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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 being 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 for implementing 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 potential and prospects for future application. Today, biorenewable routes cannot yet compete with their petrochemical equivalents. However, given that most of them are still in the early stages of development, we foresee their commercial implementation in the next two decades.

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with Prof. Hualong Xu. His research interest lies in combining knowledge of different fields to develop sustainable chemical processes.

Rolf Beerthuis has recently obtained his MSc chemistry diploma cum laude at the University of Amsterdam, focussing on heterogeneous catalysis with a minor in molecular computational chemistry. His thesis centered on catalytic biomass conversion, namely the oxidation of lactic acid to acrylic acid. Currently, he is investigating the conversion of glycerol to acrolein at the Lab of Advanced Materials at the Fudan University in Shanghai,

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He also co-founded the companies Sorbisense A/S, YellowDiesel BV, and Plantics BV. In 2007 he was voted 'teacher of the year' by the chemistry students. His latest invention is a 100% plant-based cheap biodegradable plastic.

Gadi Rothenberg is Professor and Chair of Heterogeneous Catalysis and Sustainable Chemistry at the Van't Hoff Institute for Molecular Sciences at the University of Amsterdam, and teaches catalysis, thermodynamics and scientific writing. He has published 150 papers in peer-reviewed journals and discovered two catalysts, for which he received the Marie Curie Excellence Award in 2004 and the Paul Rylander Award in 2006.

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 \$1500 per ton.

In 2012, more than 60% of all fibres produced worldwide were synthetic materials⁶ (Fig. 2, left). Of these synthetic

Fig. 1 Annual average prices for ethylene, propylene and 1,3-butadiene in \$ per ton.⁵

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Fig. 2 Overviews by weight percentage. Left: global fibre market, in 2012. Right: constituents of synthetic fibre market, by general polymer classes, in 2012.⁷

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 the production of fully biorenewable PET.⁷ Braskem produces 200 000 tons of biobased PE in Brazil,⁸ using ethylene obtained by dehydrating bioethanol. However, 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, and the 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 into a great many chemical and economical value chains. Their prices are low: below \$1500 per metric ton.¹⁰ Conversely, the bulk chemicals that we will cover here are relatively expensive, ensuring economical margins for innovative alternatives.

Acrylic acid is used for making polyacrylic acid and various acrylic esters, known for their superabsorbent properties and attractive properties in co-polymerization (Fig. 3). They are used in a range of synthetic products, including diapers, plastics, synthetic rubber, coatings and paint formulations.¹¹

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

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 the 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

Over the last few decades, much research has gone 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 of various compounds. It is therefore important to also review the influence of ‘white biotechnology’ or industrial bio-refineries, 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 feedstocks (Table 1). The benchmark prices are averaged across regions and qualities, giving a general impression of the availability of biobased feedstocks and their incorporation into chemical value chains.

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 these developments, we will examine the biobased pathways, and compare these to the petrochemical pathways. We use examples of on-purpose reactions towards target molecules, focusing on the most recent and efficient to date.

Table 1 Overview of available biomass feedstocks

Biobased feedstock	Chemical formula	Global production ^a (Mtpa)	Benchmark price ^a (U.S.\$ per ton)
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 ₂ OH)	7	900
Ethanol ^{2,24}	CH ₃ CH ₂ OH	65	750
Virgin oils ^{1,25}	Various triglycerides	155	1100
Glycerol ^{26–28}	(CH ₂ OH)-(CHOH)-(CH ₂ OH)	1	850
Lysine ^{29,30}	C ₆ H ₁₄ N ₂ O ₂	0.85	1900
Glutamic acid ^{29,31,32}	C ₅ H ₉ NO ₄	1.6	1300

^a Worldwide production and price indexes for 2012.

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 is 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 petro-based. 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 that 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.

2.1. 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

2.2. 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 a 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 This polymer is now being commercialized by Plantics B. V.

2.3. 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 processes 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 demand it.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 (eqn (1) and (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 \$1600–\$1800 per ton for low-grade and \$1900–\$2200 per ton for glacial-grade. The Asia-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 the 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 into acrylic acid in a second reactor, using a Bi/V–O catalyst at 280 °C (eqn (3)).

3.2. Alternative biorenewable processes

Here, we will discuss the most recent and noticeable alternative routes towards acrylic acid. Some advanced processes include converting glycerol, but also using platform chemicals that are already produced on a 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.

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 its process to propylene.⁴⁸ Another pathway to biopropylene is through converting

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

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 approximately 10% glycerol by weight.²⁶ Its current global production is around 1 Mtpa, with a market price of around \$850 per ton.^{27,28} For converting glycerol to acrylic acid, both 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, Chieregato *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 process using a single reactor with two consecutive reactor beds. First, the 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/SiO₂ 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 oxydehydrogenation reaction, in the presence of molecular oxygen. Optimal results were found for the first bed with 91% ZrO₂–9% WO₃ and for the second bed with a multi-metallic catalyst⁵³ (Mo₁₂V_{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 an existing capacity of over 500 ktpa. The current market prices range from \$1300 per ton (50% purity) to \$1600 per 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 thermophilus* bacteria (eqn (7)). Generally, starch is used as a 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 by reacting glycerol in the presence of Cu₂O and 1.5 equivalents of NaOH, in H₂O under 14 bar N₂ 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

The 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 temperatures, 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 H₂SO₄ increased lactide and acetaldehyde formation, while NaOH increased selectivity to acrylic acid.⁵⁹ Moreover, adding Na₂HPO₄ 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 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 its 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 a 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 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 homogeneous 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 attained at pH 6, using an Nd₄(P₂O₇)₃ catalyst calcined at 400 °C.⁷⁰ Previously, we reported the dehydration of glycerol to acrolein over Nb₂O₅/SiO₂ catalysts, showing that the conversion and selectivity depend on the niobium loading and calcination temperature.⁷¹ Elsewhere, de Oliveira and co-workers⁷² investigated liquid-phase glycerol dehydration using various zeolite catalysts. They found that the catalytic activity was not directly correlated to the Si/Al ratio. However, the catalyst structure and porosity, and the 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 CsSiW₁₂O₄₀/Al₂O₃ catalyst in a continuous flow reactor (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 MoO₃, V₂O₅, Al₂O₃ precursors in the respective ratio of 8 : 1 : 0.4 at 17.8% (by weight) supported on spongy aluminum. Using O₂ 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 an Mo–V–O catalyst supported on SiO₂ aerosil (30% by weight), with an Mo : V ratio of 5 : 1, in the presence of molecular oxygen and steam at 180 °C. The complete conversion of acrolein was observed with 96%

selectivity towards acrylic acid. However, little is known about its catalyst stability and re-use.⁸¹ The reaction mechanisms, kinetics, and the effects of promoters are reviewed elsewhere.⁸²

Recently, Aoki and co-workers achieved high acrylic acid yields, using an 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 into acrolein, which is hydrated to 3-HPA (eqn (17)). Further reduction yields 1,3-PDO at 43% overall yield, but product separation is costly. In contrast, the Shell process relies on 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⁻¹. 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 bio-based 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 0.2 M 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 concentrations; 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 on a 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 a further scale-up. In 2013, another consortium of OPX Biotechnologies and Dow Chemical, announced the successful fermentation of 3-HP 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⁻¹. The main by-products are 1,3-PDO (47%) and acetic acid (18%).⁹²

The 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 SiO₂ yielding 97%, and 60–80% aqueous solutions over high surface area γ -alumina, also yielding 97–98%. Reactions proceeded at 250 °C, with the 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, its production was around 6.0 Mtpa, with a market price of \$1600–\$2000 per 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-workers⁹⁸ in 2008. They used a V-Sb-Nb/Al₂O₃ 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 the activity is modest, these conditions are mild, solvent-free, and use inexpensive bio-based 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 is 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 its 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 an overall low yield.

The hydrolysis of acrylonitrile to acrylic acid is one of the conventional routes to acrylic acid, adopted by Mitsubishi Petrochemical, Asahi Chemical and others. However, reaction with H₂SO₄ gives stoichiometric NH₄HSO₄ waste. The more recent Mitsui Toatsu process uses only water for conversion over a B₂O₃-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⁻¹ yield was achieved. Continued research is being performed towards its optimization and scale-up conditions. Since then, various biotransformations have been 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 \$1300 per ton). Substituting petro-based propylene with its bio-based equivalent provides a bio-renewable pathway to acrylic acid. This approach preserves existing production processes and allows the industry to adapt more easily to biorenewability. Propylene may be produced from ethanol (around \$750 per ton) at 60% yield. By improving the 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 per ton) and thus provide large economic margins towards acrylic acid (\$1600–2200 per ton).

The efficient production of 3-hydroxypropionic acid from glucose is emerging rapidly, and commercialization is envisioned in the coming years. Moreover, the 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. \$1300 per ton) makes this route far from economically viable.

Glycerol is an attractive bio-based feedstock for producing acrylic acid. As a by-product from the biodiesel industry, its price (around \$850 per ton) is expected to lower in the coming years. Its continuous reaction with acrolein shows high yield (96% yield). The subsequent acrolein conversion to acrylic acid occurs with 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* the biocatalytic production of 3-hydroxypropionaldehyde from glycerol (98% yield). Its subsequent conversion produces acrolein at 97% yield. The theoretical acrylic acid yield is 86%, in three steps. However, the combined process is not yet reported. Most of the studies on glycerol conversion are done with a refined feed. Additional studies need to be performed on the catalytic performance and stability, when crude glycerol is used as the 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 \$1600 per ton (88% purity)). However, bacterial routes to lactic acid show high yields (around 90%). We expect that the expanded production and improved biotechnology will lower lactic acid prices in the coming years. The dehydration of lactic acid shows selectivity issues due to the instability of the intermediate. A possibility to overcome this problem is by

using derivative chemicals, such as 2-acetoxypropionic acid. This route is still limited to homogeneous catalysis and lacks processing conditions. Nevertheless, it is worth studying, since the 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)). Its polycondensation with hexamethylenediamine (HMDA) towards nylon 6.6 accounts for around 85% of all the adipic acid produced, with the remainder is used for polyurethanes and adipic esters.¹¹

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 \$1500–\$1700 per ton, and its major producers are Invista, DuPont, Rhodia, Ascend and BASF.¹⁰⁴ Commercial interest in biorenewable routes to adipic acid is found in the 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 the 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 already seen large improvements. Here we outline the most relevant current routes. A comprehensive overview is published elsewhere.¹⁰⁶

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-workers¹⁰⁹ 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 H₂O₂. This gave adipic acid at 90% yield, albeit after 8 h.

Freitag *et al.*¹¹⁰ then improved this biphasic system using an Na₂WO₄ catalyst and microwave radiation, reducing the 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.

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 de-

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

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

hydroxylation and (hydro)de-alkylation to phenol. One promising development is the use of liquid ammonia, which can dissolve lignin almost instantly.¹¹¹ However, yields are too low for industrial application.

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)).

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 the complete conversion of

phenol at over 95% selectivity towards cyclohexanone, under mild conditions: 140–170 °C and 1–2 bar H_2 (eqn (30)).

4.2.2. *cis,cis*-Muconic acid to adipic acid. In 2002, a biosynthetic route¹¹³ to *cis,cis*-muconic acid was reported, starting from glucose at 24% (mol mol⁻¹) 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 products 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 into 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 license¹¹⁴ 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}

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 the conversion of maleic anhydride and another is based on the hydrolysis of furfural derivatives. Various mono- and polysaccharides can be dehydrated to hydroxymethylfurfural, which is hydrolysed to a mixture of

Scheme 2 Possible applications of adipic semialdehyde.

formic acid and levulinic acid.¹¹ The most efficient glucose to levulinic acid reaction was demonstrated in the presence of 5.0% H₂SO₄ 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 the cellulose/hexose content were as high as 83%.

For the catalytic hydrogenation of levulinic acid to γ -valerolactone (GVL), both homogeneous 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, ZrO₂ and γ -Al₂O₃, and secondary alcohols as both solvents and hydrogen donors (eqn (34)). The highest GVL yield was 92%, using a ZrO₂ 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 the 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 the acid-catalysed dehydration of various sugars. For 5-hydroxymethylfurfural (5-HMF), the dehydration of fructose and cellulose shows 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 the modification of the pH and the

addition of promoters such as DMSO. Moreover, it eliminated the need for the acid pre-hydrolysis of polysaccharides. The best results were obtained using dichloromethane (DCM) as the organic solvent and a 3 : 7 water : DMSO solution 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)H₂PW₁₂O₄₀]₃ heteropoly acid catalyst, (DS = OSO₃C₁₂H₂₅ 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 A 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-workers¹²⁹ at Hydrocarbon Research Inc. showed a multi-step process towards adipic acid, consisting of: (1) acid-catalysed hydrolysis of lignocellulose in the presence of aqueous H₂SO₄ to provide 5-HMF. (2) Hydrogenation of 5-HMF over RANEY® Ni to 2,5-tetrahydrofurfurdimethanol (THFDM). (3) Converting THFDM to 1,6-hexanediol in the presence of copper chromite. (4) Bio-transformation 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/SiO₂ and a solid acid catalyst, under 80 bar H₂ at 120 °C. The reaction proceeded *via* 1,2,6-hexanetriol, with the complete conversion of THFDM and 86% selectivity towards 1,6-hexanediol (Scheme 3, (ii)).

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 was done on transforming 5-HMF to its dicarboxylic derivative,¹³² which already contains the required carboxylic moieties for adipic acid. Gupta and co-workers¹³³ catalytically oxidized

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

5-HMF to 2,5-furandicarboxylic acid (FDCA), using hydrothermalite-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-workers¹³⁵ at Rennovia Inc. in 2010. In their two-step process, FDCA was first hydrogenated using Pd/SiO₂ (4% by weight) under 52 bar H₂ at 140 °C for 3 h, yielding 88% tetrahydrofuran-2,5-dicarboxylic acid (THFDCA). Second, THFDCA was hydrogenated to adipic acid, using Pd/SiO₂ or Rh/SiO₂ in the presence of HBr or HI in acetic acid, under 49 bar H₂ 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 patent¹³⁶ 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/SiO₂ catalyst under 5 bar O₂ at 90 °C after 8 h.

(38)

The 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.

(39)

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 the 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 \$2000 per 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 CO₂ 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.

(40)

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 \$2400–\$3000 per ton,¹⁴² but it is estimated that succinic acid prices may fall below \$1000 per ton as the 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 the 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 process¹⁴⁵ for converting succinic acid to 1,4-BDO uses a 1% Pd–4% Re/TiO₂ catalyst, under 69 bar H₂ 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 into 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.

The catalytic carboxylation of 1,4-BDO to adipic acid is typically done using rhodium-based catalysts. The Monsanto process¹⁴⁶ from 1970 (eqn (42)) gives 74% yield at 175 °C, using an $\text{Rh}(\text{PPh})_3\text{COCl}$ 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 a 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, the *cis,cis*-muconic acid production from glucose (around \$500 per 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 important because the 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 in its infancy. A more promising example is the selective oxidation of glucose to glucaric acid (66% yield) and its 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 the fermentation feedstock to produce levulinic acid at 83% yield (based on the 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 the fermentation feedstock 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, these are expensive feedstocks, with current prices above \$900 per ton. The economical margin towards adipic acid (\$1500–\$1700 per 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 (43)). In 2012, over 4.0 Mt of ϵ -caprolactam were produced globally, and the current market price is \$2000–\$2500 per ton.^{11,148} Major producers are DuPont/BASF, DSM and Asahi.

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 the 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 a commercial scale, the isolation of the lactam proceeds through NH_3 addition at 98% yield (eqn (44)). Yet this final step requires organic solvents for purification and generates 1.8–5.0 kg ammonium sulfate waste (which BASF sells as a fertilizer) per 1.0 kg ϵ -caprolactam produced.

Various efforts have been made to reduce ammonium sulfate formation.^{75,149} The alternative Montedison cyclohexanone oxidation route uses NH_3 and a $\text{TiO}_2/\text{SiO}_2$ catalyst in a fluidized-bed reactor, in the presence of H_2O_2 at 40–90 °C. This provides the complete conversion of cyclohexanone and 90% selectivity towards the oxime. Another alternative approach came from DSM/Stamicarbon. Its acid-catalysed Beckmann rearrangement was performed using an acidic ion-exchange resin in DMSO at 100 °C. Bayer reported a $\text{B}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalyst in a fluidized bed reactor, at a temperature above 300 °C.^{11,150} However, only the Sumitomo route has proven to be commercially competitive. This route produces cyclohexanone oxime by direct ammoxidation from NH_3 and H_2O_2 using a TS-1 catalyst.¹⁵¹ The subsequent use of an MFI catalyst produces ϵ -caprolactam, while avoiding the formation of ammonium sulfate.¹⁵²

5.2. Alternative biorenewable processes

Here, we will discuss the most recent and noticeable biorenewable routes towards ϵ -caprolactam. Some advanced routes include 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.

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

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 the 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 (45)).

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 $\text{Ru}/\text{Al}_2\text{O}_3$ at 250 °C (eqn (46)). In 2 h, 64% ϵ -caprolactam yield was obtained. Other side-products include hexamethyleneimine (HMI) (6% yield), hexanamide (4%) and adipamide (2%).

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 few 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 rising to meet the growing demand. The

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

dimerisation of bioethanol (around \$750 per ton) provides a promising pathway to 1,3-butadiene (currently above \$1600 per ton). Two biobased methods are commercially applied today. The first is the Lebedev process, operated in Brazil and Poland, using an 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 an 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 an MgO-SiO_2 (1 : 1) catalyst and Na_2O (0.1%) at 350 °C, giving 1,3-butadiene at 87% yield (eqn (47)). 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 the 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. Its subsequent hydroformylation and amination yield 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)); Invista¹⁶⁵ and Rhodia/DuPont¹⁶⁶ or by electrolytic hydrodimerization of acrylonitrile (eqn (50); Asahi¹⁶⁷ and BASF¹⁶⁸). The production of biorenewable acrylonitrile is discussed in section 3.2.7.

The BASF process¹⁶⁹ 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)). The consecutive catalytic hydrolysis of 6-amino capronitrile yields 79% ϵ -caprolactam in 15 min, in the 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 interest recently. 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-pentenitrile, at 54% yield. The 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 the absence of a catalyst, as demonstrated by BASF¹⁷⁹ 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)).

5.2.6. Adipamide to ϵ -caprolactam. Adipamide may be obtained from adiponitrile or through the 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 were obtained, with HMI as the 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 can be produced through the fermentation of glucose. The best yields were obtained using a 5% Pd- Al_2O_3 (5 mol%) catalyst in

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
<i>t,t</i> -MA X = 88%	S = 50% Y = 44%	S = 7% Y = 6%	S = 43% Y = 38%
<i>c,t</i> -MA X = 77%	S = 70% Y = 54%	S = 9% Y = 7%	S = 23% Y = 18%
<i>c,c</i> -MA X = 79%	S = 70% Y = 55%	S = 16% Y = 13%	S = 11% Y = 9%

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).

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 the feedstock. Its biorenewable production may revive these 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 the subsequent continuous conversion of 6-aminocaproic acid to ϵ -caprolactam was proven to be efficient (95% yield). 1,3-Butadiene may be produced from bioethanol, at 87% yield. The low bioethanol price (around \$750 per ton) makes this a viable route to 1,3-butadiene (above \$1600 per ton) and leaves sufficient economical margin towards ϵ -caprolactam (\$2000–\$2500 per 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.

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

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 \$1900 per 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 can be produced from biorenewables, so can ϵ -caprolactam. Their economical difference (\$500–\$800 per 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 the 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.

‘White biotechnology’ has grown much in the last few decades, but still suffers from limitations to large-scale application, due to cost-intensive purification and separation requirements. However, the advantages of changing between various carbohydrate feedstocks, combining different processes and using 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 industries. No biorenewable routes to the target chemicals are yet competitive to their petrochemical equivalents. But, given that most of them 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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