EBIO BIOFUELS THROUGH ELECTROCHEMICAL TRANSFORMATION OF INTERMEDIATE BIO-LIQUIDS

Catalytic glucose oxidation applying electrochemically produced green oxidants

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In this study, peroxo-dicarbonate (PODIC®), a novel oxidizing agent, was evaluated for the selective oxidation of glucose to gluconic acid. The oxidation activity of PODIC® was compared with other oxidizing agents (O2 in air, H2O2 and KMnO4). High selectivity and yield of gluconic acid were achieved with PODIC® under mild conditions, with high conversion rates, suggesting promising applications of this oxidizing agent in catalytic reactions.

Introduction

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 various applications in the pharmaceutical, food, paper and concrete industries. The market demand is expected to grow over the next few years if a scalable cost-effective technology is developed (Glucaric Acid Market, 2017). Different routes to obtain gluconic acid have been developed, including fermentation and noble metal catalysed processes. Those catalysts have shown high yields of conversion and a potential scalable cost-effective technology. However, major drawbacks are unwanted side reactions and catalyst deactivation, mainly due to overoxidation of the active surface atoms [1].

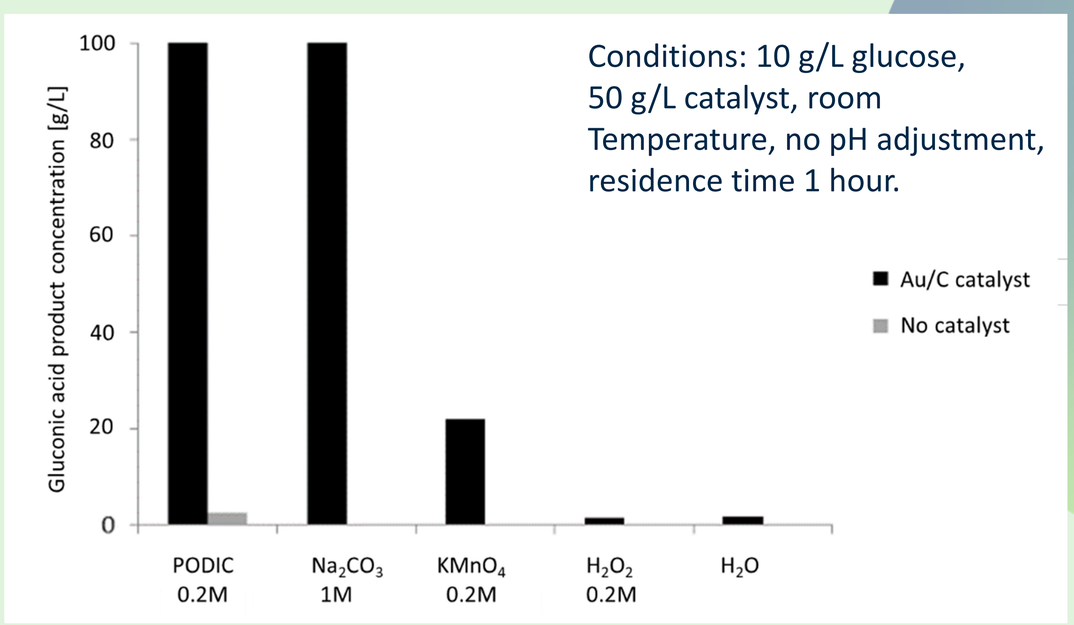

Figure 2: Gluconic acid yield by different oxidant agents with or without Au/C catalyst.

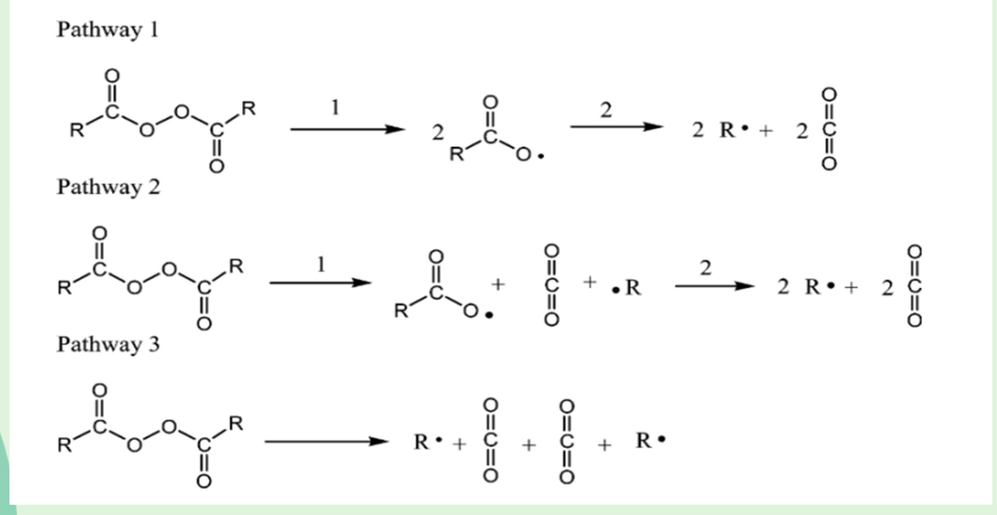

Figure 1: Mechanisms for Podic decomposition into radicals.

Experimental/methodology.

With the aim to identify glucose oxidation routes based on green oxidants, the oxidation compound of choice was disodium peroxydicarbonate (PODIC). PODIC was produced from sodium carbonate solutions by electrochemical synthesis on boron-doped diamond anodes, following the method described by Chardon et al. [2]. The consists of two circuits one for the recirculation of carbonate/PODIC and the the cooling system. For autocatalytic reactions the freshly prepared PODIC was mixed with glucose solution at different concentrations. Heterogeneously catalysed reactions were studied by applying a Au/C powder catalyst, which was prepared by homogeneous deposition precipitation. The effect of residence time under continuous operation was studied by using a fixed bed reactor.

Results and discussion

Conversion of glucose to gluconic acid by means of different oxidants is summarized in Figure 1. In a non-catalytic system only the use of PODIC resulted in the production of quantitative amounts of gluconic acid, which is with 2.6 mol% still low after the residence time of 1h. Applying Au/C in combination with the individual oxidation agents resulted in production of gluconic acid in all cases, where the conversion is of the following order: PODIC = Na2CO3 > KMnO4 > H2O2 > H2O. KMnO4 showed only a gluconic acid yield of 22.1 % with several low molecular size side products. Under continuous operation the concentration of PODIC is about three orders of magnitude higher than the dissolved oxygen concentration, resulting in significantly higher conversions than dissolved oxygen systems, including carbonate solutions. At flow rates above 6 mL/min/g catalyst, the conversion is reduced due to mass transport limitations.

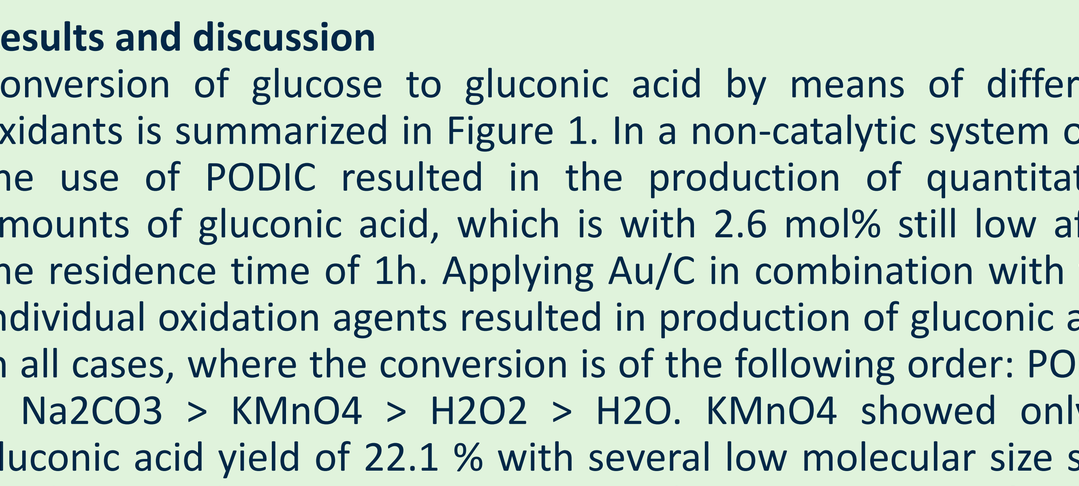

Figure 3: Conversion of glucose applying Podic and Na2CO3.

Project partners:

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