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Transforming a Threat into Fuel : A Comprehensive Exploration of CO_2 Conversion Pathway to Ethanol for a Sustainable Future in India

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ABSTRACT

The escalating dependence on fossil fuels has intensified the greenhouse effect, primarily due to carbon dioxide (CO_2) emissions. This paper investigates a potential of CO_2 conversion into ethanol, a promising biofuel alternative. Following a critical review of the current ethanol blending policy in India and it's challenges (majorly due to feedstock availability), the paper delves into the various CO_2-to-Ethanol conversion technologies and pathways including catalytic hydrogenation, electro-catalytic reduction and photo-assisted processes. Recent advancements and research efforts, including those by Covalent Projects & Engineers Pvt. Ltd., Pune India are explored to highlight the progress in this domain. The paper concludes by emphasizing the potential of CO_2-to-ethanol conversion as a sustainable solution for India's energy needs and proposes future research directions.

Keywords: Ethanol, biofuel, Co^2 emission, ethanol blending, Co_2

INTRODUCTION

India's dependence on crude oil imports has been deepening over the years and it was the highest at 87% in year 2022-23. An increased use of ethanol is likely to reduce India's crude oil dependence and save more than USD 4 Billion annually. Reducing crude oil import, reducing emissions and minimizing the depletion of fossil fuel reserves are the key drivers behind India's Fuel Ethanol Policy. The key feedstocks for producing ethanol in the country are sugarcane, rice and maize. The basic question remains if the country should prioritize achieving energy security or food security. It is always debatable whether India should divert crops such as rice, maize and sugarcane for fuel production or use them to first meet food and feed demands. The position may not be as binary in the case of sugarcane where sugar is generated as a by-product, but diverting maize and rice for ethanol production directly competes with their food and feed requirements. National Biofuel Policy states the target of 20% Ethanol blended petrol by year 2030 (which was later advanced to year 2025). However, country could achieve highest of 12% ethanol blending mainly due to shortfall in feedstocks.

The sun serves as the primary source of energy for much of our energy consumption, despite the extensive discussions and concerns regarding future energy crisis. This reliance on solar energy extends to various forms of energy, including fossil fuels such as coal, oil, and natural gas. The sun, in the natural carbon cycle, facilitates the recycling of carbon dioxide from its natural sources through the intricate process of photosynthesis. This metabolic process entails the absorption of CO_2 from the atmosphere by various photosynthetic organisms such as vegetation, plankton, and algae. Utilizing water as a hydrogen source and under the catalytic influence of green chlorophyll, solar energy initiates the synthesis of organic compounds, thereby fostering the growth of new plant life. Carbon stands as a fundamental cornerstone for the construction and sustenance of all life forms inhabiting our planet. Its perpetual cycling from the atmospheric reservoir is an indispensable process in the intricate web of Earth's ecosystems. The conversion of carbon dioxide (CO_2)

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into fuels and chemicals holds significant promise in alleviating the depletion of fossil resources and curbing carbon emissions, thereby mitigating the effects of global warming.

Commencing with an alternative perspective, the chemical carbon cycle diverges from the natural carbon cycle, driven by photosynthesis and subsequent gradual anaerobic conversion into fossil fuels. This chemical process holds potential for large-scale industrial implementation, offering a sustainable, renewable and secure carbon source. Through this cycle, hydrocarbons, derived fuels and essential synthetic products can be produced to meet societal demands. Furthermore, embracing the chemical recycling of carbon dioxide presents an avenue to mitigate or eliminate the detrimental environmental impact of excessive atmospheric carbon dioxide, a major driver of global climate change.

Carbon dioxide is a greenhouse gas which comes from extraction and burning of fossil fuels (such as coal, oil and natural gas) and it also evolves during fermentation of sugars during ethanol manufacturing process. Since the onset of industrial times in the 18th century, human activities have raised atmospheric CO_2 by 50% - meaning the amount of CO_2 is now 150% of its value in year 1750. This human-induced rise is greater than the natural increase observed at the end of last ice age 20,000 years ago. As greenhouse gas emission blanket the Earth, they trap the sun's heat. This leads to global warming and climate change. The world is now warming faster at any point in recorded history. Warmer temperatures over time are changing weather patterns and disrupting the usual balance of nature. This poses many risks to human beings and all other forms of life on Earth.

Fossil fuels – coal, oil and natural gas - are by far the largest contributor to global climate change, accounting for over 75% of global greenhouse gas emissions and nearly 90% of all carbon dioxide emissions. With major expansion in ethanol production using fermentation process, there will be enormous amount of CO_2 generation (91.3% w/w of ethanol production) which needs to be addressed.

To address the escalating levels of atmospheric carbon dioxide, reducing reliance on fossil fuels, transitioning to alternative low-carbon energy sources and enhancing natural photosynthetic recycling or deploying carbon capture and storage methods emerge as imperative strategies.

Technology

There are several possible pathways of CO_2 recycling and conversion to ethanol. It should be noted that these pathways differ with respect to their degree of maturity, their potential for emergence, duration of CO_2 sequestration, energy consumption, volume of ethanol recovery and energy efficiency. The main objective of this paper is to deepen the CO_2 electrochemical recycling by studying the technical feasibility. The proposed process consists of two main steps. The first one is the high temperature co-electrolysis of CO_2 and water vapour, using solid oxide electrolysis cells (SOEC) to produce the syngas (H_2+CO). The second step consist of converting syngas into synthetic fuel (gasoline/diesel/ethanol) via fisher tropsch reactions synthesis or convert it into ethanol via catalytic and exothermic reactions whose products depends on the operating parameters and type of catalyst.

Co-electrolysis of CO_2 and H_2O

Electrochemical recycling of carbon dioxide consists of using carbon-free energy (solar) as a source of electricity, to allow the dissociation of CO_2 and H_2O. This separation can be carried out via thermolysis, photolysis or electrolysis of water vapor and carbon dioxide. In this study we chose to use electrolysis to dissociate carbon dioxide and water vapor. There are two ways to produce syngas via electrolysis of CO_2 and H_2O - dissociate CO_2 and H_2O separately in two different electrolysis cells or simultaneously in the same electrolysis cell. Recent research has shown that co-electrolysis H_2O and CO_2 is more interesting in terms of energy consumption and conversion rate than separate electrolysis of water vapour and carbon dioxide. The co-electrolysis of water vapor and carbon dioxide can be summarized by the following reaction:

The first reaction to be considered is the reverse reaction of water gas shift.

$$H_2O + CO_2 \longleftrightarrow H_2 + CO + O_2$$

It is slightly endothermic reaction ,another side reaction that can also affect the electrolysis operation is the formation of coke (carbon deposition on the surface of the electrolysis cell) as follows:

$$CO\ C \longrightarrow + \tfrac{1}{2}\, O_2$$

At a temperature below 700 °C, and in the presence of nickel as catalyst, methane is formed according to the following reaction:

$$CO + 3H_2 \longrightarrow H_2O + CH_4$$

Therefore it is preferable to use temperatures above 700 °C to avoid the formation of methane. In order to determine the composition (mole fractions of the chemical species) at the outlet of the electrolysis cell according to the operating parameters including the current density ,the temperature and gas flow rates. H_2O and CO_2 co-electrolysis model is much more complicated than simple electrolysis of water or carbon dioxide. The reaction mechanism of co-electrolysis of H_2O and CO_2 is complicated and not fully understood because it includes three simultaneous reactions: electrolysis of CO_2, H_2O and the reverse reaction of water gas shift (RWGS). Until now it is not precisely known if the CO produced is formed by electrolysis of CO_2, or via the reverse reaction of water gas.

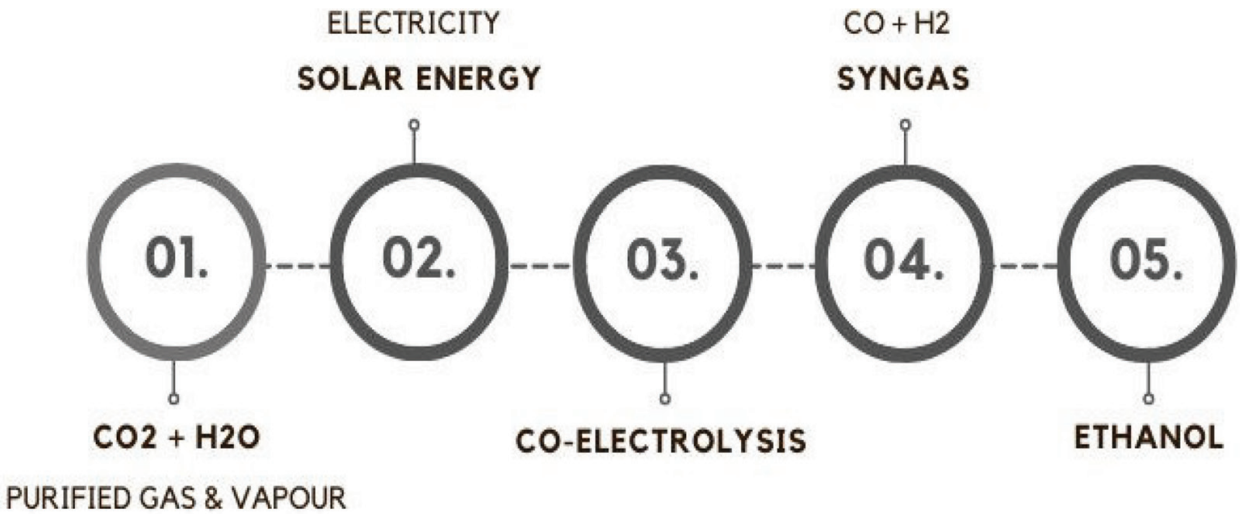

Figure 1 : Pathway for Co-electrolysis for CO_2 to ethanol conversion

Ethanol synthesis

Ethanol is a 2-carbon alcohol with a molecular formula CH_3-CH_2-OH. It is a colourless versatile solvent miscible with water. Syngas produced during co-electrolysis of CO_2 and H_2O could be converted to ethanol in three different pathways. The first pathway consists of direct synthesis of ethanol form syngas. The second pathway is syngas conversion to methanol which is converted to ethanol via methanol homologation reaction. The last pathway is known as the ENSOL process. Syngas is first converted to methanol over a methanol commercial synthesis catalyst followed by methanol carbonylation to acetic acid in the second step and, then, subsequent hydrogenation of acetic acid to ethanol. All these pathways differ in term of catalysts used, operational conditions, selectivity for ethanol and C_2 oxygenates. The pathway which adopted in this paper is the direct synthesis of ethanol from syngas.

The direct conversion of syngas to ethanol is the most studied way in terms of used catalysts and operating conditions. Thus tens of catalysts have been developed in this perspective. Considerable research has been conducted on this topic in order to understand more the reaction mechanism which remains currently poorly understood, and in order to characterize the kinetics of the reaction. The rhodium based catalysts, which is a noble metal, are known to have the best selectivity to ethanol (to C_2+ oxygenates in general) with a good carbon monoxide conversion.

Conversion of CO_2 to ethanol by electrochemical synthesis method using Cu-Zn electrode

Conversion of CO_2 into ethanol in an electro-chemical synthesis reactor is done by varying the voltage, concentration of sodium bicarbonate electrolyte solution and time of electrolysis to obtain the optimum conditions to convert CO_2 into ethanol. Sodium bi-carbonate electrolyte solution is incorporated into an electrochemical synthesis reactor which is equipped with a brass electrode plate (cathode) and a carbon electrode rod (anode). Purified CO_2 gas flows into the electrochemical synthesis reactor with controlled flow rate. The optimum voltage is studied by flowing voltages with variations. The optimum time of electrolysis is studied for 60, 90, 120, 150 and 180 minutes.

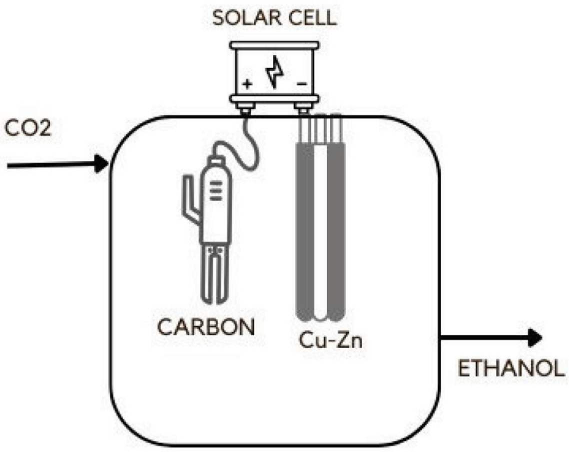

Figure 2 : Electro-chemical synthesis reactor using Cu-Zn electrode

Advantages

Although bioethanol production is considered to be sustainable from a global warming perspective, its dependence on agricultural systems, land management, and geographical limitations has sparked concern. The electrocatalytic CO_2 reduction reaction (CO_2RR) is a promising alternative pathway to produce fuels, such as ethanol, through captured CO_2 and electricity. Secondly, the CO_2 generated during fermentation of sugars can be converted to ethanol, thereby adding in overall Ethanol production and reducing emission of greenhouse gas.

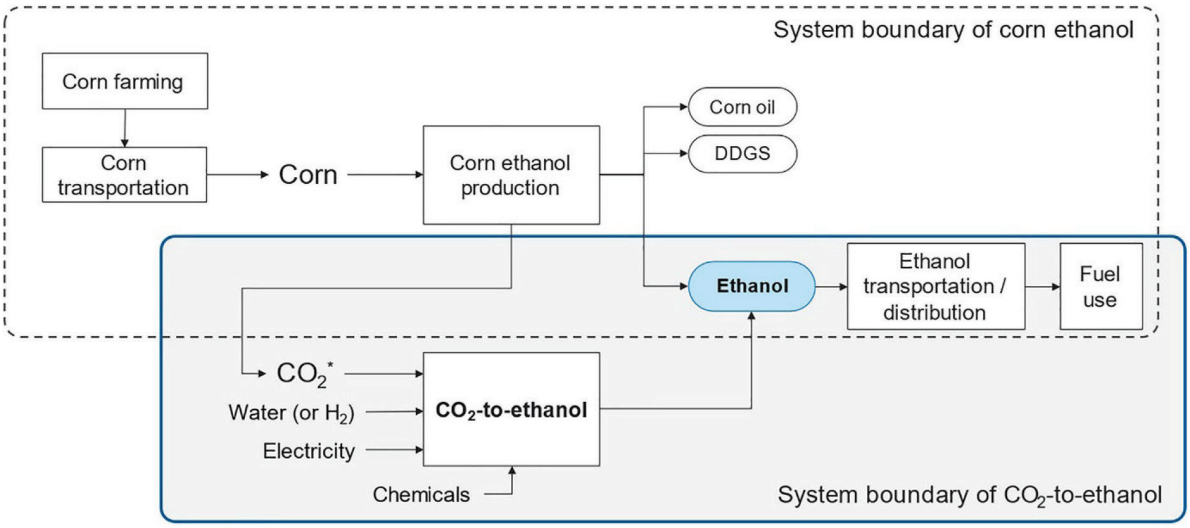

Figure 3 : Corn ethanol and CO_2 ethanol integrated production mModel

CONCLUSION

India's utilization of fossil fuels has witness a substantial surge, with coal consumption reaching 502.46 million tonnes of oil equivalent (MTOE), oil consumption standing at 245.46 MTOE, and natural gas consumption amounting to 54.63 MTOE as of the year 2023. This escalation underscores the nation's heavy reliance on traditional energy sources, posing challenges to its aspirations for biofuel adoption. India's biofuel aspirations are constantly challenged by the limited availability of feedstock, the raw materials needed for biofuel production. This scarcity significantly impacts the country's ability to achieve its ambitious biofuel blending targets. In response to these challenges, the National Policy on Biofuels (NBP) of 2018 set forth a visionary goal of achieving 20% ethanol blending in petrol by 2030, aiming to diminish reliance on imported fossil fuels and promote environmental sustainability.

However, recent government directives prioritizing sugar production over ethanol production from sugarcane juice have jeopardized the immediate 15% blending target for 2023-24. Despite these setbacks, there is a growing interest in exploring alternative feedstocks such as researching CO_2 conversion to ethanol.

In addition to this, CO_2 generated during fermentation of sugars at ethanol production facilities is being vented into atmosphere, thereby making an addition to greenhouse gases and global warming.

Grain and molasses ethanol plants generate high-purity carbon dioxide (CO_2) while producing ethanol. CO_2 production is almost 91.3% weight/weight of ethanol in proportion to their molecular weights. If that CO_2 could be converted into ethanol by carbon recycling and utilization technologies it would be possible to increase ethanol production to almost double without additional grain or molasses input.

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