# Sustainable production of glucaric acid from corn stover via glucose oxidation: an assessment of homogeneous and heterogeneous catalytic oxidation production routes

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1    **Abstract**

2    Glucaric acid is being used increasingly as a food additive, corrosion inhibitor, in deicing, and in

3    detergents, and is also a potential starting material for the production of adipic acid, the key

4    monomer for nylon-66. This work describes a techno-economic analysis of a potential bio-based

5    process for the production of pure glucaric acid from corn stover (biomass). Two alternative

6    routes for oxidation of glucose to glucaric acid are considered: via heterogeneous catalytic

7    oxidation with air, and by homogeneous glucose oxidation using nitric acid. Techno-economic

8    and lifecycle assessments (TEA, LCA) are made for both oxidation routes and cover the entire

9    process from biomass to pure crystalline glucaric acid that can be used as a starting material for

10   the production of valuable chemicals. This is the first TEA of pure glucaric acid production

11   incorporating ion exchange and azeotropic evaporation below 50°C to avoid lactone formation.

12   The developed process models were simulated in Aspen Plus V9. The techno-economic

13   assessment shows that both production routes are economically viable leading to minimum

14   selling prices of glucaric acid of ~ \$2.53 /kg and ~ \$2.91 /kg for the heterogeneous catalytic

15   route and the homogeneous glucose oxidation route respectively. It is shown that the

16   heterogeneous catalytic oxidation route is capable of achieving a 22% lower environmental

17   impact than the homogeneous glucose oxidation route. Opportunities for further improvement in

18   sustainable glucaric acid production at industrial scale are identified and discussed.

19   **Keywords:**  sustainable, environmental, glucaric acid, techno-economic, oxidation.

20

## Introduction

Increased energy usage is leading to increasing greenhouse gas (GHG) emissions (EPA, 2017; Fischedick et al., 2014) largely due to a dependence upon fossil fuel-derived energy (IEA, 2008). Manufacturing including chemical manufacturing accounts for 24% of total GHG emissions (Brown et al., 2012). This has incentivized the development of energy-efficient technologies and processes based on the use of sustainable feedstocks in chemical manufacturing. Utilization of biomass as an alternative feedstock to hydrocarbons can be the basis of sustainable processes as long as it is non-competitive with food crops (Brown et al., 2012; Fernando et al., 2006). In recent years, the potential of biomass for use in the manufacturing of industrial chemicals has been widely explored (Biddy et al., 2016; Boussie et al., 2016; Bozell and Petersen, 2010; Han et al., 2014; Mussatto and Dragone, 2016; Sen et al., 2012; Van Duuren and Wittmann, 2014; Werpy and Petersen, 2004). Improvements in biomass pretreatment, saccharification technologies and processes for the fermentative/catalytic conversion of cellulosic feedstocks into desirable products pave the way for sustainable chemical production (Van Duuren and Wittmann, 2014). Glucaric acid (GA) is a value-added biomass-derived commodity chemical listed by the US-Department of Energy as one of the top value-added chemicals (Werpy and Petersen, 2004). GA and its derivatives find many applications in food, pharmaceutical and chemical industries (Walaszek, 1990; Walaszek et al., 1996) and recently it has been proposed as a key intermediate in the production of bio-derived adipic acid (Boussie et al., 2013).

GA occurs naturally in fruits and vegetables, and can also be produced synthetically from glucose via electrochemical, chemical, biochemical and chemocatalytic oxidation (Bin et al., 2014; Gupta et al., 2016; Lee et al., 2016). The oxidation of glucose with nitric acid is the main commercial route for GA production (Smith et al., 2012), which utilises mild temperatures (25-

40°C) and pressures (1-2 bar). Through base-neutralization, GA can be isolated as its calcium or potassium glucarate salts. However, the process suffers from low GA yields (45%) due to formation of many co-products including gluconic, 5-ketogluconic, tartaric and oxalic acids (Smith et al., 2012). An alternative approach is the heterogeneous catalytic selective oxidation of glucose. This occurs in a two-step process in which the first oxidation step to gluconic acid has been widely studied over a range of monometallic and bimetallic catalysts (Besson et al., 2014; Comotti et al., 2006; Miedziak et al., 2014). The most commonly used catalyst is Pt/C with various promoters, for example by Bi (Deller et al., 1992), which serve to mitigate deactivation and increase selectivity by suppressing the unwanted formation of 2-ketogluconic acid. The second oxidation step leading to GA formation is more difficult and consequently reports on direct catalytic oxidation of glucose to GA are relatively limited, although the production of GA is receiving increasing attention. For example, Jin et al., (Jin et al., 2015) recently reported a highly active $PtCu_3/TiO_2$ catalyst for oxidation of sodium gluconate to glucarate in strong base. In a commercial patent Rennovia claimed a process for production of adipic acid via oxidation of glucose to GA (Boussie et al., 2013). Examples of glucose oxidation in non-basic conditions (in acetic acid) over a range of Pt supported catalysts were reported with maximum GA yields of 57-60% (Boussie et al., 2013). The Rennovia patent also presented examples on adipic acid production via hydrodeoxygenation of GA in the presence of HBr.

A sustainable commercial GA production process can be based on glucose oxidation by either the heterogeneously catalyzed and nitric acid-mediated routes (Boussie et al., 2013; Smith et al., 2012). However, these generally produce GA as the potassium, sodium or calcium glucarate salts. The process patented by Rennovia yields GA in acetic acid which it was claimed can be used directly in hydrodeoxygenation (HDO) to adipic acid. To address product separation,

Rennovia have recently patented a process for GA recovery via ion exchange chromatography, with selective elution by organic acids such as formic or acetic acid (Diamond et al., 2016). Yuan et al. also reported solid phase extraction of GA from aqueous solution using polymeric ion exchange resin and non-ionic adsorbents (Yuan et al., 2017). However, while these reports describe promising methods for GA purification, they lack detailed experimental analyses on the recovered GA. Recently, Armstrong et al. reported a low temperature method for isolating pure GA from dilute aqueous $K^+$ or $Ca^+$ glucarate solutions (Armstrong et al., 2017), and presented the first powder X-ray diffraction pattern of crystalline GA (Armstrong et al., 2017). In this innovative approach, a two-step process is used whereby dilute glucarate salt solutions are contacted with amberlyst-15 ($H^+$) exchange resin followed by azeotropic evaporation at low temperature, thereby avoiding lactone formation, and yielding ultimately 99.9% pure crystalline GA. In principle, production of crystalline GA as an intermediate avoids the need for a fully integrated process from biomass to final end product (adipic acid) (Boussie et al., 2016) and can simplify the potential supply chains.

In this work we present techno-economic analysis (TEA) and life cycle analysis (LCA) for the production of GA from corn stover, which is an agricultural waste available in large quantity. Both the heterogeneous catalytic (Route 1) and homogeneous-$HNO_3$ (Route 2) glucose oxidation routes have been evaluated. The process models are integrated with a GA purification step based on ion exchange and low temperature azeotropic evaporation to avoid lactone formation. The GA ion exchange adsorption data reported by Yuan et al., has been used to model the ion exchange column with integration of the azeotropic evaporation method reported by Armstrong et al., to give a novel process (Yuan et al., 2017; Armstrong et al., 2017). The comparative assessment and sensitivity analysis for pure GA production via either glucose oxidation route presented here,

1 paves the way for an economical and sustainable route to synthesis of this commodity chemical

2 at an industrial scale.

**Materials and methods**

*An innovative approach towards producing renewable, pure GA*

5 Corn stover biomass is used as a starting material for the renewable production of glucaric

6 acid. The process flow model was developed for the two production routes proposed and, in both

7 routes, include detailed mass and energy balances for the entire process from corn stover to GA.

8 The process is designed to target production capacities suitable for use of GA as a commercial

9 product or by small scale industries, or for an adipic acid demonstration plant where glucaric

10 acid is the starting material. This is done by considering ~1/3$^{rd}$ capacity of the NREL bioethanol

11 model (Humbird et al., 2011). The ready availability of pure glucaric acid would encourage

12 development of further conversions into other important glucaric acid derivatives such as esters,

13 ketones and lactones which have pharmaceutical applications (Lampe et al., 2002; Walaszek,

14 1990; Walaszek et al., 1996).

15 The overall GA process flow model consists of stepwise processes, namely (i) biomass

16 pretreatment-cellulase-catalyzed enzymatic saccharification and (ii) oxidation of glucose to GA

17 followed by (iii) its purification and recovery. The general process scheme for glucaric acid

18 production from biomass-derived glucose is shown in Figure 1. A schematic process flow

19 diagram for corn stover conversion to glucaric acid is shown in Figure S.1 of the Supporting

20 Information section S.I. A separate process model has been developed for each of the alternative

21 oxidation routes. The model also considers wastewater treatment and utilities required for GA

22 production. The latter includes cooling water, steam and electricity generation, integrating the

combustor and boiler operations into the process flowsheet. All cost estimates are given in US dollars $ (USD).

The process flow model was designed and simulated in the process simulation software Aspen Plus V9. The composition of the corn stover biomass used as a feedstock to produce GA in both production routes is specified in Supporting Information section S.I, Table S.1. The physical and chemical properties of all components were assigned according to the Aspen Plus V9 database and property data developed by the National Renewable Energy Laboratory (NREL) for biochemical conversion of lignocellulosic biomass to ethanol (Humbird et al., 2011). For GA and potassium glucarate components, the physicochemical properties were estimated based upon their molecular structures. These properties are given in the Supporting Information Table S.2 (Vasiliu et al., 2011; Joback and Reid, 1987). The simulation of a designed process model was performed using a non-random two-liquid (NRTL) thermodynamic model with Henry's law for gaseous component.

The model was designed to process 12000 kg/hr of biomass-derived glucose in both production Routes 1 and 2, to produce GA as a commodity intermediate chemical. The process flow model was divided into 9 process areas by considering each of the steps shown in Table 1.

The overall schematic process flow diagram from corn stover to glucaric acid is shown in Figure S.2. The process model involving biomass conversion to glucose, i.e. from process area A100 to A300, was designed based on an earlier article by the current authors on caprolactone production from corn stover biomass (Thaore et al., 2018) and the National Renewable Energy Laboratory ethanol production model from biomass (Humbird et al., 2011). This involves biomass conversion to cellulose by steam and acid hydrolysis followed by enzymatic

saccharification into glucose. The detailed description of each reaction as well as conditions for process areas A100 to A300 are the same as those previously reported (Thaore et al., 2018); they are reproduced in Supporting Information Table S.3. After saccharification, one more step is included for concentration of sugar stream from 13 to 50% w/w using mechanical vapor recompression (MVR) evaporator and then glucose was separated from sugars mixture by considering component separator block. For this we referred to the NREL 2017 biochemical sugar model (NREL 2017 biochemical sugar model (BC1707A), 2017). On an industrial scale, glucose could be separated using a cation exchange resin from other sugar components such as xylose and arabinose present in lignocellulosic hydrolysates stream (Chen et al., 2018). Thus, in this process a sugar stream containing xylose and arabinose is generated as a byproduct.

***Glucose oxidation to GA***



Glucose                                      Glucaric acid
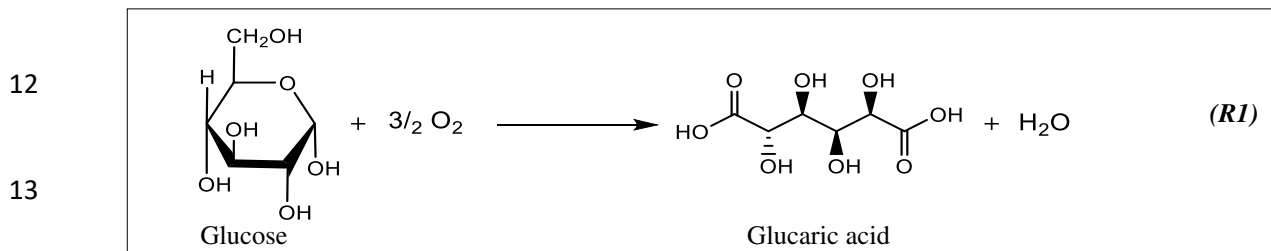
***Route 1:*** *Heterogeneous catalytic oxidation of glucose*

For the heterogeneous catalytic oxidation route, the process model was designed with 10% w/w glucose solution based on data taken from the Rennovia patent (Boussie et al., 2013), which reported heterogeneous glucose oxidation using air at pressures of 35-40 bar and temperatures of 80°C - 90°C achieving GA yields of 50-60%. A 5 wt% Pt/C catalyst has been considered for GA production based on the Rennovia patent (Boussie et al., 2013). Pt/C is a readily available commercial catalyst and its performance was reported to be amongst the best of the catalysts tested. In the present process model, glucose oxidation is represented by the reaction *R1* using the stoichiometric reactor model operating at 35 bar air pressure and a temperature of 80°C. A

GA yield of 60% has been assumed based on the experimental studies of Lee et al. (2016) and is also consistent with the reported yields in the Rennovia patent (Boussie et al., 2013) for similar catalysts. The amount of catalyst for the glucose oxidation step in Route 1 was estimated based on the reported productivity in Lee et al. (2016). The 5 wt% Pt/C catalyst initially charged corresponded to a glucose (in 1 hr): Pt molar ratio = 54 :1 or a glucaric acid productivity of 32.36 $mol_{GA} \cdot mol_{Pt}^{-1} \cdot h^{-1}$ in a continuous fixed-bed oxidation reactor. The industrial-scale Pt/C catalyst cost was conservatively assumed to be 50% of the Sigma Aldrich catalyst price (Sigma Aldrich: Platinum on carbon, 5 wt% loading, matrix activated carbon support, 2018). The catalyst amount was considered as the initial capital catalyst charge to process 12000 kg/hr of glucose.

*GA neutralization*

The oxidized mixture was neutralized by adding 45% KOH to maintain a stoichiometric ratio of 1.015:1 KOH: GA. The addition of base resulted in formation of GA's potassium salt (potassium glucarate). Following cooling to 30 °C, solid potassium glucarate was then separated using a solid-liquid separator. The separated liquid solution, which contained un-reacted glucose, was sent to the anaerobic digester for generation of biogas.

***Route 2:*** *Homogeneous oxidation of glucose using nitric acid reagent*

Route 2 was based on the controlled nitric acid oxidation of glucose to GA as reported by Smith et al (Smith et al., 2012). They used 62.3 wt% glucose at a 3:1 molar ratio nitric acid: glucose and performed the reaction at the relatively low temperature of 25-40 °C and maintained a reactor pressure of 0.25-0.5 barg with air as the oxidizing agent (Smith et al., 2012). Under these conditions Smith et al. reported 40-45% yield of GA (Smith et al., 2012). Therefore, similar conditions have been used in the present process model. Similar to reaction condition used by Smith et al, here 62.3 wt% glucose solution was maintained for nitric acid oxidation by

diluting glucose stream. The concentrated glucose solution was then oxidized to GA using 70% w/w nitric acid. The stoichiometric reactor model was used based on reaction R1 for the oxidation process operating at 2 bar air pressure and at 40°C with addition of 70% w/w nitric acid to maintain the 3:1 molar ratio of nitric acid: glucose.

*Neutralization of the oxidized mixture*

Neutralization of the glucose oxidation product mixture with KOH resulted in formation of monopotassium glucarate and potassium nitrate. Smith et al. have proposed nanofiltration and diffusion dialysis for nitric acid removal (Smith et al., 2012). It allows separation of inorganic nitrate from salts of oxidation products by passing the neutralized mixture through a nanofiltration membrane. However, in general dilute product streams (%w/w) are favored when using nanofiltration membranes. Hence, to achieve salt separation at an industrial scale, the product streams would require significant dilution with water prior to nanofiltration. Energy intensive unit operations such as evaporation or distillation are then required in isolating monopotassium glucarate. Smith et al. have also proposed the use of diffusion dialysis (DD) prior to the neutralization step (Smith et al., 2012). This would separate inorganic and organic acids. The advantage of DD over nanofiltration is that it allows for processing of low pH streams containing high nitric acid concentrations. Therefore, DD would circumvent the need for an additional dilution step if operated on an industrial scale.

In the present process model, nitric acid was separated prior to the neutralization step by employing a component separator block to represent the DD step in the process flowsheet. Thus, the spent nitric acid was recycled back to the oxidation reactor, thereby reducing the nitric acid consumption rate. Then, neutralization of the glucose oxidation mixture was performed in a similar way to that explained in Route 1 through the addition of 45 % KOH (1.015:1 molar ratio

of KOH: glucose). Solid potassium glucarate was separated from the unreacted glucose solution and then passed to the next step of GA purification, whilst the unreacted glucose solution was sent to anaerobic digester in A600 for generation of biogas.

*GA purification*

Armstrong et al. have described a procedure to obtain the pure solid form of free- GA (Armstrong et al., 2017). The first step is to contact the glucarate solution with amberlyst-15 ion exchange resin followed by water washing. Contacting the potassium glucarate solution with amberlyst-15 ion exchange resin leads to > 99% exchange of $K^+$ for $H^+$. After ion-exchange, GA can be recovered in powder form from the water washing by evaporation. However, during evaporation of water, even at a reduced pressure of 50 mbar and a temperature 50°C, extensive lactonization of GA can occur as demonstrated in the detailed NMR study (Armstrong et al., 2017). With increase in temperature, GA has the tendency to form D-glucaro-1,4:6,3-dilactone, and in acidic medium it lactonizes more rapidly to D-glucaro-1,4-lactone (Brown et al., 2007). Lactonization can be avoided using azeotropic evaporation at low temperature < 28 °C for glucaric acid recovery (Armstrong et al., 2017). In the present process, the azeotrope of GA-water wash with acetonitrile (95:5) is formed and then evaporated at a reduced pressure of 50 mbar and low temperature (22°C) to yield solid white GA with high purity (99.96%) and yield (98%).

The 10 wt% aqueous monopotassium glucarate solution obtained from the neutralization step was used for the ion exchange chromatographic purification. In our process model, the adsorption column was designed based on adsorption parameters reported by Yuan et al. for solid phase extraction of GA (Yuan et al., 2017). Simulation of the fixed bed adsorption column including pore diffusion model kinetics and Langmuir adsorption model (Supporting Information

S.II) was performed in the gPROMS process modelling platform for an adsorption column of 4 m length and 1 m diameter. A detailed simulation of the GA concentration profile with respect to bed height is shown in Figure S.3. The resin column parameters were also evaluated based on the Amberlyst-15 resin capacity provided by the resin manufacturer, Supporting Information section S.II. There was no significant difference in column design parameters from the column designed using the adsorption kinetic data of Yuan et al, 2017.

The GA-water-acetonitrile azeotrope is evaporated in a series of distillation columns at a reduced pressure of 50 mbar and 15 mbar to obtain pure solid GA with >97% purity. Table 2 gives the make-up amounts of acetonitrile required for this GA recovery step (for Route 1 and 2).

*Wastewater treatment-A600*

In Route 1, the combined streams of steam condensate from A800 and cooling water were treated in aerobic and anaerobic digesters, generating biogas. Route 2 generated an additional wastewater (WWT) stream as evaporate condensate from process area A400 which was combined with the steam condensate from A800 combine and with cooling water prior to treatment in this area. The water stream was recycled to the process water distribution area A900, whilst the remaining sludge stream containing solids, unconverted cellulose, hemicellulose, lignin and spent enzymes were sent to the combustor area (A800).

*Storage-A700*

The raw materials: ammonia, sulphuric acid, nitric acid, 45% KOH, and acetonitrile required for GA production, are shown in this section and their make-up amounts are given in Table 2.

*Combustor, Boiler and turbo-generator-A800*

The solid waste stream generated from cellulose saccharification, containing spent cellulase enzyme and unconverted cellulose combined with solid waste from A600, are combusted in this area producing steam and electricity. The biogas generated in A600 and pure methane serve as fuel for the combustor.

*Process water and utilities-A900*

This area represents the process water distribution required in various processes and also the cooling water, chilled water utilities distribution for distillation columns and many other operations. The net amount of electricity, i.e. in terms of net workload for each process area, was also tracked in this process area.

**Results and discussion**

As noted above, the process model was designed to process 12000 kg/hr of glucose derived from corn stover into GA in the each of two production routes (heterogeneous catalysis and homogeneous nitric acid oxidation). In both routes a total of 42.4 tonne/hr (20% moisture) of biomass was required to produce 12000 kg/hr of glucose. Production Route 1, heterogeneous selective catalytic oxidation using a commercial Pt/C catalyst, produced 8000 kg/hr of GA. In Route 2, 6086 kg/hr of GA was obtained by homogeneous glucose oxidation with nitric acid. During biomass pretreatment, 40% of all sugars was produced as a by-product at rates of 38000 kg/hr and is the same for both Route 1 and Route 2. The rate at which raw materials, solvents and reactants are required by these processes, complete with respective costs in USD $, are given in Table 2. The unitary costs of each input stream are presented in Supporting Information section S.III, Table S.5.

It should be noted that the data presented on the input streams of both production routes, especially solvent and the reagent-HNO$_3$, are the make-up amounts required in the GA production process model. Recycling of 98% of solvent and HNO$_3$ back into the process has been assumed.

*Financial analysis*

The equipment cost for GA production involving biomass handling (A100), pretreatment (A200) and glucose production (A300) along with that required for wastewater treatment (A600), boiler/steam generator (A800) and utilities (A900) was estimated using the NREL equipment list (Humbird et al., 2011). This equipment list was further updated based on the required equipment size and the CEPCI cost index for 2017 (CEPCI, 2017). The bottom-up approach proposed by Peters et al was used in determining the cost of equipment for the GA production area (A400) and purification process area (A500) (Peters et al., 2003). Table 3 shows the total installed cost of equipment for the bio-based production of GA in both routes.

In Route 1, 240 kg of Pt (4800 kg of 5wt% Pt/C catalyst) was loaded for oxidation of 12000 kg/hr of glucose (Glucose (in 1 hr): Pt molar ratio=54). Two reactors have been included: one for the continuous glucose oxidation reaction, the other for catalyst regeneration, which is assumed to be by a washing process. The conversion reactor contains 4.8 tonne of catalyst and the total initial outlay on the catalyst was estimated at $50.43 million, assuming the cost of the 5 wt% Pt/C catalyst is 50% of the Sigma Aldrich price. Based on the simulation results for the purification process, 8 ion exchange columns were required to adsorb 9555 kg/hr of K-glucarate in Route 1: 4 for both the adsorption and resin regeneration processes each having a length of 4 m and a diameter of 1m. Whereas in Route 2, 6 columns of the same dimensions are required (3 for adsorption and 3 in regeneration) for adsorption of 7279 kg/hr of K-glucarate. A total of

1    26875 kg of ion exchange resin (IER) was loaded into columns for Route 1 and 20625 kg for

2    Route 2. The outlay on catalyst and IER represents an initial capital cost. Thus, these values were

3    considered in the total capital investment (TCI). Financial analyses for Routes 1 and 2 are given

4    in Table 4. These represent the total capital investment (TCI) based on the total cost of installed

5    equipment, total direct cost (TDC), total indirect cost (TIC) and fixed capital investment (FCI).

6    The total capital investments are estimated to be $320 million for Route 1 and $270 million for

7    Route 2 for processing 42.4 tonne/hr of corn stover into high purity solid GA.

8        The total annual production costs of these two routes were evaluated taking into account both

9    fixed and variable operating costs. Estimated costs for consumables, feedstock, utilities and

10    electricity for Routes 1 and 2 are given in Table 5. Additionally, both processes operate a net

11    electricity surplus owing to the boiler/steam generator A800: 1.2 MW in Route 1 and 7.5 MW in

12    Route 2 (Table 3). This could be sold to the national grid. Based on this evaluation, the total

13    production cost was estimated as $70.27 million/year to produce 67.20 million kg/year GA via

14    Route 1 and $64.17 million /year for 51.12 million kg/year output via Route 2. Based on these

15    estimates, whilst there is a demonstrable difference in total capital investment required for

16    Routes 1 and 2, the total production costs are of the same order. The discounted cash flow

17    analysis method was used to determine a minimum selling price for GA by equating the net

18    present value to zero at the end of 20 years (Peters et al., 2003). Table S.6 summarises the

19    discounted cash flow analysis parameters for the new glucaric acid production plant. With an

20    assumption of constant 35% income tax rate, higher project contingency 40% for the new plant

21    and 6 years of capital depreciation with a safe acceptable investment by considering the

22    minimum acceptable annual rate of return (MARR) of 15%, the minimum selling price of GA

23    was estimated to be $2.53/kg by Route 1 and $2.91/kg by Route 2. According to a recent market

research report, the global GA market demand for 2016 was estimated at $550.4 million with key applications as detergents, food ingredients, corrosion inhibitors and de-icing chemicals (Glucaric Acid Market Analysis, 2017; Gupta et al., 2016; Walaszek, 1990; Walaszek et al., 1996). The minimum selling price of GA was estimated to be 1.8 $/kg when sugarcane-derived sugar (Sugar Price, 2019) was used as starting material. This 30% reduction in cost is due to elimination of pre-processing cost involved in the conversion of corn stover biomass into glucose. In February 2017, Johnson Matthey and Rennovia jointly announced the renewable production of glucaric acid by heterogeneously catalyzed glucose oxidation (Johnson Matthey R&D News, 2017; Rennovia Press Release, 2015). Unfortunately, there is currently no available benchmark- market data as to the minimum selling price of high purity solid GA.

A higher GA yield (60 %) has been assumed for catalytic glucose oxidation based on the Rennovia patent (Boussie et al., 2013) (Route 1) than for nitric acid-mediated oxidation (45%) (Smith et al., 2012), Route 2. This results in GA–production yields of *ca* 188 kg/tonne of corn stover biomass in Route 1, and 143 kg/tonne in Route 2. Both production routes are economically viable based on the assumptions made here. However, there remain significant challenges especially in the conversion of glucose to GA and in GA separation, which may hamper commercial application. For instance, Route 1 utilizes an expensive Pt catalyst, where improvements in performance would have a significant impact. Route 2 uses nitric acid, which although a very low-cost reagent, is highly corrosive thereby increasing operational risk and consequently both operating costs and capital investment. Also, due to the highly exothermic nature of Route 2, GA production requires efficient heat removal and temperature control to perform the reaction at a 3:1 molar ratio of nitric acid to glucose. Also, the additional capital and operating costs associated with the nitric acid removal step.

The process model could be improved by implementing a purification step for the GA salt obtained from the neutralization step. In both Routes 1 and 2 conversion of glucose was assumed to be to GA only. However, with proper experimental analysis of the glucose oxidation mixture, both quantitative and qualitative, the model could be further refined. Low temperature, stepwise crystallization would be desirable to separate GA salts from the salts of other product components: for example, the salts of other acid products formed in Route 1 and 2.

One of the problems of using precious metal catalysts is leaching of the metal leading to deactivation. Glucose and its acids have chelating properties which can enhance leaching. Carrying out the catalytic oxidation at a controlled high pH by addition of base could reduce leaching significantly and suppress lactone formation (Boussie et al., 2013). Operating the oxidation reactor in this mode would eliminate the unit operation of neutralisation after the glucose oxidation step in Route 1. It would therefore make little change to the estimated MSP of GA.

The impact of uncertainties in the various assumptions is considered further in the sensitivity analysis below

*Environmental analysis: Water balance and $CO_2$ balance*

The LCA of both routes evaluates the environmental impact of GA production by estimating the total $CO_2$ emissions and water mass balance of each process. Based on the $CO_2$ eq emission factor of the input streams (Supporting Information section S.III, Table S.7), GHG emissions were estimated for Route 1 and Route 2 (Table S.8). Figure 2 shows the total estimated $CO_2$ equivalent emissions for Routes 1 and 2 to be 1675 kg/tonne GA and 2150 kg/tonne GA respectively. Route 2 shows 28 % higher $CO_2$ emissions, generated from the nitric acid reagent

used in oxidising glucose. In Route 1, 48% of total emitted $CO_2$ came from the potassium hydroxide used in neutralizing GA. In Route 2, potassium hydroxide (37%) and nitric acid (10%) accounted for major $CO_2$ emissions. The other input streams also contributed to the total $CO_2$ emissions, specifically, corn stover biomass feed (20% in Route 1 and Route 2), ammonia used in the neutralization step (14% in Route 1 and Route 2) and the cellulase enzyme used in saccharification (14% in Route 1 and Route 2). $CO_2$ emissions from the biomass feed could, however, be utilized during biomass growth stage, making this a net $CO_2$ sink (negative $CO_2$ contribution). To mitigate $CO_2$ emissions for the enzyme usage, alternative non-enzymatic cellulose hydrolysis methods could be applied (Luterbacher et al., 2014). To achieve reductions in $CO_2$ emissions resulting from use of ammonia in pretreating the biomass would require development of new technologies. Application of novel technologies such as ionic-liquid assisted processes could eliminate ammonia from the biomass pretreatment stage and consequently reduce associated $CO_2$ emissions. However, due to a lack of comparative assessment of $CO_2$ emissions from ionic liquid and acid hydrolysis processes, the use of ammonia cannot be avoided at this stage.

An environmental assessment was also conducted based on water resources required by production Routes 1 and 2. The water mass balance of input/output streams for process areas A100 to A500 are presented in Table 6 (a). The overall water balance for GA production is presented separately in Table 6 (b). Significant water loss was observed due to evaporation from cooling towers but not from the biomass to GA conversion steps. Thus, improvements in the heat exchanger network and energy integration could reduce the cooling water requirement and consequently water loss. The cooling utility distribution for the GA production plant was estimated as total 64 MW for both production routes (Table 7). Water could also be recovered

from the dilute sugar stream (48 wt%) generated as a co-product in both production routes; 38700 kg/hr in Route 1 and Route 2. However, the dilute sugar stream could itself serve as the byproduct stream. The total water required for the process was estimated as 250 tonne/hr and 156 tonne/hr for Routes 1 and 2 respectively. Of this, cooling tower water make-up constitutes 35 % of the water required in Route 1 and 56 % in Route 2.

*Life cycle analysis on electricity generation*

For electricity generation, as described earlier, the solid waste stream generated from cellulose saccharification, biogas generated from aerobic and anaerobic digesters, and supplemental natural gas were combusted for electricity generation. As shown in Table 3, about 95% of the electricity generated by the boiler in Area 800 is used throughout the plant in Route 1 and 75% in Route 2. The surplus electricity is sold to the grid for credit. This is reflected in the economics by an operating cost credit equal to this amount of electricity in Table 3. Total $CO_2$ eq emissions is evaluated based on supplemental natural gas consumption rate in Area 800. Here, the equivalence difference between $CO_2$ biomass combustion emissions and $CO_2$ absorption during growth of plants was considered as it is commonly accepted. Minimum selling price of GA and total $CO_2$ emission were estimated without the use of natural gas and then purchasing the required net electricity for the plant. This resulted decrease in operating cost and therefore minimum selling price of glucaric acid decreased by 5 % in route 1 and route 2 and with decrease in total $CO_2eq$ emissions also by 3 % in both production routes 1 and 2. However, total $CO_2eq$ emission for electricity purchased could not be accounted and thus for accurate estimation of $CO_2eq$ emission use of supplemental natural gas along with combustion of solid biomass fractions were considered in electricity generation.

*Sensitivity analysis for sustainable production of GA*

A sensitivity analysis has been performed to determine the economic and environmental sustainability of manufacturing bio-based GA via both production routes with consideration of the effect of key economic and operational parameters. This was done by varying one parameter at a time and estimation of the effect on the minimum selling price of glucaric acid. The considered variation in parameters from the base case condition are given in Table 8. For both Route 1 and Route 2, the effect of project contingency, income tax rate, fixed capital investment, feedstock cost and recyclability of acetonitrile solvent on the minimum selling price of GA are shown in Figure 3 (a) and (b), respectively. With increase in feedstock cost from 88 $/tonne to 97 $/tonne, the minimum selling price of GA increases by 2.46 % in Route1 and 2.0 % in Route 2. Whereas, an increase in the fixed capital investment by 30%, causes the minimum selling price of GA to increase by 14 % in Route 1 and 2. With 5% decrease in recyclability of acetonitrile solvent, the minimum selling price of GA increases by 17% in Route 1 and 10% in Route 2. Further detailed investigation of highly uncertain parameters is discussed below which affect the economic and environmental viability of both routes.

i)      *Heterogeneous Catalyst deactivation and Pt/C catalyst cost*

The heterogeneous and homogeneous oxidation routes appear to be competitive in terms of overall GA yield and selling price. For both routes, the glucose oxidation step has a significant impact on the techno-economic and life cycle assessment of bio-derived GA. In Route 1, the activity and robustness of the supported platinum catalyst is a key consideration in the glucose oxidation step (Boussie et al., 2013; Lee et al., 2016; Wenkin et al., 1997a). At industrial scale, one of the major problems related to heterogeneous catalysis is loss of catalyst activity with time on stream. A number of studies have reported aerobic glucose oxidation using supported

precious metal catalysts in combination with co-catalysts such as Bi, Sn and Te, which can prevent oxidative deactivation of the noble metal (Abbadi and van Bekkum, 1995; Dirkx et al., 1977; Jin et al., 2015; Shaner et al., 2016; Sheldon and van Bekkum, 2007; Wenkin et al., 1997b, 1996). Other issues such as leaching of the precious metal component can also impact on catalyst lifetime. Catalyst deactivation can also result from the co-products such as HMF and furfural formed during saccharification of the corn stover. Recent papers by Derrien et al. have demonstrated that the presence of furanic compounds in the feed strongly reduces the catalytic glucose oxidation reaction rate (Derrien et al., 2017, 2016). Thus, a sensitivity analysis has been performed on the minimum selling price of the GA by consideration of major uncertainty parameters such as a decrease in GA yield due to catalyst deactivation.

A 5% decrease in GA yield/annum relative to the base case 60% yield has been investigated. To maintain catalyst activity, regeneration of the catalyst could be performed by a thermal regeneration processes using water with the resultant wastewater stream being treated in the WWT plant in A600. Nevertheless, in the current process model the catalyst regeneration step was not defined as more experimental data is required on suitable regeneration procedures. Figure 3(a) shows that with a decrease in GA yield from 60% to 55%, the minimum selling price of GA increases by 7%. The cost of the Pt/C catalyst also significantly affects the minimum selling price of GA. Assuming a change in discount % of the catalyst price, changes the total cost of the Pt/C catalyst. For example, by decreasing the cost from 5237 $/kg to 2619 $/kg, the minimum selling price of GA decreases by 4%. This preliminary analysis shows that fixed capital investment including catalyst cost is the most significant variable with the potential to significantly affect the economic performance of Route 1 at industrial scale. Given the abundant availability of biomass and a Pt/C catalyst with a reasonably high operating stability and a cost

appropriate for bulk quantity, Route 1 could be applicable for the large-scale production of GA. However, for more accurate TEA analysis, further studies of catalytic glucose oxidation with the real feedstock are required.

## *ii)      C$_5$ sugars as by-product*

In lignocellulosic biomass conversion, a mixture of sugars stream, ~38000 kg/hr, is generated in both routes considered here. This is one of the main by-products of the present process which was not assigned any economic value in estimating MSP of GA. Direct selling of this stream to market or valorisation by conversion into high value chemicals would further improve the overall process economics. Figure 3 (a) and (b) shows with change in the market selling price of sugars mixture from 0.1 $/kg to 0.2 $/kg, minimum selling price of GA varies from 2 $/kg to 1.5 $/kg in Route 1 and 2.2 to 1.6 $/kg in route 2, respectively.

## *iii) Recovery of nitric acid reagent*

In Route 2, the use of inexpensive high strength nitric acid reagent requires effective temperature control of the glucose oxidation process. Smith et al. have reported nitric acid oxidation performed at a milder reaction temperature (40°C) and pressure (2 bar) and also proposed downstream methods for removal of nitric acid after oxidation (Smith et al., 2012). In our model we assumed that 98% $HNO_3$ is recycled back to the reactor. It was observed that a slight variation in $HNO_3$ recyclability could affect the required $HNO_3$ make-up and consequently the total $CO_2$ emissions of the process. The sensitivity analysis shown in Figure 4 indicated 11 % increase in the $CO_2$ emissions, i.e. from 2150 kg $CO_2$eq to 2378 kg $CO_2$eq per tonne of GA, when the $HNO_3$ recyclability was reduced by 3% from 98% to 95%. With a further 5% reduction in $HNO_3$ recyclability, the $CO_2$ emissions increased by 31%, reaching 2824 kg $CO_2$ eq/tonne of

GA. Thus, efficient unit operations in nitric acid recovery are a key consideration for scale up of Route 2.

One of the advantages of glucose oxidation using heterogeneous catalysis in the presence of base that it could reduce leaching of precious metal catalyst and the separation of other salts by employing a simple crystallisation step. Additionally, it would reduce the unit operation of neutralisation after the glucose oxidation step. These findings recommend glucose oxidation as a significant important step to decide the overall sustainability of bio-based GA production. Therefore, we need either a selective glucose oxidation process restricting formation of GA only or the potential method for the separation of by-products generated during glucose oxidation.

*General remarks*

The current investigation shows that both production routes, heterogeneous oxidation (Route 1) and homogeneous oxidation (Route 2), have the potential to produce GA from biomass such as corn stover at large scale. The pure GA obtained in this process model could serve as the feedstock for synthesis of adipic acid and a range of other products. However, it is necessary to perform systematic TEA and LCA studies of these additional processes before translating the laboratory scale process to industrial scale. The production scale also dictates potential applications for the highly pure GA produced and thereby which of Routes 1 or 2 are more favorable. Route 2 is favored at a small scale due to ready availability of $HNO_3$ and relatively efficient temperature control. In this way Route 2 would be preferable for synthesis of GA for use in detergents or for application such as an alternative to toxic-phosphorous based corrosion inhibitors. The large scale of global demand for adipic acid would necessitate large volumes of GA under which circumstances catalytic glucose oxidation via Route 1 would be favored.

This study shows the comparative assessment of these two routes whilst also integrating GA purification into the process model. The formation of pure GA as a dry, crystalline solid could reduce product transportation costs and potentially extend its shelf life. Further decreases in transportation costs and $CO_2$ emissions could also be achieved by locating GA production in close proximity to the biomass feedstock source. In contrast, in manufacturing adipic acid from GA via hydrodeoxygenation (HDO), it may be more economical to situate the hydrogenation plant close to the hydrogen source. This approach would affect the overall supply chain of adipic acid production. Indeed, continuously supplying hydrogen to the HDO process would circumvent the costs related to large scale hydrogen storage, whilst also reducing the associated supply chain $CO_2$ emissions. Well considered sourcing of the input hydrogen stream could also lead to significant improvements in economic and environmental aspects of the process. In this paper, we have reported TEA and LCA analyses for GA production. In the future, it would be beneficial to carry out a combined study which also integrates the production and distribution of hydrogen into a flowsheet for large scale production of commodity chemicals in an economically and environmentally benign manner.

**Conclusion**

The production of pure, crystalline GA from corn stover, which is an abundant and cheap source of biomass, has been investigated. Two routes for oxidation of glucose have been evaluated and compared: via either nitric acid or catalytic glucose oxidation. TEA and LCA assessments of the designed processes demonstrate the suitability of both in producing GA on a commercial scale. Based on ion-exchange adsorptive separation and azeotropic evaporation, 98 % pure GA was recovered in solid form. TEA analysis shows due to higher GA yield in heterogeneously catalyzed aerobic glucose oxidation of *ca.* 183 kg/tonne of biomass is

economically and environmentally more sustainable route to GA production than nitric acid-mediated glucose oxidation, as the latter incurs high GHG emissions associated with nitric acid production. Both routes could be developed for commercial production of GA. However, the commercial viability would be improved by valorization of the by-product streams, for example utilization of the waste sugars from enzyme hydrolysis, and the efficient separation of the glucarate salt from the by-product salts. For the catalytic oxidation route, a stable catalyst preferably with improved yield of glucaric acid remains a key issue. For homogeneous glucose oxidation, nitric acid recovery needs to be addressed to make a more environmentally friendly process. The promising GA production routes investigated here could be further extended to consider downstream manufacturing of either small scale products such as pharmaceuticals or large-scale commodity chemicals such as adipic acid.

**Supporting Information**: Additional information as noted in text is available in Supporting Information.

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**List of Tables**

**Figure Captions**

1

**Table 1:** Process areas in glucaric acid production process model (ASPEN process flowsheet)

| Process Area | Description |
|---|---|
| **A100** | Feedstock handling |
| **A200** | Pretreatment with steam and sulphuric acid |
| **A300** | Enzymatic Cellulose saccharification |
| **A400** | Glucose oxidation |
| **A500** | Glucaric acid purification<br>(a) Solid phase extraction of glucaric acid: K-glucarate adsorption<br>(b) Purification of glucaric acid by azeotropic evaporation |
| **A600** | Wastewater treatment and Biogas generation in anaerobic and aerobic digester |
| **A700** | Storage of raw material and solvent |
| **A800** | Combustor |
| **A810** | Steam and electricity generation |
| **A900** | Process utilities and process plant water distribution |

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**Table 2:** Input streams material balance for glucaric acid production routes

| Input stream | Production Route 1 Pt/C-air | | Production Route 2 $HNO_3$ | |
| --- | --- | --- | --- | --- |
| | Rate (tonne/hr) or (GJ/hr) | Cost US \$/hr | Rate (tonne/hr) or (GJ/hr) | Cost US \$/hr |
| Biomass | 42.44 | 2994 | 42.44 | 2994 |
| $H_2SO_4$ | 0.81 | 60 | 0.81 | 60 |
| $NH_3$ | 0.82 | 526 | 0.82 | 526 |
| Cellulase | 0.24 | 775 | 0.24 | 775 |
| $HNO_3$ | 0.00 | 0 | 0.44 | 126 |
| 45% KOH | 5.01 | 1824 | 3.76 | 1368 |
| make-up Acetonitrile | 0.11 | 179 | 0.09 | 137 |
| Water | 124 | 34.22 | 120 | 32.9 |
| Natural gas (energy basis) | 194.13 | 1437 | 194.13 | 1437 |

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**Table 3:** The equipment cost and electricity required by each process area in the glucaric acid

production process model

| | Production Route 1 | | Production Route 2 | |
|---|---|---|---|---|
| **Process Area** | **Total Installed equipment cost (million US $)** | **Power required in MW** | **Total Installed equipment cost (million US $)** | **Power required in MW** |
| A100 | 15.43 | 0.35 | 15.45 | 0.350 |
| A200 | 20.63 | 2.71 | 20.63 | 3.08 |
| A300 | 25.27 | 5.4 | 25.27 | 3.93 |
| A400 A500 | 9.13 | 15.23 | 7.42 | 12 |
| A600 | 7.91 | 0.706 | 7.81 | 0.68 |
| A700 | 6.14 | 0.029 | 5.97 | 0.027 |
| A800 | 50.89 | 0.82 | 52.86 | 0.86 |
| A900 | 4.33 | 2.013 | 4.3 | 2.07 |
| **Total equipment cost** | **124.30** | | **124.35** | |
| **Total Power generated (MW)** | **-28.18** | | **-30.158** | |
| Surplus Electricity generated (MW) | -1.2 | | -7.55 | |

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2    **Table 4:** Total capital investment for bio-based glucaric acid production processes

| Item | Production Route 1 Cost (in million US $) | Production Route 2 Cost (in million US $) |
|---|---|---|
| **Total installed cost of equipment** | **124.30** | **124.35** |
| Warehouse (4 % of ISBL) | 2.20 | 2.13 |
| site development (9% of ISBL) | 4.95 | 4.80 |
| Additional piping (4.5% ISBL) | 2.48 | 2.40 |
| **Total direct cost (TDC)** | **133.93** | **133.68** |
| Prorateable expenses (10% of TDC) | 13.40 | 13.37 |
| Field expenses (10% of TDC) | 13.40 | 13.37 |
| Home office and construction fee (20% of TDC) | 26.79 | 26.74 |
| Project contingency (40% of TDC) | 53.57 | 53.47 |
| Other costs (10% of TDC) | 13.19 | 13.37 |
| **Total Indirect Cost (TIC)** | 120.57 | 120.31 |
| **Fixed Capital Investment (FCI)** | **254.46** | **254.05** |
| Land | 2.70 | 2.70 |
| working capital (5% FCI) | 12.72 | 12.70 |
| Catalyst-oxidation | 50.43 | - |
| Ion exchange Resin | 0.07 | 0.05 |
| **Total Capital investment (TCI)** | **320.40** | **270** |

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**Table 5:** Total production cost estimated for glucaric acid production process model

| Cost | Production Route 1 value in million US $/yr | Production Route 2 value in million US $/yr |
|---|---|---|
| Utilities | 12.36 | 12.35 |
| Consumables | 28.25 | 25.12 |
| Feedstock | 25.15 | 25.15 |
| Grid +A100 Electricity | -0.62 | -3.61 |
| **Variable operating cost** | **65.15** | **59.01** |
| Maintenance (3% ISBL) | 1.38 | 1.60 |
| Insurance (0.7% FCI) | 1.78 | 1.78 |
| Labor | 1.95 | 1.77 |
| **Fixed operating cost** | 5.11 | 5.15 |
| **Total Product Cost** | 70.26 | 64.16 |

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2 **Table 6(a):** Water balance for glucaric acid production processes

| | Production route 1 | Production route 2 |
|---|---|---|
| **Input streams** | $H_2O$ | $H_2O$ |
| | **Rate (tonne/hr)** | **Rate (tonne/hr)** |
| Biomass | 8.49 | 8.47 |
| $H_2SO_4$ | 0.06 | 0.06 |
| Enzyme | 0.94 | 0.95 |
| KOH | 2.75 | 2.07 |
| $HNO_3$ | - | 5.40 |
| Dilution | 342 | 230.7 |
| Steam | 10.12 | 15.94 |
| Water generated-in A300 | 0.74 | 0.55 |
| **Total** | **364.4** | **264.15** |

| *Table 6(a) continued..* | **Production route 1** | **Production route 2** |
|---|---|---|
| **Output** | **Rate (tonne/hr)** | **Rate (tonne/hr)** |
| | $H_2O$ | $H_2O$ |
| Vent | 12.58 | 9.13 |
| WWT | 196 | 210 |
| Water consumed during enzyme hydrolysis and A300 | 2.56 | 1.13+1.43 |
| Product stream-sugar | 22.54 | 21.97 |
| WWT | - | 6.54 |
| Other Product streams | 130.95 | 14.17 |
| **Total** | **364.4** | **264.14** |

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3 **Table 6(b):** Overall water balances for glucaric acid production plants

| Input | Rate (tonne/hr) $H_2O$ | Rate (tonne/hr) $H_2O$ |
|---|---|---|
| Biomass | 8.74 | 8.49 |
| $H_2SO_4$ | 0.04 | 0.06 |
| Enzyme | 0.94 | 0.95 |
| KOH | 2.75 | 2.07 |
| $HNO_3$ | - | 5.40 |
| Water generated-in A300 | 0.74 | 0.55 |
| WWT air intake | 0.16 | 0.16 |
| CIP water | 0.15 | 0.07 |
| Combustion air intake | 2.15 | 3.44 |
| Water generated in combustor | 17.63 | 18.87 |
| water make up | 127 | 27.91 |
| Cooling tower water make up | 88.98 | 88.74 |
| **Total** | **249** | **156.71** |

*Table 6(b) continued..*

| Output | Rate (tonne/hr) $H_2O$ | Rate (tonne/hr) $H_2O$ |
|---|---|---|
| Sugars product stream | 22.54 | 21.98 |
| other Product streams | 111.15 | 15.96 |
| Vent | 0.218 | 0.240 |
| water from the combustor stack | 30.49 | 32.97 |
| boiler blowdown vent | 1.35 | 1.43 |
| Water consume in A600 and A810 | 2.42 | 2.63 |
| water consumption in enzyme hydrolysis and A300 | 2.56 | 1.4+1.1 |
| water evaporated from cooling tower | 78.89 | 78.68 |
| **Total** | **249.62** | **156.40** |

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3    **Table 7:** Cooling utility distribution for glucaric acid production plants

| Cooling water usage for Process area | Route 1 MW | Route 2 MW |
|---|---|---|
| A200 | 4.34 | 4.65 |
| A300 | 6.32 | 6.30 |
| GA purification | -7.50 | -8.24 |
| A800 | 54 | 54.22 |
| Evaporator condensation | 7.50 | 7.50 |
| **Total cooling utility** | **64.59** | **64.42** |

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2 **Table 8:** The base case values for Route 1 and Route 2 used for the estimation of minimum

3      selling price of pure glucaric acid

| Parameters | Base case value | Units |
|---|---|---|
| Corn stover biomass cost (79:88:97) | 88 | $/tonne |
| Pt/C catalyst cost (10%: 50%: 75%) | 5237[#] | $/kg |
| GA yield (55: 60 %) | 60[#] | % |
| Acetonitrile recycling (95: 99%) | 99 | % |
| Project contingency (10%:40%) | 40 | % |
| Fixed capital investment (± 30%) | 254 | M $ |
| Income tax rate (25% :35%) | 35 | % |
| By-product Sugars cost (0: 0.2) | 0 | $/kg |

*# For production Route 2, GA yield = 45% using nitric acid reagent for glucose oxidation*

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**Production Route 1:** Biomass to glucaric acid via heterogeneous catalysed glucose oxidation

**Production Route 2:** Biomass to glucaric acid via Homogeneous glucose oxidation using nitric acid reagent
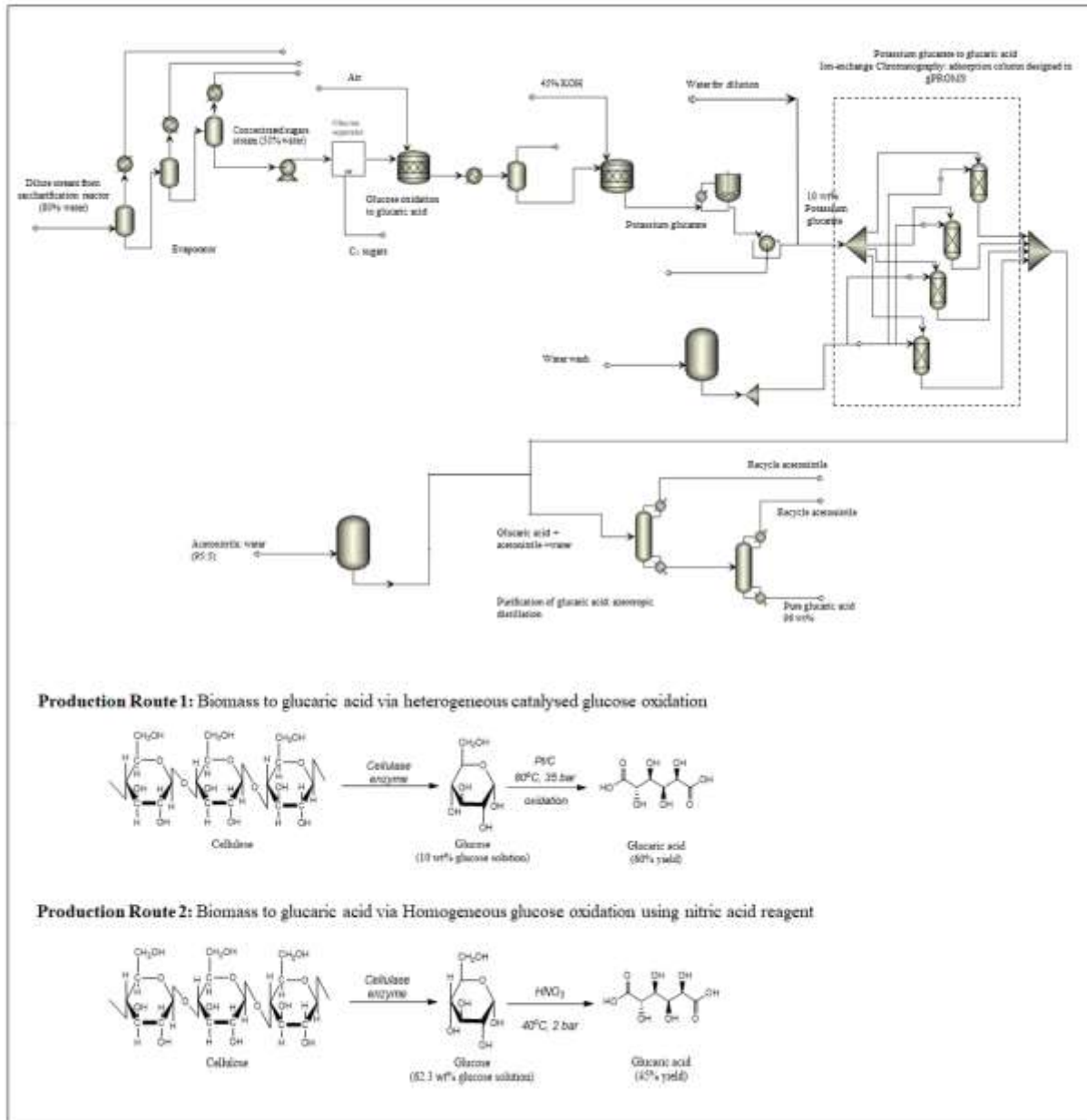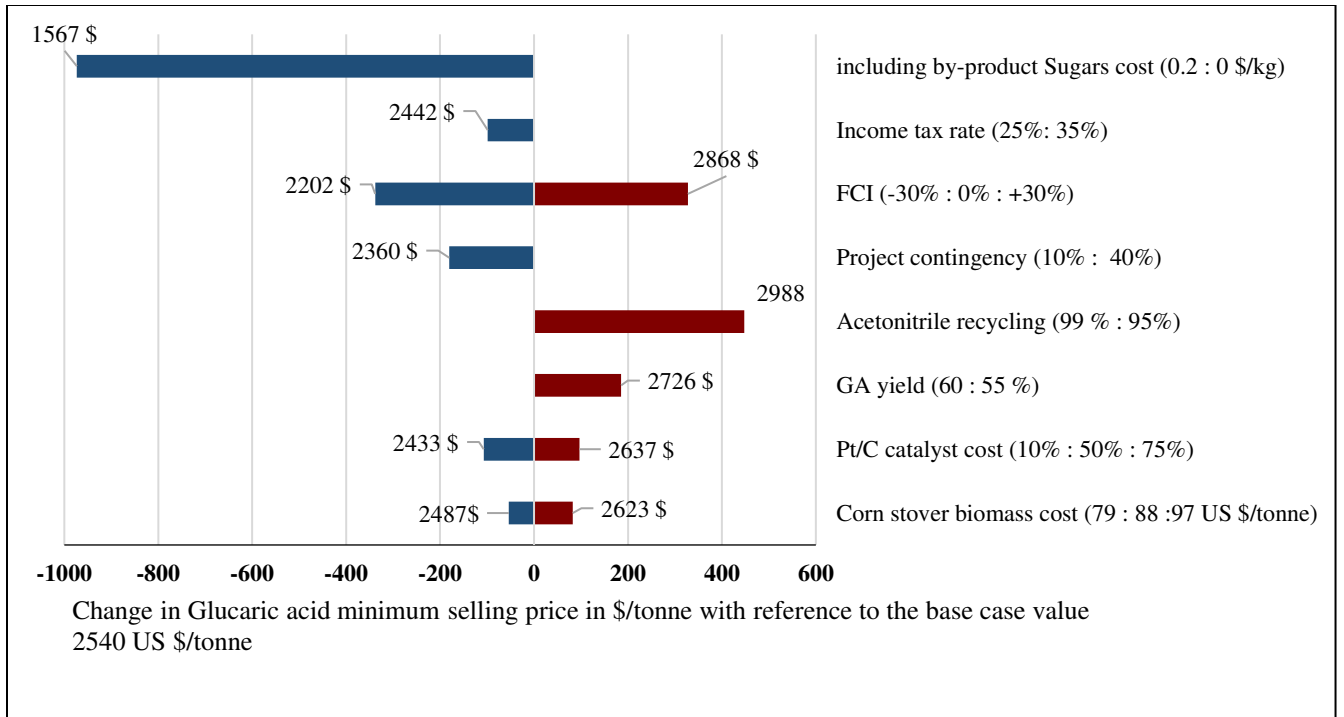
**Figure 1:** General Process scheme for conversion of sugars derived from corn stover to pure glucaric acid

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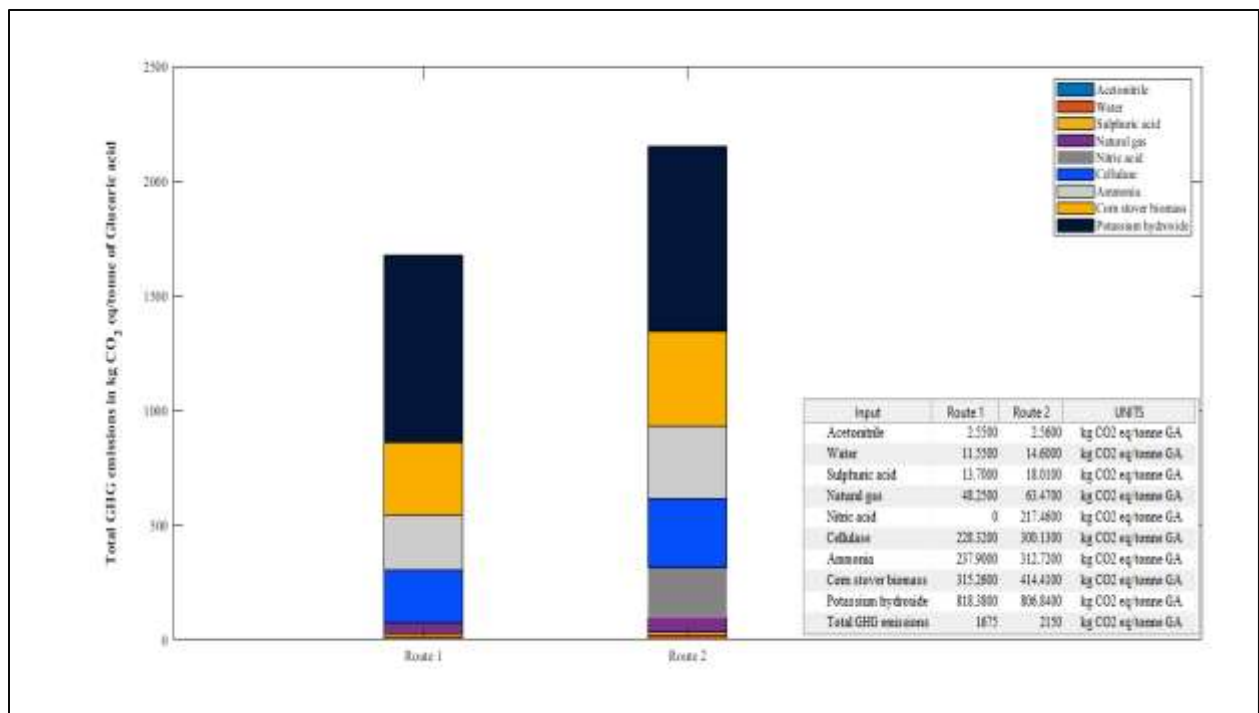
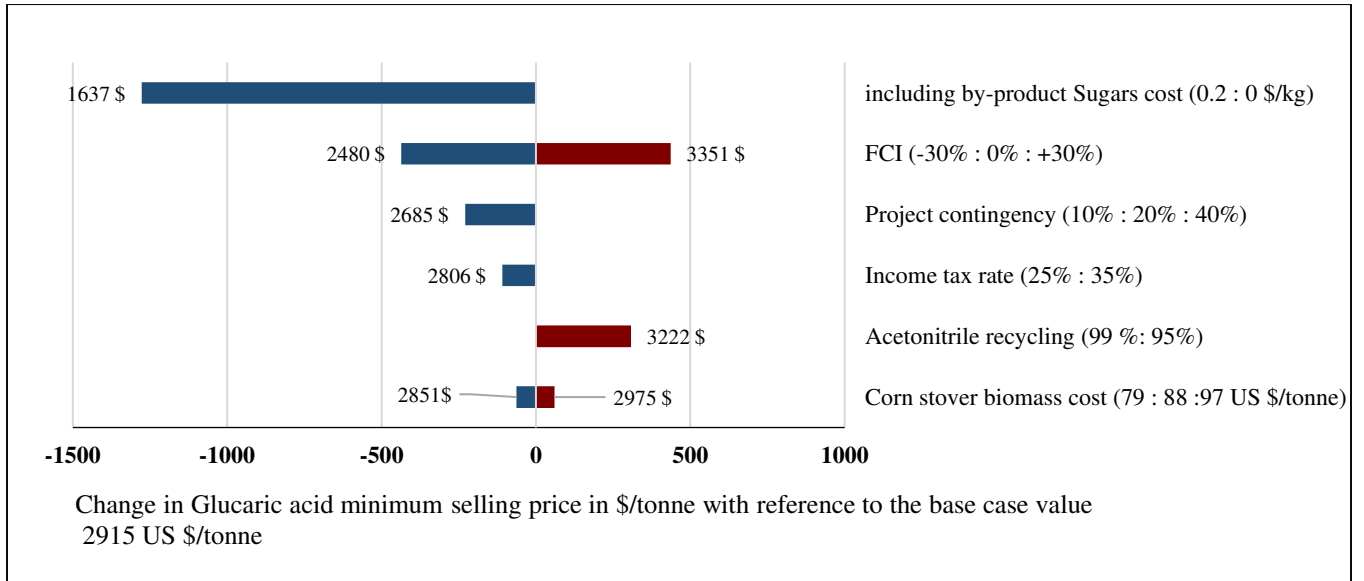**Figure 2:** Total CO$_2$eq emissions for bio-derived glucaric acid production processes via Route 1 and Route 2
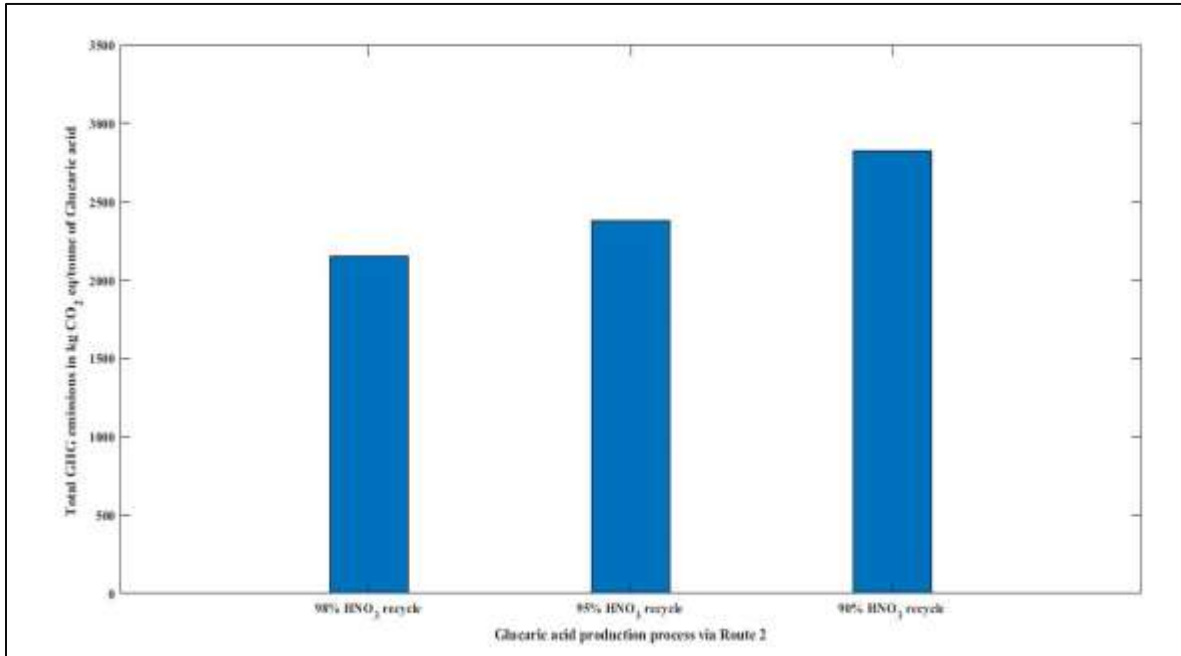
(a)



(b)

**Figure 3:** Sensitivity analysis on minimum selling of glucaric acid in **(a)** Route 1 **(b)** Route2

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3    **Figure 4:** Sensitivity analysis on total $CO_2$eq emission per tonne of glucaric acid in Route 2

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