyclohexanone, using a bifunctional supported palladium catalyst containing alkaline earth oxides, with Lewis acid functionality. This approach was demonstrated using a

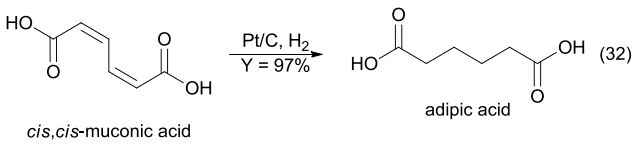
Pd/(CaO/Al_2O_3) catalyst, obtaining complete conversion of phenol at over 95% selectivity towards cyclohexanone, under mild conditions: 140–170 °C and 1–2 bars H_2 (eqn (30)).

4.2.2. *Cis,cis*-muconic acid to adipic acid

In 2002, a biosynthetic route[113] to *cis,cis*-muconic acid was reported, starting from glucose at 24% (mol/mol) yield. The patent rights were recently bought by the Amyris Company, but the biobased process is not yet commercially competitive. The reaction requires little energy and its waste is non-toxic, but recovery does not yet yield resin-grade product and the system suffers from low turnover numbers (eqn (31)).

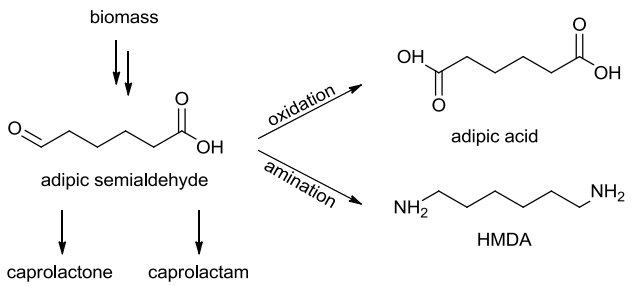


Biobased *cis,cis*-muconic acid from glucose can be catalytically hydrogenated to adipic acid at 97% yield. This means that the biosynthesis translates nearly quantitatively to the conversion of glucose to adipic acid, bearing in mind the additional hydrogenation step (eqn (32)) and the difficulties in separation/purification.[113]



4.2.3. Adipic semialdehyde to adipic acid

Recently, the BioAmber Company, a pioneer in biobased succinic acid, bought the Celexion Pathway license[114] to explore biotechnological pathways to adipic semialdehyde.[115] This compound can be used as a starting material for caprolactone, ε-caprolactam and HMDA (Scheme 2). Moreover, its oxidation may provide an attractive route to adipic acid.[114, 115]

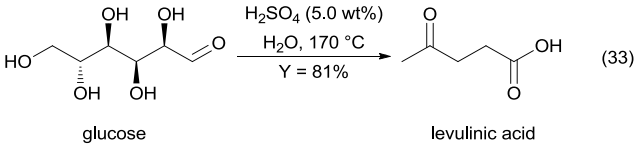


Scheme 2 Possible applications of adipic semialdehyde.

4.2.4. γ-Valerolactone to adipic acid

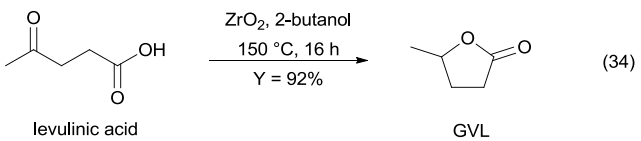
The technical improvements in levulinic acid production are increasing interest in the production of γ-valerolactone (GVL).

For producing levulinic acid, a versatile platform chemical[116, 117] and potential biofuel feedstock,[118] there are currently two main routes. One relies on conversion of maleic anhydride and another is based on hydrolysis of furfural derivatives. Various mono- and polysaccharides can be dehydrated to hydroxymethylfurfural, which is hydrolysed to a mixture of formic acid and levulinic acid.[11] The most efficient glucose to levulinic acid reaction was demonstrated in presence of 5.0% H_2SO_4 at 170 °C, giving 81% yield (eqn (33)).[119]

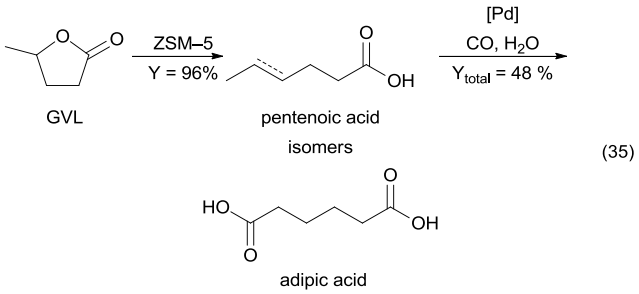


The direct conversion of sugarcane bagasse, the fibrous residual waste of sugarcane juice extraction, showed 23% levulinic acid yield per biomass weight in the presence of 4.45% (w/w) HCl at 220 °C in 45 min.[120] Yields based on cellulose/hexose content were as high as 83%.

For the catalytic hydrogenation of levulinic acid to γ-valerolactone (GVL), both homogenous and heterogeneous catalysts were used.[121, 122] Noble metals (especially ruthenium) give high yields, but are too expensive for large-scale implementation. An example using a non-noble metal catalyst came in 2011 from Chia and co-workers, who used base metal oxides, ZrO_2 and γ-Al_2O_3, and secondary alcohols as both solvent and hydrogen donor (eqn (34)). The highest GVL yield was 92%, using a ZrO_2 catalyst and 2-butanol solvent, in 16 h at 150 °C.[123]



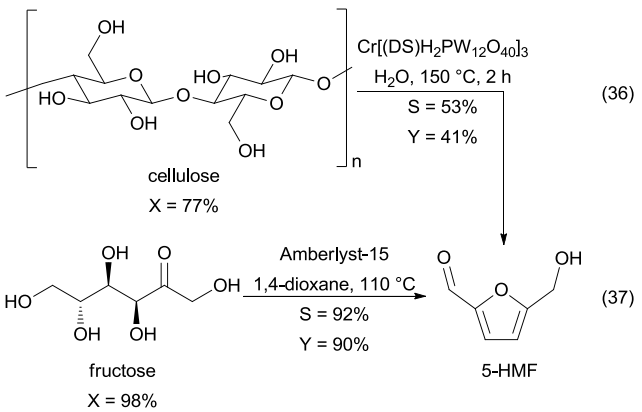
In 2012, Wong *et al.*[124] presented a two-step process for adipic acid from GVL, through a mixture of pentenoic acid isomers, in absence of water and oxygen. First, they ran a reactive distillation in the presence of ZSM–5, obtaining a mixture of pentenoic acid isomers at 96% yield. These were then converted to adipic acid in 48% overall yield using a homogeneous bidentate diphosphine palladium based catalyst (prepared *in situ*) in the presence of CO and water (eqn 35)).



4.2.5. 5-Hydroxymethylfurfural (5-HMF) to adipic acid

Several furan derivatives can be produced by acid-catalysed dehydration of various sugars. For 5-hydroxymethylfurfural (5-HMF), dehydration of fructose and cellulose show the highest yields for mono- and polysaccharides, respectively.

In 2007, Chheda *et al*.[125] reported the conversion of a series of mono- and polysaccharides to 5-HMF, using a biphasic system, which allowed for modification of the pH and the addition of promoters such as DMSO. Moreover, it eliminated the need of acid pre-hydrolysis of polysaccharides. The best results were obtained using dichloromethane (DCM) as organic solvent and a mixture of water and dimethyl sulfoxide (DMSO) in 3:7 ratio as the aqueous phase. The best results were obtained for fructose (complete conversion and 87% selectivity, in 2 h) and starch (91% conversion at 40% selectivity, in 11 h).

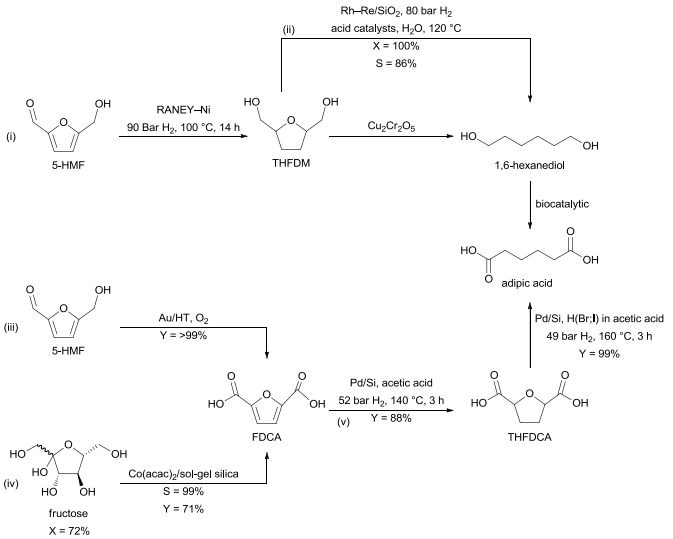


In 2011, Zhao *et al*.[126] showed the hydrolysis of cellulose to 5-HMF, using a $Cr[(DS)H_2PW_{12}O_{40}]_3$ heteropoly acid catalyst, (DS = $OSO_3C_{12}H_{25}$ dodecyl sulfate). In this one-pot reaction, 77% conversion at 53% selectivity was obtained, after 2 h at 150 °C. Moreover, catalyst stability was proven and re-use ensued *via* a facile separation process (eqn (36)).

In 2012, Aellig *et al*. demonstrated the continuous dehydration of fructose, using a single-phase reactor with solvent regeneration.[127] High conversion (98%) of fructose with 92% selectivity to 5-HMF was attained in 1,4-dioxane at 110 °C, in the presence of Amberlyst–15 (eqn (37)). A review on the syntheses of various furfurals was published by Ebitani *et al*.[128]

The potential of lignocellulose as a biobased feedstock was already demonstrated in 1981. Faber and co-workers[129] at Hydrocarbon Research Inc. showed a multi-step process towards adipic acid, consisting of: 1) Acid-catalysed hydrolysis of lignocellulose in presence of aqueous H_2SO_4 to provide 5-HMF. 2) Hydrogenation of 5-HMF over Raney-Ni to 2,5-tetrahydrofurdiomethanol (THFDM). 3) Converting THFDM to 1,6-hexanediol in presence of copper chromite. 4) Biotransformation of 1,6-hexanediol to adipic acid using *Gluconobacter oxydans subsp. oxydans*. (Scheme 3, (i)).

Recently, Buntara *et al*.[130, 131] improved the conversion of THFDM to 1,6-hexanediol, using a bifunctional system of Rh–Re/SiO_2 and a solid acid catalyst, under 80 bar H_2 at 120 °C. The reaction proceeded *via* 1,2,6-hexanetriol, with complete conversion of THFDM and 86% selectivity towards 1,6-hexanediol (Scheme 3, (ii)).



Scheme 3 Overview of possible routes from 5-HMF and FDCA to adipic acid.

These pathways show the potential of producing adipic acid from 5-HMF, but still depend on the biotransformation of 1,6-hexanediol to adipic acid. To supersede this, much research is done on transforming 5-HMF to its dicarboxylic derivative,[132] which already contains the required carboxylic moieties for adipic acid. Gupta and co-workers[133] catalytically oxidized 5-HMF to 2,5-furandicarboxylic acid (FDCA), using hydrotalcite-supported gold nanoparticles (Au/HT), in the presence of O_2 (Scheme 3, (iii)). At a substrate: catalyst ratio of 40:1, they obtained near quantitative FDCA yield (>99%).

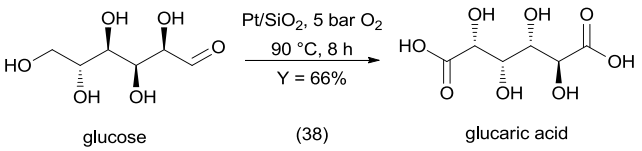
Ribeiro *et al*.[134] showed the direct conversion of fructose to FDCA, using a bifunctional cobalt-acetylacetonate catalyst encapsulated in sol-gel silica. The enhanced cooperative acidic and redox performance resulted in 72% conversion with 99% selectivity towards FDCA (Scheme 3, (iv)).

A fully chemical process towards adipic acid came from Boussie and co-workers[135] at Rennovia Inc. in 2010. In their two-step process, FDCA was first hydrogenated using Pd/SiO_2 (4% by weight) under 52 bar H_2 at 140 °C for 3 h, yielding 88% tetrahydrofuran-2,5-dicarboxylic acid (THFDGA). Second, THFDCA was hydrogenated to adipic acid, using Pd/SiO_2 or

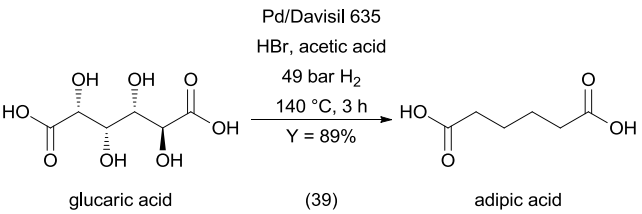
Rh/SiO_2 in presence of HBr or HI in acetic acid, under 49 bar H_2 at 160 °C, yielding 99% adipic acid in 3 h (Scheme 3, (v)).

4.2.6. Glucaric acid to adipic acid

In 2010, Boussie and co-workers at Rennovia filed a patent[136] on the oxidation of glucose to glucaric acid, and its reduction to adipic acid (eqn (38)). The oxidation yields 66% glucaric acid, using a Pt/SiO_2 catalyst under 5 bar O_2 at 90 °C after 8 h.



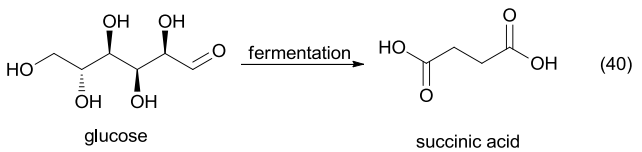
Hydrodeoxygenation of glucaric acid using a Pd–Rh/Davisil 635 catalyst gave 89% yield (eqn (39)).[136] Though catalyst stability is not described, research on similar platinum-catalysed oxidations[137-140] suggests that deactivation is a problem here.



Currently, Rennovia is testing a 4 tpa pilot plant for converting glucaric acid to adipic acid, and has announced plans for scaling-up to 165 tpa. The company claims that its biobased production will compete economically with current technology through lower capital, operational and feedstock costs.[141]

4.2.7. 1,4-Butanediol to adipic acid

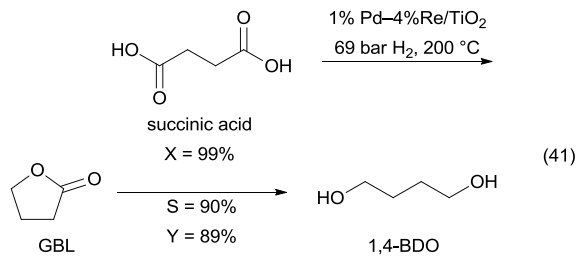
The current global production of 1,4-butanediol (1,4-BDO) is 1.3 Mtpa, at a market price of around $2,000/ton. The biobased production of succinic acid offers a pathway to biorenewable 1,4-BDO on an industrial scale. Converting glucose to succinic acid (eqn (40)) has several advantages. The most important is that it uses CO_2 during fermentation.[142] Conventionally, succinic acid is mainly produced from maleic anhydride. Recent biotechnological improvements, such as water-splitting electrodialysis and liquid/liquid extraction have lowered separation costs, leading to the first commercial fermentation process (30 ktpa) in January 2010, by BioAmber.



In 2012, around 40–45 ktpa of succinic acid and succinate were produced globally, with an estimated market growth to 100 ktpa in 2015. The current market price is $2,400–$3,000/ton,[142] but it is estimated that succinic acid prices may fall to below $1,000/ton, as fermentation technology matures.[143] Its major producers are Myriant, using BioEnergy's D(-)lactic acid technology (13.6 ktpa), and DSM in a joint venture with Roquette Frères called Reverdia (10 ktpa). Other companies investing in biobased succinic acid production, include BASF, Purac, BioAmber, Mitsubishi and Amyris.

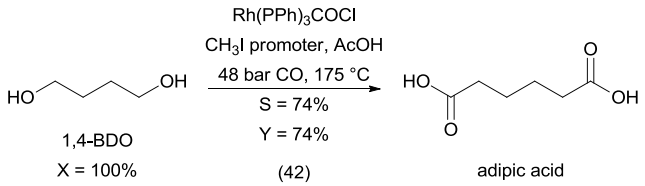
The use of waste-stream feedstocks enhances the eco-friendly image of the process. Recently, food-waste was demonstrated as a sustainable feedstock for succinic acid biorefineries. By simultaneous hydrolysis and fungal autolysis of bakery-waste, a reaction mixture rich in glucose and free amino acids was obtained. This was fermented, using a species of *Actinobacillus succinogenes*. Vacuum distillation and crystallisation of fermentation products afforded highly-crystalline succinic acid, at up to 35 % overall yield.[144]

The DuPont process[145] for converting succinic acid to 1,4-BDO uses a 1% Pd–4% Re/TiO_2 catalyst, under 69 bar H_2 at 200 °C, providing 1,4-BDO at 89% overall yield (eqn (41)).



BioAmber is scaling up its biosuccinic acid hydrogenation to multi-ton capacity, using the DuPont license. The process allows the conversion of succinic acid to a range of products, including 1,4-BDO, THF and γ-butyrolactone (GBL). Elsewhere, BASF and Genomatica aim at producing 1,4-BDO by directly fermenting glucose-containing biobased feedstocks.

Catalytic carboxylation of 1,4-BDO to adipic acid is typically done using rhodium-based catalysts. The Monsanto process[146] from 1970 (eqn (42)) gives 74% yield at 175 °C, using a $Rh(PPh)_3COCl$ catalyst and 48 bar CO. The reaction is well-studied,[147] but not applied commercially.



4.3. Adipic acid – summary and analysis

The petrobased synthesis of adipic acid depends on processing benzene-derived KA-oil. Moreover, the dominant nitric acid oxidation route emits nitrous oxides quantitatively. Alternatively, direct cyclohexene oxidation is an example of more eco-friendly route to adipic acid. This gives adipic acid at 90% yield in 8 h, or 68% yield in 90 min using microwave

radiation. However, the feedstock price and current process technology limit direct cyclohexene routes. Producing biobased KA-oil is theoretically possible from lignin, but yields are low. Moreover, using biobased KA-oil still depends on the nitric acid oxidation.

The biobased *cis,cis*-muconic acid route is a typical combination of biotechnology and chemocatalysis. Converting *cis,cis*-muconic acid to adipic acid provides near quantitative yield (97%). However, *cis,cis*-muconic acid production from glucose (around $500/ton) suffers from low yield (24%), combined with difficulties in separation/purification. Until biotechnological improvements allow better turnover numbers, this route has no near-future application. This is noticeable, because conversion of *cis,cis*-muconic acid alone seems very promising. The adipic semialdehyde route is another combination of biotechnology and chemocatalysis. However, the route is very much in its infancy. A more promising example is selective oxidation of glucose to glucaric acid (66% yield) and subsequent reduction to adipic acid (89% yield). The theoretical overall yield is promising (59%), but catalyst deactivation is a problem. A stable and efficient combined process would open a viable pathway to adipic acid.

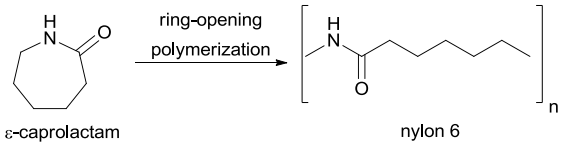
Producing adipic acid *via* levulinic acid and γ-valerolactone gives a theoretical overall yield of around 34%, in four steps. However, bagasse food-waste may be used as fermentation feedstocks to produce levulinic acid at 83% yield (based on sugar content). The succinic acid route to adipic acid *via* 1,4-butanediol shows 66% theoretical yield, in two steps. Similarly, bakery food-waste may be used as fermentation feedstocks for succinic acid, at 35% overall yield. Additionally, the prices of levulinic acid and succinic acid are expected to fall radically as their (bio)technological production methods improve. These routes provide both interesting societal and economic perspectives.

The 5-hydroxymethylfurfural route to adipic acid has seen much research. Starting from fructose, up to 78% theoretical adipic acid yield may be achieved. Yet, those are expensive feedstocks, with current prices above $900/ton. The economical margin towards adipic acid ($1,500–$1,700/ton) is small, considering the four required process steps. 5-Hydroxymethylfurfural from cheaper feedstocks would provide larger economical margins, promoting viability.

5. ε-Caprolactam

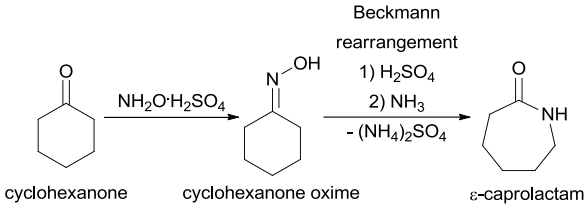
5.1. Introduction

ε-Caprolactam is used solely as a precursor for its catalytic ring-opening polymerization to nylon 6 (eqn (46)). In 2012, over 4.0 Mt of ε-caprolactam were produced globally, and the current market price is $2,000–$2,500/ton.[11, 148] Major producers are DuPont/BASF, DSM and Asahi.



(46)

The dominating production process of ε-caprolactam relies on the conversion of cyclohexanone (mainly derived from petrobased benzene or phenol) to cyclohexanone oxime. This reaction typically occurs in presence of hydroxylamine sulfate, under pH buffered conditions (*e.g.* by H_3PO_4) at 85 °C. The oxime is converted to ε-caprolactam by Beckmann rearrangement in the presence of fuming sulfuric acid, at 90–120 °C. On commercial scale, isolation of the desired lactam proceeds through NH_3 addition at 98% yield (eqn (43)). Yet, this final step requires organic solvents for purification and generates 1.8–5.0 kg ammonium sulfate waste (which BASF sells as fertilizer) per 1.0 kg ε-caprolactam produced.



(43)

Various efforts have been made to reduce the ammonium sulfate formation.[75, 149] The alternative Montedison cyclohexanone oxidation route uses NH_3 and a TiO_2/SiO_2 catalyst in a fluidized-bed reactor, in the presence of H_2O_2 at 40–90 °C. This provides complete conversion of cyclohexanone and 90% selectivity towards the oxime. Another alternative approach came from DSM/Stamicarbon. Its acid-catalysed Beckmann rearrangement was performed by using an acidic ion-exchange resin in DMSO at 100 °C. Bayer reported a B_2O_3/Al_2O_3 catalyst in a fluidized bed reactor, at temperature above 300 °C.[11, 150] However, only the Sumitomo route has proven commercially competitive. This route produces cyclohexanone oxime by direct ammoximation from NH_3 and H_2O_2 using a TS-1 catalyst.[151] Subsequent use of a MFI catalyst produces ε-caprolactam, while avoiding formation of ammonium sulfate.[152]

5.2. Alternative biorenewable processes

Here, the most recent and noticeable biorenewable routes towards ε-caprolactam will be discussed. Some advanced routes include including pathways *via* lysine and muconic acid. However, we also introduce more novel routes, *e.g.* through adiponitrile and 6-aminocaproic acid. Fig. 6 summarizes both the conventional petrobased routes towards adipic acid in grey, and the alternative biorenewable routes in light blue.

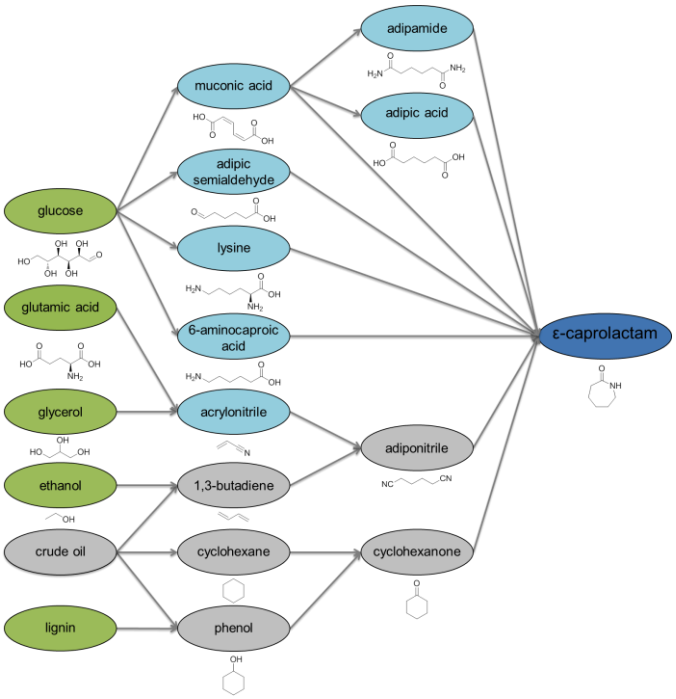
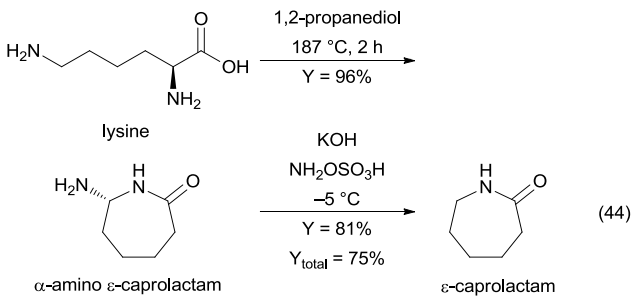


Fig. 6 Outline of the production routes to ε-caprolactam, showing biobased feedstocks (green), biobased platform chemicals (light blue), and existing petrobased routes (grey).

5.2.1. Lysine to ε-caprolactam

ε-Caprolactam was used in the 1940s by DuPont, as a commercial intermediate for synthesizing L-lysine.[153, 154] Lysine is now commercially available by fermentation of glucose, using *Corynebacterium glutamicum* bacteria, at an estimated yield of 40–50 mol %. The main producers are Ajinomoto in Japan and France, ADM in the U.S., Evonik Degussa in Germany and DSM in the Netherlands. It is a promising precursor for the industrial biobased production of ε-caprolactam, since the carbon skeleton of lysine contains the required carboxylate and ε-amine moieties.[5]

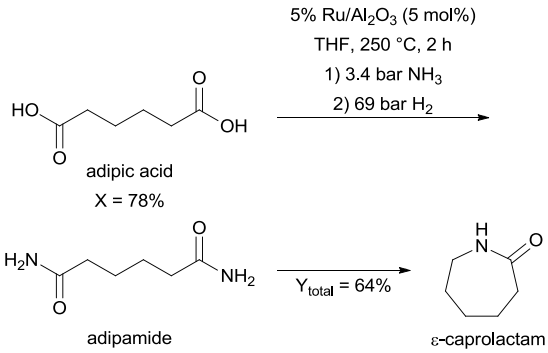


(44)

In 2005, Frost *et al.*[155, 156] at Amyris reported the conversion of lysine to α-amino-ε-caprolactam. Refluxing in 1,2-propanediol provided 96% yield in 2 h. Successive deamination was done at –5 °C, in the presence of KOH (8 equiv.) and hydroxylamine-*O*-sulfonic acid (4 equiv.) with formation of N_2 and K_2SO_4. ε-Caprolactam was purified by sublimation at 75% yield. The preferred solvent for the cyclization was 1,2-propanediol. This may be made from lactic acid, supporting the concept of sustainability (eqn (44)).

5.2.2. Adipic acid to ε-caprolactam

The biobased production of adipic acid may promote new biobased pathways to ε-caprolactam. Recently, Frost *et al.*[157, 158] demonstrated the direct one-pot conversion of adipic acid to ε-caprolactam, catalysed by Ru/Al_2O_3 at 250 °C (eqn (45)). In 2 h, 64% ε-caprolactam yield was obtained. Other side-products include hexamethyleneimine (HMI) (6% yield), hexanamide (4%) and adipamide (2%).

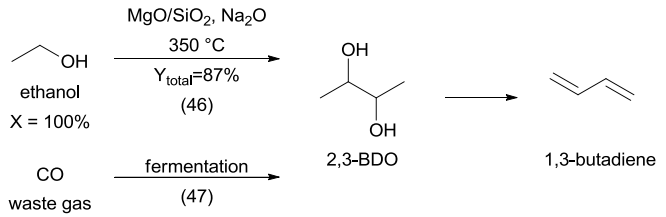


(45)

5.2.3. 1,3-Butadiene to ε-caprolactam

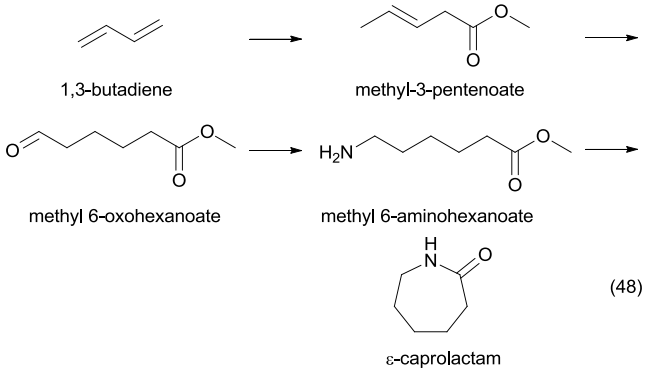
As early as 1886, 1,3-butadiene was produced by dehydration of ethanol. However, its petrochemical production soon became economically favourable. Over the last decades, co-production in hydrocarbon cracking processes and on-purpose catalytic dehydration of butane accounted for around 95% of all 1,3-butadiene produced globally. Recently, however, co-production in hydrocracking processes is declining, and alternative on-purpose processes are raising to meet the growing demand.

Dimerisation of bioethanol (around $750/ton) provides an promising pathway to 1,3-butadiene (currently above $1,600/ton). Two biobased methods are commercially applied today. The first is the Lebedev process, operated in Brazil and Poland, using a $MgO–SiO_2$ catalyst at 370–390 °C to dehydrogenate and dimerise bioethanol, giving 70% selectivity to 1,3-butadiene. The second is the Ostromislensky process, using bioethanol and bioacetaldehyde (obtained from bioethanol) and a unspecified supported catalyst, yielding 70% 1,3-butadiene.[11] An alternative route by Ohnishi *et al.*[159] shows high yield, but is currently not commercial. It uses a MgO/SiO_2 (1:1) catalyst and Na_2O (0.1%) at 350 °C, giving 1,3-butadiene at 87% yield (eqn (46)). For a comprehensive review on the pathways from ethanol to 1,3-butadiene see Angelici *et al.*[24]



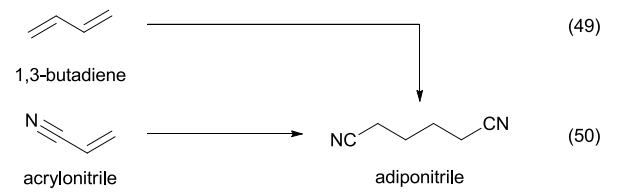
Multiple collaborations of biotechnological and chemical companies are combining genetic engineering and fermentation technology with experience in catalysis and process engineering. Examples of such partnering are Genomatica and Versalis,[160] Global Bioenergies and Synthos,[161] and Invista and LanzaTech.[162] Currently, LanzaTech has a 55 klpa pilot plant in New Zealand and a 380 klpa plant in China, where carbon monoxide waste gas is fermented to ethanol and 2,3-butanediol (2,3-BDO).[163] Direct carbon monoxide fermentation to 1,3-butadiene and catalytic dehydration of 2,3-BDO are also being investigated (eqn (47)).

DSM's ALTAM process (ALTernative caprolactAM) consists of carbonylation of 1,3-butadiene to obtain methyl-3-pentanoate. Subsequent hydroformylation and amination yields 6-aminocaproate, a precursor to ε-caprolactam (eqn (48)).[164] However, only a few details are disclosed.

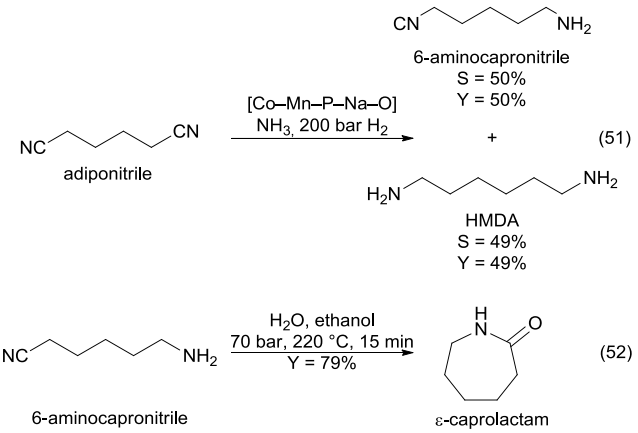


5.2.4. Adiponitrile to ε-caprolactam

Adiponitrile is produced today either by reacting 1,3-butadiene with hydrogen cyanide (eqn (49); Invista[165] and Rhodia/DuPont[166]) or by electrolytic hydrodimerization of acrylonitrile (eqn (50); Asahi[167] and BASF[168]). Producing biorenewable acrylonitrile is discussed in Section 3.2.7.

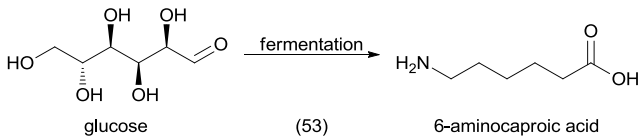


The BASF process[169] describes the catalytic hydrogenation of adiponitrile, using a tube reactor and catalyst based on oxides of 90% Co, 5% Mn, 3% P, 2% Na (by weight) in the presence of excess NH_3 and H_2 under 200 bar at 280 °C. The process depends on adiponitrile recycling to achieve full conversion, with 70% conversion of adiponitrile per cycle. This reaction gives equal amounts of 6-aminocapronitrile and HMDA, and over 99% combined selectivity for both products (eqn (51)). Consecutive catalytic hydrolysis of 6-amino capronitrile yields 79% ε-caprolactam in 15 min, in presence of water and ethanol, under 70 bar at 220 °C (eqn (52)).

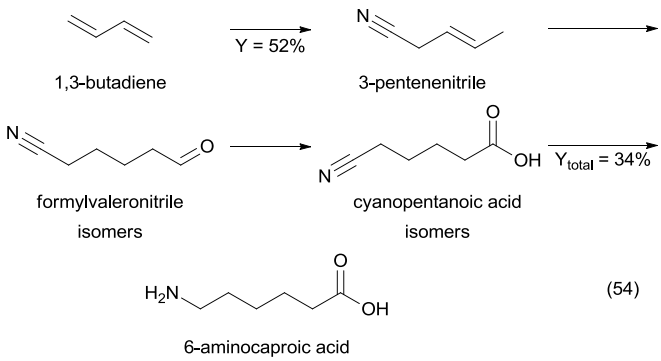


5.2.5. 6-Aminocaproic acid to ε-caprolactam

The direct biotechnological production of 6-aminocaproic acid from sugars has gained much recent interest. Companies such as DSM,[170] Genomatica,[171] and Celexion LLC,[172] all claim such pathways, but none give process details (eqn (53)).

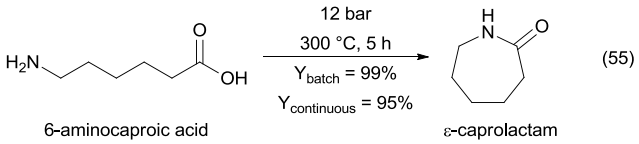


Conventionally, the DuPont process to 6-aminocaproic acid[173-178] starts with 1,3-butadiene conversion to 3-pentenenitrile, at 54% yield. Subsequent hydroformylation affords a mixture of formylvaleronitrile (FVN) isomers. Consecutive oxidation of the FVN mixture yields a mixture of cyanovaleric acid isomers, which is then hydrogenated to 6-aminocaproic acid at 34% overall yield (eqn (54)).



6-Aminocaproic acid may be converted to ε-caprolactam in absence of a catalyst, as demonstrated by BASF[179] and DSM[180].

A batch reaction using superheated steam, gave 99% yield after 4–5 h, under 12 bar at 300 °C. A continuous process under similar conditions gave 95% ε-caprolactam yield (eqn (55)).

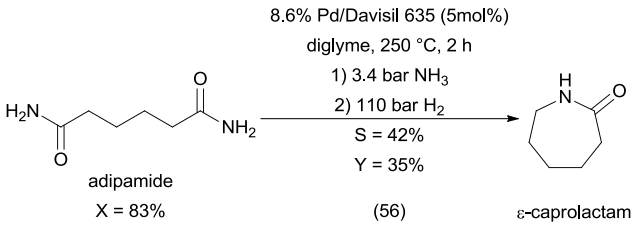


(55)

5.2.6. Adipamide to ε-caprolactam

Adipamide may be obtained from adiponitrile or through amidification of adipic acid. Moreover, it is a common by-product in muconic acid reactions and ε-caprolactam syntheses.

For directly converting adipamide to ε-caprolactam, Frost *et al.*[157] used a 8.6% Pd/Davisil 635 (5.6% mol) catalyst in diglyme, at 250 °C. They first saturated the substrate with NH_3 under 3.4 bar, before introducing H_2 up to 110 bar (eqn (56)). In 2 h, 83% adipamide conversion and 35% ε-caprolactam yield was obtained, with HMI as major side-product (28% yield).

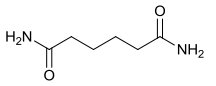
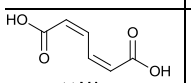
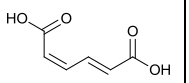
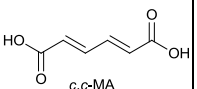


5.2.7. Muconic acid to ε-caprolactam

Muconic acid may provide adipic acid, which can be converted to ε-caprolactam. However, the direct conversion of muconic acid has recently shown promising results. The biosynthetic route to *cis*,*cis*-muconic acid is discussed in Section 4.2.2.

Recently, Frost *et al.* [158] demonstrated the production of ε-caprolactam from three muconic acid (MA) isomers, all may be produced through fermentation of glucose. The best yields were obtained using a 5% Pd/Al_2O_3 (5 mol %) catalyst in dioxane at 250 °C. The reactor was first saturated with NH_3, before introducing H_2. The results after 2 h show varying yields for the different isomers; *t*,*t*-MA shows 88% conversion, with 44% ε-caprolactam yield and side-product formation of 6% HMI and 38% adipamide. The *c*,*t*-MA isomer showed 79% conversion, with 54% ε-caprolactam yield, 7% MHI and 18% adipamide. Lastly, the *c*,*c*-MA isomer showed 77% conversion, with 55% ε-caprolactam yield, 13% MHI and 9% adipamide (Table 2).

Table 2 Overview of available biomass feedstocks.

5% Pd/Al_2O_3 (5 mol%) dioxane, 250 °C, 2 h 1) 3.4 bar NH_3, 2) 34 bar H_2	 ε-caprolactam	 HMI	 adipamide
 *t*,*t*-MA X = 88%	S = 50% Y = 44%	S = 7% Y = 6%	S = 43% Y = 38%
 *c*,*t*-MA X = 77%	S = 70% Y = 54%	S = 9% Y = 7%	S = 23% Y = 18%
 *c*,*c*-MA X = 79%	S = 70% Y = 55%	S = 16% Y = 13%	S = 11% Y = 9%

5.3. Caprolactam – summary and analysis

The petrochemical synthesis of ε-caprolactam depends on processing benzene/phenol-derived cyclohexanol. Its dominant process produces stoichiometric ammonium sulfate waste. Though multiple green alternatives are available, few have been commercialized. Besides, these still use petrobased feedstocks.

In many conventional ε-caprolactam syntheses, 1,3-butadiene is used as feedstock. Its biorenewable production may revive those processes. The hydrogen cyanide reaction of 1,3-butadiene provides a route to adiponitrile. Reacting this platform chemical provides both HMDA and ε-caprolactam. Conversely, 1,3-butadiene may be converted to 6-aminocaproic acid, in several steps. Yields are low (34% overall), but subsequent continuous conversion of 6-aminocaproic acid to ε-caprolactam was proven efficient (95% yield). 1,3-Butadiene may be produced from bioethanol, at 87% yield. The low bioethanol price (around $750/ton) makes this a viable route to 1,3-butadiene (above $1,600/ton) and leaves sufficient economical margin towards ε-caprolactam ($2,000–$2,500/ton) Also, research producing 1,3-butadiene from carbon monoxide is emerging rapidly. However, the overall processes are not yet likely, having low overall yields.

Lysine may be used as a feedstock, because of its similar structure to ε-caprolactam. Its chemical modification shows high yield (75% overall). However, high lysine feedstock prices (around $1,900/ton) limit current commercial application.

Various emerging routes towards ε-caprolactam are observed. For example, the novel adipic acid to ε-caprolactam route, giving 64% yield. When adipic acid may be produced from biorenewables, so could ε-caprolactam. Their economical difference ($500–$800/ton), would allow for versatile changes in the synthetic fibre market.

Converting muconic acid to ε-caprolactam is another recent route. Yields of 55% were obtained and are likely to improve rapidly. However, the biotechnological production of muconic acid still suffers from low yield and high processing costs.

We also observe the valorisation of adipamide, a common by-product in muconic acid reactions and ε-caprolactam

syntheses. The maximum yield achieved so far for adipamide to ε-caprolactam is only 35%. However, its utilization is crucial from an economical aspect and likely to improve in the coming years.

6. Conclusions and outlook

The past decade has seen important advances in the development of routes to acrylic acid, adipic acid and ε-caprolactam starting from biorenewables. These three bulk chemicals are used mostly for making synthetic fibres. Their petrobased processes may be replaced altogether by biorenewable alternatives, from feedstock to end-product. However, most of the new routes cannot yet compete with the long-standing petrochemical processes, for logistic and economic reasons. Alternatively, we see that petrochemical intermediates may also be replaced with biorenewable equivalents. This "compromise solution" is more likely, as manufacturers can more easily adapt their current processes.

We consider biomass feedstocks and compare the most recent and promising pathways towards the desired end-products. Here, we emphasise the importance of examining the entire route in each case. Focusing on specific reactions may lead to exaggerated claims and/or unsupported economical estimations. Avoiding this, we focused on the potential of current routes and on-going developments in the field, rather than on their current values. Table 3 summarises the feasibility of the key emerging biobased processes (a table comparing all the main routes discussed in this review is included in the ESI). Note that these biobased routes can (and will!) still improve, while conventional routes are often already fully optimised.

Table 3 Summary of the most feasible biorenewable processes.

Product	Feedstock	Platform chemical	Maximum yield (%)	Year of innovation	Ref.
acrylic acid	glycerol	acrolein	75	2012	52
	starch	lactic acid	78	2014	63
adipic acid	glucose	glucaric acid	59	2010	136
	fructose	5-hydroxy-methylfurfural	78	2010	134, 135
ε-caprolactam	lysine	direct synthesis	75	2013	155, 156

'White biotechnology' has grown much in the last decades, but still suffers from limitations to large-scale application, due to cost-intensive purification and separation requirements. However, the advantages to change between various carbohydrate feedstocks, combine different processes and use the water content of wet plant material are major strengths. These are typically unseen in chemocatalytic processing. As a result, many companies already have biotechnological divisions in their portfolio, as useful tools in the search for biorenewable pathways towards valuable chemicals.

Societal pressure and government legislation may trigger a transition from petrobased to biobased chemicals, but this will only be effective if capital and operating costs for the new processes give a bona fide financial advantage. 'Green' alone is insufficient. Process efficiencies, feedstock prices and stabilities, and processing costs will determine which routes will be adopted by industry. No biorenewable routes to the target chemicals are yet competitive to their petrochemical equivalents. But, given that most are just in the early stages of development, we foresee that they will become competitive – it is only a matter of time.

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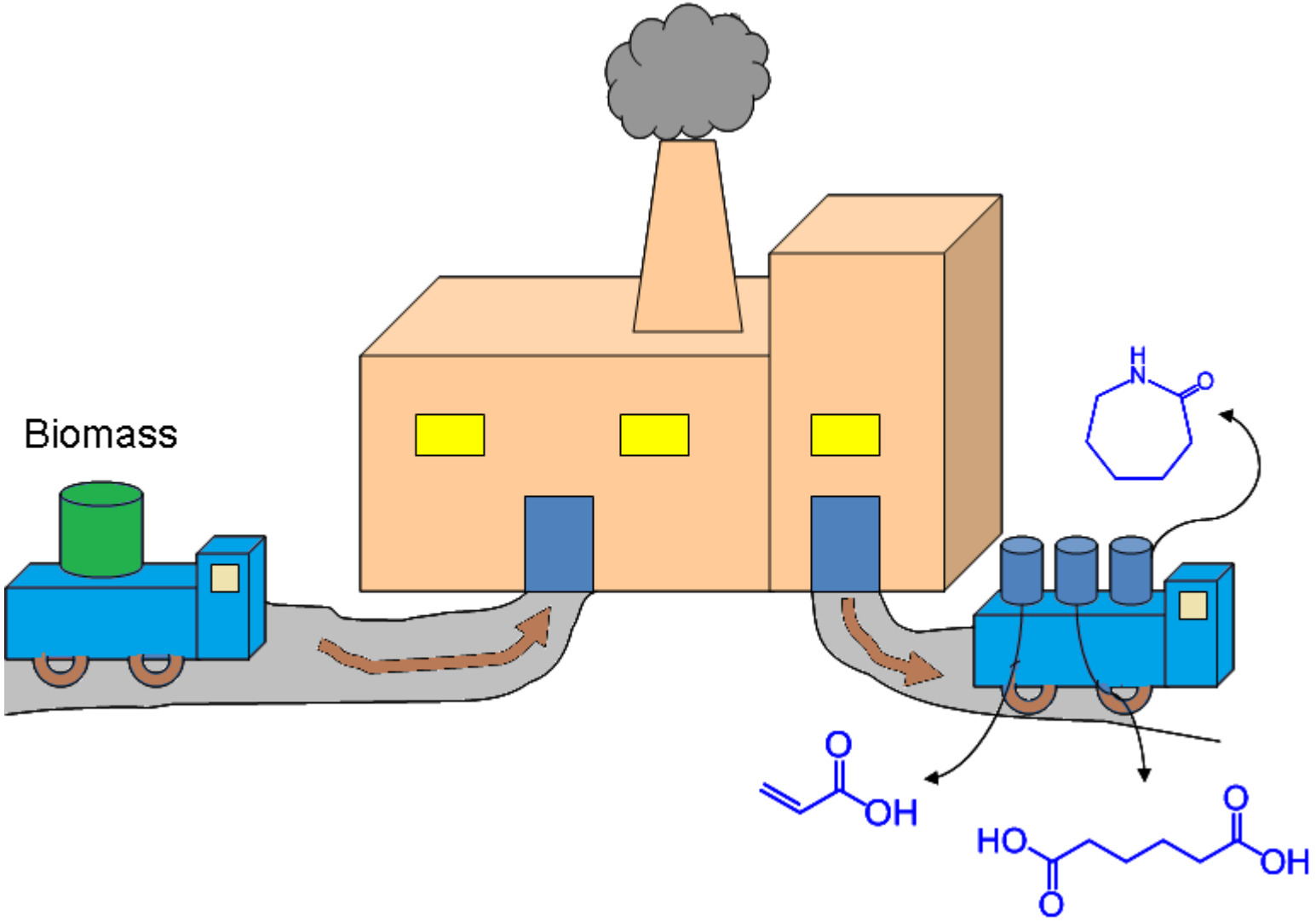

Go bio! We assess the biobased productions of three important bulk chemicals: acrylic acid, adipic acid and ε-caprolactam. These are the key monomers for high-end polymers and are all produced globally in excess of two million metric tons per year.