Research and Reviews Journal of Chemistry

e-ISSN: 2319-9849
p-ISSN: 2347-2324

Glucaric Acid: Applications & Synthesis

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SHORT COMMUNICATION

Received date: 24/07/2021
Accepted date: 23/07/2021
Published date: 30/07/2021

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Keywords: Depolymerization, Glucaric acid, Oxidation.

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Today the whole world is dependent on fossil fuels to satisfy its demand in the energy sector. Lignocelluloses biomass is one such sustainable resource that can be used as a replacement for fossil fuels and thus conversion of biomass to value added chemicals is of great interest and biggest challenge to the scientific community. Lignocellulose has advantages over starch and sugar crops, as it does not compete with food supplies. Major challenge in using lignocellulosic biomass is the efficient depolymerization of cellulose and hemicelluloses into their monomers. Cellulose is a major component of biomass but due to its highly crystalline structure its depolymerization to monomer glucose is difficult. Hemicelluloses is a mixture of C5 and C6 sugars and its depolymerization leads to monomers mainly xylose, arabinose, glucose, mannose etc. These monomers can be separated and offer a versatile platform that can provide a range of useful molecules. Thus, glucose is the most abundantly available biomass component and can be converted into variety of useful chemicals such as sorbitol, 2, 5-furandicarboxylic acid, 5hydroxymethylfurfural, gluconic acid, glucaric acid etc. In 2004, U.S. Department of Energy has identified glucaric acid as one of the top 12 value added chemical. Glucaric acid is a very important chemical as it finds uses in variety of industries such as polymer industry, paint industry, food industry, chemical industry and construction industry. Currently in 2020, the global market for glucaric acid is 1.0 billion$ and is expected to increase to 1.3 billion$ by 2025. Glucaric acid contains dicarboxylic acid groups at terminal ends of C-6 sugar and can be used as an alternative to fossil derived adipic acid and thus can be used in synthesis of nylon. It is used as an additive in cement industry as it has corrosion inhibition property. Derivatives of glucaric acid also find use in medical applications such as diabetes treatment, antitumor agent etc. Glucaric acid occurs naturally in fruits and vegetables and can also be produced synthetically from glucose using chemical, biochemical and electrochemical oxidation strategy **(Figure 1).**

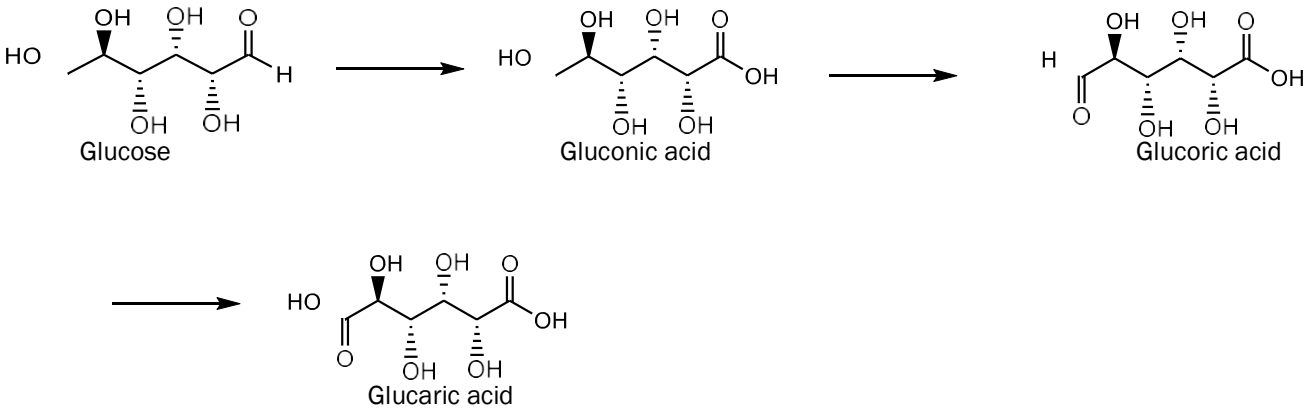

Figure 1. Step involved in oxidation of glucose to glucaric acid.

Traditionally, glucaric acid is mainly synthesized from glucose (an abundant biomass feedstock) using nitric acid as an oxidant in 40% moderate yield [1]. Use of stoichiometric nitric acid as an oxidant gives rise to various problems of pollution by generating waste and also trouble in separation of products.

e-ISSN: 2319-9849
p-ISSN: 2347-2324

Major drawback of current technology is use of inorganic oxidants. A US based company named Rivertop Renewables Inc. produces glucaric acid on 25,000 tons from glucose by using this catalytic oxidation process. In an alternative approach, the nitroxide-mediated oxidation of glucose using bleach and NaBr produces glucaric acid in a yield of >90%. Till date very few catalytic methods are available for selective oxidation of glucose to glucaric acid whereas more literature is available on comparatively easier and simpler selective oxidation of glucose to gluconic acid [2]. The heterogeneous catalytic methods used in the synthesis of glucaric acid either from glucose or gluconic acid uses noble metal catalysts such as palladium, platinium, gold etc using O_2 as an oxidant at relatively high pressure. Various mono and bimetallic catalysts have been used and evaluated in the synthesis of glucaric acid from glucose. Platinum on carbon support Pt/C catalyst was studied for synthesis of glucaric acid from glucose that was found to give 53% yield **(Table 1: Entry 1)** [3].

Table 1. Catalysts reported in literature for oxidation of glucose to glucaric acid.

Entry	Catalysts	Conversion (%)	Selectivity (%)	Yield (%)
1.	Pt/C	-	-	53
2.	Au-Bi/AC	100	-	31
3.	Au-Pt/ZrO_2	100	-	50
4.	Pt/C	-	-	74
5.	Pt/CeO_2	28	47	-
6.	Pt/TiO_2	70	38	-
7.	Pd/TiO_2	41	44	-
8.	Pt-Cu/TiO_2	100	32	-
9.	Cu/TiO_2	2.8	31	-
10.	Co/CeO_2	5.5	21	-

Bimetallic AuBi/AC was used in the synthesis of glucaric acid giving 29% yield of glucaric acid with 100% conversion of glucose **(Table 1: Entry 2)** [4]. AuPt/ZrO_2 gave 50% yield of glucaric acid with 100% conversion **(Table 1: Entry 3)** [5]. Vlachos et al. reported glucaric acid yield of 74% using Pt/C catalyst **(Table 1, Entry 4)** [6]. Pt was supported on various supports such as TiO_2 and CeO_2 giving 47% and 38% selectivity with 28% and 70% conversion respectively **(Table 1: Entries 5 & 6)**. Pd supported on TiO_2 support gave about 44% selectivity of glucaric acid with 41% conversion **(Table 1: Entry 7)**. Bimetallic catalyst Pt-Cu/TiO_2 giving 32% selectivity with complete conversion of glucose to glucaric acid **(Table 1: Entry 8)**. Non-noble metal based catalysts Cu/TiO_2 and Co/CeO_2 gave about 31% and 21% selectivity of glucaric acid with less conversion **(Table 1: Entries 9 & 10)** [7].

The drawbacks of these catalysts are use of precious metal catalysts, high pressure reaction conditions, low yields and low selectivity of glucaric acid. The major drawback of chemical synthesis is formation of various side products such as tartonic acid, oxalic acid etc having similar properties which affects its selectivity and hence makes the process troublesome for separation of glucaric acid. Another disadvantage is use of high pressure reaction which requires use of high pressure vessels and safety issues always remain a priority. There still remains a challenge for researchers to develop an efficient catalytic method for selective synthesis of glucaric acid. Currently, gluconic acid is commercially produced from glucose fermentation by fungi, such as a niger too [8]. Microbial fermentation an another way for synthesis of glucaric acid also has several disadvantages such as long time required for fermentation process, low selectivity and also difficulty in separation of glucaric acid from other side products. Fermentation methods are generally not considered economical. Another way for synthesis of glucaric acid is electrochemical oxidation process. This process has advantages such as use of non-hazardous

Chemicals and also high pressure reaction conditions are not required. The selectivity of the product formed can also be controlled by electrode potential. It can be called as an environmentally friendly process but has limitations of scaling up. It can be used for smaller scale reaction but when it comes to manufacturing of glucaric acid on bulk scale, this method will have its limitations. Anodic oxidation of glucose is done using noble metals catalyst, but due to its high cost and scarcity, researchers focus more on using transition metal based catalyst for oxidation of glucose on anode [9]. For all the available ways known for oxidation of glucose to glucaric acid, all methods have their own limitations in terms of yield, selectivity, economical process, scale up etc. Further efforts are also required to produce glucaric acid directly from biomass. A simple, inexpensive, high yielding and highly selective green technology for synthesis of glucaric acid on commercial scale still remains an unsolved problem and is truly a challenge for researchers working in this field.

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