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Separation of Organic Acids through Direct Catalysis from Sugars

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4/28/23

Table of Contents

List of Figures

List of Equations

Abstract

Society relies on plastic products, whether they are single use or durable. A downside of plastic is that the most common type is a product of oil and oil is not only a limited resource but also a climate-damaging resource. Polylactic acid (PLA) is a bio-based, biodegradable plastic. However, the process of converting biomass to polylactic acid polymer has the largest environmental impact of the PLA production process, so alternative methods of conversion are needed (Moretti et al., 2021). The polylactic acid polymer can be made with lactic acid, which can be converted from glucose.

Introduction

Plastic is a key part of our modern world; however, it is also a limited resource. The purpose of this research project is to theorize about an alternative method for producing lactic acid with an end usage in PLA plastic. This alternative method would ideally be easier to commercialize and scale up to the point of mass production than other previously researched methods of lactic acid production.

Background and Literature Review

The goals of this literature review include an explanation of lactic acid production the reasoning behind the method of research chosen, as well as the basics of electrodeionization and the review of other research in related fields. Some key texts are "Recent trends in lactic acid biotechnology: A brief review on production to purification" and "Electrochemical biomass upgrading: degradation of glucose to lactic acid on a copper(II) electrode". These sources were found using select databases like Compendex and Web of Science, and keywords including "Lactic acid", "deionization", "production" and "electrochemical". Several sources were found with the assistance of University of Arkansas research librarian Jay McAllister. Articles were selected based on their relevance to the main research topic, publishing date and the credibility of the publisher and author.

There are a few broad ways of approaching the conversion of glucose to lactic acid, biological, chemical, and electrochemical. Each method has a different basic approach with different benefits and downsides associated with them. Literary research was done into each approach to evaluate which method was the ideal method to achieve the research project's goals.

The biological production of lactic acid involves fermentation through bacteria, a specific type of microbes. Fermentation is a process that uses the anaerobic respiration of specific bacterias, to cause chemical changes (*Bacteria*, n.d.; Martin, 2010a; Schaschke, 2013). As shown in Figure 1, the fermented broths are required to go through extensive purification by the use of several membrane-based separation columns (Ghaffar et al., 2014).

This biological production method has some potential benefits in that it can be used to obtain pure lactic acid. However, biological conversion can involve other issues like contamination, which is hard to prevent and eliminate. Another downside of the biological conversion is the necessary media. These media are traditionally expensive and can raise production costs in cases of scaled-up production.

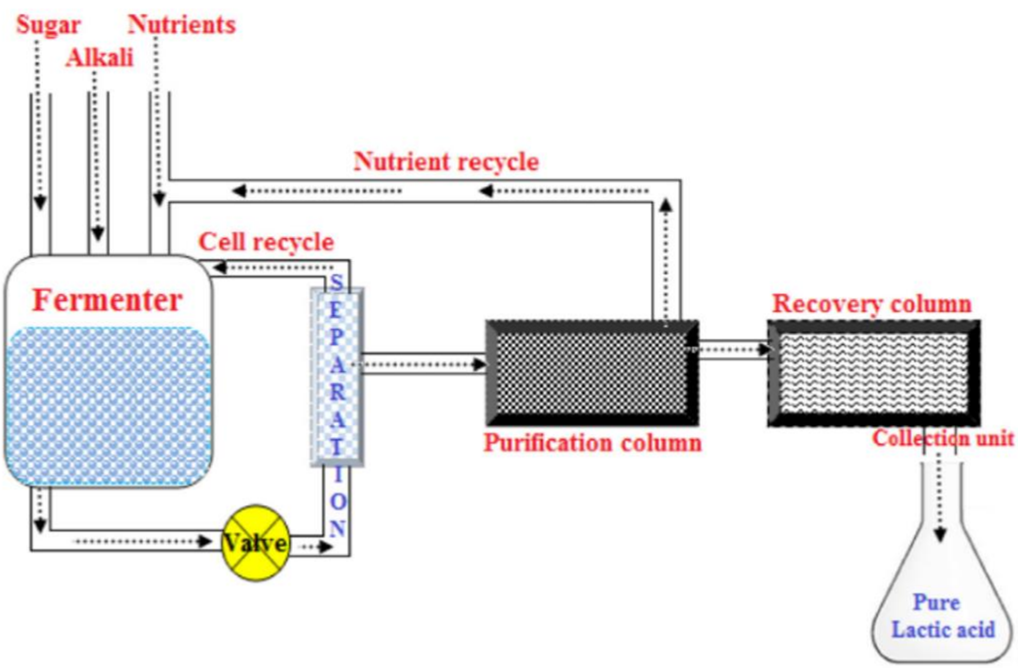

Figure 1: An example of a biological conversion of glucose to lactic acid through the usage of fermentation (Ghaffar et al., 2014).

The chemical production of lactic acid starts with acetaldehyde. Acetaldehyde with the addition of hydrogen cyanide in the presence of a catalyst is converted into lactonitrile. Lactonitrile, water, and sulfuric acid react together to produce ammonium salt and lactic acid. Lactic acid is combined with methanol to produce methyl lactate and water. Finally, the methyl lactate goes through hydrolysis in the presence of water to produce methanol and lactic acid (Ghaffar et al., 2014).

Equation 1: Addition of Hydrogen Cyanide Catalyst (Ghaffar et al., 2014)

$$CH_3CHO + HCN \longrightarrow CH_3CHOHCN$$

Equation 2: Hydrolysis by H_2SO_4 (Ghaffar et al., 2014)

$$CH_3CHOHCN + H_2O + \frac{1}{2}H_2SO_4 \longrightarrow CH_3CHOHCOOH + \frac{1}{2}(NH_4)_2SO_4$$

Equation 3: Esterification (Ghaffar et al., 2014)

$$CH_3CHOHCOOH + CH_3OH\ CH_3 \longrightarrow CHOHCOOCH_3 + H_2O$$

Equation 4: Hydrolysis by H_2O (Ghaffar et al., 2014)

$$CH_3CHOHCOOCH_3 + H_2O \longrightarrow CH_3CHOHCOOH + CH_3OH$$

This chemical route of lactic acid production has some benefits and drawbacks. While the chemical route of lactic acid production avoids the drawbacks of the biological version like the contamination risks and expensive medias, it does have some drawbacks. These drawbacks include the type of lactic acid that is produced. The chemical reactions produce a racemic mixture of DL-lactic acid, where this mixture is simply an equal mixture of the d- and l- forms of lactic acid (Martin, 2010b). This racemic mixture can cause a decrease in the crystallinity and decrease the melting point of the resulting PLA.

Finally, the electrochemical production of lactic acid starts with glucose, and a copper catalyst that an electrical current is applied to, this leads to the conversion of glucose to lactic acid. Two possible reaction schemes for the electrochemical production of lactic acid are shown below in Figure 2. A potential electrochemical setup for the conversion of glucose to lactic acid is shown in Figure 3.

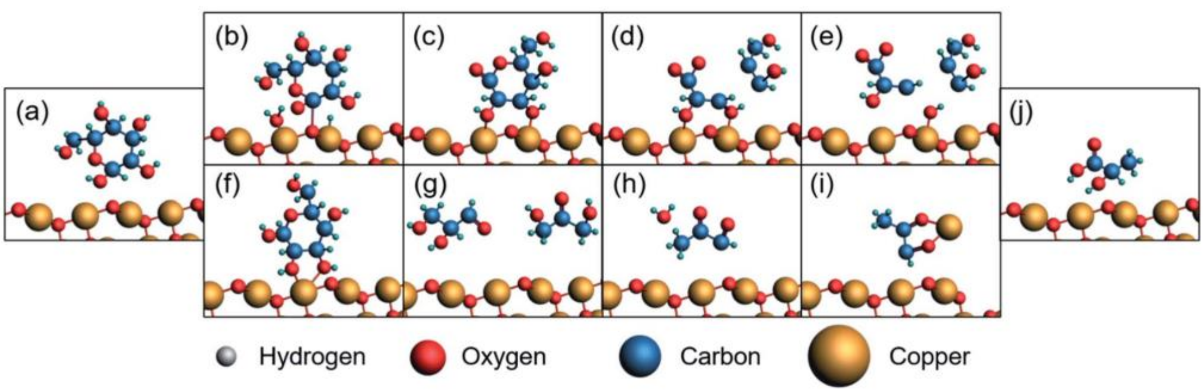

Figure 2: Possible electrochemical reaction scheme from glucose to lactic acid using a CuO surface. This includes 2 pathways b-e and f-i. The pathways are further explained in the cited paper (Lars Ostervold et al., 2021).

The benefits of the electrochemical conversion include the potential for usage of plant matter and food waste as a source of glucose, and the simplicity of the electrochemical setup when compared to the additional materials needed for the biological production method, and the long series of reactions used in the chemical production method. However, a current drawback of the electrochemical method is the production yield, which is low due to the reaction continuing to degrade into other organic acids. This is why research is ongoing regarding the separation of lactic acid from these other organic acids within the original product stream so that the lactic acid is unable to continue to degrade and a higher yield of lactic acid will be produced.

This breakdown of benefits and downsides to each method of lactic acid production demonstrates the reasoning behind the selection of the electrochemical production method of lactic acid production as the chosen method of lactic acid production for this research project.

Deionization is defined as the process which uses ion exchange resins to remove mineral ions from water (*Deionization - Dictionary of Chemical Engineering*, 2014). This research project plans to use a similar method, also using ion exchange resins and membranes to remove lactic acid from a mixture containing formic acid, glucose, and fructose.

Research has been conducted about removing lactic acid from other mixtures, like removing organic acids, including lactic acid, from wastewater with a lactic acid removal percentage of 33.36% when a 24-hour PANI coating was used (Khurram et al., 2020). Selective separations of an organic acid from other organic acids have also been done before. Butyric acid production through continuous formation required the use of electrodeionization to separate the butyric acid from lactic acid and acetic acid (Du et al., 2012). Lactic acid has also been separated from other organic acids by utilizing absorbent resin (Nam et al., 2012). However, no research has been done to date on using electrodeionization or EDI to separate an electrochemical catalyst produced lactic acid from formic acid, glucose, and fructose.

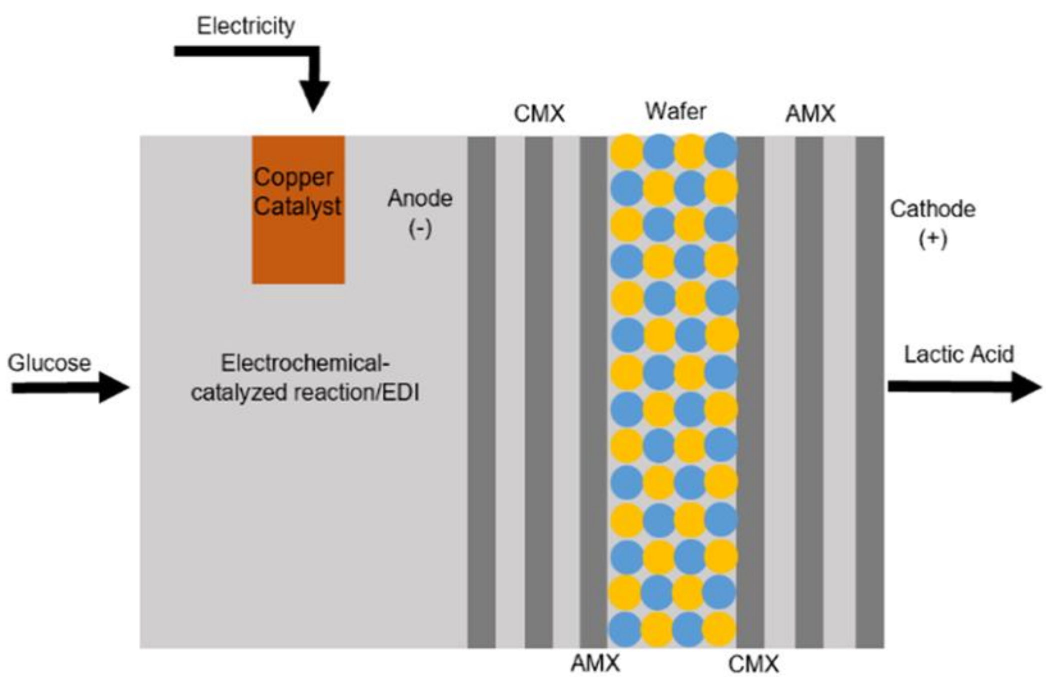

Figure 3: The electrochemical production method of lactic acid from glucose that is discussed in this research thesis (Robinson, 2021b).

Lactic acid has a long list of applications in many several different key industries. Beyond just being used to produce polylactic acid, lactic acid is also used in the food and beverage industry, the personal care industry, and in industrial applications. Figure 4 shows the diversity of industries lactic acid is used in.

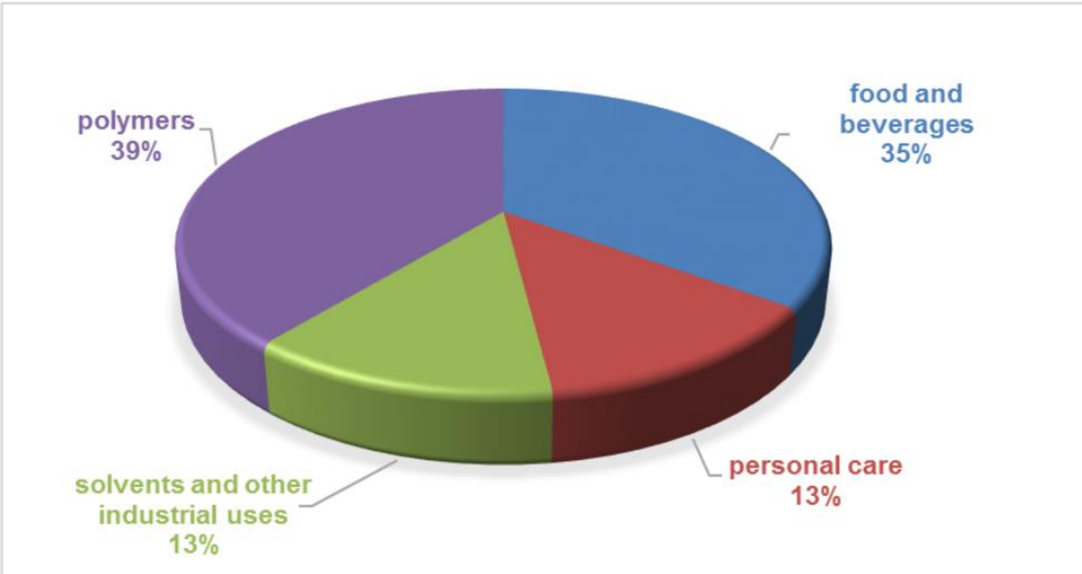

Figure 4: Industries with Lactic Acid application and the industry's demand for Lactic Acid (Komesu et al., 2017).

In the polymer industry, lactic acid is used to produce other compounds, like polylactic acid, ethanol, and acetaldehyde. The next industry with a large demand is the food industry. Lactic acid is used as a flavoring agent, to regulate the pH of a product, and to inhibit bacterial growth. Another industry that uses lactic acid is personal care, where it is used in pharmaceuticals, cosmetics, and in oral hygiene products (Komesu et al., 2017).

Polylactic acid has other applications that should also be considered. PLA is a common 3-D printing polymer. 3-D printing is used in areas like small business product production, rapid prototyping, and in medicine. For students, 3-D printing allows for more hands-on learning for all ages and schools.

Specifically in the medical field, 3-D printing can allow for a more personalized and interactive discussion of treatment plans between the doctor and the patient. 3-D printing can also assist doctors in the diagnosis process. Additionally, PLA and 3-D printing also have a place in orthopedics and bone repair (Chen et al., 2020). Overall, 3-D printing is a widely applicable technology that can be used in a wide variety of industries.

This literature review found that the electrochemical conversion of glucose to lactic acid has potential and should be further researched. It was also found that while research has been conducted regarding the removal of organic acids from other substances, the use of an EDI to separate the separation of lactic acids has yet to be explored. These gaps in current knowledge are what this research project plans to investigate and eventually fill. This literature review has shown where this research project needs to go to ensure that it is advancing current scientific research.

Foundational Research

This deionization project was proposed so that an electrochemical-catalyzed product stream would be used as the dilute stream to be separated. The electrochemical experiment was focused on the production of lactic acid from glucose. This project used a Biologic SP-300 potentiostat/galvanostat. The electrodes consisted of a copper foil as the working electrode, Hg/HgO as the reference electrode, and a platinum coil as the counter electrode. The Nernst equation was used to convert the potentials to potential vs. RHE (Lars Ostervold et al., 2021).

There were three parameters that were varied to determine their effect on the product yield: voltage, alkalinity, and oxidation time allowed when preparing the copper (working) electrode. The analyzed product streams are shown below in Figure 5 (Lars Ostervold et al., 2021).

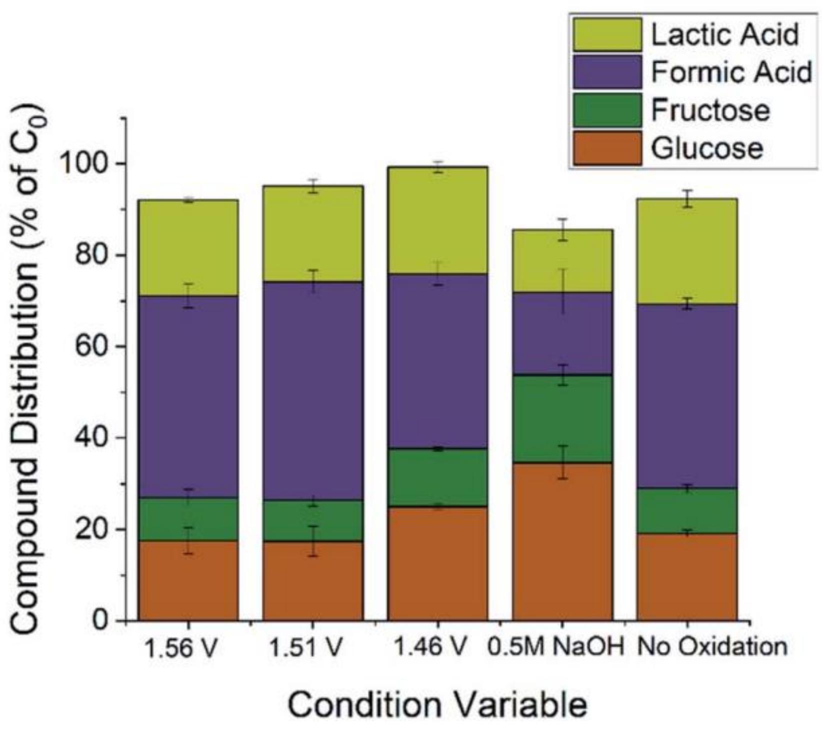

Figure 5: Product analysis for each of the varied parameters outlined above, with constant conditions besides the varied parameters (Lars Ostervold et al., 2021).

It was found that when converting biomass to lactic acid, the lactic acid produced would continue to react causing the production of other organic acids, like the high production of formic acid, rather than a higher yield of lactic acid as seen in the reported results (Figure 4).

The goal of this separation project is to remove the lactic acid as it is produced. This separation would mean that the lactic acid would be unable to continue to react into other organic acids. Also, by removing the lactic acid, the reaction would continue to occur, therefore leaving less of the reactants unreacted that would either be assigned as waste or would have to be recycled back into the reaction vessel. This separation would overall create a positive impact on the electrochemical reaction's results as more lactic acid would be produced with smaller amounts of byproducts like formic acid and reactants like glucose appearing in the product stream.

Completed Research

This research was focused on using electrodeionization (EDI) to remove lactic acid from the product stream of the electrochemical conversion of glucose to lactic acid. This product stream included unreacted glucose, as well as other organic acids, formic acid in particular. The experimental setup included the EDI stack and 4 liquid pumps which would feed the streams into the EDI stack. This EDI stack was made of thin pieces of plastic, and a few ion exchange membranes that were adhered together using silicone. The EDI stack was assembled in a particular order as shown in Figure 6.

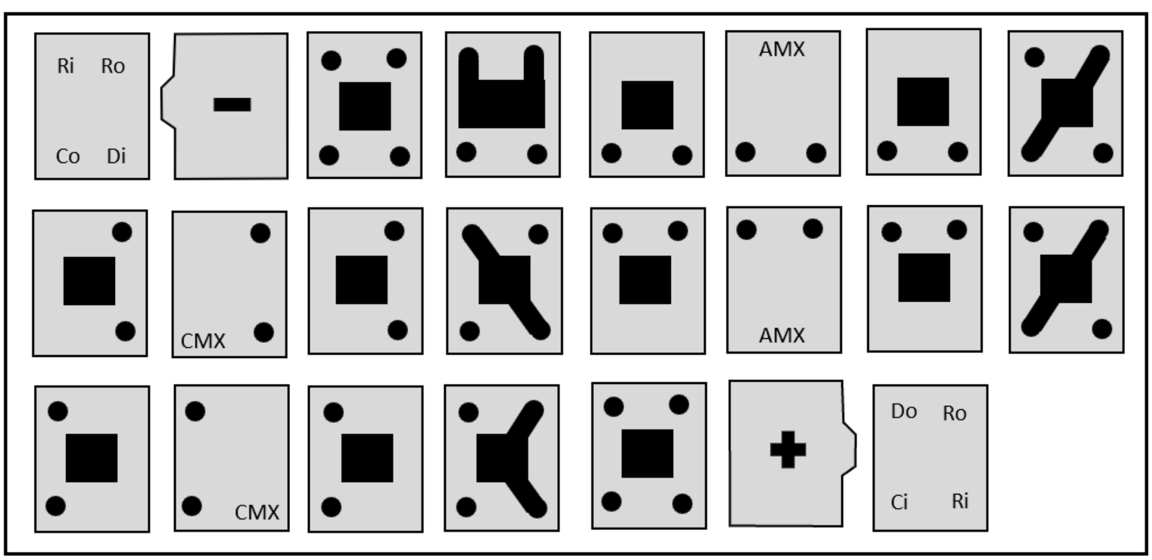

Figure 6: EDI Stack Assembly Order from the Anode (Top Left) to the Cathode (Bottom Right). Assembled from Left to Right then Top to Bottom (Robinson, 2021a).

The chemical solutions used in this experiment include a dilute stream of 1g/L of sodium lactate at neutral pH, a concentrate stream of 1g/L sodium chloride, and redox streams of 42.6g/L of sodium sulfate. The current goal of this setup is to determine the amount of lactic acid that is removed when no other compounds are present. The experiment is conducted at room temperature and atmospheric pressure since a goal of this project is commercialization and maintaining a specific temperature and pressure can be costly on a manufacturing plant scale. The experiment ran for 4 hours with samples collected every hour. 3-4mL samples are collected from the input and output of the concentrated, dilute, and both redox streams.

The samples were analyzed using high performance liquid chromatography (HPLC) with a refractive index detector, an infrared sensor, and a Bio-Rad Aminex HPX-87H column at 25°C. Sample were ran through the HPLC with stock solutions.

The analysis of the results experienced difficulties due to the HPLC becoming nonoperational for several months once the samples had been collected. While the HPLC was nonoperational, the samples were stored in a lab refrigerator for several months. Once the HPLC was repaired, it was found that both the run method and the export method had to be recreated in the HPLC computer software. After the methods were recreated, the stock solutions were remade, and the samples were removed from the refrigerator. The samples were then defrosted and ran through the HPLC. The HPLC data was exported from the HPLC computer and analyzed using Origin 2021. Standards were also ran and analyzed through the same method. These standards included a deionized water sample, and lactic acid samples of the following concentrations, 0.25M, 0.5M, 1M, 1.5M, and 1.25M.

Within Origin 2021, a plot was developed, and a baseline was found. Then a peak analyzer tool was used to identify the peaks located on the plot's baseline and determine the area within the peaks. An example of the developed plots is found below Figure 7.

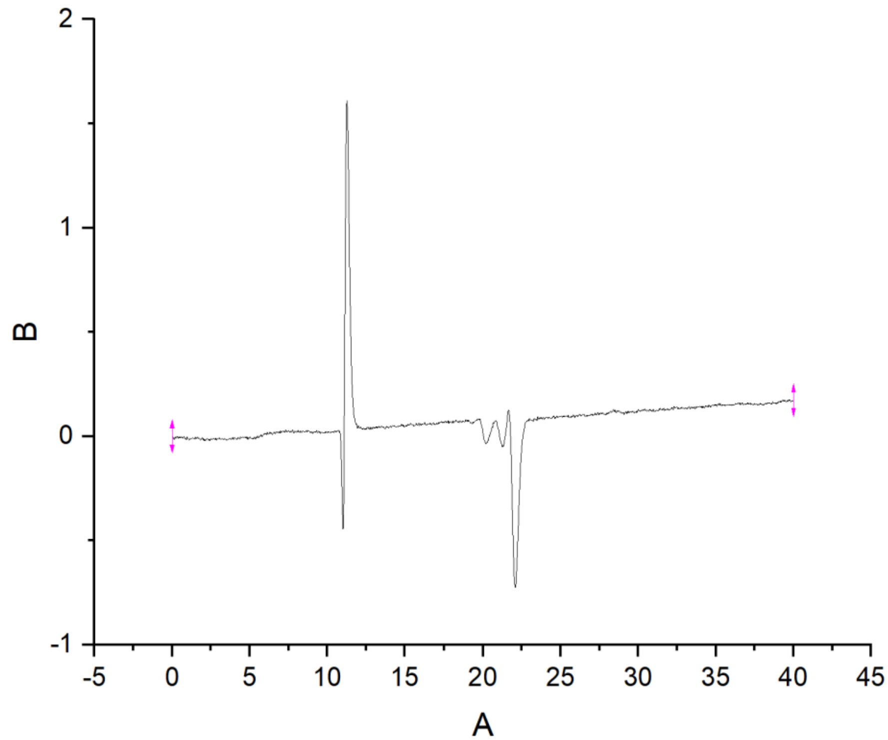

Figure 7: Example Orgin 2021 Plot (Robinson, 2022a).

The Origin plots of the deionized water and the lactic acid standards were compared and used to select the peak that was believed to be lactic acid. The lactic acid standard plots were also used to create a lactic acid calibration curve. The calibration curve would allow for the peak areas to be converted into concentration in units of M.

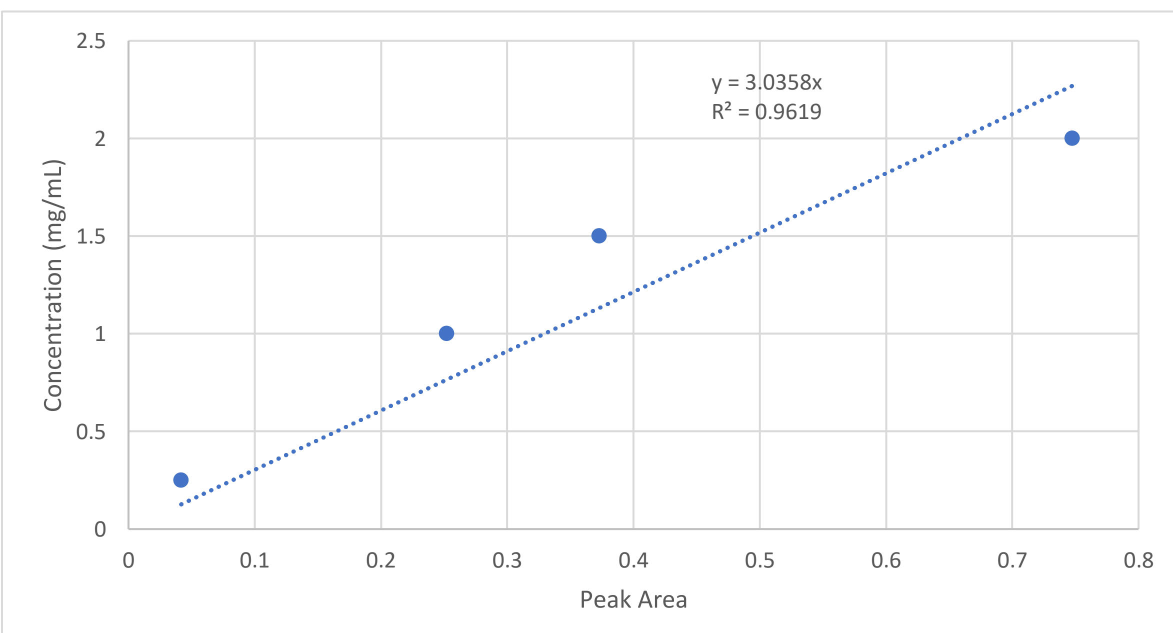

Figure 8: Lactic Acid Calibration Curve Example (Robinson, 2022b).

The results of this project appear to be inconclusive at this time since the concentration of lactic acid appears to be increasing in both the concentrate and dilute streams of the EDI. This is different than the expected results of the concentration of lactic acid decreasing in the dilute stream while the lactic acid concentration increases in the concentrate stream. Due to this unexpected trend as well as the issues in analyzing the experimental samples, repeat trials should be conducted to either confirm this result's trend as incorrect or determine that the original result's trend is correct and a change in method is required to achieve the desired separation of organic acids.

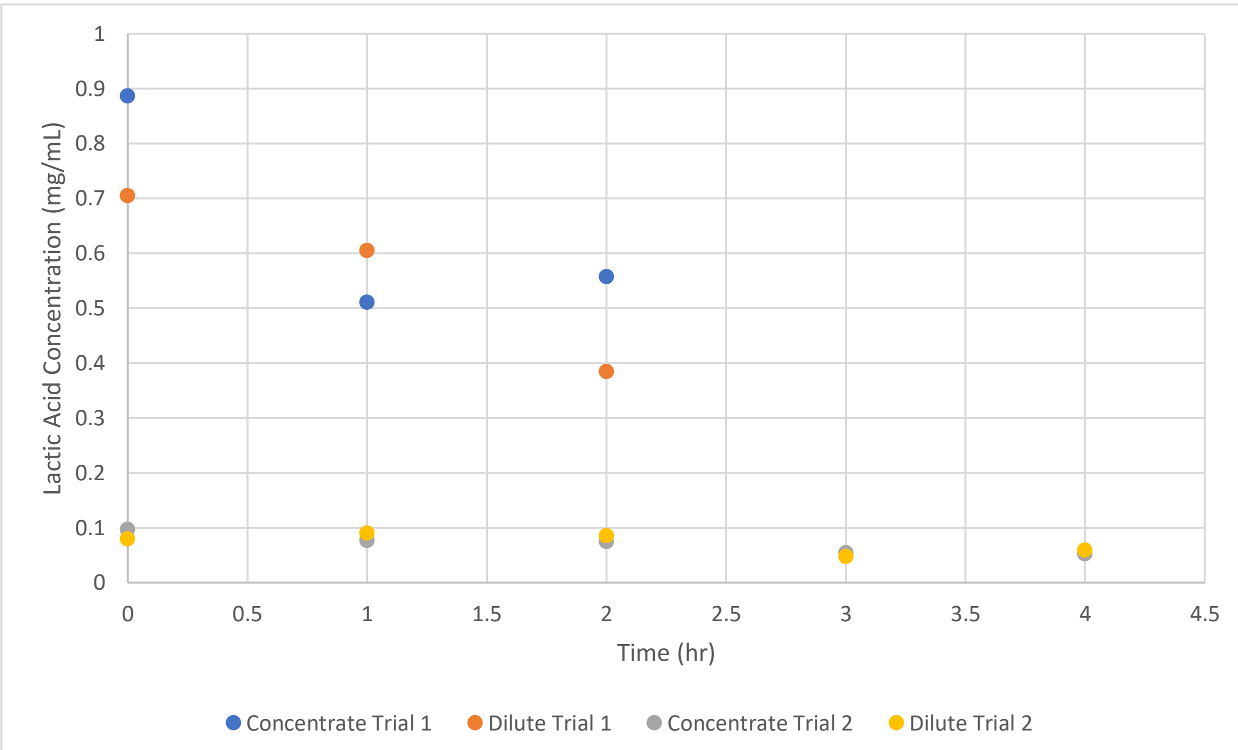

Figure 9: Lactic Acid Concentration Results from Two Trials (Robinson, 2023).

Potential Further Research

Further experiments will be conducted with a variety of different organic acid mixtures with the end goal of running the experiment with the electrochemistry's product stream. These experiments will also be conducted at room temperature and atmospheric pressure so that potential commercialization plans won't have to include the cost of maintaining a specific temperature and pressure. Other experiments will be ran on a longer time basis to determine if a longer runtime would yield a higher percentage of lactic acid removed. Experiments will also be conducted on the effects different ion exchange wafers can have on the removal of lactic acids, some of these variations would be the ratio of cation to anion exchange beads, the size of the resin beads (ground or unground), as well as the strength of the exchange beads themselves. Future research may also include the separation of the other organic acids in the production stream to be potentially used in the production of other products. A techno-economic analysis will also be completed, this analysis will assess the economic potential of a production process and to help stimulate the possible operation of a commercial-sized manufacturing plant that uses this production process. Research is also ongoing regarding the electrochemical-catalyzed production of lactic acid regarding the use of different catalysts to increase the yield of lactic acid.

After the completion of the techno-economic analysis, the research could begin in combining the electrochemical reaction and the deionization separation so that they could take place in one contained device. This potential device was previously shown in Figure 3.

The project could then go into commercialization of this lactic acid production method since that is the overarching end goal of this project. By scaling up the combined device, a pilot plant of the production method could be built and used to find and solve any issues that come with scaling up a previously lab-sized production method.

Conclusion

Overall, the literature review shows the importance of this research and where it can fill in gaps in the current understanding of EDI and lactic acid separation. However, the current results of this research are inconclusive. The results are considered inconclusive due to trends not following the expected results. The expected results are that the concentration of lactic acid would decrease in the dilute stream while increasing in the concentrate stream due to the transfer of ions. The current results show that the concentration of lactic acid increases in both the dilute and concentration streams. This is why repeat trials are recommended in order to support or disprove the current results. If the current results are supported then a change in the separation method would need to be considered to meet the requirements of the project. If the current results are disproven then further research for this project will continue as outlined. This further research has been recommended to further simulate the separation of the electrochemical-catalyzed product stream. By completing the suggested further lab trials, the research could then focus on the industrial commercialization and scale-up of the process.

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