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CO_2 ELECTROREDUCTION: CIRCULAR INNOVATION IN PULP & PAPER

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ABSTRACT

The pulp and paper sector significantly impacts global CO_2 emissions, which makes it necessary to explore inventive solutions that endorse sustainability and circularity in the industry. This paper delves into the potential of the CO_2 electrochemical reduction process, an innovative approach poised to address the sector's environmental hurdles and bolster its circular economy.

CO_2 electrochemical reduction, colloquially known as CO_2 electroreduction, is an emerging technology adept at transforming carbon dioxide into beneficial chemicals and fuels, including carbon monoxide, formic acid, and various hydrocarbons. This process provides a two-pronged benefit: it helps curb CO_2 emissions and simultaneously generates valuable byproducts, which can be reincorporated into the pulp and paper manufacturing cycle, thus fostering a circular economic model.

In this paper, we initially sketch an overview of the existing state of the pulp and paper sector, emphasizing its environmental footprint and underscoring the need for inventive strategies to curtail its carbon emissions. Following this, we introduce the notion of CO_2 electroreduction, elucidating its foundational principles, the catalysts involved, and the diverse products that can be synthesized through this mechanism.

Subsequently, we venture into the potential applications of CO_2 electroreduction within the pulp and paper industry, specifically focusing on how the end-products of the process can be leveraged to create a more circular and sustainable industry. We discuss the use of carbon monoxide and hydrocarbons as alternative energy sources or raw materials for paper production and related goods. We also consider the possibility of using formic acid as an eco-friendly alternative to conventional pulping and bleaching chemicals, which could further diminish the industry's environmental imprint.

We then present recent case studies and advancements in CO_2 electroreduction research, highlighting its potential for large-scale integration within the pulp and paper industry. As part of a chemical plant and equipment manufacturing company, we also address the challenges of implementing this technology, touching on aspects such as the need for efficient catalysts, energy consumption, and scalability of the process.

The paper wraps up with a highlight of the role innovation plays in promoting circularity in the pulp and paper sector. The deployment of CO_2 electroreduction technology could not only help reduce the industry's environmental consequences but also herald a more sustainable and circular future. By fostering cooperation among researchers, industry stakeholders, and policymakers, we can expedite the development and execution of such innovative solutions, which ultimately pave the way towards a greener and more sustainable global environment.

Keywords: *Carbon Utilization, Circular Economy, CO_2 Electroreduction, CO_2 Valorization, Sustainable Innovation*

INTRODUCTION

The pulp and paper (P&P) industry is a significant contributor to global carbon dioxide (CO_2) emissions, accounting for approximately 1.1% of global industrial energy use and similar proportions of global industrial CO_2 emissions (Sajna et al., 2023). In certain countries, the contribution of this industry to CO_2 emissions is even more pronounced. For instance, the pulp and paper industry is responsible for 7% of Austria's industrial CO_2 emissions alone (Mobarakeh, 2021). This contribution results from the energy-intensive nature of the industry, coupled with the use of carbon-rich feedstocks. Consequently, there is an urgent need to explore innovative solutions that promote circularity and sustainability within the sector. One such promising solution is the CO_2 electrochemical reduction process, which transforms CO_2 emissions into valuable chemicals and fuels.

The CO_2 electrochemical reduction process, also known as CO_2 electroreduction, is a promising technology that converts carbon dioxide into valuable chemicals and fuels, such as carbon monoxide, formic acid, and hydrocarbons. This process not only mitigates CO_2 emissions but also generates valuable products that can be reintegrated into the P&P production cycle, thereby fostering a circular economy. By reducing the amount of carbon dioxide released into the atmosphere and simultaneously creating valuable products, this technology presents a dual advantage - environmental protection and economic gain.

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The circular economy is a model that seeks to decouple economic growth from the use of natural resources by circulating products, components, and materials at their highest utility and value at all times. In the context of the P&P industry, this involves minimizing wastewater, optimizing resource use, and creating more sustainable production and consumption systems. Implementing the CO_2 electroreduction process within this industry aligns perfectly with these goals. It not only reduces the industry's carbon emissions but also transforms these emissions into useful products, thus closing the loop in the production cycle.

This paper delves into the potential of this transformative approach in addressing the environmental challenges faced by the P&P industry and enhancing its circularity.

METHODS

CO_2 electroreduction is an electrochemical technique that reconfigures CO_2 into beneficial outputs such as carbon monoxide, formic acid, and diverse hydrocarbons. This procedure is expedited by catalysts that diminish the activation energy required for the CO_2 reduction reaction to occur (Farooqi et al., 2023). This paper provides a comprehensive overview of the current situation in the P&P industry, shedding light on its environmental consequences and emphasizing the necessity for innovative strategies to lessen its carbon footprint. The concept of CO_2 electroreduction is introduced next, providing an in-depth explanation of the principles that govern it, the array of catalysts deployed in the process, and the multitude of products that can be synthesized through this methodology. To arrive at these insights, we conducted a thorough literature review of the contemporary research and economic analyses centered around CO_2 electroreduction, with a particular focus on its potential applications within the P&P industry.

RESULTS AND DISCUSSION

The Pulp and Paper (P&P) sector is recognized for its high energy demand and substantial water usage, two factors that directly contribute to its carbon footprint. Various elements of paper manufacturing contribute to carbon emissions, to wit:

- Energy use: The P&P industry is particularly dependent on energy, with significant quantities derived from the black liquor obtained during the pulping process, as well as from bark or biomass and recovery boilers. In many instances, gas or coal-fired boilers are used to generate the steam necessary for paper production, and the combustion of these fossil fuels results in the emission of CO_2.
- Chemical processes: Numerous chemicals are employed throughout the pulping, bleaching, and papermaking processes. The production and application of these chemicals result in carbon emissions, especially when they originate from fossil fuel sources.
- Liquid waste management: A significant by-product of the P&P industry is liquid waste, including crude tall oil and process sludge effluents, which can release emissions if not properly managed.
- Sustainability in sourcing: Wood, a renewable raw material, is central to the pulp and paper industry. However, when wood fiber is harvested without the implementation of sustainable forestry practices, it can lead to a reduction in the natural carbon absorption capacity of forests.

In order to mitigate the P&P industry's carbon footprint, it's essential to integrate innovative technologies and solutions, including:

- Energy-efficient methods: The introduction of energy-saving technologies and methodologies, such as combined heat and power systems, can contribute significantly to the reduction of energy use and the related carbon emissions.
- Utilization of renewable energy: Transitioning to renewable energy sources like hydroelectric, solar, or wind power can substantially decrease carbon emissions produced by the P&P industry.
- Sustainable sourcing: Advocating for sustainable forestry practices and using recycled paper can help prevent deforestation and the subsequent carbon emissions associated with the procurement of raw materials.
- Enhanced production processes: By adopting cleaner and more efficient pulping, bleaching, and papermaking processes, the industry can decrease chemical use and its associated carbon emissions.
- Waste management and recycling: The deployment of efficient waste management strategies, such as recycling, waste-to-energy conversion, as well as carbon capture and utilization, can help limit greenhouse emissions.

Carbon Capture and Utilization (CCU)

Carbon Capture and Utilization (CCU) represents a significant opportunity for the pulp and paper industry to reduce its emissions. This strategy involves capturing the waste CO_2 generated during processing operations and then repurposing or converting it into value-added products.

Numerous sources of CO_2 emissions at pulp and paper mills can be exploited for CCU, such as flue gases from boilers, lime kilns, and power plants. By capturing these concentrated CO_2 streams, direct emissions to the atmosphere are reduced. Moreover, the industry's existing expertise in managing and processing carbon-rich feedstocks provides an advantage in effectively implementing CCU.

An especially promising CCU solution for the P&P industry is the electrochemical reduction process of CO_2. This cutting-edge technology transforms CO_2 into valuable chemicals and fuels, including carbon monoxide and hydrocarbons. It operates based on the principles of electrochemistry, employing electricity to drive chemical reactions that reduce CO_2 to more reduced states, generating products such as carbon monoxide,

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formic acid, methane, ethylene, methanol, and even complex hydrocarbons. A high-level overview of the process includes:

1. **Setup of Electrolysis Cell:** The CO_2 electroreduction process is conducted within an electrochemical cell, containing two electrodes: an anode and a cathode, separated by an electrolyte. The cathode is the site where the CO_2 reduction reaction happens, while the anode usually serves to oxidize water, generating oxygen and protons.
2. **Implementation of Electrolyte and Catalysts:** The electrolyte, which can be either liquid (such as water containing dissolved salts) or solid (such as a proton-exchange membrane), enables ion movement between the anode and the cathode. On the cathode side, catalysts are often employed to hasten the CO_2 reduction reaction. These catalysts can be derived from a range of materials, including metals, metal oxides, and even intricate organic molecules.
3. **Execution of CO_2 Reduction:** When electricity is supplied to the electrochemical cell, it stimulates the reaction at the cathode. Here, CO_2 molecules acquire electrons and are reduced to different products. The specific end products depend on the catalyst used and the reaction conditions, including the voltage applied and the reaction temperature. The following reactions represent possible reduction outcomes:

$$CO_{2(g)} + 2H^+ + 2e^- \rightarrow CO_{(g)} + H_2O_{(l)}$$
$$CO_{2(g)} + 2H^+ + 2e^- \rightarrow HCOOH_{(l)}$$
$$CO_{2(g)} + 6H^+ + 6e^- \rightarrow CH3OH_{(l)} + H_2O_{(l)}$$
$$CO_{2(g)} + 8H^+ + 8e^- \rightarrow CH_{4(g)} + 2H_2O_{(l)}$$
$$2CO_{2(g)} + 12H^+ + 12e^- \rightarrow C_2H_{4(g)} + 4H_2O_{(l)}$$
$$2CO_{2(g)} + 12H^+ + 12e^- \rightarrow C_2H_5OH_{(l)} + 3H_2O_{(l)}$$
$$3CO_{2(g)} + 18H^+ + 18e^- \rightarrow C_3H_7OH_{(l)} + 7H_2O_{(l)}$$

4. **Formation of Products:** By fine-tuning the catalysts and reaction conditions, the process can yield a variety of chemicals, ranging from simple compounds such as carbon monoxide and methane to more complex molecules like ethylene and ethanol.

The potential for applying the CO_2 electroreduction process in the P&P industry is immense. For instance, carbon monoxide, a product of the process, can serve as an alternate energy source in the P&P industry, thus reducing dependency on fossil fuels (Wang et al., 2022). Furthermore, hydrocarbons produced from CO_2 electroreduction can be utilized as raw materials for the manufacture of paper and related products (Table 1). This not only helps to reduce waste but also promotes a circular economy where waste from one process is repurposed as a resource in another.

Formic acid, another product of the process, can be used as a green alternative to traditional pulping and bleaching chemicals, which are often harmful to the environment. By substituting these chemicals with formic acid, the environmental impact of the P&P industry can be further reduced.

Oxalic acid, a liquid-phase product of the electroreduction process, has potential use in the bleaching of pulp, particularly to produce high-grade white paper. Its use can significantly improve the quality of paper products while reducing the amount of harmful chemicals used in the process.

Formaldehyde, a gas-phase product, can be utilized in resin production for bonding fibers. This contributes to the structural integrity of paper products, ensuring their durability and functionality.

Acetic acid, another liquid-phase product, can be used in the production of modified cellulose, a vital component of many paper products. In addition, it can be sold to the pharmaceutical and food industries.

Figure 1. High-level overview of the CO_2 electroreduction process. Instead of releasing carbon dioxide emissions into the atmosphere, a chemical plant captures them and directs them to a carbon dioxide reuse (CO2R) reactor within the same facility. The CO_2 is then transformed into products that are purified via separation technologies and recycled back into the main production process. © GIG Karasek

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Table 1. Gas-phase and liquid-phase products resulting from the electrochemical reduction of CO2 and their potential uses in the P&P industry

Product	Phase	Potential Use in P&P Industry
Carbon Monoxide (CO)	Gas	Used in the synthesis of various chemicals used in the P&P industry such as acetic acid
Methane (CH_4)	Gas	Can be used to power boilers and other equipment, reducing reliance on fossil fuels
Ethylene (C_2H_4)	Gas	Key raw material in the production of ethyl cellulose, a common paper-coating material
Formic Acid (HCOOH)	Liquid	Can be used as a pulping agent and in the bleaching process to brighten paper and remove residual lignin
Methanol (CH_3OH)	Liquid	Can serve as a solvent, is used as a raw material in the production of formaldehyde, is sold as an "industrial chemical" or is used as a fuel in recovery boilers.
Ethanol (C_2H_5OH)	Liquid	Is mainly sold as fuel, which is then added to gasoline.
Oxalic Acid ($C_2H_2O_4$)	Liquid	Used in bleaching of pulp to remove impurities, especially for high-grade white paper
Formaldehyde (CH_2O)	Gas	Used in resin production for bonding fibers and adhesives industry (e.g., urea resin, melamine resin).
Acetic Acid (CH_3COOH)	Liquid	Used in the production of modified cellulose, a component of many paper products

Furthermore, methane, a gas-phase product of the CO_2 electroreduction process, can serve as an alternative energy source for powering boilers and other equipment in the P&P industry. This not only helps reduce greenhouse gas emissions but also represents a significant cost-saving measure for the P&P industry.

Figure 2 illustrates the energy requirements for the electrochemical reduction of CO_2 into various products. These values are specified in kilowatt-hours per kilogram (KWh/kg) of each product. As depicted, methane has the highest energy requirement (23.6 KWh/kg), followed by ethylene (22.4 KWh/kg), and Ethanol (13.4 KWh/kg). On the lower end of the spectrum, oxalic acid requires the least amount of energy for its production (1.7 KWh/kg), with formic acid (2.9 KWh/kg) and CO (4.3 KWh/kg) also being relatively energy-efficient products of CO_2 electroreduction.

These energy requirements are critical considerations for the P&P industry, as they directly impact the feasibility and economic viability of implementing CO_2 electroreduction technology. Consequently, understanding these energy

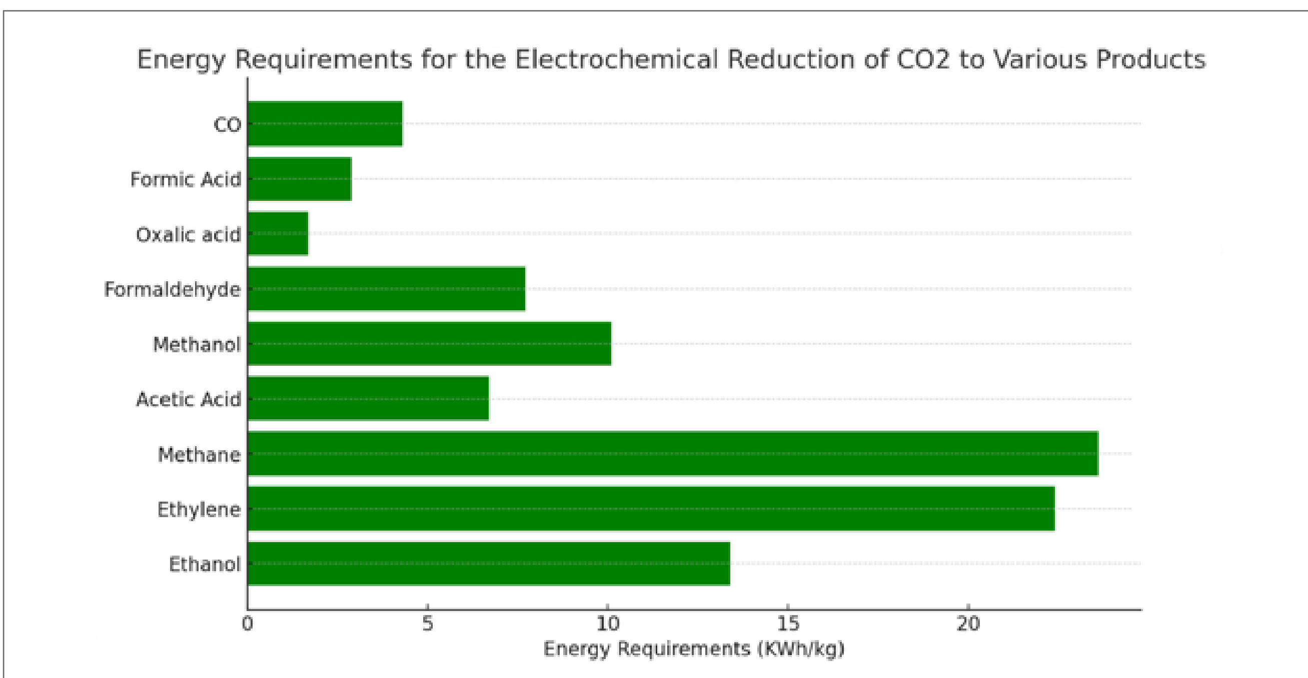

Figure 2. Energy requirements for the electrochemical reduction of CO2 into various products.
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requirements can guide decision-making and strategy development for incorporating this technology into the industry's operations.

Based on the methods developed by Barecka et al., 2011, a preliminary techno-economic assessment was conducted to evaluate the potential for electrochemical CO_2 reduction to produce methanol in a 400 kta pulp and paper plant. Based on an available CO_2 stream of 79 mol/s and assumptions of 50% CO_2 conversion, 1.7V cell voltage, and 0.3 A/cm2 current density, the analysis showed an electrolyzer size of 690 million cm^2 would be needed. The electrolyzer size was calculated using "Equation (1)":

Electrolyzer size (cm^2) = (Available CO_2 (mol/s) x CO_2 conversion) / (CO_2 converted per cm^2 (mol/s)) (1)

With a methanol production of 28.7 mol/s, electricity cost of \$0.02/kWh, and methanol price of \$0.4/kg, the estimated net value generated is \$7.2 million per year.

The return-on-investment period is projected to be 0.8 years at a production scale of 50,000 units per year. Operational costs are estimated at \$0.11/kg CO_2 recycled, with a product value of \$0.26/kg CO_2. This generates a 54% potential reduction in pulp and paper production costs calculated as "Equation (2)":

Cost reduction = - (OPEX + Product value + CO_2 tax) x (CO_2 conversion) x (Emissions density) / Product price (2)

The preliminary techno-economic analysis included a sensitivity analysis to evaluate the impact of electricity prices on the process economics. Electricity price is a key variable as it largely determines the operating costs for electrochemical CO_2 reduction.

The analysis was performed by varying the electricity price from \$0.01/kWh to \$0.045/kWh and assessing two key metrics - the return on investment (ROI) period and the potential reduction in pulp/paper production costs through CO_2 utilization (Figure 3).

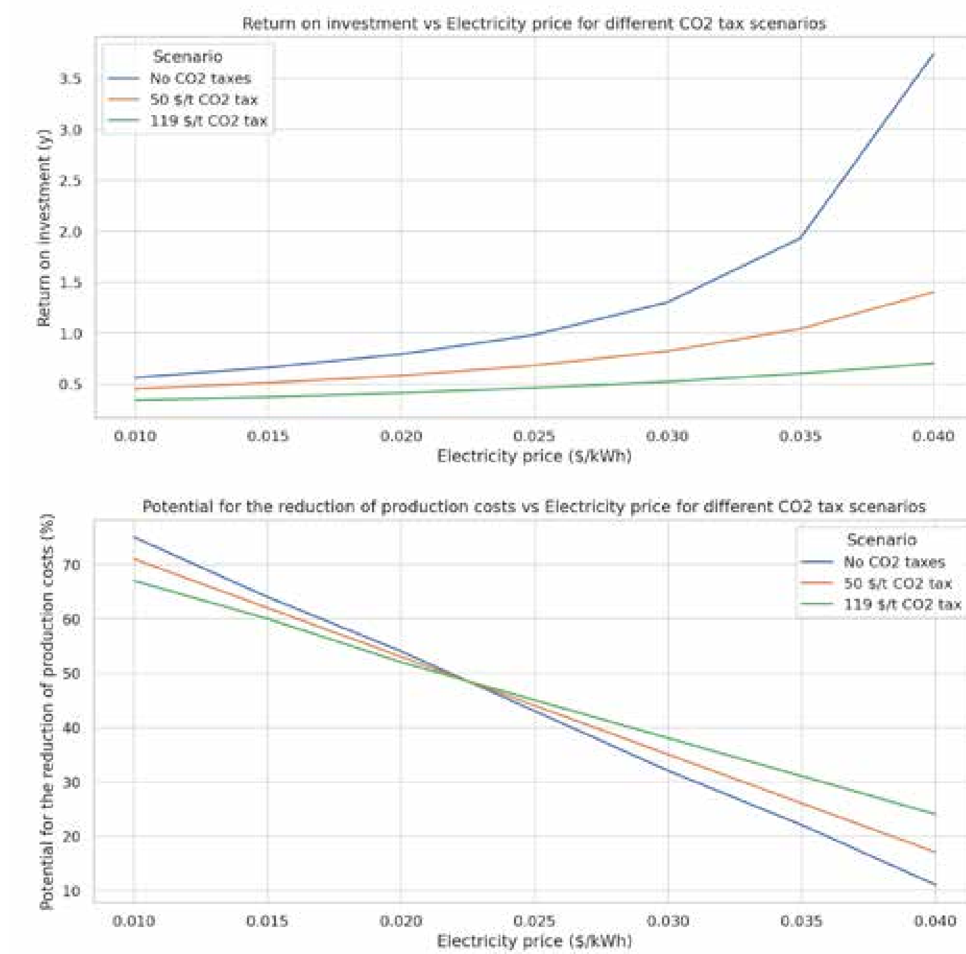

Figure 3. Comparison of Return on Investment and Cost Reduction Potential Across Different CO_2 Tax Scenarios: This figure presents the impact of varying electricity prices on the return on investment and potential for production cost reduction in three scenarios - No CO_2 taxes, a CO_2 tax of 50 \$/t, and a CO_2 tax of 119 \$/t. The plots illustrate that CO_2 taxes can enhance both the economic viability and cost-effectiveness of operations, with higher taxes providing more pronounced benefits.
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The results showed that at an electricity price of $0.01/kWh, the ROI period is just 0.41 years due to the low operating costs. The potential production cost reduction is also over 100%, indicating that CO_2 utilization could yield net cost savings for the mill.

As electricity price increases to $0.03/kWh, the ROI period rises moderately to 0.69 years, still quite attractive. Potential cost savings decrease but are still significant at around 60%. At a price of $0.045/kWh, the ROI period approaches 1.5 years, which may be near the upper limit of viability for such projects. Cost reduction potential also falls to around 30%.

It should be noted that the cost reduction lines intersect because the rate at which the potential for cost reduction decreases with increasing electricity prices differs for each scenario. In other words, as the electricity price increases, the potential for cost reduction decreases more rapidly in the "No CO_2 taxes" scenario compared to the scenarios with CO_2 taxes. This is because, in scenarios with CO_2 taxes, some of the operational costs are offset by the tax, making the operation more cost-effective. Thus, at lower electricity prices, the "No CO_2 taxes" scenario has a higher potential for cost reduction. But as the electricity price increases, the scenarios with CO_2 taxes become more cost-effective, leading to a higher potential for cost reduction. This causes the lines to intersect.

These promising preliminary results showcase the potential for electrochemical CO_2 reduction to enable profitable methanol production while lowering the carbon footprint of pulp and paper manufacturing. Further optimization of catalysts, reactors, and process integration can help improve the techno-economics and support adoption at large scales.

CONCLUSIONS

The techno-economic analysis conducted shows that with the right conditions, integrating CO_2 electroreduction into pulp and paper mills can be financially viable while delivering environmental benefits. Electricity prices below $0.03/kWh enable profitable production of methanol from CO_2, with the potential to cut manufacturing costs. The adoption of CO_2 electroreduction technology can significantly reduce the environmental impact of the pulp and paper industry and pave the way for a more sustainable and circular future. Through collaboration between researchers, industry stakeholders, and policymakers, the development and implementation of such innovative solutions can be accelerated, ultimately contributing to a greener and more sustainable world. ■

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