

Glucose Oxidation Applying Electrochemically Produced Green Oxidants

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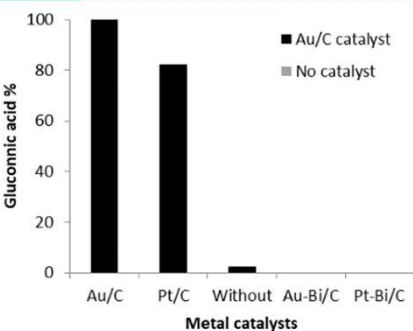
Background

In recent years, the oxidation of glucose has been widely studied. The main product of its oxidation is gluconic acid, in which only is oxidized the aldehyde group (Nikov, 1995). Gluconic acid is a mild, non corrosive, non-toxic and readily biodegradable organic acid (98% after 2 days) with an excellent sequestering power which is of great interest for many applications. It is used in the pharmaceutical, food, paper and concrete industries and, it is estimated that 100,000 tons are being produced per year (Anastassiadis, 2007). Since glucose is a cheap and renewable material, its oxidation is an economical and sustainable trade. The market demand is expected to grow over the next few years if a scalable cost-effective technology is developed (Gluconic Acid Market, 2017).

The aim of this study was to identify glucose oxidation routes based on green oxidants that can be produced on-site. In this work the oxidation compound of choice was disodium peroxy-dicarbonate (PODIC[®]), developed by CONDIAS. Its oxidation activity is based on direct electron transfer as well as a range of decomposition pathways, including carbonate - and hydroxyl radicals. PODIC[®] is produced electrochemically from sodium carbonate by applying boron-doped diamond (BDD) anodes with high selectivity and at reasonable concentrations of about 0.2 M PODIC[®] (Chardon, 2017). The aim of this work was to evaluate the applicability of this oxidant for the selective oxidation of bio-based model components. Based on this work industrial feedstocks will be selected for further conversion studies.

Screening of oxidant-catalyst combinations for glucose oxidation

Conversion of glucose to gluconic acid by means of different catalysts was performed in simple beaker-type experiments. The results are summarized in Figure 3. Interestingly, the use of bismuth, a common co-catalyst for oxygen shuttling, did not result in any Application of oxidants without catalyst did not result in significant glucose conversion, only PODIC showed 2.6 % of gluconic acid conversion after 1 h reaction. When using catalyst-oxidant combinations PODIC (0.2 M) and air (using a 1M sodium carbonate solution as solvent) gave the best performance with a quantitative



glucose conversion and gluconic acid selectivity of >98% after 1 hour. $KMnO_4$ showed 22.1 % gluconic acid yield and several side products, due to over-oxidation. The lowest yields were obtained hydrogen peroxide (0.2 M) with a gluconic acid yield of 1.7%.

Figure 3: Gluconic acid yields applying different PODIC-catalyst combinations.

References

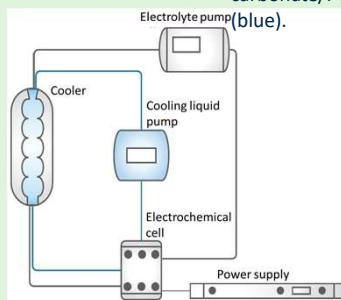
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 Chardon, C. P., Mattheé, T., Neuber, R., Fryda, M., & Comninellis, C. (2017). ChemistrySelect (Vol. 2, Issue 3).
 Gluconic Acid Market (2017) Global Industry Analysis, Size, Share, Growth, Trends And Forecast, 2015 To 2022.

Electrochemical production of PODIC as green oxidant



Figure 1: CONDIAS Synthesis Starter Kit.

Small amounts of PODIC were produced applying the CONDIAS Synthesis Starter Kit consisting of a circulation pump, immersed into the electrolyte, and an electrochemical cell. AS PODIC-producing anode a BDD electrode with a geometric surface area of 3,14 cm² was applied. As hydrogen-producing cathode the stainless steel frame of the cell was used. The reservoir consisted of a wall-cooled glass autoclave connected to a circulation cooling bath with a temperature of 10 °C. Applying the recommended currents of 2.2 A after 1.5 h of operation a PODIC concentration of around 160 mMol was produced. For the production of PODIC solutions in litre scale a CONDIAS 100 cm² cell setup as schematized in Figure 3 was applied. This consists of two circuits one for the recirculation of carbonate/PODIC (grey) and other for the cooling system

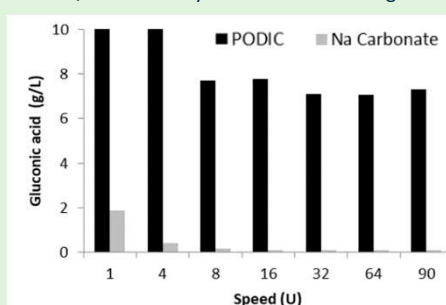


Sodium carbonate solution (1M) was cooled down (10-11°C) inside the cooling tank. Current was set up at 47 A so that potential reaches values around 6.7 V, recirculation flow was kept high around 10 L/min, and, after 1 hour reaction time, ~0.2 M of PODIC was obtained (molarity determined by iodometric titration). The prepared solution was either used directly or cooled at temperatures below 10 °C to minimise decomposition of PODIC.

Figure 2: Bench scale PODIC production rig.

Continuous operation at lab scale

When passing a mixture of glucose and PODIC over a catalyst bed the limits of low oxygen concentration are overcome. Even when using only a PODIC concentration of 150 mM, this is still three orders of magnitude higher than the oxygen concentration at ambient pressures. The use of PODIC significantly simplifies the glucose oxidation. Simple liquid-solid contacting fixed bed reactors can be applied instead of more complex reactors, such as slurry bubble columns or agitated reactors with gas sparging.



Neither elevated oxygen pressures is required to reach quantitative yields within a few minutes. The initial set of experiments showed a steady state of high glucose conversion. Catalyst over-oxidation was not detected during the limited set of experiments, but needs to be evaluated in a separate study.

Figure 4: Gluconic acid yields feeding aqueous mixtures of glucose and PODIC over a fixed bed of Au/C.

Next steps

As PODIC is the consumed oxidation agent, the main focus is now to increase the PODIC:glucose ratio to enable industrial highly concentrated glucose streams.

Project partners:



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