

Sustainable Methanol Production via Integrated Supercritical CO₂ Cycle: Process Optimization and Energy Efficiency Analysis

Zhu Ling^a, Chakib Bouallou^{b,*}

^aSJTU-Paris Elite Institute of Technology, Shanghai Jiao Tong University, Shanghai 200240, China

^bMINES Paris - PSL University, Centre Energie Environnement Procédés, 60 Boulevard Saint Michel, 75272, Paris, France
chakib.bouallou@minesparis.psl.eu

This paper outlines the work on optimizing methanol production by incorporating a supercritical CO₂ cycle. The primary goal was to enhance methanol production efficiency and address environmental concerns by reducing greenhouse gas emissions. The integration of the supercritical CO₂ cycle helps improve process efficiency, thereby increasing methanol production from 2,085.63 to 2,174.65 kg/h, a 4.3 % increase in production. This integration is in line with the mission to advance sustainable energy solutions. A sensitivity analysis was conducted to assess the impact of CO₂ flow rates on methanol production. Increasing the CO₂ flow rate from 500 kg/h to 1,000 kg/h led to a minor increase in methanol output, which indicated that the process's sensitivity to CO₂ flow rate changes is relatively low. This finding demonstrates that while the supercritical CO₂ cycle has potential benefits, the adjustments in flow rates have a limited impact on the final methanol production volume. Overall, the integration of the supercritical CO₂ cycle has shown potential for enhancing methanol production processes. The results underscore the effectiveness of incorporating advanced technologies to achieve better process performance and contribute to environmental sustainability.

1. Introduction

With increasing global energy demands and environmental concerns, clean energy sources are essential to replace traditional fossil fuels. Methanol, known for its ease of storage and transport, serves as a versatile energy carrier and a feedstock for numerous chemical processes. However, traditional methanol production relies heavily on natural gas or coal, processes that contribute significantly to CO₂ emissions and exacerbate global warming. To overcome these challenges, enhancing the economic feasibility and competitiveness of methanol production processes is essential. This can be achieved by reducing energy losses and improving overall energy efficiency. Advancements in more sustainable and efficient production methods for methanol will not only reduce greenhouse gas emissions but will also support the global transition toward cleaner, renewable energy solutions.

Biomass represents a significant category of solid waste with high production rates, creating an urgent need for environmentally friendly treatment methods and effective energy utilization strategies. Although direct combustion of biomass can recover some energy, it also generates harmful by-products like nitrogen oxides and sulfur oxides, contributing to secondary pollution. As a result, finding sustainable methods to manage biomass while optimizing waste recovery has become essential. Thermal processes such as pyrolysis or gasification can convert biomass into syngas, primarily composed of carbon monoxide and hydrogen, with smaller amounts of CO₂, CH₄, and water. This syngas can be used as a feedstock for subsequent methanol synthesis. Studies support the theoretical feasibility of utilizing biomass-derived syngas for methanol production. For example, Adil et al. (2022) used Aspen Plus to model methanol synthesis and found that the syngas from biomass gasification closely matches the composition of feedstock syngas used in conventional methanol synthesis, providing a solid theoretical foundation for this process. Further supporting the viability of biomass-derived methanol, Harris et al. (2021) conducted a commercial assessment comparing methanol production from biomass to CO₂. Their analysis introduced a new methodology for evaluating the economic viability of

renewable methanol technologies. The findings indicated that biomass gasification-based methanol production meets competitive market costs, establishing it as a promising commercial process for sustainable methanol production.

Hydrogen is gaining recognition as a potential zero-carbon energy carrier, owing to its ability to store and deliver substantial amounts of energy. One of the primary methods for producing hydrogen is through the electrolysis of water, which is commonly referred to as "green hydrogen." Electrolysis splits water into hydrogen and oxygen by applying an electric current through two electrodes immersed in a conductive solution. Hydrogen gas is produced at the cathode, while oxygen is generated at the anode.

However, the hydrogen content in syngas from biomass gasification is typically insufficient to fully react with all the carbon elements present in the gas stream (Zhang et al., 2023). Therefore, utilizing hydrogen produced via water electrolysis can significantly enhance the methanol synthesis process. To achieve cleaner and more efficient methanol production, optimizing process structures is essential. This includes improving the recovery of both material and energy within the system, increasing the overall efficiency of hydrogen utilization, and promoting sustainability across the entire process.

This paper investigates a more sustainable methanol production method using biomass gasification, hydrogen from water electrolysis, and a supercritical CO₂ cycle (Weiss and Bouallou, 2024) to enhance energy efficiency and reduce emissions. By optimizing the process, we aim not only to increase methanol production but also to significantly lower the carbon footprint associated with its synthesis.

2. Process Simulation

2.1 Alkaline Water Electrolysis

Hydrogen production through water electrolysis is an environmentally sustainable and clean process. It involves breaking down water into hydrogen and oxygen gases using an electric current. Among various electrolytic methods, Alkaline Electrolysis (AEL) stands out as a commercially mature technology unlike high-temperature technology which is still in the process of being developed (Petipas et al., 2014). This process uses potassium hydroxide (KOH) as the electrolyte and typically operates at a temperature range of 65-100 °C and a pressure range of 25-30 bar.

The electrolyzer, also called a stack, is the core equipment in the AEL process. Since a direct model for an electrolyzer is not available in Aspen Plus, it is represented using conversion reactors and separators in Aspen HYSYS. The process modeling involves three critical parameters: the cell voltage, the power requirement of the electrolyzer, and the efficiency of water conversion into hydrogen. From referential research by Sanchez et al. (2020), the electrolyzer voltage is set at 2 V, and the theoretical power requirement is 3.66 kWh per kilogram of hydrogen, with a stack conversion efficiency of 58 %. By recycling unreacted water back into the electrolyzer, the process effectively increases the overall conversion of water into hydrogen. This recycling minimizes the consumption and enhances the efficiency of hydrogen production.

To simulate the AEL process, the input streams must be specified. Stream 1 is water with a mass flow rate of 1,000 kg/h, an initial temperature of 25 °C, and a pressure of 1 atm. Stream 2 is a mixture of 80 % KOH and 20 % water, with a mass flow rate of 500 kg/h, and the same initial conditions as Stream 1. The mass fractions of the mixed components are water (0.6914) and potassium hydroxide (0.3086), meeting the recommended range of 25–35 % KOH by weight.

The process involves preheating the feed mixture and pressurizing it to the required operating conditions. The outlet pressure of the pump is set to 27 bar, and the pressure drop across the heater is 30 kPa, heating the stream to 65 °C. The heated liquid is then fed into the electrolyzer, represented as a conversion reactor in ASPEN HYSYS, where a heat flow power of 500 kW is used to drive the reaction.

Inside the electrolyzer, water is decomposed into hydrogen and oxygen gases. The hydrogen-to-oxygen production ratio is carefully monitored, and the products are separated in subsequent steps. Hydrogen is separated using a gas separator with a pressure drop of 30 kPa and an outlet temperature of 70 °C. To enhance the process efficiency, unreacted water is recycled back to the electrolyzer. A second separator with a pressure drop of 20 kPa removes oxygen, while the remaining liquid stream is recirculated.

The properties of hydrogen produced in this process are summarized in Table 1. The simulation demonstrates that the AEL process is an efficient method for hydrogen production, especially when a recycle loop is implemented to enhance conversion efficiency and minimize resource consumption. The generated hydrogen can be further utilized in downstream applications, such as methanol synthesis.

Table 1: Outlet hydrogen production of water electrolysis

Temperature [°C]	Pressure [kPa]	Molar flow rate [kmol/h]	Mass flow rate [kg/h]
70.00	2,640.00	5.48	11.04

To increase conversion efficiency, unreacted water is recycled. The produced hydrogen is separated from by-products and mixed with syngas for subsequent methanol synthesis.

2.2 Decomposition and Pyrolysis

The decomposition and pyrolysis stages are crucial components of the biomass gasification process. In Figure 1, decomposition is performed at 700 °C and 1 atm, with biomass properties characterized through proximate and ultimate analyses based on peer-reviewed data. The proximate analysis indicates the following composition: 10.63 % moisture, 27.23 % fixed carbon, 55.00 % volatile matter, and 7.14 % ash. The ultimate analysis reveals 7.13 % ash, 54.18 % carbon, 5.37 % hydrogen, 1.28 % nitrogen, 0.13 % chlorine, 0.21 % sulfur, and 31.70 % oxygen. Sulfur is further categorized into 0.09 % pyritic, 0.03 % sulfate, and 0.09 % organic sulfur.

To ensure the reliability of these data, specific criteria must be met: (1) proximate and ultimate analyses must sum to 100 %; (2) sulfur subcategories must total the sulfur content in the ultimate analysis; and (3) ash proportions must be consistent across analyses. Furthermore, ash components are defined using both proximate and ultimate data, excluding sulfur.

Decomposition occurs at 700 °C, with water yield equating to the moisture fraction of biomass. In the subsequent pyrolysis step, also conducted at 700 °C and 1 atm, an RGibbs reactor is used for chemical equilibrium, while an RYield reactor calculates yields based on stoichiometric ratios and conversion efficiencies.

A nitrogen stream, introduced at 25 °C, 1 atm, and a flow rate of 100 kg/h, supports the reaction environment. Mass flow analysis shows complete biomass conversion in the yield reactor, producing preliminary hydrogen. Additional hydrogen generation is expected in the next gasification stage, with mass fractions aligning with the yield reactor specifications.

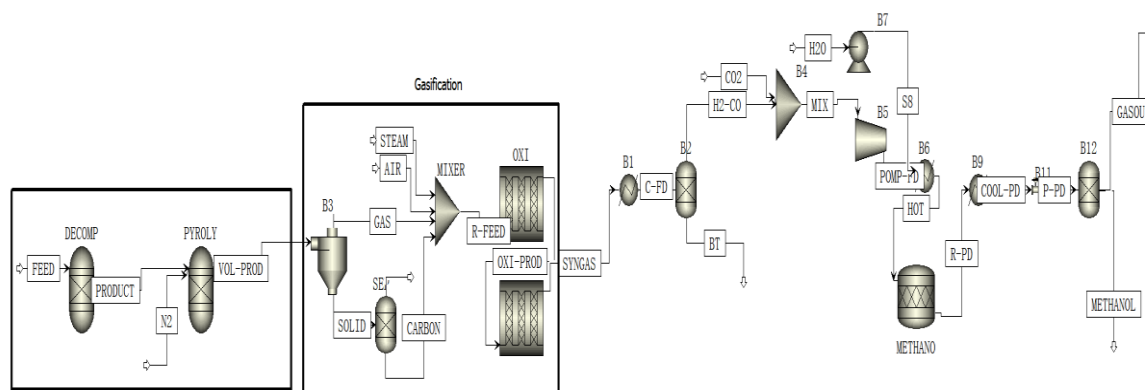


Figure 1: Flow Diagram of the Process

2.3 Gasification

Following the decomposition and pyrolysis, the next stage involves separating the gaseous products from the solid residues (ASH and CARBON) using a separator. The gaseous products are then mixed with steam, air, and 80 % of the carbon from the solid product. The remaining carbon and ASH are reserved for potential further processing or utilization. Introducing 80 % of the carbon back into the gasification process helps maintain the reaction's carbon balance, ensuring sufficient carbon is available for methanol production. This step is crucial to support the subsequent chemical reactions and maximize the conversion of biomass into useful syngas for methanol synthesis. The steam is introduced at 100 °C, 1 atm, with a flow rate of 100 kg/h, while the air is introduced at 65 °C, 1 atm, with a flow rate of 500 kg/h. The air composition is defined as 21 % oxygen and 79 % nitrogen, with the inlet quantities adjusted to ensure that the oxygen-to-biomass ratio falls within the range of 0.2 to 0.3 (Cao et al., 2024).

The separated gaseous flow is then directed into kinetic gasification reactors where both oxidation and reduction reactions occur. A Plug Flow Reactor is selected to simulate the oxide-reduction process. Both oxidation and reduction reactions are modeled using the POWERLAW type, which provides a convenient way to represent

reaction kinetics. The reaction parameters, including coefficients, activation energies (E_a), and component exponents, are specified in Table 2.

Table 2: Oxidation and Reduction Reactions and their parameters

	Reaction	k	E_a (kJ/kmol)	Component (Exponents)
Oxidation	(R1) $\text{CO} + 0.5\text{O}_2 \rightarrow \text{CO}_2$	1.78×10^7	180,000	CO(1) O ₂ (0.25) CO ₂ (0.5)
	(R2) $\text{CH}_4 + 0.5\text{O}_2 \rightarrow \text{CO} + 2\text{H}_2$	2.4×10^8	126,000	CH ₄ (0.7) O ₂ (0.8)
	(R3) $\text{C} + \text{H}_2\text{O} \rightarrow \text{CO} + \text{H}_2$	2×10^2	49,900	C(1) H ₂ O(1)
Reduction	(R4) $\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2$	3×10^5	125,000	CH ₄ (1) H ₂ O(1)
	(R5) $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$	2.78	12,600	CO(1) H ₂ O(1)
	(R6) $\text{C} + \text{CO}_2 \rightarrow 2\text{CO}$	1.05×10^{10}	135,000	C(1) CO ₂ (1)

The reactor is configured as a "reactor with specified temperature" at 800 °C. For the purposes of this study, the reactor size is set at 100 m in length and 15 m in diameter, to ensure that the residence time of the reactants is sufficient for the gasification reactions to proceed effectively, thereby providing a realistic representation of the process within the simulation environment.

To analyze hydrogen production, the feed conditions, reaction temperature, and the dimensions of the Plug Flow Reactor are examined. Additionally, the mass flow rates of steam and air are adjusted to ensure the oxygen-to-biomass mass flow ratio remains between 0.2 and 0.3 (Cao et al., 2024). It is therefore noted that hydrogen production through water electrolysis might be helpful to meet the overall hydrogen demand.

Following the pyrolysis and gasification processes, the next step involves cooling the syngas using a heat exchanger. The syngas, initially at 800 °C, is cooled to 25 °C at a pressure of 81.3 kPa, reducing its temperature significantly for subsequent processing.

The cooled syngas is then subjected to separation to isolate the useful gases required for methanol production. The target components for separation include hydrogen (H₂), carbon monoxide (CO), with a minor amount of carbon dioxide (CO₂) and water (H₂O). Specifically, it is necessary to separate all hydrogen and CO, along with 5 % CO₂ and 5 % H₂O from the remaining products. It is important to note that CO₂ and water were fully consumed during the oxidation and reduction reactions; therefore, they must be added separately. The CO₂ and H₂O introduced are at 25 °C, 1 atm, with a flow rate of 50 kg/h each.

The water needs to be pumped before it can enter the mixing and heating stages. The pump is set with an outlet discharge pressure of 50.3 bar and an efficiency of 85 %. The gas mixture is then compressed using an isentropic compressor. The outlet discharge pressure of the compressor is set to 50.3 bar, with an isentropic efficiency of 85 %. After compression, the gas mixture is heated to 250 °C and maintained at 50 bar, with an anticipated pressure drop of approximately 30 kPa.

These operating conditions above define the setup for the reactor, ensuring that the syngas is prepared adequately for the next stage of methanol production.

2.4 Methanolation

For the methanol production process, an RStoic reactor is employed, operating at a temperature of 250 °C and a pressure of 50 bar. The reaction is configured with the assumption that the fractional conversion of hydrogen is 85 %. Following the reaction, the product stream is initially cooled using a heat exchanger to a temperature of 65 °C and a pressure of 47.7 bar. Subsequently, a valve is used to further reduce the pressure to 130 kPa. This pressure reduction results in a decrease in the mixture's temperature. To account for this, the initial cooling temperature in the heat exchanger is set higher, ensuring that the final methanol temperature is close to room temperature (25 °C). The main components of the GASOUT stream are CO and H₂. This stream is redirected to the syngas recovery system for further processing.

Finally, methanol is separated from the remaining components using a separator. This separation process isolates the methanol from the other products, completing the methanol production sequence.

2.5 Results

The final properties of the produced methanol are as follows: a temperature of 25.19 °C, a pressure of 1.3 bar, and a mass flow rate of 2,085.63 kg/h. The temperature indicates that the methanol is in a liquid state, given that its normal boiling point is around 64.7 °C at atmospheric pressure. This suggests that the methanol produced has been adequately cooled and is being maintained at a temperature suitable for storage and handling. The pressure of 1.3 bar is typical for the storage and transport of methanol to prevent its evaporation and ensure stability. This pressure setting helps maintain the methanol in its liquid phase, avoiding any phase change that might occur at lower pressures. The mass flow rate indicates a substantial production capacity, reflecting the efficiency of the methanol production process. This result suggests that the process is effective in generating methanol at an industrial scale, meeting substantial demand.

3. Optimizations of the Process with s-CO₂ cycle

3.1 Integration of s-CO₂ cycle

The supercritical CO₂ (s-CO₂) combined cycle represents an advanced power generation that utilizes CO₂ in its supercritical state as the working fluid to enhance efficiency and reduce greenhouse gas emissions. This technology merges the benefits of both gas turbine and steam turbine cycles by employing supercritical CO₂ as a substitute for the traditional water/steam heat cycle fluid.

Research by Pan et al. (2021) explored the optimization of the supercritical CO₂ combined cycle within a solid oxide fuel cell gas turbine system, calculating system efficiency, exergy efficiency, and performing an economic analysis to demonstrate the feasibility of the s-CO₂ cycle in such systems. Nami et al. (2017) proposed a novel system that integrates a gas turbine, s-CO₂ cycle, and organic Rankine cycle, analyzing and calculating its power generation efficiency. Their findings indicate that the power generation efficiency of this system exceeds 40 %. Balafkandeh et al. (2019) developed a new biomass-based combined heat and power system that incorporates the s-CO₂ cycle with an absorption chiller. Compared to conventional Rankine cycles, the s-CO₂ power cycle offers significant advantages within its operational temperature range.

As is shown in Figure 2, in the Aspen Plus simulation's, the flow rate of CO₂ is assumed 500 kg/h. The blue lines represent the flow of CO₂ in the cold part of the cycle, while the red lines indicate the flow in the hot part. The turbine within the system generates 7,400 kW of power and operates at a pressure of 20 MPa, with an inlet temperature of 375 °C. The compressor in the cycle has a power consumption of 1,800 kW. It receives CO₂ at an inlet temperature of 32 °C and a pressure of 7.3 MPa. The outlet temperature of the CO₂ from the compressor is 500 °C.

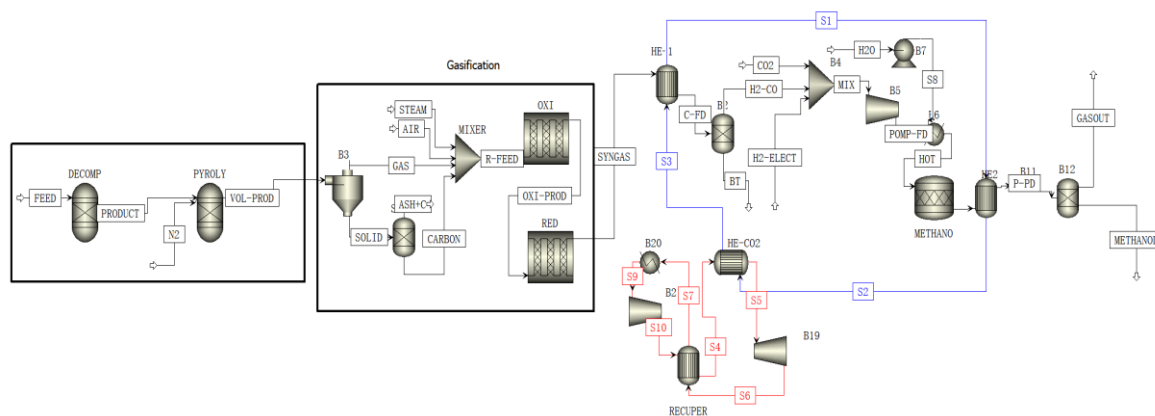


Figure 2: Process Flow Diagram of the Process with s-CO₂ cycle

3.2 Results

In the improved methanol production process, the integration of a supercritical CO₂ cycle has been implemented to optimize the overall system. The final properties of the produced methanol are as follows: a temperature of 29.76 °C, a pressure of 1.3 bar, and a mass flow rate of 2,159.94 kg/h. The impact of this improvement on the production process and its performance can be evaluated.

The introduction of the supercritical CO₂ cycle primarily aims to enhance the system's overall efficiency and economic viability. This cycle effectively increases the production rate by 4.3 %, thereby reducing energy consumption and lowering production costs. The methanol produced at nearly ambient temperature and

relatively low pressure with a high mass flow rate indicates that the improved process demonstrates good stability and efficiency in terms of methanol yield and production conditions.

However, when considering the energy losses and economic costs associated with the supercritical CO₂ cycle, the efficiency gains from this improvement may be limited. The CO₂ cycle involves complex components, including compressors and turbines, which introduce additional energy consumption and operational costs.

Based on the need to evaluate how variations in CO₂ flow rate impact the overall process efficiency and methanol production, a sensitivity analysis was conducted to evaluate the impact of varying the CO₂ flow rate on methanol production. Specifically, the CO₂ flow rate was increased from 500 kg/h to 1,000 kg/h. After this adjustment, the methanol production rate was observed to be 2,174.65 kg/h. The relatively minor change in methanol output indicates that the process is not highly sensitive to variations in the CO₂ flow rate.

This limited sensitivity suggests that while CO₂ flow rate adjustments do affect the overall production, the extent of these effects is relatively small within the operational range tested. Therefore, other factors such as energy losses, economic costs, and system efficiency may play a more significant role in optimizing the methanol production process. This finding underscores the importance of considering multiple factors in process optimization and highlights that adjustments to the CO₂ flow rate alone may not substantially enhance overall process efficiency.

4. Conclusion

The integration of the supercritical CO₂ cycle into the methanol production process significantly improved efficiency and reduced greenhouse gas emissions. This optimization resulted in a final methanol output with a temperature of 29.76 °C, a pressure of 1.3 bar, and a mass flow rate of 2,159.94 kg/h. Sensitivity analysis demonstrated that variations in CO₂ flow rate had minimal impact on production, indicating that the process is stable and optimized. The integration of the supercritical CO₂ cycle is expected to contribute to a more sustainable and efficient methanol production process by reducing the overall carbon footprint through improved energy efficiency and reduced emissions.

References

- Adil A., Rao L., 2022, Methanol Production from Biomass: Analysis and Optimization. *Materials Today: Proceedings*, 57, 1770–1775.
- Balafkandeh S., Zare V., Gholamian E., 2019, Multi-Objective Optimization of a Tri-Generation System Based on Biomass Gasification/Digestion Combined with S-CO₂ Cycle and Absorption Chiller. *Energy Conversion and Management*, 200, 112057.
- Cao Y., Bai Y., Du J., 2024, Parametric Study on Biomass Gasification by Using Air, Oxygen-Enriched Air, Air/Steam and Oxygen-Enriched Air/Steam Agents: An Aspen Plus Modeling. *International Journal of Hydrogen Energy*, 73, 265–273.
- Harris K., Grim R.G., Huang Z., Tao L., 2021, A Comparative Techno-Economic Analysis of Renewable Methanol Synthesis from Biomass and CO₂: Opportunities and Barriers to Commercialization. *Applied Energy*, 303, 117637.
- Nami H., Mahmoudi S.M.S., Nemati A., 2017, Exergy, Economic and Environmental Impact Assessment and Optimization of a Novel Cogeneration System Including a Gas Turbine, a Supercritical CO₂ and an Organic Rankine Cycle (GT-HRSG/SCO₂). *Applied Thermal Engineering*, 110, 1315–1330.
- Petipas F., Brisse A., Bouallou C., 2014, Benefits of external heat sources for high temperature electrolyser systems. *International Journal of Hydrogen Energy*, 39(11), 5505 - 55134.
- Pan M., Zhang K., Li X., 2021, Optimization of Supercritical Carbon Dioxide Based Combined Cycles for Solid Oxide Fuel Cell-Gas Turbine System: Energy, Exergy, Environmental and Economic Analyses. *Energy Conversion and Management*, 248, 114774.
- Sanchez, M., Amores, E., Abad, D., Rodríguez, L., Clemente-Jul, C., 2020, Aspen Plus model of an alkaline electrolysis system for hydrogen production. *International Journal of Hydrogen Energy*, 45, 3916–3929.
- Weiss F.G., Bouallou C., 2024, Supercritical Carbon Dioxide Power Cycles with Oxy-Combustion Capture: Towards A New Improved Cycle Layout for Energy Production. *Chemical Engineering Transactions*, 114, 145-150.
- Zhang Q., Chen H., Li B., Pan P., Xu G., Zhao Q., Jiang X., 2023, A Novel System Integrating Water Electrolysis and Supercritical CO₂ Cycle for Biomass to Methanol. *Applied Thermal Engineering*, 225, 120234.