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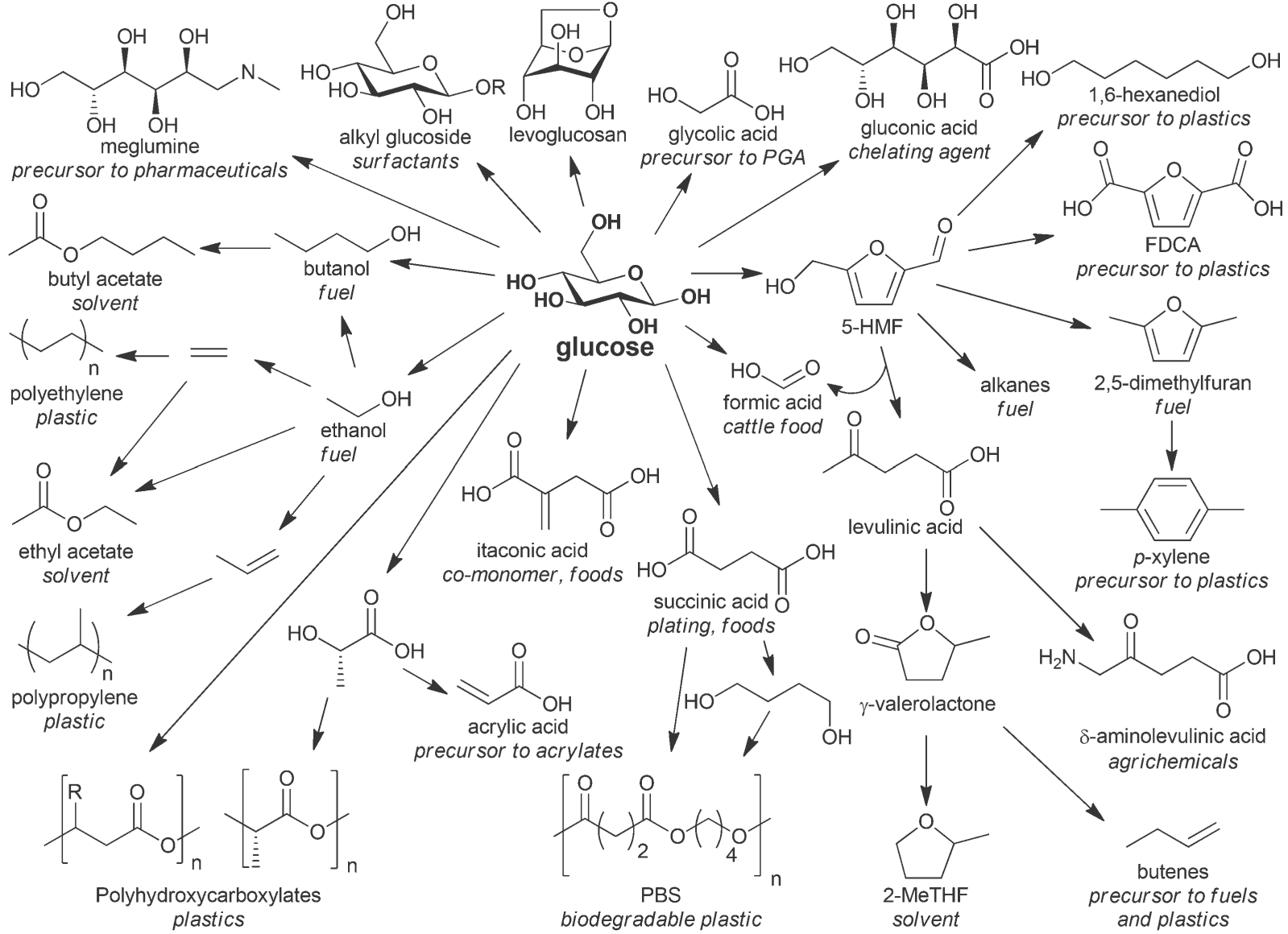
Catalytic routes towards bio-renewable glucaric acid

**KEYWORDS:** *Glucaric acid, gluconic acid, adipic acid, catalysis, biomass.*

**ABSTRACT:** Biomass-derived glucaric acid has the potential to become an important bio-derived chemical due to its wide range of potential industrial applications, but most notably due to its application as detergent builder as a substitute for phosphates or citric acid and, as a precursor to renewable adipic acid. Typically, glucaric acid is synthesised from the oxidation of glucose, which involves using nitric acid as a stoichiometric oxidant, which brings about problems in pollution, separation and increased greenhouse gas emissions. Other routes are being explored and chemo-catalysis has received considerable interest, with several companies taking steps to begin large-scale commercialisation of these routes to glucaric acid and derivatives using heterogeneous catalysts. In this perspective review, we summarise the recent scientific and patent literature and critically evaluate the merits of each of the emerging routes towards glucaric acid.

# Introduction

One of the most widely available and well-studied biomass feedstocks is glucose, which it is the monomeric unit contained in widely abundant cellulose and starch. In general, industrial-scale glucose production involves firstly isolating starch from the plant source, followed by acidic or enzymatic hydrolysis to give glucose ([1](#_ENREF_1)). The high abundance of starch-containing compounds and thus the relatively low price of glucose, makes it a prime candidate for biomass conversions. As a result, glucose is one of the most important bio-based feedstock for various biomass conversions, ranging from fermentations to bioethanol for fuels, to dehydrations to polymer precursors, as seen in Figure 1 ([2](#_ENREF_2)).



**Figure 1.** Diagram showing glucose, its derivatives and their applications. Reproduced (adapted) with permission from Kobayashi and Fukuoka ([2](#_ENREF_2)). Copyright 2013 Royal Society of Chemistry.

The US department of energy classified glucaric acid (also saccharic or glucosaccharic acid) as one of the top 12 value added chemicals from biomass in 2004 ([3](#_ENREF_3)). Today, it is mostly synthesised by the non-selective nitric acid oxidation of glucose (Figure 2), forming 85 lbs of waste nitric acid per 100 lbs of glucaric acid produced ([4](#_ENREF_4)). The use of nitric acid as the oxidising agent was cited as one of the reasons for removing glucaric acid from this list in a review by Bozell and Petersen in 2010 ([5](#_ENREF_5)). On the other hand, little scientific research has yet been carried out to elucidate catalytic routes to selectively oxidise glucose to glucaric acid and most of the available literature focuses on the much easier selective oxidation towards gluconic acid ([6-10](#_ENREF_6)) . Bozell also highlighted the stagnation in glucaric acid research between 2004 and 2010 and the absence of any commercial successes. However, arguments can be made for improvements in all three of these areas since 2010, presenting a case for the return of glucaric acid to this list.

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**Figure 2.** Possible pathways for the production of glucaric acid from glucose, where [O] represents an oxidant, such as nitric acid or molecular oxygen.

Glucaric acid itself has a diverse market potential with uses ranging from detergents ([11](#_ENREF_11)) to polymers ([12](#_ENREF_12)) to food additives (due to its health benefits) ([13](#_ENREF_13)) as shown in Figure 3. Very importantly, the dicarboxylic acid functionalisation also makes it an attractive bio-derived precursor to adipic acid, which could be used as a more sustainable alternative to fossil-fuel derived adipic acid in nylon production plants ([14](#_ENREF_14)). A wide range of other biodegradable polymers are also possible including methacrylates ([15](#_ENREF_15)), hydroxylated nylons ([16](#_ENREF_16)) and other ester/amide polymers ([17](#_ENREF_17)). Furthermore, its corrosion inhibition properties have been recognised in other fields, such as in construction as a cement additive ([18](#_ENREF_18)).

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**Figure 3.** Overview of uses of glucaric acid in different sectors as mentioned in text.

A large market opportunity has presented itself with the increase in governmental taxes on phosphates in detergents in Europe and more regulation can be expected in the future to fully eradicate the use of phosphates in detergents ([19](#_ENREF_19)). Since the 1970s, significant amounts of scientific evidence have linked these phosphates to eutrophication and subsequent decrease in water quality ([20](#_ENREF_20), [21](#_ENREF_21)). This realisation led to the economic disincentive policies in the EU and outright bans in the U.S. on phosphates in detergents ([22](#_ENREF_22)). Despite limitations in performance and cost, this market gap has been partially plugged by citric acid, with around 13 % of global citric acid consumption for the manufacture of detergents ([23](#_ENREF_23)). Glucaric acid is a compelling drop-in substitute for these banned substances due to its chelating properties in sequestering metal ions in building detergents ([24](#_ENREF_24)). The current supply of glucaric acid is very limited and not sufficient for such large market, however, if glucaric acid could be produced at scale and with a price competitive to that of citric acid, then this multi-billion dollar market would be available and bio-sourced. Table 1 outlines the catalytic oxidation studies of glucose to glucaric acid from scientific and patent literature, which will be discussed in more detail later in the text.

Table . Overview of the results achieved in oxidation of glucose (conversion (X)) to glucaric acid (yield (Y)) presented in this review. Additive/note refers to the compound usually present in the reaction mixture or how the reaction was carried out.

a trickle bed reactor (210 cm long with 4 cm diameter) (2520 mL catalyst, 150 mL/h of 9.25 % glucose solution); b 2,2,6,6-tetramethylpiperidin-1-yl)oxyl;

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| Catalyst | T, °C | p, bar | t, h | additive/note | X, % | Y, % | Ref. |
| NaNO2 (HNO3) | 25-30 | 1.25-1.5 (O2) | 4.9 | NaNO2 | NA | 45 | ([4](#_ENREF_4)) |
| 10%Pt/C | 50 °C | 1 (O2) | 12 | KHCO3 | NA | 54 | ([25](#_ENREF_25)) |
| 3%Pt/C | 50 °C | 1 (O2) | NAa | Na2CO3 | 84.6 | NA | ([26](#_ENREF_26)) |
| 1.5%Pt 1.5%Au/TiO2 | 100 °C | 34.5 (air) | 5 | none | NA | 55 | ([27](#_ENREF_27)) |
| 4%Au 4%Pt/TiO2 | 119 °C | 27.6 (O2) | 3 | none | 100 | 71 | ([28](#_ENREF_28)) |
| 5%Pt/C | 80 °C | 13.8 (O2) | 10 | none | 100 | 74 | ([29](#_ENREF_29)) |
| 0.91%Pt 0.95%Pd/TiO2 | 45 °C | 1 (O2) | 24 | NaOH | 100 | 40 | ([30](#_ENREF_30)) |
| 0.71%Au 0.2%Bi/C | 60 °C | 10 (O2) | 3 | NaOH | 100 | 31 | ([31](#_ENREF_31)) |
| TEMPOb | 5 °C | NA (NaOCl) | NA | NaOCl+NaBr/electro | NA | 90 | ([32](#_ENREF_32)) |
| TiO2 | 30 °C | 1 (air) | 5 min | CH3CN/UV photo | NA | 16.6 | ([33](#_ENREF_33)) |

# Chemo-catalytic routes to glucaric acid

## Homogeneous catalysis

One of the key reasons for developing chemicals from biomass is that fossil-fuel derived chemicals produce significant amounts of the greenhouse gas, CO2. It is however sometimes disregarded that, N2O, one of the major by-products from nitric acid oxidations, has a 180 times higher global warming potential than CO2 ([34](#_ENREF_34)). As a consequence, in addition to generating routes for glucose valorisation, there is a strong motivation that such routes will avoid the release of N2O associated with nitric acid oxidations.

A very positive step in this direction was carried out by the group of Donald E. Kiely at the University of Montana, who was able to improve on the traditional method by recycling the nitric acid in the process ([4](#_ENREF_4)). The method is simple in concept, and a blanket of pressurised oxygen is used to prevent the release of nitrogen oxides forcing the regeneration of nitric acid. This effectively makes the process catalytic in nitric acid, using up stoichiometric amounts of molecular oxygen instead. The use of nanofiltration or diffusion dialysis are identified as potential separation techniques for isolating the products and attempts are made to prove their effectiveness. However, on a bigger commercial scale, these techniques might be expensive, time consuming and/or energy intensive and further research is required. Despite these limitations, the recycling technology has been put to use by Montana-based company Rivertop Renewables, who have reached the benchmarking stage of their first commercial plant. In a recent press release, they announced that this plant is “now capable of producing more than 9 million dry pounds of sodium glucarate product per year” ([35](#_ENREF_35)). The technology could be equally applied to other nitric acid oxidations of aldoses, such as mannose, arabinose, xylose or ribose, to their corresponding aldaric acids ([36](#_ENREF_36), [37](#_ENREF_37)).

## Heterogeneous catalysis

One of the earliest mentions of heterogeneously catalysed synthesis of glucaric acid is from 1949 patent by Alexander and Mehltretter ([25](#_ENREF_25)). They reported 54 % yield of potassium D-glucosaccharate achieved over 10 % Pt/C catalyst (43.7 g/g ratio of substrate to Pt). Dextrose hydrate was catalytically oxidised by air bubbled at atmospheric pressure through a vigorously stirred solution containing potassium bicarbonate to keep the pH alkaline (50 °C, 12 h).

Johnson Matthey Company Ltd. led by Acres and Budd patented a heterogeneous continuous catalytic process to produce both gluconic and glucaric acids in 1971 ([26](#_ENREF_26)). Both reactions were conducted under basic conditions to enable the reaction or to improve the reaction rate. While palladium on carbon or alumina support produced gluconic acid selectively, platinum on carbon gave glucaric acid. Trickle-bed oxidations of concentrated glucose solutions (1 and 0.5 M, 150 mL/h) gave 100 and 84.6 % conversion of the substrate at 50 °C, 1500 mL/h oxygen, over 840 mL of 1 % Pd/α-Al2O3 and 2520 mL of 3 % Pt/C with 1 M sodium bicarbonate and 0.5 M sodium carbonate, respectively.

More recently, Rennovia Inc. have developed a number of heterogeneous catalysts comprising various transition metals on a selection of different supports for the base-free, aerobic oxidation of glucose to glucaric acid in water ([27](#_ENREF_27), [28](#_ENREF_28)). Importantly, Rennovia Inc. developed their catalysts using high-throughput screening using automated robots for synthesis and testing of the heterogeneous catalysts comprising supported metal catalysts of a variety of compositions. Although the best catalyst and its composition was not specified, the first patent from 2010 identified commercial 1.5 % Au/TiO2 catalyst from Süd Chemie, promoted by 1.5 % Pt as the most active catalyst (based on specific activity per amount of metal present in catalyst) giving 55 % yield of glucaric acid (100 °C, 5 h). The high activity of Au and Pt in the selective glucose oxidation was reported before and after the release of this patent also in the literature ([6](#_ENREF_6), [7](#_ENREF_7), [9](#_ENREF_9)). In the follow up Rennovia patent, Murphy and co-workers ([28](#_ENREF_28)) expanded the optimisation of the composition of gold and platinum and found the Au deposition is promoted by base and formed AuPt nanoparticles should be between 8-12 nm and in Pt/Au molar ratio 2:1-1:1 and that platinum would be reduced from Pt(II) to Pt(0). Catalysts in the majority of the shown examples were prepared by successive deposition of gold and then platinum and 4 wt. % Au 4 wt. % Pt supported on TiO2 gave up to 71 % yield of glucaric acid at 100 % conversion of glucose at 119 °C and 3 hours of reaction. Importantly, the process removes the need for nitric acid, utilising pressurised oxygen as the oxidant instead. Based on these discoveries, the California-based company started a pilot plant for the conversion of glucose to glucaric acid in partnership with Johnson Matthey in 2015 ([38](#_ENREF_38)). Rennovia’s approach also involves a second catalytic step for the subsequent hydrodeoxygenation of glucaric acid to adipic acid in the same facility.

Since then, they have taken a further step towards commercialisation and this year they have licensed the production of glucaric acid to a third company, Archer Daniels Midland Company ([39](#_ENREF_39)).

Meanwhile, researchers from the University of Delaware achieved the highest reported yield of glucaric acid from glucose using heterogeneous catalysts, under base-free conditions ([29](#_ENREF_29)). They were able to tune the reaction conditions for a commercially available Pt/C catalyst, to oxidise glucose at 80 °C and 13.8 bar oxygen pressure over 10 hours, achieving 74 % selectivity to glucaric acid at >99 % conversion. They also found that increasing oxygen pressure resulted in faster reactions, but lowered the calculated carbon mass balance. Neutral and mildly basic conditions gave much higher selectivities.

In the last couple of years, a research group at the University of Kansas considered bimetallic Pt1Cu3 and PtPd on titania supports for glucose oxidations targeting glucaric acid, with yields of 25 % and 40 %, respectively ([30](#_ENREF_30), [40](#_ENREF_40)). A clear synergistic effect was seen in both catalytic systems, where the bimetallic system significantly outperforms the monometallic catalyst in terms of glucose conversion and glucaric acid selectivity. Furthermore, their approach involves milder conditions than others, with reactions conducted at just 45 °C and atmospheric pressure, bubbling oxygen through the reaction at 60 ml/min. However, these milder conditions are partially balanced by the longer reaction times of up to 24 hours to achieve comparable yields. The bimetallic catalysts were also reported to retain their activity, with <4.2 % leaching of Pt or Pd over three 24-hour reaction cycles, demonstrating their stability. From a commercial perspective, these very long reaction times appear largely unattractive.

Perhaps, part of the success of these reactions could be attributed to the slow addition of base to the reaction mixture. One possible explanation for this enhancement could be that the addition of base drives the equilibrium of glucose from the stable cyclic form to the more reactive linear form ([41](#_ENREF_41)). Furthermore, acidic conditions are known to promote lactonisation of glucaric acid to the corresponding mono or dilactone forms ([42](#_ENREF_42), [43](#_ENREF_43)), as seen in Figure 4. Over the course of a typical glucose oxidation reaction, many different organic acids are generated, dropping the pH of the reaction mixture and potentially forming the lactone. Theoretically, addition of a base could hinder this process by reducing the acidity of the solution, driving the equilibrium back towards glucaric acid.

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**Figure 4.** Lactonisation pathway of glucaric acid to a mixture of glucaro-1,4-lactone, glucaro-6,3-lactone and glucaro-1,4:6,3-dilactone.

Another possible explanation is that under acidic conditions, the strongly-binding carboxylic acids that are formed in the oxidation remain adsorbed on the catalyst surface, poisoning the catalyst ([44](#_ENREF_44)). Therefore, reactions conducted at basic pH avoid this “self-poisoning” phenomenon and proceed at higher rates. Previously, the presence of base in glucose oxidation with gold catalysts has been shown to aid the reaction to gluconic acid ([45](#_ENREF_45)). Since gluconic acid is thought to be the intermediate in the glucaric acid production, it is reasonable to assume that addition of base would result in a subsequent increase in glucaric acid yields. Supported gold nanoparticles have been used extensively in the oxidation of glucose to gluconic acid, where 100 % selectivity to gluconic acid can been achieved ([45](#_ENREF_45)). Most recently, Solmi *et al.* used Au/C and AuBi/C for the direct oxidation of glucose to glucaric acid at 60 °C and 10 bar oxygen pressure ([31](#_ENREF_31)). A 3:1 ratio of Au:Bi gave the maximum yield of glucaric acid of 31 % at 100 % glucose conversion. Glucose concentration was found to be a key factor in optimising the catalyst performance, with lower concentrations aiding both conversion and selectivity. Furthermore, smaller gold particles were linked to increased activity, but also to lower selectivity due to the formation of further oxidation products. These two observations appear fundamental in order to further increase the selectivity of the glucose to glucaric acid reaction, although highlight that very high selectivity towards glucaric acid while avoiding over-oxidation (often observable in lower carbon mass balances) comes at a significant price in terms of process parameters and productivity. Taking this in consideration, it is important to understand the oxidation of gluconic acid to glucaric acid separately and realise whether the limitations in activity are unavoidable.

One could consider the potential utilisation of sugar-rich waste generated in the pulp paper industry, which is currently burnt to regenerate some of the energy used in the process ([46](#_ENREF_46)). The carbohydrate-rich hydrolysate of hemicellulose, such as that found in pulp paper waste, presents a good renewable feedstock for this conversion. However, the utilisation of such biomass presents further problems due the interactions of other compounds in the mixture with the catalysts. For example, residues from acidic hydrolysis of hemicellulose, such as guaiacol, furfural and hydroxymethylfurfural, have been shown to hinder the heterogeneously catalysed glucose oxidations to glucaric acid ([47](#_ENREF_47)). Thus, a decision would need to be made on whether to spend energy and resources on purifying the feedstock, or dealing with the problems arising from using a contaminated feedstock. The advantage of purifying the feedstock by extracting the other compounds is that almost all chemicals generated will have a higher value than the feedstock, including guaiacol, furfural and HMF.

# Other Routes

## Electrocatalytic routes

In 2001, Thaburet *et al.* were able to produce glucaric acid in over 90 % yield, using an oxidation system consisting of sodium hypochlorite (NaOCl), sodium bromide (NaBr) and the stabilised radical 2,2,6,6‑tetramethylpiperidin‑1‑yl)oxyl (TEMPO) ([32](#_ENREF_32)). While these oxidants do allow milder conditions, which in turn lead to fewer side products, the toxicity of the reagents and by-products results in a less environmentally friendly process. Not to mention that the cost of stoichiometric amounts of NaOCl and NaBr economically disincentives this process. However, more recently, they have been able to replace the chlorine and bromine oxidants by using an electrochemical method, greatly decreasing the amount of toxic side products ([48](#_ENREF_48)). The new method employs a graphite anode and a stainless steel cathode and under optimum conditions, the product mixture analysed was over 90 % glucaric acid, comparable to the chlorine and bromine oxidised systems. The reaction conditions of 5 °C and atmospheric pressure are much milder than those used on the chemo-catalytic processes mentioned previously. These mild conditions may be able to compensate for the electrochemical reactions tendency to lead to over-oxidation products. To further compensate for this, the reaction was held at more basic pH values (>12), where degradation products were minimised.

## Photocatalytic routes

Very little research has been conducted on photochemical selective glucose oxidation, but this research is gaining some momentum across academic research ([33](#_ENREF_33), [49-53](#_ENREF_49)). In these reports, typically only trace quantities of glucaric acid are found among a product distribution that typically includes gluconic acid and formic acid as the two main compounds obtained. Our very recent research work clearly indicated that gluconic acid was the main reaction product when using both titania and plasmonic nanoparticles, whereas visible light resulted in higher seletcivities as comapred to UV light irradiation([50](#_ENREF_50), [51](#_ENREF_51)). However, using a different photocatalytic system, the group of Colmenares reports some of the highest yields to glucaric acid under photocatalytic conditions. Colmenares *et al.* employed TiO2 photocatalysts under illumination by a 125 W mercury lamp (λmax=365 nm) to selectively oxidise glucose ([33](#_ENREF_33)) and were able to achieve 16.6 % yield of glucaric acid after just 5 minutes of illumination with a TiO2 photocatalyst prepared by an ultrasound-assisted sol-gel method. Under these conditions, longer reaction times and aqueous solvent compositions tended to lead to mineralisation (complete conversion of glucose to CO2 and H2O) instead of the desired selective oxidation. To overcome this, they used relatively short reaction times and a mixed solvent system composed of acetonitrile and water. More recently, the same group found that mounting the titania photocatalysts on zeolite supports increased the selectivity to gluconic and glucaric acid, showing a total selectivity of 68 % to these acids (individual selectivities were not reported) ([49](#_ENREF_49)). The enhancement in selectivity is probably a result of the porous nature of the zeolite support, which allows the substrate to undergo nanoscale reactions within the pores and then quickly diffuse out again. A significant increase in absorption of visible light is observed when mounting the TiO2 on a zeolite support, which could be contributing to this increased selectivity through electronic effects. Further improvements in the photocatalytic activity can be seen when doping the TiO2 with other metals, such as Fe ([54](#_ENREF_54)), or Cr ([55](#_ENREF_55)).

# Conclusions

Although the electrocatalytic and photocatalytic routes towards glucaric acid might not yet be sufficiently understood and uneconomic, they present some interesting opportunities in the longer term when much higher selectivities and yields are achieved. The use of heterogeneous catalysts is substantially more mature and attarcts high interest from academia and industry alike. The oxidation of glucose to gluconic acid is readily carried out with heterogeneous catalysts and, although higher catalytic activity is highly desired in order to intensify the process (i.e. continuous), the limitation resides in obtaining high selectivity to consecutive products.Whenglucaric acid is targeted, overoxidation and C-C breaking become a real problem. Despite of this, the oxidative selective oxidation of glucose to glucaric acid continues to attract important industrial interest aligned with the ultimate production of bio-derived adipic acid or for its direct use. And the development of very selective systems is stillthe key.

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