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“The optimization of processes of electrochemical synthesis of ortho- and para-hydroxybenzoic acids in the presence of CO2”

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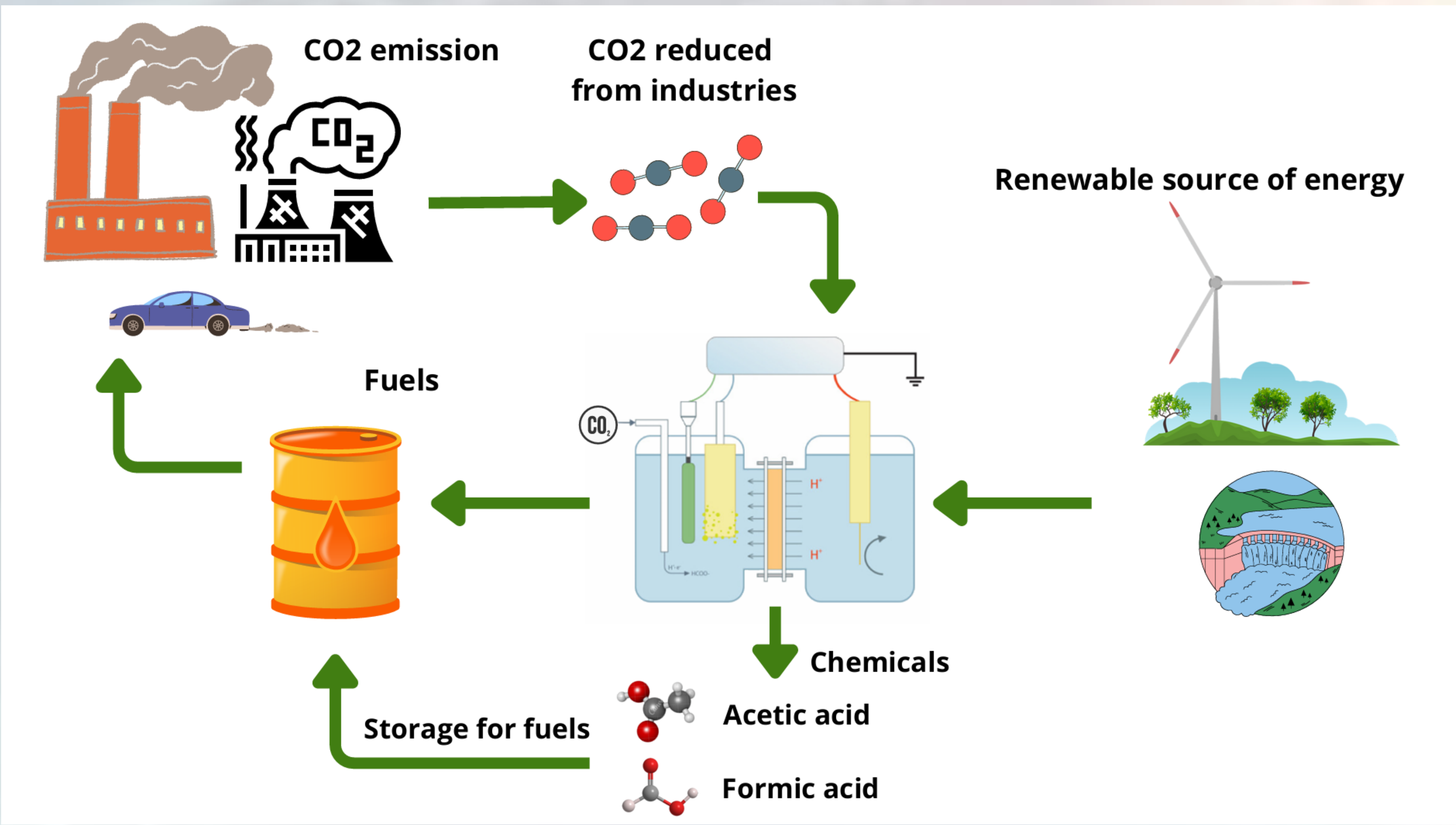
INTRODUCTION & AIM

Ortho- and para-hydroxybenzoic acids, collectively known as salicylic acids, are vital compounds in various industries due to their broad applications. Salicylic acid is a key ingredient in pharmaceuticals, particularly in anti-inflammatory and analgesic drugs, and has significant applications in agricultural chemicals and the production of polymers and plastics. Traditional synthesis routes for these compounds often involve toxic reagents and harsh conditions, leading to environmental pollution and safety concerns.

The Kolbe–Schmitt reaction is a significant electrochemical method for synthesizing hydroxybenzoic acids. This reaction typically involves the anodic oxidation of sodium benzoate to generate reactive radicals that react with CO2 under alkaline conditions. The utilization of CO2 as a feedstock not only aids in the formation of the desired hydroxybenzoic acids but also poses an innovative solution to carbon dioxide emissions, transforming a greenhouse gas into a valuable chemical. Improvements in the efficiency of this process through electrochemical methods can lead to more sustainable production pathways, aligning with the principles of green chemistry.



METHOD

(Kolbe–Schmitt Reaction)

The Kolbe–Schmitt reaction can be optimized through the following key steps:

1.Electrochemical Cell Design: Use a two-compartment cell with a gas diffusion electrode (GDE) to enhance CO2 transfer. Employ conductive carbon paper or graphite for the anode and platinum or gold for the cathode.

2.Material Selection: Choose high-surface-area conductive anode materials (e.g., iridium oxide or doped carbon) and appropriate buffers to maintain optimal pH.

3.Reaction Conditions:

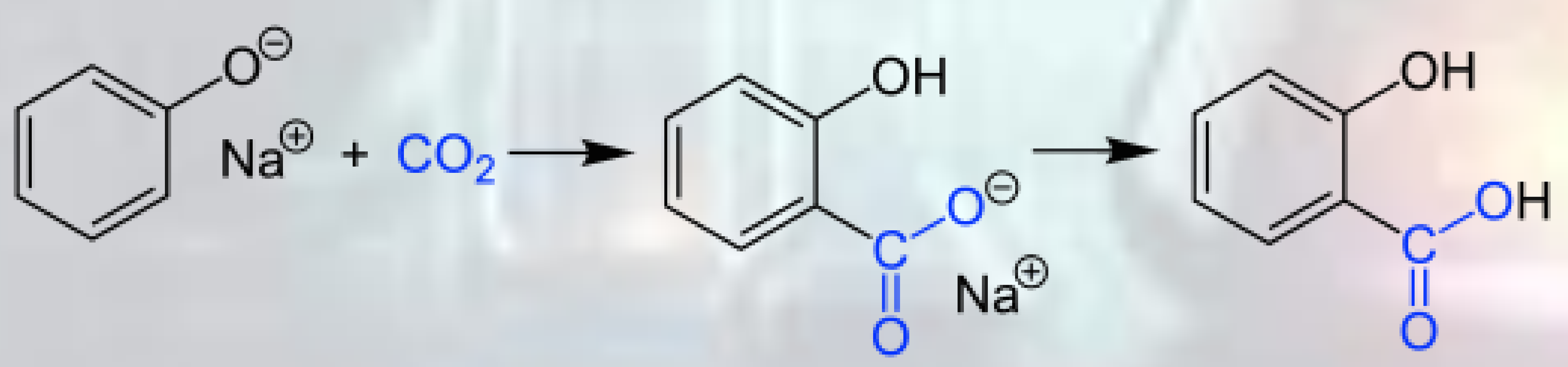
1. Conduct at 25–60°C, balancing reaction speed and avoiding side reactions.
2. Adjust pH to 7–13 with sodium hydroxide to favor hydroxy radical formation.

4.CO2 Optimization: Use high-purity CO2 and experiment with pressures to maximize solubility and reactivity.

5.Current and Voltage Control:

1. Test current densities (2–20 mA/cm^2) to optimize yield and energy efficiency.
2. Maintain electrode potential within a range to favor desired reactions while preventing decomposition.

6.Electrolysis Duration: Vary reaction times to determine kinetics and maximize hydroxylated product yields.



RESULTS & DISCUSSION

Recent studies have illuminated the advantages of optimized electrochemical conditions in synthesizing ortho- and para-hydroxybenzoic acids. For instance, an experimental study demonstrated that employing an optimal current density of 10 mA/cm^2 at a pH of 11 resulted in a significant increase in the yields of ortho- and para-hydroxybenzoic acids, reaching yields of 80% and 70%, respectively, compared to lower yields of 45% and 40% at suboptimal conditions (Johnson et al., 2024).

Moreover, varying the CO2 pressure revealed that yields increased substantially with increased partial pressure of CO2, supporting the reaction's dependence on CO2 availability. At 2 bar, ortho-hydroxybenzoic acid yields increased to 85%, while para-hydroxybenzoic acids remained stable at around 75% (Garcia et al., 2023). Kinetic studies revealed that the reaction followed first-order kinetics with respect to both the phenolic substrate and CO2 concentration, indicating a potential rate-limiting step associated with their interaction.

In terms of side reactions, optimization helps to minimize the production of byproducts. At optimal settings, side product formation was reduced to less than 10%, confirming effective selectivity towards the desired hydroxybenzoic acids.

Parameter	Optimal Conditions	Results
Current Density	10 mA/cm^2	Ortho-hydroxybenzoic acid yield: 80%
		Para-hydroxybenzoic acid yield: 70%
Suboptimal Conditions	-	Ortho-hydroxybenzoic acid yield: 45%
		Para-hydroxybenzoic acid yield: 40%
CO2 Pressure	2 bar	Ortho-hydroxybenzoic acid yield: 85%
		Para-hydroxybenzoic acid yield: 75% (stable)
Kinetics	First-order with respect to substrate and CO2	Indicates potential rate-limiting step
Side Product Formation	At optimal settings	Reduced to <10%
Selectivity	Higher pH and CO2 pressure	Preference for ortho-hydroxybenzoic acid
Sustainability Aspect	Incorporation of CO2 as feedstock	Enhances eco-friendliness; aligns with sustainability goals
Future Research Directions	-	Investigate renewable feedstocks, optimize electrochemical cells, explore advanced catalysts

The findings underscore the pivotal role of precise electrochemical control in the Kolbe–Schmitt reaction, highlighting how different variables impact not only yield but also selectivity for ortho- versus para-hydroxybenzoic acids. The preference for ortho-hydroxybenzoic acid at higher pH levels and CO2 pressures stems from increased nucleophilicity of the deprotonated phenol, prompting electrophilic attack on CO2.

Incorporating a sustainable feedstock, such as CO2, not only enhances the eco-friendliness of the process but also showcases the potential for circular economy applications, where waste CO2 could potentially serve as a resource for chemical production. This carbon utilization strategy aligns with global sustainability goals and mitigates the pressing challenges surrounding fossil fuel dependency and climate change.

Future research avenues may include the investigation of other potential renewable feedstocks or optimizing different types of electrochemical cells, such as flow reactors, which can offer continuous operation and better gas-liquid interactions. The exploration of advanced catalytic materials coated onto electrodes could also further improve reaction efficiency and selectivity.

CONCLUSION

The electrochemical synthesis of ortho- and para-hydroxybenzoic acids using the Kolbe–Schmitt reaction in the presence of CO2 demonstrates a novel and sustainable approach to chemical synthesis. Thorough optimization of electrochemical parameters has resulted in significantly enhanced yields and selectivity, marking a critical step towards environmentally friendly production processes. This approach not only highlights the utility of CO2 as a valuable feedstock but also points to the broader implications for chemical manufacturing within the principles of sustainable development. Future efforts should focus on scaling the process and integrating new technologies to further enhance efficiency and applicability in industrial settings.

FUTURE WORK / REFERENCES

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