

Advanced Biomass Conversion: Sustainable e-methanol production with enhanced CO₂ utilization

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Abstract

Amid escalating concerns over climate change and emissions, this study presents a novel approach to develop sustainable fuels, leveraging advanced process modeling that uses waste CO₂ streams from the biological ethanol fermentation process to produce e-methanol. Using Aspen Plus software, this research focuses on the conversion of biomass such as sugar cane and sugar beet to reduce reliance on fossil fuels and fortify energy resilience in a sustainable manner. In the first phase, bagasse, a byproduct of sugar production that is rich in carbon is used as a precursor for gasification and as a fuel to generate high-pressure steam. Oxygen obtained from electrolysis of water using renewable energy is used to preheat the biological exothermic fermentation phase. The CO₂ captured during the fermentation phase is mixed with hydrogen obtained from the electrolysis process to synthesize e-methanol. Lignin, a byproduct of second-generation bioethanol, and surplus bagasse are identified and converted into ethanol and e-methanol, respectively, optimizing the use of CO₂ from fermentation and O₂ from electrolysis. Lastly, gasification of the carbon-rich bagasse serves to further enhance methanol production, culminating in the generation of enriched e-methanol. This results in enhanced bioenergy, bio-carbon recovery and consequently reduced fossil CO₂ emissions, offering a holistic CO₂ and biomass management solution. This research introduces a groundbreaking approach to sustainable fuel production, significantly advancing over traditional methods by implementing a closed carbon cycle that fully utilizes every carbon atom from biomass feedstock. This contrasts sharply with conventional practices where carbon dioxide is often released as a byproduct, aggravating greenhouse gas emissions. A key innovation is the waste-to-value conversion, where byproducts like bagasse and lignin are transformed into valuable fuel sources, adding a new dimension of resource optimization absent in traditional fuel production. The environmental impact is profound, with a potential substantial reduction in greenhouse gas emissions, particularly in the transport sector, positioning this method as a sustainable alternative aligned with global environmental goals. Economically, it promises enhanced viability through improved resource utilization and efficiency, presenting a holistic solution that addresses both energy needs and environmental concerns, a significant leap forward from the limitations of traditional fossil fuel-based methods.

Introduction

The transportation sector represents roughly 26% of global energy consumption, contributing to 22% of worldwide CO₂ emissions from

fossil sources [1]. The present atmospheric CO₂ level is 400 ppm [2]. A significant 94% of its energy source is anchored in petroleum-based fuels. Due to the implications of climate change and the strategic emphasis on energy diversification, there is a shift towards exploring low-carbon alternative fuels. Predictions suggest that conventional energy sources will be exhausted in the coming decades, given their rapid extraction and slow rate of renewal [3]. Given the significance of biofuels in everyday life and the urgency to combat environmental degradation from fossil fuel consumption, there's a pressing need for eco-friendly energy alternatives. As traditional energy reserves diminish, solutions such as biofuels including biodiesel, and bioethanol emerge as vital replacements [3].

Eliminating subsidies for fossil fuels is crucial for effective transitions to clean energy, a point emphasized in the Glasgow Climate Pact [4]. The International Energy Agency (IEA) identifies several core strategies for decarbonization, comprising energy efficiency enhancements, modifications in consumer behavior, increased electrification, renewable energy sources expansion, the development and integration of hydrogen and fuels based on hydrogen, bioenergy utilization, and the advancement of carbon capture, utilization, and storage technologies [5, 6]. Biomass-derived and other renewable energy sources are viable contenders to replace petroleum in this context [5, 7].

Energy carriers suitable for transportation encompass liquid and carbon-based fuels [8, 9], hydrogen [10], and electricity [11, 12]. To generate these carriers with a low fossil-carbon footprint, it is essential to harness renewable sources like biomass, solar, and wind energy [13]. There is considerable scope to enhance the adoption of biomass-based fuels, electricity, and hydrogen within the transport realm. However, there remains ambiguity regarding the feasibility of batteries and fuel cells for sectors like aviation, maritime transport, and long-haul road movement [14, 15]. Primary approaches to lowering Greenhouse gas emissions focus on electrifying the transportation sector [16]. However, certain areas, due to logistical and safety challenges, find this solution challenging to adopt [17].

There are challenges in adopting electrification in sectors like aviation [18], heavy-duty vehicles [19], and marine transport due to their high energy requirements and the limited energy storage capacity [20] of batteries [17, 21]. For such scenarios, the solution lies in converting electricity into alternative energy forms [22, 23]. Depending on the specific technology or system, electricity can be used directly, as seen in battery electric vehicles (BEVs), or transformed into adaptable energy carriers suitable for storage, transport, and diverse energy applications [24]. This has led to the introduction and growing

prominence of the term "Power-to-Fuels" (PtF) in recent years, given its expanding range of applications and versatility [25]. Essentially, PtF transforms electricity—primarily from renewable sources such as solar, wind, and hydro—into carbon-neutral synthetic fuels poised to replace traditional fossil fuels [25]. These newly produced fuels, known as "e-fuels" or "electro-fuels", are generated either from capturing carbon dioxide and then combining it with hydrogen from water electrolysis [2, 26].

Consequently, e-fuels present an avenue for amplifying the incorporation of green electricity in transport, bolstering energy reliability [27]. Within the framework of both European and national strategies to advance energy transition, the topic of alternative, renewable liquid fuels is distinctly highlighted [27-29]. Over the past decade, Europe has seen the development of several pilot facilities. Notably, Carbon Recycling International (CRI) in Iceland has been harnessing geothermal energy to produce methanol since 2011 [30]. Audi AG's ETOGAS in Germany has established a plant powered by wind energy to generate methane [31]. Additionally, a German experimental facility had successfully produced high-quality diesel using renewable electricity and captured CO₂. These fuels are integral to fostering the expansion of eco-friendly mobility, aiming for a net-zero emissions target. These fuels hold potential across various modes of transportation. Some can be utilized in traditional combustion engines without necessitating substantial infrastructure modifications. These are known as drop-in fuels [32]. Besides serving as a potential alternative for future transport fuels, electrofuels can enhance biofuel production by utilizing the surplus CO₂ associated with them. Moreover, they can play a role in stabilizing fluctuating electricity output.

The transport sector demands vast amounts of energy, especially in populated areas and during peak times. This poses a multifaceted problem for the energy industry, requiring timely energy provision, storage solutions, grid enhancements, and political considerations. A solution is converting energy into chemical carriers using renewables which are compatible with the current systems [33]. Meanwhile, the ethanol industry aims to boost its greenhouse gas reductions by capturing and using CO₂ produced during fermentation [34].

One of the most widely produced e-fuels is methanol [35]. Methanol is a vital chemical that offers an alternative to liquid fossil fuels, allowing for cleaner combustion without necessitating significant infrastructure modifications [36]. Additionally, it serves as a precursor in the production of various other chemicals.

Given the objectives set for both medium and long-term horizons concerning decarbonization and the evolution of sustainable technologies, this study focuses on e-fuels derived using bio-feedstocks. These e-fuels are synthesized using hydrogen obtained from water electrolysis—powered by renewable energy—and CO₂ captured during bio-ethanol fermentation processes.

In our investigation, we focused on Christian Schweitzer's 'CO₂mbined cycle' from BSE Engineering, a pivotal initiative aimed at enhancing the efficient and flexible generation of energy from biomass, a critical factor in the reduction of anthropogenic greenhouse gas emissions. Schweitzer's innovative approach emphasizes the urgent need for more efficient biomass utilization to counteract the escalating demand for land in energy production. The CO₂mbined plant, a remarkable

innovation in technology, integrates existing mass flows to create a unique product.

The essence of the CO₂mbined plant lies in its unique technical concept, which harmonizes four primary process units into a single, efficient system.

The first process involves an electrolyser that harnesses surplus grid power to generate pressurized Hydrogen and Oxygen. The second process employs a steam generator that utilizes Oxygen from the first step to minimize NO_x emissions and produce steam, thereby boosting boiler efficiency. The third step involves biological endothermic fermentation, which leverages steam from the second and fourth processes to produce atmospheric green CO₂ and market-ready fuel through fermentation. The final step, exothermal methanol synthesis, combines compressed Hydrogen and green CO₂ to yield steam and methanol. This integrated approach not only maximizes biomethanol production from renewable resources but also capitalizes on the benefits offered by existing bioethanol plant locations. The ready availability of substantial quantities of green CO₂, coupled with optimal infrastructure achieved through this four-step combination, significantly enhances both the technical and commercial viability for specific customers. This results in a more efficient biomass fuel yield and reduced production costs. [37]

In this paper, our aim is to examine the feasibility of producing e-fuels via carbon capture and utilization (CCU), bagasse gasification and electrolysis, harnessing renewable energy sources.

The integrated plant system is designed around four principal processes, each contributing to the overarching objective of sustainable fuel production. Initially, the system employs an electrolyzer, which utilizes surplus electricity from the grid—preferably sourced from zero-carbon power—to generate pressurized hydrogen and oxygen. The oxygen produced in this stage is then strategically used to facilitate the decomposition of sucrose and fructose, derived from sugarcane processing byproducts, to produce bagasse.

Subsequently, the system engages in a biological fermentation process. This phase leverages the steam generated earlier to produce green CO₂ while concurrently synthesizing ethanol, which is then prepared for market distribution. Following this, the plant undertakes exothermal methanol synthesis. This critical phase involves the combination of the compressed hydrogen, sourced from the electrolyzer, with the green CO₂, a byproduct of the fermentation process. This reaction not only results in the production of steam but also yields e-methanol.

In the final stage of the process, bagasse obtained from the pre-treatment or filtration phase is subjected to gasification. This gasification process is then followed by the conversion of the resultant product into bio-methanol. This bio-methanol, when combined with the e-methanol produced earlier, significantly enhances the overall methanol output of the system. The primary objective of this integrated approach is to ensure the transformation of all carbon atoms within the system into fuels, thereby eliminating any residual CO₂ emissions and

Methanol Synthesis Methodologies

Various methodologies for methanol synthesis have been delineated in literature, with CO₂ hydrogenation emerging as an environmentally-friendly approach [60 - 62]. A comparative study by Zhang et al. [63] assessed the merits of merging biomass-to-methanol synthesis with a solid oxide electrolysis cell (SOEC) against its union with a water-gas-shift reaction. The former, leveraging the SOEC, exhibited an exergy efficiency of 59.1%, outstripping the latter by an 11.1% point margin. In the context of CO₂ hydrogenation via the so-called S-Graz cycle, Nami et al. [64] conceptualized a trigeneration framework, concurrently generating power, hydrogen, and methanol. This innovative model achieved a methanol synthesis rate of 65.58 kg/h and an overall exergy efficiency of 40.7%.

Bos et al. [65] assessed methanol synthesis using CO₂ captured from the atmosphere and H₂ generated via wind-driven electrolysis process. Their findings indicated a power-to-methanol efficiency of approximately 50%. Ishaq et al. [66] introduced a system comprising wind turbines, a PEM electrolyzer, and a methanol production mechanism to harness industrial CO₂ emissions. Under varying operational conditions, the system demonstrated simultaneous methanol and hydrogen production with exergy and energy efficiencies of 38.2% and 39.8%, respectively. Meunier et al. [67] analyzed methanol production by leveraging CO₂ from a cement facility using a monoethanolamine (MEA) - based capture approach, emphasizing the economic viability's dependence on electricity and H₂ production expenses. Zhang et al. [68] explored a large-scale power-to-methanol system utilizing a solid oxide electrolyzer with co-electrolysis capabilities. Their research revealed the system's potential to maintain high energy efficiency (72%) and carbon conversion (93.6%) while using 146.7 kton of CO₂ annually. Xin et al. [69] studied carbon-neutral, coal-centric polygeneration system that integrated a methanol synthesis supercritical CO₂ cycle with syngas from coal gasification directed to the methanol reactor. Their findings suggested a fuel savings rate of approximately 5.3% and a 10.8% reduction in exergy destruction compared to standalone systems. He et al. [70] conducted energy and exergy evaluations on an innovative methanol-electricity polygeneration system using coal-steam gasification, reporting an energy efficiency close to 63%.

Zhang et al. [71] conducted an assessment of the viability of transforming biomass into fuels, utilizing steam electrolysis and co-electrolysis methods for the creation of synthetic fuels such as natural gas and methanol. Their approach, when integrated with steam electrolysis, yielded a peak energy efficiency of 68% for synthetic natural gas and 64% for methanol. Wei et al. [72] proposed a new process for methanol production based on renewable hydrogen, emphasizing a sustainable and economic production future that embarked on an innovative exploration of flue gas utilization. Their approach centered CCS techniques, aiming to transform captured carbon into an e-fuel such as methanol.

Our methodology leverages carbon dioxide captured during fermentation, pairing it with hydrogen from electrolysis to produce methanol. Importantly, no carbon dioxide is released into the atmosphere; all emitted CO₂ is captured and transformed into e-fuels. This approach not only optimizes the use of resources but also offers a sustainable method to reduce greenhouse gas emissions by using the alcohols produced to offset fossil fuel utilization. By merging innovative biomass processing techniques with carbon capture from fermentation, our research aims to produce both e-methanol and ethanol. Recognizing the significance of bagasse and the captured CO₂, our study addresses the need for eco-friendly fuel alternatives.

Through this work, we present a streamlined and scalable process for e-methanol and ethanol production, hoping to influence the biofuel sector and support a greener energy future.

Methodology

Process Technology

For the analysis of the fermentation of ethanol and synthesis of e-methanol Aspen Plus was employed, this being a computational tool. The software was chosen due to its ability to define unconventional fuels through both ultimate and proximate analysis, along with its comprehensive built-in database of physical properties that can be utilized in all simulation calculations. The process of producing ethanol from sugarcane juice incorporates techniques found in contemporary Brazilian ethanol distilleries. These include dry sugarcane cleaning, juice concentration using multi-effect evaporators, pre-fermentation sugarcane juice sterilization, and ethanol dehydration.

The choice of specific system boundaries in our study was made to comprehensively capture and simulate the entire ethanol, e-methanol and bio-methanol production process, from the initial biomass feedstock processing to the final synthesis of the products.

The Aspen model developed has 6 hierarchies namely – extraction, clarification, ethanol formation, electrolysis e-methanol formation and methanol by gasification as shown by Figure 2.

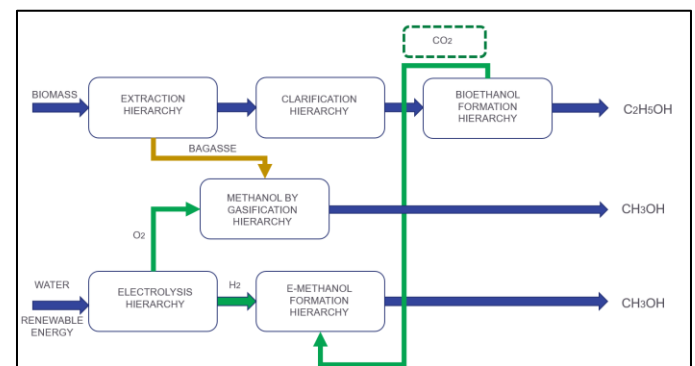


Figure 2. Process flow diagram involving all the hierarchies.

In our process simulation, depicted through a detailed block diagram in figure 3, the following general sequence of operations unfolds for ethanol and bagasse formation from various feedstock.

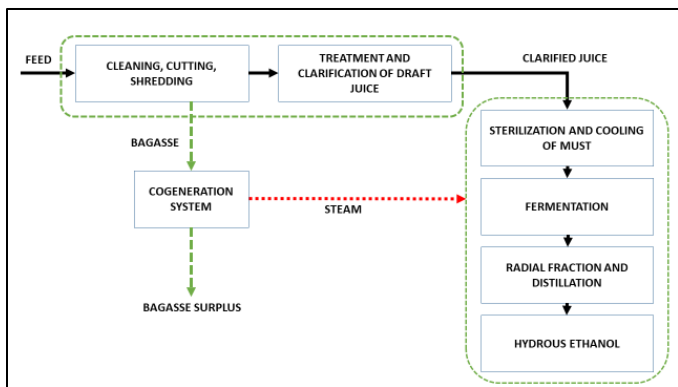


Figure 3. Sequential operations for producing ethanol and bagasse from various feedstock.

Guest et al. [73] modeled and verified the Aspen model for a sugar cane biorefinery based in South Africa. For the purpose of our model we adopted the principle of the extraction and clarification hierarchies with modifications from Guest et al. [73]. Figure 3 demonstrates the sequence of operations involved in extracting and clarifying the biomass to produce bioethanol.

In this study, we adopted a hierarchical modeling approach in Aspen Plus to efficiently manage the complexity of ethanol and e-methanol production processes. This structured approach, dividing the process into distinct hierarchy blocks, enhances model clarity and scalability. Key to this methodology is the application of specific property methods tailored to each process stage. The NRTL model is utilized for accurate liquid-liquid equilibrium in fermentation, UNIQUAC for detailed activity coefficient predictions, ELECNRTL for electrolyte systems, and PENGROB for phase behavior in hydrocarbon-rich sections. This strategic selection of property methods within our hierarchical framework ensures precise simulation of diverse process interactions, aligning with industry standards and enhancing the scientific rigor of our study.

Hierarchy 1: Extraction hierarchy

The feedstock undergoes a preparatory phase, where it is finely chopped and shredded to facilitate juice extraction. This juice extraction is achieved using a modeled diffuser. The residual biomass, termed 'bagasse', is subsequently dewatered. The derived bagasse is then channeled to the gasification hierarchy, while the draft juice exiting the hierarchy is passed through the clarification hierarchy.

In our study, we've adopted the UNIQUAC model, which is a recognized method for predicting how different substances interact in a mixture, to form the foundation of our hierarchy. This approach was refined using parameters specific to a three-component system of sucrose, water, and non-sucrose substances, drawing on the regression analysis of experimental data from Starzak et al. [77].

The feedstock is generally composed of roughly 70% water, 15% dissolved substances, and 15% fibre, as outlined by Rein et al. [74] and Guest et al [73]. The fiber portion, which accounts for 15% of the sugarcane, is mostly made up of bagasse, a type of biomass. This bagasse is typically burned to create steam for the boilers, according to observations by Rein et al [74]. However, our study proposes a different use: we allocate bagasse merely to undergo gasification, transforming it into methanol. For each 100 tonnes of feedstock processed, the result is about 30 tonnes of bagasse and 4 tonnes of

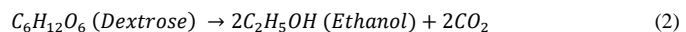
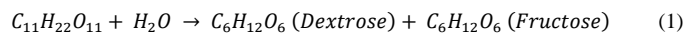
molasses as by-products, as indicated by references [75, 76]. To simulate the processing conditions, we relied on data from Starzak et al. [77] and Guest et al. [73], setting our model at a temperature of 27 degrees Celsius, a pressure of 1.01 bara, and a sugarcane mass flow rate of 244 tonnes per hour. The process includes several stages and components: cutting devices known as knives, pulverizing tools like hammers (represented in our model by a duplicator block that maintains the original feed composition), a diffuser, and dewatering mills (modeled by a Separation Block). The heating and cooling are managed by units called Heater, DJCOOL, Heater 2, and DJCOOL2 (all modeled by the Heater Block), alongside a Pump (modeled by the Pump block), culminating in a storage tank (represented by a Mixer in the model).

Hierarchy 2: Clarification hierarchy

The extracted raw juice undergoes clarification, involving a combination of heaters and a flash tank. These components serve the dual purposes of juice heating and air removal. Subsequent pH neutralization readies the juice for clarification, effectively eliminating suspended particles with the addition of lime. In the simulation, the juice heaters are represented by three shell and tube heat exchangers (modelled by HeatX Block).

Hierarchy 3: Bioethanol formation hierarchy

Post-clarification, the sucrose-laden clear juice is introduced in an RSTOIC reactor, where it splits into dextrose and fructose. After heating, this mixture is subjected to fermentation in another reactor (RSTOIC2), yielding an ethanol and carbon dioxide aqueous solution. Carbon dioxide is captured, and the ethanol solution undergoes a radial fractionation (RadFrac) process to distill ethanol out. The reactions for the hydrolysis of sucrose to form dextrose and fructose is shown in reaction (1). Similarly the fermentation reaction to produce ethanol and carbon dioxide from dextrose is shown in (2).



The clear juice is cooled down to room temperature, about 25 degrees Celsius, to prepare it for neutralization. A special type of reactor, called an RSTOIC reactor in the model, is used to simulate the chemical breakdown of sucrose into dextrose and fructose, with the process assumed to be 99% effective at 30 degrees Celsius. After that, the temperature of the mixture is brought back down to 25 degrees Celsius for fermentation.

In the fermentation step, dextrose is transformed into ethanol through a natural process that doesn't use oxygen and also produces carbon dioxide. The carbon dioxide is then removed from the mix using a separation component in the model. Any dextrose that didn't turn into ethanol is sent back for another round of fermentation to increase the ethanol yield. The resulting liquid, now enriched with ethanol, is passed through a complex separation process designed in the model as a 20-stage RadFrac block with a specific parameter called the reflux ratio set to 4.

In our study, we've chosen to maintain ethanol in an aqueous state to avoid the energy-intensive dehydration process. Dehydration significantly increases energy consumption and production costs. Our decision aligns with recent findings highlighting the benefits of using

high-water-content ethanol, termed 'wet ethanol' or 'hydrous ethanol' especially for water volumes exceeding 5%.

Hierarchy 4: Electrolysis hierarchy

An integral component of the process is the electrolysis, where water is dissociated into its constituent hydrogen and oxygen elements. The oxygen aids in the gasification process while the hydrogen serves multiple purposes, including methanol synthesis and synergies in the various chemical processes. The carbon-enriched bagasse undergoes gasification, which leverages oxygen produced via electrolysis. The reaction for the electrolysis of water is shown in (3).



The model is designed to reflect an Alkaline electrolyser similar to the one described by Sanchez et al.[52], including a detailed representation of the stack based on the polarization curve parameters from Amores et al.[78]. The electrolyzer's main goal is to produce green hydrogen using electricity from renewable sources. The design, including the number of cells in the stack and their surface area, was influenced by the work of Gallandat et al.[79].

In this system, KOH (potassium hydroxide) is used to increase water's conductivity, which makes the electrolysis more efficient. Although systems with KOH tend to produce less product per unit of time, they convert a higher percentage of the electrical energy into chemical energy, making them more energy-efficient. The following specific parameters were set for the Alkaline Electrolyser (AEL):

Current Density: 2000 A/m²

Electrical Energy Supplied: 7.8 MW

Chemical Energy Conversion in Electrolyzer: 2.5 MW

Hydrogen Production Rate: 0.1 t/h

Water Feed Rate: 1.2 t/h

Process Temperature: 85°C

Liquid KOH serves as the electrolyte in the electrochemical processes. Metals like nickel or iron are used as catalysts to improve the reactions. While KOH is effective, it is also a strong base and corrosive, which means the materials used must resist corrosion and safety measures must be in place to handle the substance safely. The modeling involves a stoichiometric reactor (RSTOIC) for the breakdown of water into hydrogen and oxygen. The produced hydrogen and oxygen, along with the electrolyte—a 30% KOH solution by weight—are moved to their respective separation tanks (SEP-H2 for hydrogen and SEP-O2 for oxygen).

Hierarchy 5: E-Methanol formation hierarchy

During the process of making ethanol, carbon dioxide was captured as it emerged from the fermentation. Alongside this, hydrogen was produced through the electrolysis of water. The carbon dioxide was then combined with hydrogen at a ratio of 1 to 6. This combination was subjected to a series of pressure increases using a lineup of compressors, each progressively raising the pressure to a specified level. The first compressor increased the pressure to 2.7 bar, the second

to 8.8 bar, and the third to 28.3 bar. After each stage, the temperature of the gas was carefully adjusted for optimal processing conditions. The pressurized gases were then directed into a specialized reactor, designed to maintain a constant high temperature of 284 degrees Celsius. To model the methanol reactor in our study, we employed an RSTOIC reactor (B7) under specific operating conditions. The reactor was maintained at a temperature of 284 degrees Celsius and a pressure of 15 bar. Our goal was to achieve a fractional conversion rate of 90%. This targeted conversion rate was chosen to ensure that the captured carbon from fermentation and the hydrogen obtained from the electrolyzer would undergo the desired transformation, resulting in the production of e-methanol as a key output. Inside the reactor, with the aid of a catalyst, the carbon dioxide and hydrogen underwent a chemical transformation into methanol and water. The conditions within the reactor were fine-tuned to enhance the efficiency of this conversion. Upon completion of the reaction, the methanol and water mixture was further pressurized to 74 bar and the temperature set to 92 degrees Celsius, completing the transformation process and preparing the methanol for subsequent purification and use. The reaction for methanol synthesis is given by (4).

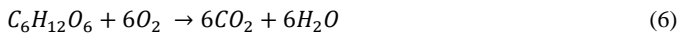


Following the production of the e-methanol mixture, we further processed it using radial fractionation. This separation was carried out using a RADFRAC model, employing an 'equilibrium' calculation type. A kettle reboiler was utilized, and the reflux ratio was set at 1.2 on a mole basis. The separation process spanned 44 stages to achieve the desired product composition and purity.

Hierarchy 6: Bio-Methanol by gasification hierarchy

The leftover solid material from squeezing out the juice from sugarcane is made up of fiber, sucrose, and some other non-sugar substances. Gasifying bagasse presents distinct challenges due to its high ash content, unlike woody biomass. Bagasse ash's elevated mineral levels can cause operational issues like slagging, fouling, and agglomeration within the gasifier, hindering efficiency and flow. These concerns demand tailored reactor design and more frequent maintenance. Moreover, ash composition can impact syngas quality as it may engage in undesirable secondary reactions, contrasting with woody biomass, which offers smoother gasification with lower ash content and more consistent composition, resulting in higher gasifier efficiency and fewer operational complications. When this solid mix is exposed to oxygen, which we get from an electrolyzer, it breaks down. This happens in an oxidative combustion reactor modeled by (RSTOIC) at a high temperature of 500 degrees Celsius and a pressure of 4 bar. During this process, the sucrose and the fiber turn into solid carbon, and the non-sugar parts react with oxygen to form carbon dioxide. After this step, the material is heated even more to 850 degrees Celsius while still at 4 bar pressure. It's then put into a gasifier modeled by (RGIBBS) reactor where it's a bit cooler at 800 degrees Celsius and still under 4 bar pressure. In our modeling approach, we utilized an RGIBBS reactor to simulate the gasification process for syngas production. The calculation type employed was focused on both phase equilibrium and chemical equilibrium. We specifically identified the potential products as carbon monoxide (CO), carbon dioxide (CO₂), and hydrogen (H₂). To ensure accuracy and reliability, we also incorporated a rigorous hydrate check into the simulation. Here, a gas mixture called syngas is created. This syngas is then cooled down to 134 degrees Celsius and gets compressed in three stages until it reaches a high pressure of 78 bar. After compression, it's heated again to 210 degrees Celsius and goes into yet another reactor for the methanol-making process. In this reactor, three chemical reactions turn the

syngas into methanol. To model the conversion of syngas to biomethanol, we employed an RPLUG reactor with specific configuration parameters. The reactor was set to operate at a temperature of 284 degrees Celsius. The reactor design involved a multitube configuration with a total of 8000 tubes. Key characteristics of this configuration included a bed voidage of 0.5 and a particle density of 2000 kg/cubic meter. Next, the mixture is cooled to 92 degrees Celsius. Any gases that are produced are separated out and sent back to be used again in the system. Finally, the mixture goes through a process to specifically pull out the methanol. This step is done with a device that's set to a particular setting, known as a reflux ratio, of 0.4 to make sure methanol is produced from the gasified material. The reactions during the decomposition, syngas formation and synthesis of methanol is given by (5), (6), (7), (8) and (9) respectively.



Results and Discussions

Process Technology Results

The process simulation conducted in Aspen Plus software yielded the following results for the diverse biomass feedstock we utilized. Sugar cane and sugar beet biomass were the selected feedstock for a simulation study performed in Aspen Plus software. Sugar beets have historically been underutilized for ethanol production compared to sugarcane, and as a result, detailed information on commercial-scale processes is not widely available. However, interest in sugar beet-based ethanol is increasing, especially in the European Union and Japan. Due to the chemical similarity between sugars from sugarcane and sugar beets, it is likely that sugar beet extracts can also be efficiently fermented into ethanol by industrial yeast. This was demonstrated when a flocculating yeast strain, *S. cerevisiae* IR2, immobilized on a loofa sponge, produced 9.5 percent ethanol by volume in about 15 hours from raw sugar beet juice, which had a 16.5 percent sucrose content by weight. Remarkably, this process did not require any pH modification or additional nutrients for the juice. Projections indicate that in the European Union, it is possible to produce ethanol from sugar beets at a volume of 86 liters per metric ton of feedstock, or roughly 5000 liters per hectare of land. In Germany, cost estimates for producing ethanol from sugar beet were evaluated and compared with production costs using wheat as the feedstock [80]. The chemical properties used to define sugar cane and sugar beet were adapted from the work of Starzak et al.[77], Gruska et al.[80], Dias et al.[81], and Hutnan et al[82].

The results and process flow diagram for each hierarchy is presented in the Appendix.

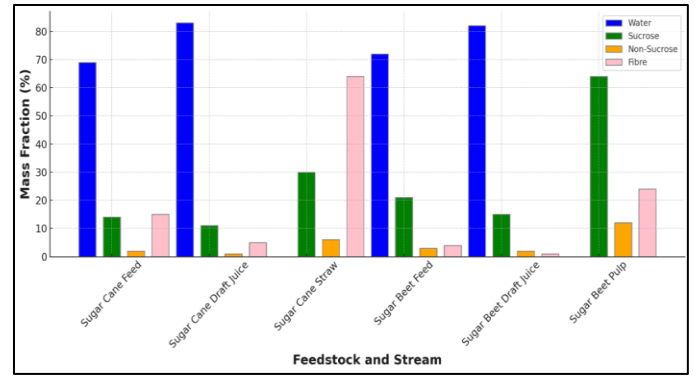


Figure 4. Mass Fraction Distribution in Sugar Cane and Sugar Beet Processing Streams.

Figure 4, clearly indicates the efficiency of sugar extraction, with a higher percentage of sucrose (apart from water – as it constitutes the major fraction) in the juice compared to the by-products. However, it also suggests that a non-negligible amount of sucrose remains with the by-products, potentially representing an area where extraction efficiency could be further improved. The absence of water in the by-products (straw and pulp) indicates that the processes used are effective in removing moisture from the solid residues, which can be beneficial for subsequent uses of these by-products. Overall, the graph provides a comparative view of the mass fractions of different components in the processing streams of sugar cane and sugar beet, which can be useful for understanding the efficiency of the extraction process and for identifying opportunities for optimization in biofuel production.

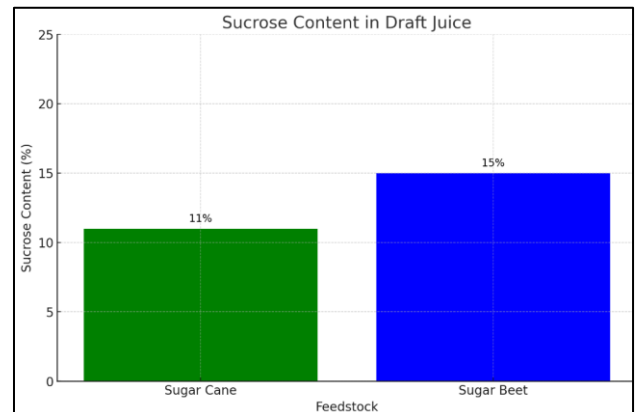


Figure 5. Comparison of sucrose content in the draft juice from sugar cane and sugar beet.

Comparing the feedstock – sugar cane and sugar beet, Sugar beet draft juice contains a higher percentage of sucrose (15%) compared to sugar cane draft juice (11%). This higher sucrose content suggests that sugar beet could potentially yield more ethanol per unit mass, making it a more efficient feedstock for bioethanol production.

From hierarchy 1, the processing of sugar cane and sugar beet feedstock demonstrated distinct mass flow conversions into intermediate and by-product streams. For sugar cane, the initial feed of 244 t/hr is partitioned into two primary outputs: draft juice and straw. The draft juice accounts for 200,835 kg/hr of the feed mass, predominantly composed of water (83%) and sucrose (11%), with a minor fraction of non-sucrose solids (1%). The remaining mass forms

the straw, amounting to 43,346 kg/hr, characterized by a high fiber content (64%) alongside water and sucrose fractions.

In contrast, sugar beet processing converts the feed into draft juice and pulp. The draft juice derived from the sugar beet feed amounts to 213,956 kg/hr, with water making up 82% and sucrose 15%, indicating a slightly more efficient extraction of sugar compared to sugar cane. The by-product pulp represents 30,225 kg/hr of the feed, with sucrose still prominent at 64%, accompanied by non-sucrose solids (12%) and a considerable quantity of fiber (24%).

These conversions from feed to draft juice and straw or pulp illustrate the efficiency of the extraction process for both feedstock. The higher percentage of sucrose in the sugar beet draft juice and pulp suggests a more favorable yield for subsequent bioethanol production processes.

The conversion efficiency of draft juice to clear juice is a critical parameter in assessing the performance of the clarification stage in sugar processing. This efficiency is quantified by the ratio of the mass flow rate of the resulting clear juice to the mass flow rate of the input draft juice, expressed as a percentage.

From hierarchy 2, in the case of sugarcane, the mass flow rate of the draft juice subjected to clarification was 200,835 kg/hr, which resulted in a clear juice with a mass flow rate of 195,613 kg/hr. This corresponds to a conversion efficiency of approximately 97.4%, indicating a high retention of liquid phase through the clarification process, with only a minor fraction being relegated to the removed solids.

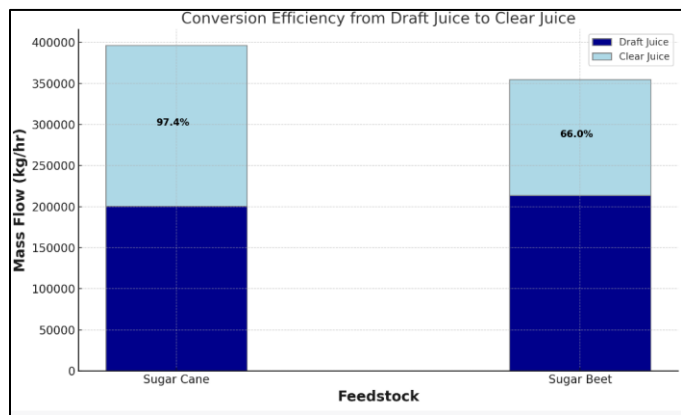


Figure 6. Clarification Conversion Efficiency: Sugar Cane vs. Sugar Beet.

Conversely, sugar beet processing began with a draft juice mass flow rate of 213,956 kg/hr, from which only 141,168 kg/hr was obtained as clear juice. The conversion efficiency here was about 66.0%, reflecting a notably lower yield of clear juice post-clarification. This disparity suggests a higher rate of solid-liquid separation, with a consequential increase in sucrose loss to the removed impurities or a higher retention of water within the pulp.

The comparative analysis of these conversion efficiencies reveals a significant variance in the performance of the clarification process between the two feedstock. The higher conversion efficiency in sugarcane processing implies a more optimal separation of non-soluble components, thereby enhancing the purity of the clear juice and potentially improving the downstream processing yield. Conversely, the reduced efficiency observed in sugar beet processing may

necessitate process optimization to minimize sucrose losses and enhance the overall sugar recovery rate from the provided biomass.

In hierarchy 3, for the sugar cane feedstock, the clear juice entering the fermentation process has a water content of 174,224 kg/hr, representing 89.1% of the mass. Post-fermentation, the ethanol stream contains 861 kg/hr of water, which is approximately 8% of the mass flow in the ethanol stream (92% being pure ethanol) – before dehydration. This significant decrease in water content from the clear juice to the ethanol stream highlights the concentration of ethanol after fermentation and the removal of water during the subsequent stages of ethanol recovery, such as radial fraction.

Similarly, in the sugar beet feedstock, the clear juice begins with 109,864 kg/hr of water, amounting to 77.8% of the mass. Following fermentation, the water content in the ethanol stream is reduced to 850 kg/hr, making up 8.0% of the stream's mass (92% being pure ethanol). This illustrates a comparable level of water removal and ethanol concentration in the sugar beet process to that of the sugarcane.

The water ratios in the ethanol streams of both feedstock are quite similar post-fermentation, indicating that the fermentation process has a consistent impact on the concentration of ethanol regardless of the initial sugar content. The presence of water in the ethanol stream is a normal part of the process, as ethanol and water form an azeotrope that is typically separated to a certain extent by distillation. The slight differences in the percentage of water may also reflect the efficiencies of the radial fraction systems used in the ethanol recovery from the fermentation broth for each feedstock. The data suggest that both feedstock are effective in reducing the water content through the ethanol production process, which is a crucial step for achieving the desired ethanol purity for fuel use.

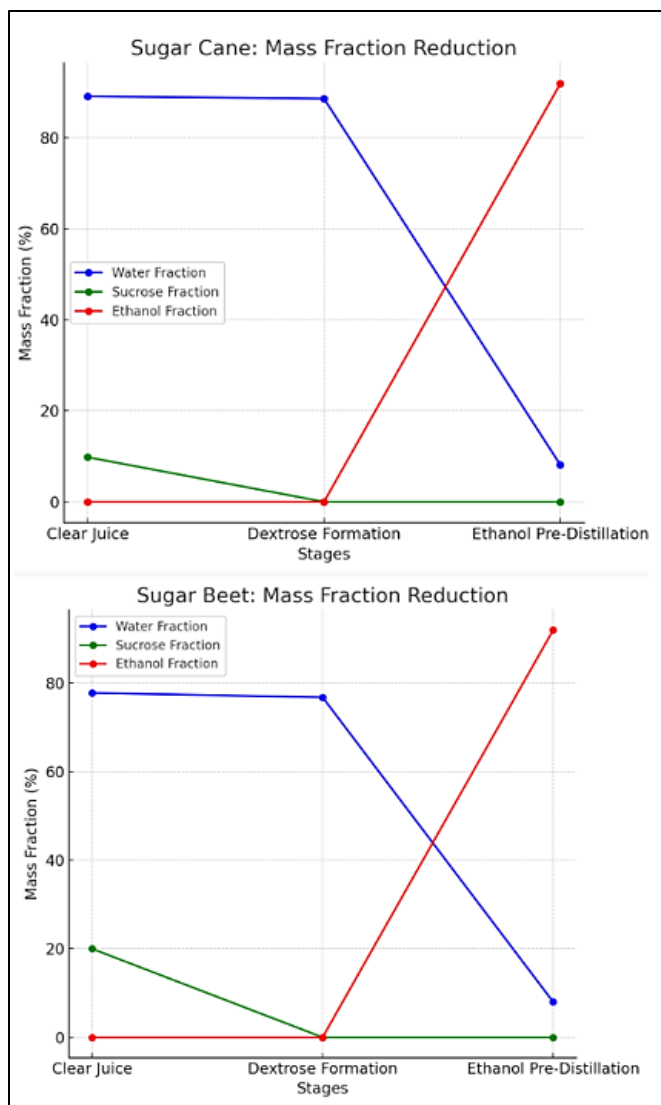


Figure 7. Transformation of Mass Fractions in Ethanol Production from Sugar Cane and Sugar Beet.

The mass fraction line graphs as shown in Figure 7, for sugar cane and sugar beet show a marked reduction in water content as the process moves from the clear juice stage to ethanol pre-distillation. In both cases, the sucrose content is completely converted by the dextrose formation stage, resulting in zero sucrose in the ethanol stream. The ethanol fraction in both the feedstock experiences a significant increase at the ethanol pre-distillation stage, underscoring the efficient conversion of sugars to ethanol within the production process.

From hierarchy 5, it was observed that the conversion of captured carbon dioxide from ethanol fermentation into e-methanol for both sugar cane and sugar beet feedstock. This process exemplifies a closed carbon loop, which is pivotal for sustainable fuel production, as it utilizes all captured CO₂ to synthesize a renewable fuel without any carbon waste.

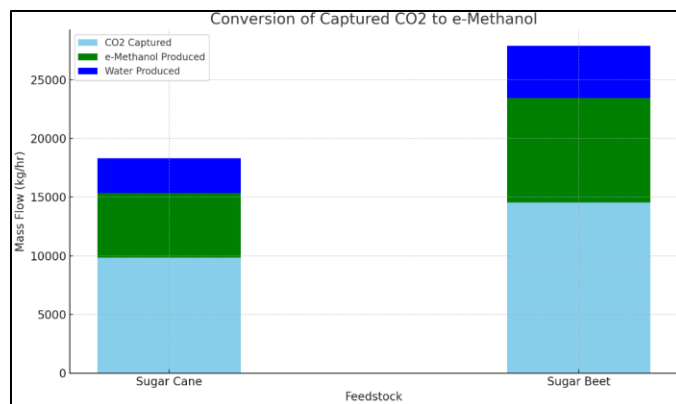


Figure 8. Complete Conversion of Captured CO₂ into E-Methanol for Sugar Cane and Sugar Beet.

The bar graph as shown in Figure 8, presents the full conversion of captured CO₂ into e-methanol for sugar cane and sugar beet feedstock, with the bars divided into segments representing the mass flow in kilograms per hour. The sky blue segment at the base illustrates the initial amount of captured CO₂, which is then entirely transformed into e-methanol, as shown by the green segment. The process efficiency is further highlighted by the top blue segment, which indicates the water byproduct. The graph shows no residual CO₂, indicating a 100% conversion into e-methanol, consistent with the provided data.

For sugar cane, 9,829 kg/hr of CO₂ was captured and used in the production of e-methanol. The e-methanol production stream before distillation consisted of 5,498 kg/hr of methanol and 2,980 kg/hr of water, resulting in a total output of 8,478 kg/hr. This indicates that the process was efficient, with all the captured carbon being converted into methanol, and the water by-product likely arising from the reaction process itself, as methanol synthesis from CO₂ and hydrogen typically produces water as a by-product.

Similarly, for sugar beet, 14,535 kg/hr of CO₂ was captured. The e-methanol production stream from this feedstock resulted in 8,906 kg/hr of methanol and 4,433 kg/hr of water, totaling 13,339 kg/hr. Again, the entire amount of captured CO₂ was utilized in the e-methanol production, showcasing the system's capability to convert all available carbon into fuel. The percentage of methanol content in the e-methanol stream before distillation for sugar cane is approximately 65%, and for sugar beet, it is approximately 67%. This indicates that in both cases, over half of the stream's mass consists of methanol, with sugar beet having a slightly higher percentage of methanol compared to sugar cane.

Regarding the conversion of CO₂ to e-methanol, the data demonstrates a complete utilization of captured CO₂ from ethanol fermentation, indicating a highly efficient carbon conversion process. This is significant as it implies that the process is not only generating renewable fuel but also contributes to a reduction in the carbon footprint by converting CO₂, a greenhouse gas, into a usable form of energy without leaving any carbon residues. This aligns with circular carbon economy principles, enhancing the sustainability of the biofuel production process.

Lastly, from hierarchy 6, the results for the methanol produced by gasification from both sugar cane and sugar beet feedstock illustrates a process that yields high purity methanol with minimal by-product formation. Remarkably, the streams show no presence of carbon

dioxide and only traces of hydrogen in the sugar beet output, indicating an efficient conversion process where carbon molecules are fully utilized in the formation of methanol, leaving no residual carbon in the streams.

Utilizing sugar cane as the lignocellulosic feedstock, we obtained syngas with the following composition, expressed as mass fractions: carbon monoxide (CO) at 0.69, carbon dioxide (CO₂) at 0.25, and hydrogen (H₂) at 0.06. The total mass flow rate of the syngas was recorded as 25670.91 kg/hr. Employing sugar beet as the lignocellulosic feedstock, we obtained a syngas composition characterized by mass fractions: 0.70 for carbon monoxide (CO), 0.24 for carbon dioxide (CO₂) and 0.06 for hydrogen (H₂). The total mass flow rate of the syngas was 25903.58 kg/hr.

For sugar cane, the methanol production via gasification yields a stream with a mass flow of 5,140 kg/hr of methanol, which constitutes 97% of the total stream. The remaining 3% is water, with a mass flow of 166 kg/hr. The absence of carbon dioxide and hydrogen in this stream highlights the completeness of the reaction, where all carbon from the feedstock is incorporated into the methanol product. In the case of sugar beet, the methanol output is even higher, with a mass flow of 8,160 kg/hr, making up 98% of the total stream. The water content is relatively lower at 1%, with a mass flow of 108 kg/hr. The trace amounts of hydrogen, less than 1%, do not significantly impact the overall purity of the methanol produced.

The high percentages of methanol in both streams — 97% for sugar cane and 98% for sugar beet — indicate a very high purity of the product, which is desirable for methanol to be used as a fuel or as a feedstock for chemicals. The low water content further underscores the efficiency of the gasification process, as water is typically a by-product of methanol synthesis and must be minimized to reduce downstream processing costs and complexity.

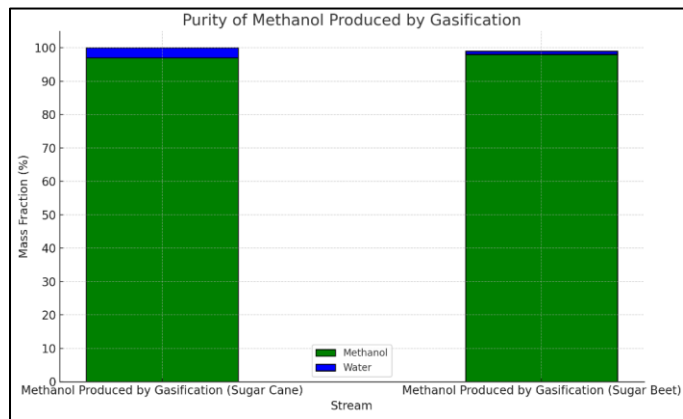


Figure 9. Composition of Methanol Streams from Sugar Cane and Sugar Beet Gasification.

The complete conversion of carbon to methanol without any detectable carbon dioxide emissions is an excellent outcome based on our hypothesis for these processes, as it demonstrates a carbon-efficient technology. This not only maximizes the use of biomass as a feedstock but also aligns with environmental goals by avoiding the release of CO₂, a greenhouse gas, into the atmosphere.

In summary, the gasification processes for both sugar cane and sugar beet feedstock show remarkable efficiency, with nearly all carbon molecules from the biomass being converted into a high-purity

methanol product. This is indicative of an advanced level of process control and optimization, reflecting the potential for these pathways to contribute to sustainable fuel and chemical production. Table 1 presents a summary of the fuel outputs—specifically, ethanol and methanol—derived from a singular feedstock, as well as the corresponding quantities of carbon dioxide that have been successfully captured during the fermentation process.

Table 1. Variety of fuels developed from a single feedstock source

FEEDSTOCK	BIO-ETHANOL (kg/hr)	CO ₂ CAPTURED (kg/hr)	E-METHANOL PRODUCED BY CCUS (kg/hr)	BIO-METHANOL (kg/hr)	E-Methanol +Bio-Methanol Produced
SUGAR CANE	10637	9829	8478	5306	13784
SUGAR BEET	10656	14535	13339	8268	21607

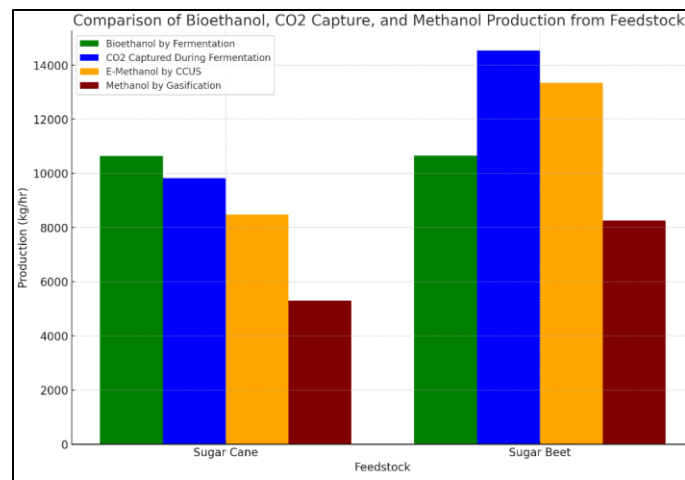


Figure 10. Comparative Analysis of Bioethanol and Methanol Production from Sugar Cane and Sugar Beet.

In conclusion, the primary intention of this study was to convert every single carbon atom within the system into fuel, thereby maximizing the efficiency and sustainability of renewable energy generation from biomass. Operating at a feed throughput of 244 tons per hour, the process was designed to ensure that no carbon atom was wasted. Utilizing sugar cane as a feedstock resulted in the production of 10,637 kg/hr of bioethanol and the capture of 9,829 kg/hr of CO₂, from which 8,478 kg/hr of e-methanol was produced via Carbon Capture Utilization, and Storage (CCUS) technology, culminating in a total methanol output of 5,306 kg/hr. Conversely, sugar beet as a feedstock yielded a slightly higher bioethanol production rate at 10,656 kg/hr and a more substantial CO₂ capture at 14,535 kg/hr, leading to an e-methanol production of 13,339 kg/hr by CCUS, with an overall methanol production of 8,268 kg/hr. These findings not only exemplify the successful conversion of each carbon atom from biomass into renewable fuels but also signify a noteworthy progression in bioenergy technology, indicating a move towards more carbon-efficient fuel production practices.

Conclusion

This investigation propels advancements in biomass conversion, spotlighting a comprehensive carbon atom utilization strategy for the sustainable production of bioethanol, e-methanol and biomethanol. It

underscores the transition towards eco-friendly wet alcohol fuels, like ethanol and methanol, which inherently contain water, thus promoting a cleaner and more efficient combustion process.

The study presents ethanol as an azeotropic blend, lauded for its lower emissions of particulates and carbon monoxide compared to conventional gasoline. Methanol, typically produced with a higher water content, also demonstrates environmental advantages, particularly when blended with other fuels to enhance the desirable attributes of each component. Such blends can facilitate a leaner burn in engines, curbing nitrogen oxides (NO_x) emissions, while the water content helps cool the combustion chamber, reducing the likelihood of engine knock and enabling higher compression ratios for improved efficiency.

The research reveals significant production volumes of bioethanol from sugar cane (10,637 kg/hr) and sugar beet (10,656 kg/hr), with the carbon dioxide captured during fermentation amounting to 9,829 kg/hr for sugar cane and 14,535 kg/hr for sugar beet. The e-methanol yield through Carbon Capture, Utilization, and Storage (CCUS) is marked at 8,478 kg/hr for sugar cane and a notable 13,339 kg/hr for sugar beet. Moreover, methanol production via gasification processes further contributes with 5,306 kg/hr from sugar cane and 8,268 kg/hr from sugar beet. This indicates a promising conversion rate of carbon to fuel, aligning with the goal of ensuring that every carbon atom is effectively transformed into a usable energy source.

The focus of this research has been to guarantee that the carbon atoms are fully converted into fuel, paving the way for 'wet' alcohol fuels to be optimized for use in combustion engines. This study establishes a foundation for future research focusing on the synergistic production and utilization of wet ethanol (WE) and wet methanol (WM). Future directions will involve deeper exploration of their unique properties and potential applications, particularly in internal combustion engines, with an emphasis on optimizing blending ratios and combustion dynamics. The azeotropic nature of ethanol, its lean burn qualities, and the cooling effect of wet alcohols in engines are all highlighted as keys to improving environmental outcomes.

Looking to the future, the process will be refined to enhance cost-effectiveness while maintaining the ecological benefits. The objective is to streamline the production of these renewable fuels, making them not just byproducts of biomass but central components of a sustainable energy framework. This approach promises to not only further the use of renewable fuels but also contribute significantly to the reduction of greenhouse gas emissions, particularly in the transportation sector.

In conclusion, the study demonstrates a forward-thinking approach to biomass conversion, integrating the principles of sustainability with tangible environmental advantages. It lays out a visionary trajectory where bioethanol and e-methanol emerge as pivotal elements in the renewable energy spectrum, marking a stride towards a greener transportation future.

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ETOGAS	Electrochemical Conversion of CO ₂ to Synthetic Natural Gas
F-T	Fischer-Tropsch
GHG	Greenhouse Gas
IEA	International Energy Agency
KOH	Potassium Hydroxide
PtF	Power to Fuels
SOEC	Solid Oxide Electrolysis Cell
UNIQUAC	Universal Quasi-Chemical Activity Coefficient Model

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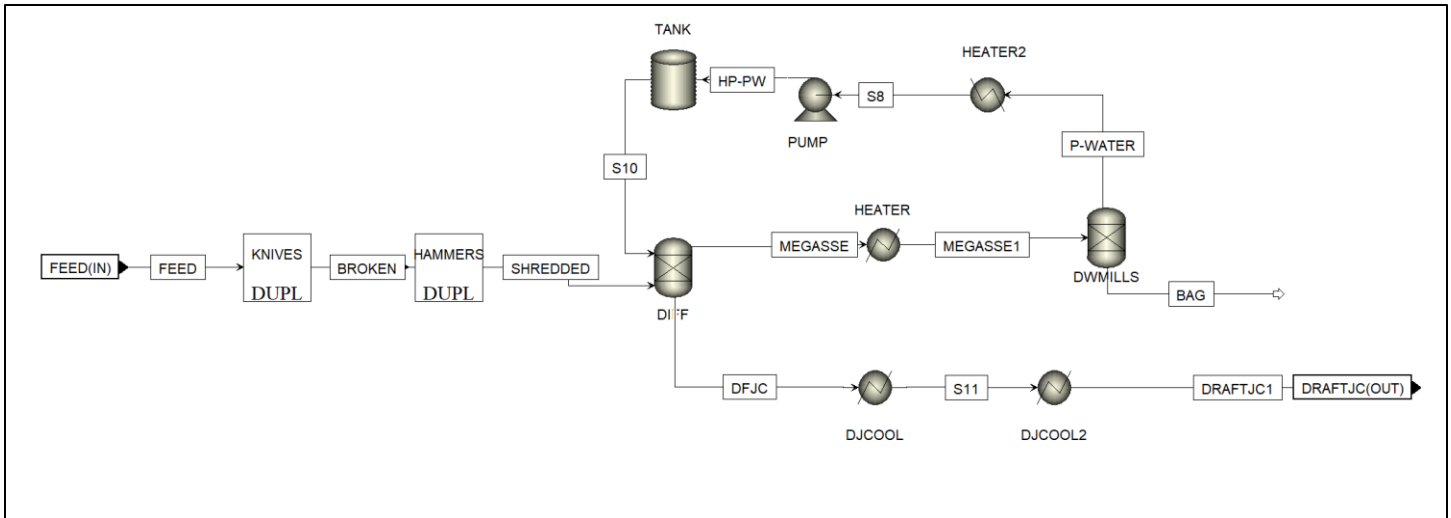
Definitions/Abbreviations

AEL	Alkaline Electrolyzer
BEV	Battery Electric Vehicle
BIG-GT	Big Gas Turbines
BOP	Balance of Plant
CCS	Carbon Capture and Storage
CCU	Carbon Capture and Utilization

Appendix

HIERARCHY 1

Process Flow Diagram

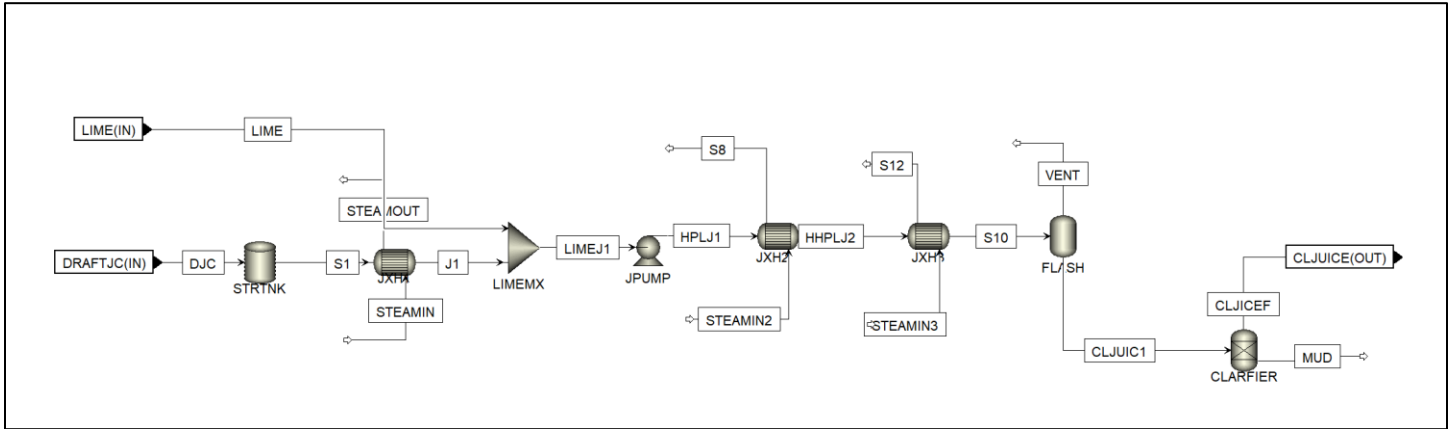


RESULTS

FEEDSTOCK	SUGAR CANE						SUGAR BEET					
	FEED		DRAFT JUICE		STRAW		FEED		DRAFT JUICE		PULP	
	Mass Flow (kg/hr)	Mass Fraction (%)	Mass Flow (kg/hr)	Mass Fraction (%)	Mass Flow (kg/hr)	Mass Fraction (%)	Mass Flow (kg/hr)	Mass Fraction (%)	Mass Flow (kg/hr)	Mass Fraction (%)	Mass Flow (kg/hr)	Mass Fraction (%)
WATER	167334	69%	167334	83%	NIL	NIL	175960	72%	175960	82%	NIL	NIL
SUCROSE	34602	14%	21606	11%	12996	30%	51165	21%	31949	15%	19217	64%
NON-SUCROSE	5469	2%	2701	1%	2768	6%	7309	3%	3610	2%	3699	12%
FIBRE	36776	15%	9194	5%	27582	64%	9746	4%	2436	1%	7309	24%
TOTAL	244181		200835		43346		244181		213956		30225	

HIERARCHY 2:

Process Flow Diagram

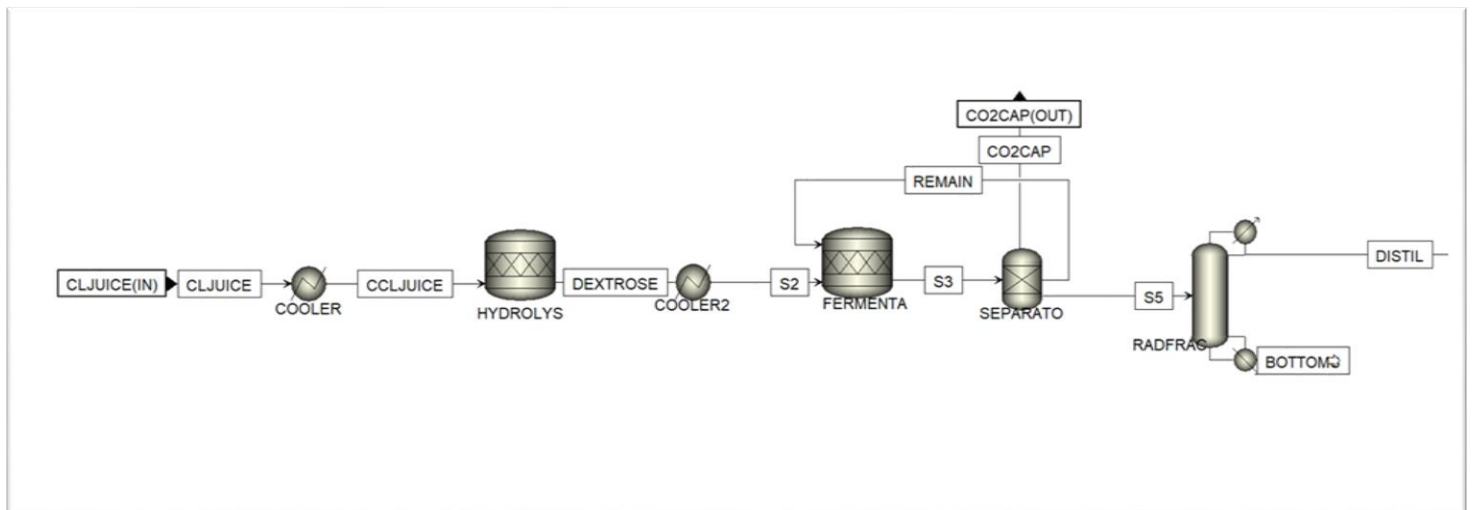


RESULTS:

FEEDSTOCK	SUGARCANE				SUGAR BEET			
	DRAFT JUICE (FROM HIERARCHY 1)		CLEAR JUICE		DRAFT JUICE (FROM HIERARCHY 1)		CLEAR JUICE	
	Mass Flow (kg/hr)	Mass Fraction (%)	Mass Flow (kg/hr)	Mass Fraction (%)	Mass Flow (kg/hr)	Mass Fraction (%)	Mass Flow (kg/hr)	Mass Fraction (%)
WATER	167334	83.3%	174224	89.1%	175960	82%	109864	77.8%
SUCROSE	21606	10.8%	19113	9.8%	31949	15%	28262	20.0%
NON-SUCROSE	2701	1.3%	2276	1.2%	3610	2%	3042	2.2%
FIBRE	9194	4.6%	NIL	NIL	2436	1%	NIL	NIL
TOTAL	200835		195613		213956		141168	

HIERARCHY 3:

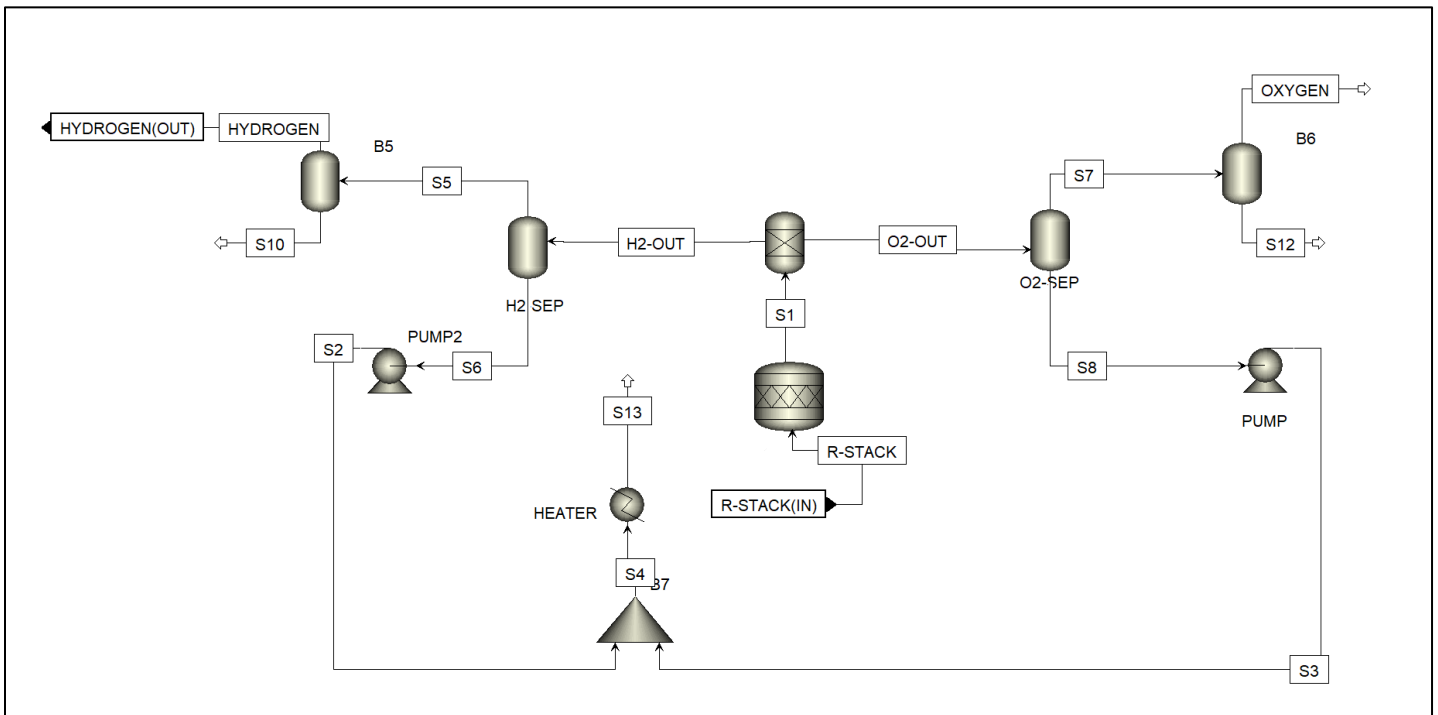
Process Flow Diagram



RESULTS

FEEDSTOCK	SUGARCANE							SUGAR BEET						
	CLEAR JUICE		DEXTROSE FORMATION		ETHANOL FORMATION BEFORE DEHYDRATION		CO2 CAPTURED DURING FERMENTATION	CLEAR JUICE		DEXTROSE FORMATION		ETHANOL FORMATION BEFORE DEHYDRATION		CO2 CAPTURED DURING FERMENTATION
	Mass Flow (kg/hr)	Mass Fraction (%)	Mass Flow (kg/hr)	Mass Fraction (%)	Mass Flow (kg/hr)	Mass Fraction (%)		Mass Flow (kg/hr)	Mass Fraction (%)	Mass Flow (kg/hr)	Mass Fraction (%)	Mass Flow (kg/hr)	Mass Fraction (%)	
WATER	174224	89.1%	173218	88.6%	861	8.1%	NIL	109864	77.8%	108376	76.8%	850	8.0%	NIL
SUCROSE	19113	9.8%	0	0.0%	0	0.0%	NIL	28262	20.0%	NIL	0.0%	0	0.0%	NIL
NON-SUCROSE	2276	1.2%	2276	1.2%	ALMOST NEGLIGIBLE	NIL	NIL	3042	2.2%	3042	2.2%	0	NIL	NIL
DEXTROSE	NIL	NIL	20119	10.3%	0	0.0%	NIL	NIL	NIL	29749	21.1%	0	0.0%	NIL
ETHANOL	NIL	NIL	NIL	NIL	9776	91.9%	NIL	NIL	NIL	NIL	NIL	9806	92.0%	NIL
CARBON DIOXIDE	NIL	NIL	NIL	NIL	NIL	NIL	9829	NIL	NIL	NIL	NIL	NIL	NIL	14535
TOTAL	195613		195613		10637		9829	141168		141168		10656		14535

HIERARCHY 4:



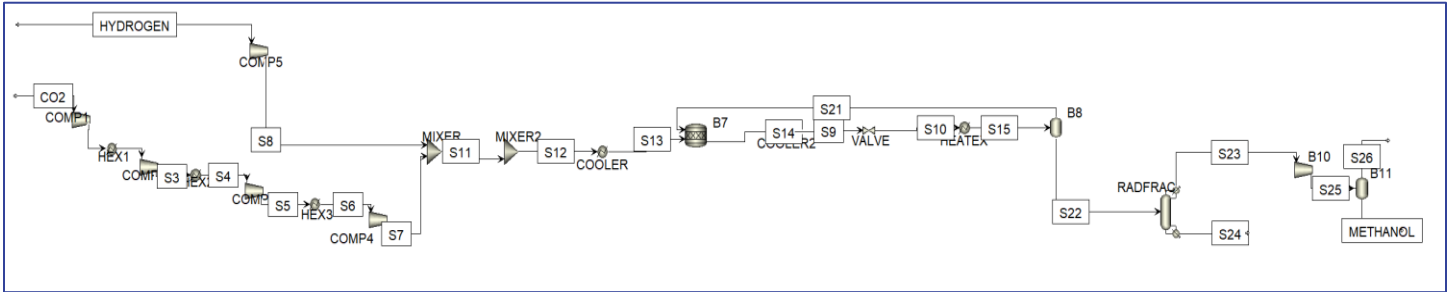
POLARIZATION CURVE PARAMETERS:

Parameter	Value	Unit
r1	3.29E-04	$m^2 \cdot ^\circ C^{-1}$
r2	2.15E-06	$m^2 \cdot ^\circ C^{-1}$
s	0.100601624	V
t1	114,609.51	$m^2 \cdot A^{-1}$
t2	12,397,438.71	$m^2 \cdot ^\circ C \cdot A^{-1}$
t3	409,431,775.5	$m^2 \cdot ^\circ C^2 \cdot A^{-1}$

RESULTS:

STREAM	WATER	HYDROGEN	OXYGEN
	Mass Flow (kg/hr)	Mass Flow (kg/hr)	Mass Flow (kg/hr)
WATER	1200	103	818

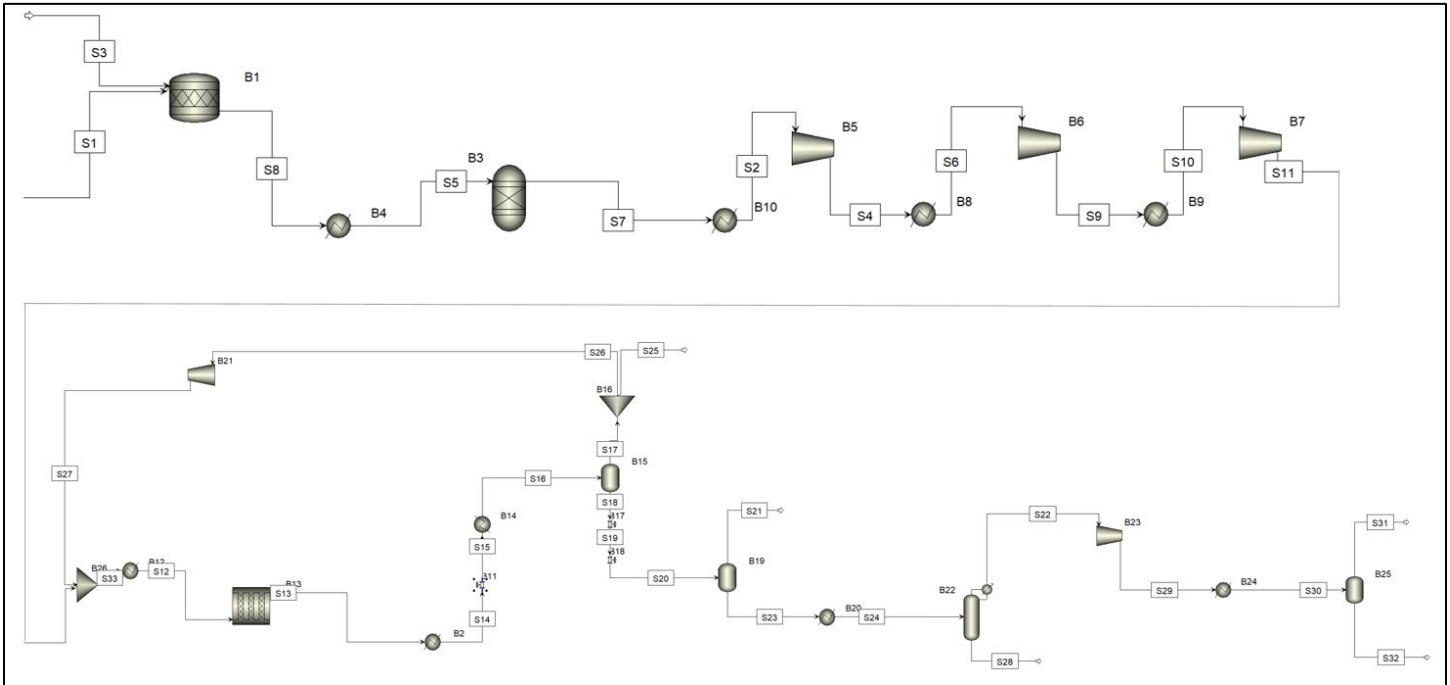
HIERARCHY 5:



RESULTS:

SUGAR CANE				SUGAR BEET			
CARBON DIOXIDE CAPTURED		E-METHANOL PRODUCED BEFORE DEHYDRATION		CARBON DIOXIDE CAPTURED		E-METHANOL PRODUCED BEFORE DEHYDRATION	
Mass Flow (kg/hr)	Mass Fraction (%)	Mass Flow (kg/hr)	Mass Fraction (%)	Mass Flow (kg/hr)	Mass Fraction (%)	Mass Flow (kg/hr)	Mass Fraction (%)
9829	100%	0	0%	14535	100%	0	0%
0	0%	0	0%	0	0%	0	0%
0	0%	5498	65%	0	0%	8906	67%
0	0%	2980	35%	0	0%	4433	33%
9829		8478		14535		13339	

HIERARCHY 6:



RESULTS:

STREAM	METHANOL PRODUCED BY GASIFICATION (SUGAR CANE)		METHANOL PRODUCED BY GASIFICATION (SUGAR BEET)	
	Mass Flow (kg/hr)	Mass Fraction	Mass Flow (kg/hr)	Mass Fraction (%)
CARBON DIOXIDE	0	0%	NIL	NIL
HYDROGEN	0	0%	Traces	<1%
METHANOL	5140	97%	8160	98%
WATER	166	3%	108	1%
TOTAL	5306		8268	