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Gluconic Acid from Biomass Fast Pyrolysis Oils: Specialty Chemicals from the Thermochemical Conversion of Biomass

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Fast pyrolysis of biomass to produce a bio-oil followed by catalytic upgrading is a widely studied approach for the potential production of fuels from biomass. Because of the complexity of the bio-oil, most upgrading strategies focus on removing oxygen from the entire mixture to produce fuels. Here we report a novel method for the production of the specialty chemical, gluconic acid, from the pyrolysis of biomass. Through a combination of sequential condensation of pyrolysis vapors and water extraction, a solution rich in levoglucosan is obtained that accounts for over 30% of the carbon in the bio-oil produced from red oak. A simple filtration step yields a stream of high-purity levoglucosan. This stream of levoglucosan is then hydrolyzed and partially oxidized to yield gluconic acid with high purity and selectivity. This combination of cost-effective pyrolysis coupled with simple separation and upgrading could enable a variety of new product markets for chemicals from biomass.

Introduction

Fast pyrolysis of biomass is not typically regarded as an effective primary conversion path for the production of specialty chemicals, which require high purity while pyrolysis of biomass produces a liquid containing over 400 compounds[1–4] that cannot be easily separated. Owing to the complexity and thermal instability of the compounds present in the whole mixture, approaches to produce specialty chemicals usually require excessive amounts of catalyst to produce a family of aromatic products, for example, benzene, toluene, and xylene.[5]

Sugar acids such as gluconic acid are attractive intermediates for numerous applications ranging from the food to paper industries.[6–12] D-Gluconic acid has the potential as a co-monomer for the production of a variety of biocompatible, biodegradable polymers.[13] The estimated market of D-gluconic acid is 60 000 tons per year.[12,14] Currently, gluconic acid is produced via fermentation of glucose,[6] which is limited by a narrow range of operating conditions and separation challenges.[15]

While glucose may be produced via the acid pretreatment and enzymatic hydrolysis of cellulose, this is a slow process when compared to fast pyrolysis and requires expensive separation steps that limit potential for commercial application. Fast pyrolysis is an appealing process for the large-scale production of liquids from biomass due to the relatively low footprint required when compared to other alternatives.[4,16] The main challenge associated with the upgrading lies in the separation of the numerous components present in the bio-oil. Recent advancements in biomass pretreatment and optimization of pyrolysis conditions have led to increases in the amount of the anhydrosugar, levoglucosan, from the degradation of cellulose in the biomass.[17] While these advancements alone do not yield great potential for specialty chemical production of biomass, pure streams can result when combined with advancements in separation. Recent results from Brown et al. demonstrate a bio-oil recovery system based on sequential condensation and separation vapors and aerosols in the pyrolysis product stream to yield bio-oil fractions with distinctive compositions.[18] The heaviest fraction consists of water-soluble anhydrosugars and water-insoluble phenolic oligomers. A simple water washing procedure is able to separate these into a concentrated anhydrosugar solution consisting mostly of levoglucosan and a tarry phenolic oligomer fraction.[19]

Herein, we describe a catalytic strategy to convert this levoglucosan-rich stream into glucose via hydrolysis with solid resins, followed by subsequent partial oxidation to gluconic acid with supported metal catalysts. While selective oxidation via the use of heterogeneous catalysts has been an area of extensive study in an effort to improve rates and ease catalyst separation,[20–24] to the best of our knowledge, this is the first report on the production of high-purity gluconic acid from biomass through a combination of thermochemical conversion and catalytic partial oxidation.

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Table 1. Weight and carbon yields in each biomass fraction obtained after pyrolysis and extraction.

Fraction	Amount [kg]	Normalized yield (wet bio-oil basis) [%]	Carbon content [wt%]	Carbon content [kg]	Carbon yield (wet bio-oil basis) [%]
Clean Phenolic Oligomers	7.04	24.4	54.3	3.82	37.4
Anhydrosugar	6.54	22.6	47.5	3.11	30.5
Middle	2.6	9	47.6	1.24	12.1
Light Oxygenates	12.7	44	16.1	2.04	20
Total	28.88	100		10.21	100

Results and Discussion

Analysis of bio-oil fractions

The carbon content of the various fractions obtained from the pyrolysis oil is shown in Table 1. It is important to note that the anhydrosugar fraction, obtained from the separation of the heavy ends as described in the experimental section followed by water extraction, contains over 30% of the carbon in the bio oil.

Composition of the anhydrosugar solution

The anhydrosugar solution obtained from the pyrolysis of biomass was caramel-colored, indicating the presence of polymeric species. The solution was diluted with distilled water at a ratio of 1:20 to facilitate analysis by GC-MS and HPLC. The pH of the diluted oil was measured as 3.23. The GC-MS results revealed that the most abundant compound boiling low enough to elute from the column was levoglucosan, along with low concentrations of furanic compounds. In general, the anhydrosugar solution may also contain some larger soluble carbohydrates that could not be identified by GC-MS. In an effort to quantify these compounds, the anhydrosugar solution was analyzed by HPLC. The HPLC results also confirmed that levoglucosan was the main component in this fraction, with a low concentration of furanics, mannose, and sorbose. The concentration of the identified compounds was quantified by a normalization curve of standard compounds as represented in Table 2. The carbon weight of each compound was then calculated and compared to the total carbon in the fraction as measured by elemental analysis to determine the weight percentage of unidentified compounds too heavy to elute from GC or HPLC. These would include humin compounds and suspended char.

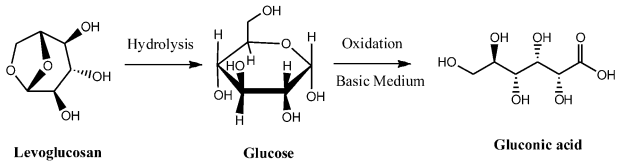
Table 2. The initial molar composition and carbon concentrations of compounds in the anhydrosugar solution. Concentrations were determined with HPLC, with the total carbon content estimated via elemental analysis.

Compound type	Concentration [M]	Carbon in anhydrosugar solution [$g_{carbon}\,L^{-1}$]	Carbon in fraction [wt%]
Furanics	0.46	28	6
HMF	0.06	4	1
Levoglucosan	2.2	158	34
Mannose	0.26	19	4
Sorbose	0.15	11	2
Unidentified Heavies	–	250	53
Total	–	470	100

Upgrading strategy

Because levoglucosan was identified as the pyrolysis product with the highest purity, a strategy for the conversion of levoglucosan to gluconic acid has been developed, as shown in Scheme 1. This strategy contemplates an initial hydrolysis step followed by partial oxidation as described in the following sections. While Table 1 indicates that levoglucosan is the most-abundant monomer present in the anhydrosugar solution, in order to improve the purity of this compound a simple purification step was employed, as will be described in the next section.

Purification of the anhydrosugar solution



Scheme 1. Upgrading strategy of anhydrosugar solution.

It is anticipated that the presence of furanics and larger polymeric species in the anhydrosugar solution results in generation of humins (polymers) under the acidic conditions required for hydrolysis, and the basic conditions necessary for partial oxidation. These polymeric species are expected to accelerate rates of catalyst deactivation. Therefore, it is essential to remove the furanic compounds and humins prior to the hydrolysis step. To accomplish this task, silica and activated carbon were chosen as adsorbent materials to filter the anhydrosugar solution prior to hydrolysis. Results after stirring in the presence of the adsorbent material are shown in Figure 1. While a moderate improvement in feed quality was observed when silica was used as a filtering material, activated carbon was much more effective for the removal of polymeric species as well as furanic compounds in the solution. It is remarkable that while the furanic and polymeric species were removed from the solution below the detection limits, the levoglucosan concentration was virtually unchanged, as confirmed by HPLC analysis. In order to demonstrate the removal of heavy polymeric species, it is necessary to quantify the carbon content before and after filtration.

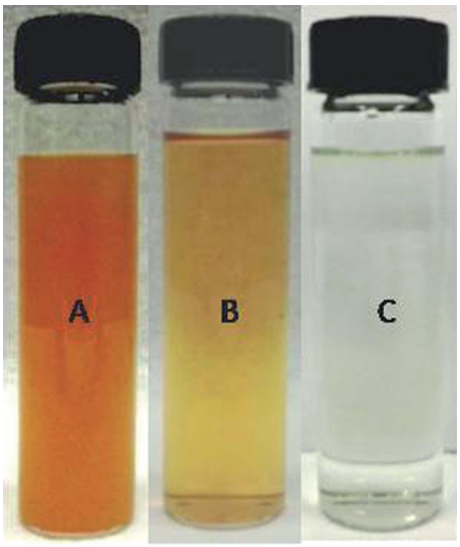


Figure 1. Diluted anhydrosugar solution (A) before, and (B) after filtration with silica gel and (C) activated carbon.

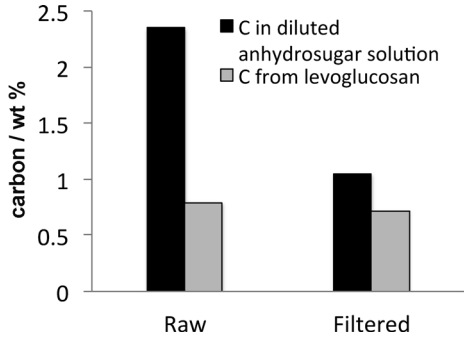


Figure 2. Carbon content in the diluted anhydrosugar solution before and after filtration with activated carbon. Note: the corresponding carbon content in the undiluted stream will be 20× the values reported here.

The carbon weight percentages of the corresponding liquids prior to and after filtration are shown in Figure 2. It should be noted that the carbon wt% values reported here are for the fraction that has been diluted 1:20 with water to facilitate analysis. Thus, the corresponding fraction of carbon in the raw material will be 20-fold the values reported in Figure 2. The results confirm that almost 50% of carbon is still retained after the filtration process, and the great majority of that carbon is now in the form of levoglucosan. Notably, acid wash pretreatment of biomass has been proven to increase yields of levoglucosan.[17] The amount of levoglucosan and its subsequent products reported herein are likely to be increased even further by applying such pretreatments.

Hydrolysis of anhydrosugar solution (rich in levoglucosan)

Prior to hydrolysis the anhydrosugar solution was diluted in water at a volume ratio of 1:20. Hydrolysis of the levoglucosan present in the activated-carbon purified and diluted anhydrosugar solution was conducted at 110 °C in the presence of 0.5 M H_2SO_4. These conditions yield 88% conversion of levoglucosan to glucose after 24 h of reaction with 100% selectivity. While sulfuric acid demonstrates high conversion, the major problem associated with sulfuric acid is the separation challenges and the resulting increase in acidity of the anhydrosugar solution. In addition, this low pH enhances the rate of polymerization of any furanic compounds present in the anhydrosugar solution. These polymerized compounds may cause a serious inhibition of the catalyst active sites in the subsequent step, decreasing the rate of selective oxidation of glucose to gluconic acid. Moreover, the highly acidic mixture would increase corrosion rates in industrial scale systems, and catalyst separation would be problematic. In comparison, solid acid catalysts have a distinct advantage. For example, Amberlyst-15 is a strong polymer-based solid acid with high SO_3H density and very high activity for a range of reactions.[25–28] Likewise, HY zeolites (Si/Al = 2.6) are potential acidic catalysts that can potentially be used for hydrolysis. To compare these solid acid catalysts, the reaction was carried out using the same weight of catalyst in all cases (0.3 g). The activity of each catalyst is shown in Figure 3. The results demonstrate that Amberlyst-15 is a very efficient and promising catalyst for the hydrolysis of levoglucosan to glucose when compared with an equal weight of HY, which demonstrated no measurable conversion of levoglucosan under these conditions. This conclusion is in qualitative agreement with the results of Van de Vyver et al., where Amberlyst-15 was found to have dramatically greater activity than HY for the hydrolysis of cellulose when compared on an equal catalyst weight basis.[29] Also, Amberlyst-15 was found to yield 100% selectivity to glucose, which is in agreement with results obtained in the presence of a 0.5 M solution of H_2SO_4 at comparable conversions.

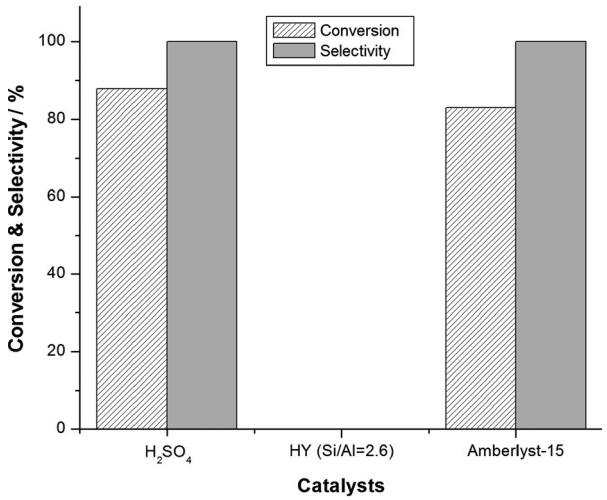


Figure 3. Hydrolytic conversion of diluted anhydrosugar solution (rich in levoglucosan) over different acid catalysts. Reaction conditions: initial conc. 0.11 M levoglucosan; conc. H_2SO_4 0.5 M; catalyst 0.3 g, reaction time 24 h; temperature 383 K.

Selective oxidation to gluconic acid

Several papers and patents demonstrate that the presence of an alkaline medium (pH 9–10) is essential for selective oxidation of glucose to gluconic acid. Uncontrolled pH in the reaction medium quickly deactivates the catalyst and the oxidation process is stopped immediately.[30] Benkó et al. reported that the use of a carbonate buffer is an easier way to control the solution pH as compared to titration with NaOH.[31] The improvement of reaction rates and heterogeneous catalyst stability for the oxidation of sugars at lower pH values is a current area of significant research interest.[32–38]

The oxidation of the diluted anhydrosugar solution after hydrolysis with Amberlyst-15 was conducted in a carbonate buffer to maintain the pH at 9.3 during the course of the reaction. It is important to note that when the reaction was conducted with the diluted hydrolyzed anhydrosugar solution without the activated carbon purification step, rapid polymerization took place, as indicated by the black color of the solution, which is likely due to the polymerization of furanic compounds in strong alkaline medium.[39] Because polymerized compounds may strongly deactivate the noble metal catalysts necessary for the oxidation reaction, additional purification is necessary. For this reason, the reactions described below were all conducted with the diluted anhydrosugar solution after purification with the activated carbon filter and subsequent hydrolysis.

The selective oxidation of the purified glucose post-purification and hydrolysis stream was conducted in alkaline medium using air as the oxidant and 5% Pd/C as catalyst. Air was bubbled into the solution with a flow rate of 60 mL min^{-1} and, as mentioned above, the carbonate buffer was used to maintain the pH at 9.3. Figure 4 depicts the conversion of glucose present in the anhydrosugar solution to sodium gluconate as a function of time. Notably, glucose was converted to sodium gluconate with 100% selectivity in each case. The reaction profile demonstrates the decrease in reaction rates as the glucose is consumed.

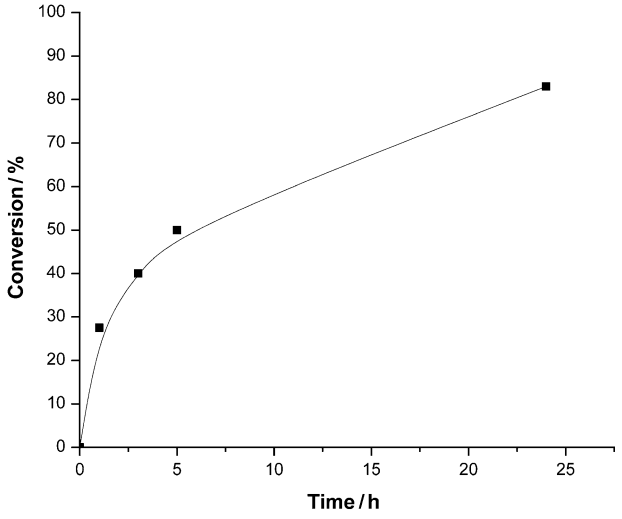


Figure 4. The effect of reaction time on the conversion of glucose present in the diluted and purified anhydrosugar solution to sodium gluconate. Reaction conditions: temperature 50 °C; flow rate of air 60 mL min^{-1}; initial conc. of glucose 0.02 M; catalyst 5% Pd/C; pH 9.3.

Deactivation studies

In order to study the sustainability and reusability of the catalysts, a deactivation study was carried out over 5% Pd/C catalyst. After 24 h of reaction in a batch reactor, the reactant concentration was adjusted back to the original feed concentration (0.02 M glucose) by adding more hydrolyzed anhydrosugar solution (Figure 5). After this, the reaction was allowed to run for another 3 h. We found that the catalytic activity was practically the same as the original after the reactants were re-introduced over the spent catalyst. That is, this experiment confirms that no measurable loss in catalyst activity occurs after 24 h of reaction with this purified feedstock. This result suggests that the filtration procedure used here is adequate to remove any heavy species that might otherwise rapidly deactivate the catalyst.

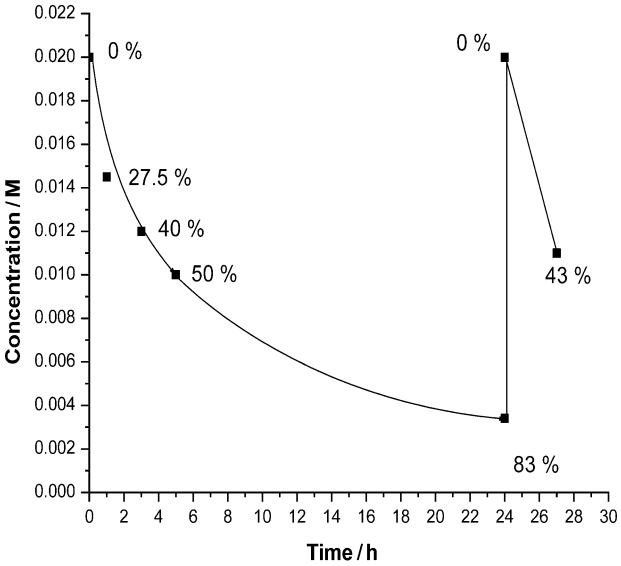


Figure 5. Deactivation studies on conversion of glucose (rich in hydrolyzed anhydrosugar solution) to sodium gluconate; Reaction conditions: temperature 50 °C; flow rate of air 60 mL min^{-1}: initial conc. of glucose 0.02 M; catalyst 5% Pd/C; pH 9.3.

Conclusion

A thermochemical route for the production of a high-purity gluconic acid stream from bio-oil is presented. Sequential condensation followed by washing was used to separate anhydrosugars from the bio-oil to create a stream consisting of primarily levoglucosan with some furanics and humins. Simple contact with activated carbon selectively removes the heavy char, humins, and furanics while preserving the levoglucosan in solution. This is the first report of the production of gluconic acid at high purity from pyrolysis products. Because a relatively clean anhydrosugar solution is obtained, a simple contact with

activated carbon removes the impurities to produce gluconic acid. The purity of the stream offers potential for long catalyst lifetimes, with no measurable decrease in catalyst activity after 24 h of oxidation.

Experimental Section

Reagents and analytical

The bio-oil used in this study was produced from fast pyrolysis of red oak. Silica gel (Merck) and Activated carbon (Fluka) were used for cleaning the bio-oil fraction prior to the reaction. Commercial 5% Pd/C (Sigma Aldrich), Amberlyst-15, and HY zeolite (Si/Al = 2.6) (Zeolyst) were used as catalysts. Gluconic acid, fructose, glucose, and levoglucosan from Aldrich were used as standard compounds. All the chemicals were used as-received.

Production of pyrolysis stage fractions

Bio-oil was produced by pyrolyzing red oak (*Quercus rubra*) purchased from Wood Residual Solutions of Montello, WI (USA) in a fluidized bed fast pyrolysis system operated at 450–500 °C. Bio-oil fractions were recovered in stages using a series of condensers and electrostatic precipitators (ESPs). Stages 1, 3, and 5 were water-cooled condensers operated at progressively lower temperatures to collect SFs of bio-oil according to condensation temperatures of the different compounds in the vapor stream. Stages 2 and 4 were ESPs designed to collect aerosols generated downstream from these stages. Stages 1 and 2 collected viscous, high-boiling point compounds referred to collectively as "heavy ends" of the bio-oil. Stages 3 and 4 captured the compounds of intermediate molecular weight while stage 5 recovered an aqueous phase containing "light oxygenates," including acids and aldehydes. Further details on the fractionating bio-oil recovery system can be found in the literature.[18,40]

The Association of Analytical Communities, Inc. (AOAC) Method 988.12 (44.1.30) Phenol-Sulfuric Acid Assay for Total Carbohydrate Determination was used to quantify total sugar in combined SFs 1 and 2. Levoglucosan was used as the standard.[41,42]

Elemental analysis was performed using a LECO TruSpec carbon, hydrogen, and nitrogen (CHN) (LECO Corp., St. Joseph, MI) analyzer with the determination of oxygen by difference as has been previously described.[18] Ethylenediamine tetraacetic acid was used as a standard for the CHN determinations.

The water-soluble anhydrosugars were separated from the water-insoluble phenolic oligomer-rich raffinate using a 1:1 ratio of water-to-heavy ends bio-oil and mixed thoroughly with a batch-style mixer. The mixed samples were placed on a shaker table (MaxQ 2506, Thermo Scientific, Hanover Park, IL) for 30 m at 250 motions min^{-1} and centrifuged (accuSpin 1R, Thermo Scientific, Hanover Park, IL) at 2561 g force for 30 min. The water-soluble portion (anhydrosugar-rich solution) was decanted. The water in the anhydrosugar solution was then removed with a rotary evaporator at 40 °C until the moisture content of the solution was measured as 8.3 ± 0.9%. Ultimate analysis (carbon content) was conducted after the separation and evaporation steps.

Analysis of anhydrosugar solution

The received anhydrosugar solution was analyzed by GC-MS (Shimadzu QP2010S GC-MS equipped with an RTX-1701; 60 m, 0.25 mm ID, 0.25 μm) and HPLC equipped with both UV (486 UV2075) and refractive index (ERC 7515ARI) detectors, (Aminex HPX-87H column; operating temperature, 303 K; mobile phase, 5 mM sulfuric acid (0.6 mL min^{-1}). Carbon in the solution was analyzed via elemental analysis (CE-440 Elemental analyzer).

Precleaning the bio-oil fraction

The anhydrosugar solution was diluted with water (1:20 volume ratio). 4 g of activated carbon were added to the diluted fraction and stirred using a magnetic stir bar for 30 min at room temperature and filtered through a Buchner funnel using Whatman filter paper. The anhydrosugar solution was analyzed before and after filtration by HPLC and the carbon content was determined by elemental analysis (CE-440 Elemental analyzer).

Hydrolysis

The hydrolysis reaction was carried out in a 100 mL glass reactor equipped with a reflux condenser. The reactor was submersed in an oil bath while the temperature was controlled by a heating plate. Analysis of the reaction products was performed by HPLC. The concentrations of identified compounds were quantified by constructing a calibration curve of standard compounds with an internal standard.

Partial oxidation

Selective oxidation of either an aqueous D-glucose mixture or the hydrolyzed anhydrosugar solution (rich in D-glucose) was carried out in a temperature-controlled, magnetically stirred batch reactor while bubbling air at atmospheric pressure. The reaction was initiated by adding the catalyst to the reaction medium, maintaining the pH at a constant value of 9.3 using a carbonate/bicarbonate (2:3 *v/v*) buffer solution. The diluted hydrolyzed anhydrosugar solution was added to the buffer solution with a volume ratio of 4:1 (buffer/hydrolyzed anhydrosugar solution). Typical reaction parameters were: concentration of buffer 0.1 M, temperature 323 K, stirring rate 600 rpm, concentration of glucose 0.02 M, air flow rate 60 mL min^{-1}. Analysis of the reaction products was performed by HPLC on a Waters instrument equipped with 486 UV2075 and ERC 7515ARI detectors. Glucose and gluconic acid peaks overlapped but glucose did not adsorb at the wavelength (210 nm) used for UV detection, thus the amount of glucose was determined by subtracting the gluconic acid contribution, quantified at 210 nm, from the signal in the RI detector, enabling the measurement of glucose concentrations in the presence of gluconic acid. The conversion was calculated on the basis of the concentration of gluconic acid produced and glucose consumed. Under these conditions, any selectivity to products other than gluconic acid and the corresponding salt were below detection limits.

The catalytic measurements are expressed in terms of degree of conversion (X,%) and selectivity (S,%), defined as [Equations (1), (2)]:

$$X(\%) = 1 - \frac{FC_R}{IC_R} \times 100 \quad (1)$$

$$S(\%) = \frac{C_P}{IC_R - FC_R} \times 100 \quad (2)$$

Herein, IC_R was the initial molar concentration of reactant, FC_R was the final concentration of reactant, and C_P was the concentration of product after reaction.

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Keywords: biomass · heterogeneous catalysis · gluconic acid · oxidation · pyrolysis

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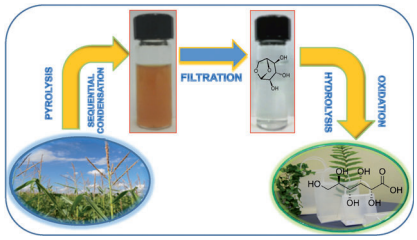
Chemicals from pyrolysis: We demonstrate the production of gluconic acid from the fast pyrolysis of biomass. Because a relatively clean anhydrosugar solution is obtained, a simple contact with activated carbon removes the impurities to produce gluconic acid. The purity of the stream offers potential for long catalyst lifetimes, with no measurable decrease in catalyst activity after oxidation.



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Gluconic Acid from Biomass Fast Pyrolysis Oils: Specialty Chemicals from the Thermochemical Conversion of Biomass