

Review

Efficient Utilization of Carbon Dioxide in Power-to-Gas and Power-to-Liquid Processes: A Vital Path to Carbon Neutrality

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Abstract: A large number of CO₂ emissions caused a serious greenhouse effect, aggravating global warming and climate change. Therefore, CO₂ utilization has been a research hotspot, especially after the Paris Agreement, and among the various CO₂ utilization technologies, the power-to-gas (PTG) and power-to-liquid (PTL) processes have recently attracted significant attention because they can transform CO₂ into fuels and/or chemicals. Considering the lack of detailed information in the literature with regard to process design and economic analysis, we have critically and comprehensively summarized the recent research progresses concerning the PTG and PTL processes. Herein, we mainly focus on the power-to-methane in the case of PTG and the power-to-syn crude, power-to-methanol, and power-to-ethers in the case of PTL. From the technical point of view, the bottleneck problem of PTG and PTL processes is the low system efficiency, which can be improved by heat integration and/or process integration. Meanwhile, from the economic point of view, the production cost of PTG and PTL processes needs to be further reduced by the following measures, such as by increasing the carbon tax, lowering the electricity price, improving the electrolysis efficiency, reducing the capital expenditure of the electrolytic cell, and formulating sustainable incentive policies. The main purpose of the paper is to present a comprehensive updated review of CO₂ utilization in PTG and PTL processes from process system integration, the techno-economic aspects, such as, state-of-the-art synthesis technologies, process system integration and the production cost, and provide useful information and reliable suggestions for the future development trends of the PTG and PTL processes.

Keywords: CO₂ utilization; power-to-liquid; power-to-gas; system integration; production cost



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1. Introduction

According to the research report of the IEA, global CO₂ emissions have exceeded 36.8 billion tons [1]. This is mainly attributed to fossil fuel burning [2], among which the energy-intensive sectors, dominated by electricity and heat, cover 45%, while the industrial sectors, including metal production and manufacturing, account for 23%, with the remaining portion mainly consisting of the transportation sector [3]. It is now widely recognized that the rising levels of CO₂ leads to global warming and severe environmental problems such as a rise in sea levels, the melting of the polar regions, and ocean acidification [4]. More specifically, according to the prediction of the fifth assessment report of the Intergovernmental Panel on Climate Change (IPCC), if the emission of a greenhouse gas such as CO₂ continues to increase, the global sea level will rise by 0.52–0.98 m until 2100 [5]. Simultaneously, extreme weather will increase significantly, which would pose a great threat to human survival. Therefore, it is necessary to reduce CO₂ emissions and to limit the global temperature increase to 1.5–2 °C by the end of the 21st century [6].

Generally, there are four main ways to reduce CO₂ emissions:

- Improving the utilization rate of fossil energy. This way means using less energy to meet the energy service demand and directly reduce the use of fossil energy. However, burning fossil fuels inevitably produces CO₂.
- Using renewable energy with near-zero CO₂ emissions, such as wind energy and solar energy. However, the widespread deployment of renewable energy is challenging due to its intermittent in time and space and low capacity factors [7].
- Carbon capture and storage (CCS). In the case of CCS, CO₂ is captured from the industrial flue gas and atmosphere, and then the CO₂ is permanently stored in underground space, such as deep geological caves, salt aquifers, abandoned oil and gas fields, coal mines, and the seafloor [8]. CCS has been proven to be feasible from the technical aspect, but economic competitiveness, social acceptance, and environmental impacts are barriers to the development of CCS [9].
- Carbon capture and utilization (CCU). In the case of CCU, CO₂ is converted into various high value-added end products, such as methanol, dimethyl ether, synthetic natural gas (SNG), and liquid fuels [10]. Recently, various processes based on CCU are developed, which mainly include reforming, hydrogenation, carboxylation, mineralization, electrochemical, photochemical, plasma catalysis, and polymeric processes [11,12].

Among the various CO₂ reduction ways, the CCU has gained widespread attention, especially power-to-gas (PTG) and power-to-liquid (PTL) processes based on CO₂ catalytic conversion, which are further introduced from technical and economic aspects in the following sections. PTG and PTL processes realize the efficient utilization of CO₂ and convert unstable renewable energy into stable chemical energy for storage [13,14]. In general, the PTG and PTL processes contain three sections: H₂ production via water electrolysis using surplus renewable energy, CO₂ capture from flue gas, and CO₂ hydrogenation. This review mainly focuses on the CO₂ hydrogenation technologies in the PTG and PTL. Hence, the water electrolysis and CO₂ capture technologies are excluded from this review.

The products of PTG and PTL mainly depend on different CO₂ hydrogenation processes. For the PTG process, the product SNG is injected into the existing natural gas pipe network or is transported by CNG tankers (Figure 1) [15]. For the PTL process, the product liquid hydrocarbons (C₅₊) are suitable to produce transportation fuels with a higher volumetric energy density, such as jet fuel, diesel, and gasoline. In addition, the product of PTL, such as methanol, olefin, and dimethyl ether, are used as the essential platform chemical (Figure 2) [16,17].

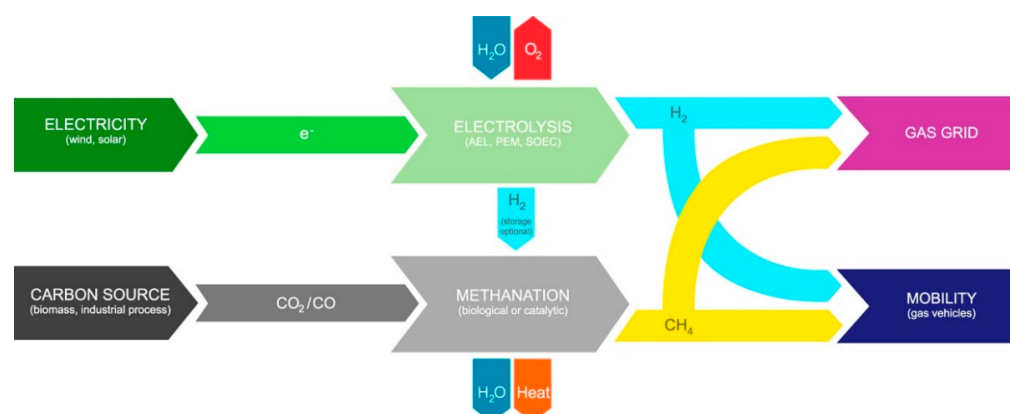


Figure 1. The schematic diagram of PTG process. Reprinted with permission from Götz et al. [15]. Copyright (2016) Elsevier.

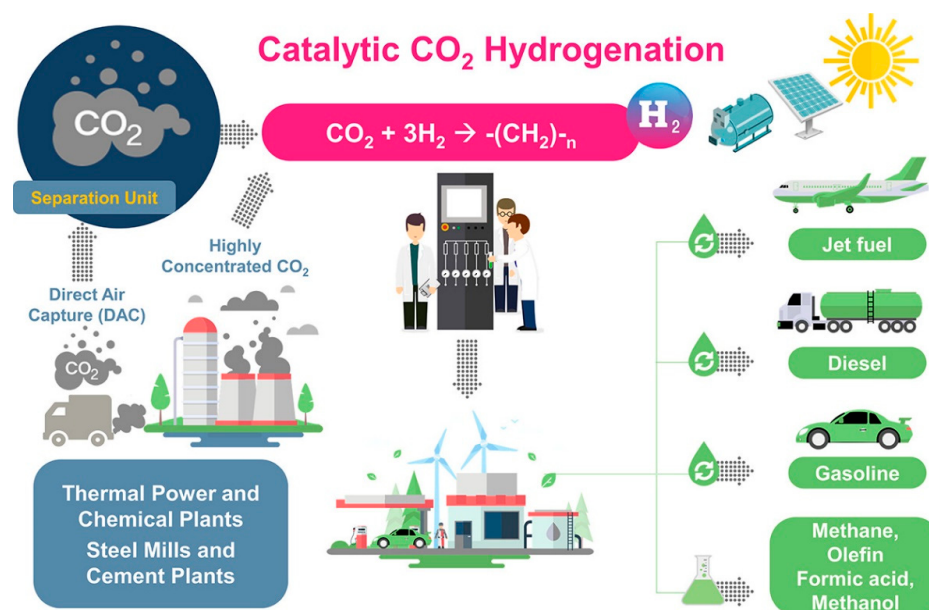
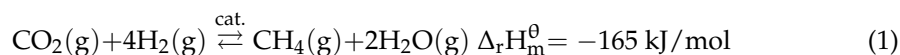


Figure 2. The schematic diagram of PTL process. Reprinted with permission from Ra et al. [17]. Copyright (2020) American Chemical Society.

At present, low system efficiency and high production cost are the primary barriers to the large-scale deployment of PTG and PTL processes. Therefore, in this review, the recent research progresses of CO₂ utilization in PTG and PTL processes are summarized, particularly in the aspects of synthesis technologies, technical performance improvement, and process system integration. In addition, the production cost of different products from PTG and PTL processes is illustrated and analyzed. Hence, the current study provides an extensive overview of PTG and PTL technologies in terms of system integration, process performance improvement, and production cost analysis. It aims to provide primary boundary conditions for future concepts with regard to performances and process designs, ultimately guiding subsequent advancements and facilitating benchmarking efforts.

2. CO₂ Utilization in Power-to-Gas Process

The PTG process primarily converts water and CO₂ into SNG, in which the CO₂ methanation (see Equation (1)) is an essential step [18]. The operating conditions, reactor configuration, product purification, process integration of CO₂ methanation and H₂O/CO₂ co-electrolysis, and production cost analysis are presented in the following sections.



2.1. Effect of Operating Conditions on CO₂ Methanation

2.1.1. Effect of Operating Temperature

Considering that CO₂ methanation is strongly exothermic, low temperature is therefore beneficial for CO₂ methanation from a thermodynamic perspective. For example, Gao et al. found that CO₂ conversion can reach 100% at about 200 °C [19]. However, from the aspect of reaction kinetics, high temperature tends to accelerate the reaction rate. However, when the temperature surpasses 450 °C, it is easy to cause an increase in CO by-product and a decrease in CO₂ conversion due to dominating reverse water–gas shift (RWGS) side reaction [20]. Therefore, the typical operating temperature is generally at 450 °C [21].

2.1.2. Effect of Operating Pressure

In the typical temperature range of 200–600 °C, the CO₂ conversion and CH₄ selectivity increase as the operating pressure increases, which is attributed to a volume reduction in CO₂ methanation. However, when the operating pressure exceeds 30 bar, the influence

of pressure on the CO₂ conversion is non-significant, while the operating cost is further increased. Therefore, an operating pressure of 10–30 bar is generally considered the most suitable from the technical and economic aspects [22].

2.2. Effect of Reactor Configuration on CO₂ Methanation

As highlighted above, an excessive operating temperature tends to cause a decrease in CO₂ conversion and catalyst deactivation. Therefore, reactor temperature control has been the primary process constraint to realize full implementation in industry [23]. Some researchers have developed different reactors, which can be roughly divided into fixed-bed reactors, fluidized-bed reactors, three-phase reactors, and structured reactors.

2.2.1. Fixed-Bed Reactors

The fixed-bed reactors comprise multiple adiabatic reactors in series and interstage condensers to control the temperature rise. The number of reactors generally varies from one to four. At present, most of the commercial methanation processes have employed multiple fixed-bed reactors in series with interstage condensers, such as the Lurgi/BASF high temperature (HT) methanation process and Haldor Topsoe's TREMP™ process (See Figure 3) [24,25]. Taking the three fixed-bed reactors in series with interstage condensers as an example, Iaquaniello found that CO₂ conversion rose to more than 90% in the temperature range of 400–500 °C [26]. In addition, multiple reactors in series allow high catalyst load and space velocity, and the steam generated in the condensers can be used as utilities. However, the primary disadvantages of such reactors are high thermal resistance and hotspots, which can cause catalyst sintering.

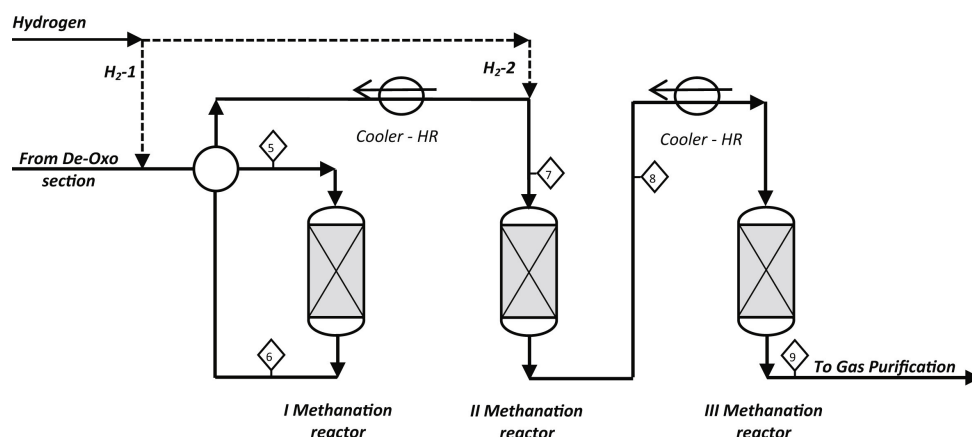


Figure 3. The schematic diagram of TREMP™ process [26]. Copyright (2018) Elsevier.

2.2.2. Fluidized-Bed Reactors

The fluidized-bed reactors were developed by the US Bureau of Mines, and a pre-commercial fluidized-bed reactor was built and commercialized in 1982 [27]. In the fluidized-bed reactors, the catalyst particles are fluidized in the gaseous reactant, and the contact between the reaction gas and the catalyst particles is uniform. Therefore, the fluidized-bed reactors can achieve high mass and heat transfer and almost isothermal operating conditions. In addition, another significant advantage of the reactors is to remove, supplement, and recycle the catalyst continuously and easily during operation [28]. However, the attrition and the entrainment of the catalyst particles and the fluidization velocity limitation are major barriers to a large-scale application [29].

2.2.3. Three-Phase Reactors

The three-phase reactors were developed by Chem Systems Inc. in the 1970s, and the operating pressure of such reactors is up to 70 bar [24]. In the three-phase reactors, the solid catalyst particles are suspended in an inert liquid, such as dibenzyl toluene, and

the reaction gas is in countercurrent contact with the catalyst. Similar to the fluidized-bed reactors, the three-phase reactors can achieve precise temperature control. The three-phase reactors are suitable for the dynamic operations of methanation [30,31]. When the feedstock fluctuates, the three-phase reactors are less prone to quick temperature changes. It is due to the fact that the inert liquid has a relatively large heat capacity. However, the evaporation and decomposition of the inert liquid are significant issues for three-phase reactors [32]. Table 1 presents the comparison of the reactor performance in the methanation process.

Table 1. Comparison of reactor performance in the methanation process [26,28,29,32].

	Fixed-Bed Reactor	Fluidized-Bed Reactor	Three-Phase Reactor
Operating mode	Adiabatic	Isothermal	Isothermal
Catalyst state	Catalyst bed	Catalyst in fluidized bed	Catalyst suspended in liquid
Advantages	(1) High reaction rate (2) Wide operating range (3) Simple construction	(1) Effective heat removal (2) Uniform temperature gradient (3) Good mass transfer	(1) Precise temperature control (2) Excellent heat transfer performance (3) Suitable for strongly exothermic reactions
Disadvantages	(1) Ineffective regions in the reactor (2) Catalyst deactivation (3) Difficult temperature control	(1) Large reactor size (2) Catalyst entrainment (3) High catalyst attrition	(1) Difficult separation of inert liquids (2) High mechanical stress of catalysts (3) Expensive reactor cost

2.2.4. Structured Reactors

Structured reactors mainly include micro-channel reactors, membrane reactors, and enhanced-adsorption reactors [24].

(1) Micro-channel reactors

Micro-channel reactors contain multiple rectangular metal channels. The inner surface of the metal channel is covered by a thin layer of catalyst, while the outer surface is in contact with the cooling medium [33]. In fact, the metal channel can be regarded as the special catalyst carrier. Different from common catalyst carriers (alumina, zeolites, etc.), the carrier based on metal has excellent heat transfer properties and better temperature control ability [34]. In addition, the high surface-to-volume ratio significantly decreases the reactor volume [35]. Micro-channel reactors have been at a demonstration scale [36]. However, it should be pointed out that the micro-channel reactors are single-use systems. That is, if the catalyst is deactivated irreversibly, the whole reactor has to be replaced [37].

(2) Membrane reactors

Membrane reactors achieve the in situ reaction and separation in the same reactor simultaneously. Meanwhile, the membrane reactor could further facilitate the forward reaction and break the limitation of thermodynamic equilibrium by selectively removing the targeted products [38]. According to the selectivity and permeability of the membrane, the membrane reactor removes products in situ and breaks the thermodynamic limitation to further improve the CO₂ conversion. For example, compared with the traditional fixed-bed reactors, the membrane reactors remove the steam via hydroxy sodalite (H-SOD) membrane in situ and increase the CO₂ conversion by 26% [39]. However, high cost and the regular replacement of the membrane are the major disadvantages for membrane reactors.

(3) Enhanced-adsorption reactors

The enhanced-adsorption reactors control the reaction conditions to change the concentration of reactants and products and increase the conversion and yield [40]. The reactors can be divided into two types according to different adsorbents.

One kind of reactor is similar to the membrane reactors, and uses adsorbents to remove steam in situ and increase methane yield. The adsorbents generally choose zeolites that can be regenerated by pressure swing adsorption (PSA) technology. For example, Walspurger et al. used a Ni-based catalyst and zeolite 4A adsorbent, and found that the CO₂ conversion reached close to 100% when operating pressure is atmospheric pressure, and the operating temperature is 250–350 °C [41]. Florian et al. investigated the thermodynamic performances of enhanced-adsorption CO₂ methanation in a fixed bed reactor. As a result, it was found that the application of the enhanced-adsorption technology is beneficial for the highly exothermic CO₂ methanation reaction [42].

Another kind of reactor employed bifunctional materials to integrate the CO₂ capture and CO₂ methanation. Bifunctional materials refer to nano-scale CO₂ adsorbents uniformly dispersed on the surface of the catalysts. In the bifunctional materials, the adsorbents, such as CaO and hydrotalcite, directly capture CO₂ from flue gas, and then the heat generated by CO₂ methanation can promote CO₂ desorption [43]. It should be noted that the process conducts the CO₂ capture and CO₂ methanation in the same reactor. Hence, the equipment investment is significantly decreased. In addition, under the action of the bifunctional materials, the CO₂ conversion can reach 99% at 300 °C [44].

2.3. Product Purification

The crude product obtained by CO₂ methanation generally contains H₂O, unreacted H₂ and CO₂, which cannot be directly injected into the current natural gas pipelines. Therefore, purification of the crude product is necessary [45]. CO₂ can be captured by amine absorption technologies, which is a well-known and implemented industrial method. For example, Becker et al. captured 90% of CO₂ in the crude SNG via MDEA, captured 90% of H₂ in the crude SNG via polysulfone membrane, and then recycled CO₂ and H₂ to the methanation reactor to improve total CO₂ conversion and CH₄ yield [46]. However, other CO₂ capture technologies such as absorption, distillation, and flash separation have been widely used [47]. In addition to the aforementioned technologies, some emerging technologies, including membrane separation and PSA, also show enormous application potentials [48].

The presence of water in crude SNG causes severe damages. For example, water and methane form hydrate blockage on the valves and pipeline [49]. In addition, the surplus water decreases the transmission capacity of the pipeline and consumes additional electrical energy [50]. Hence, it is necessary to remove the water. The widely used technology in industry is absorption with triethylene glycol (TEG). The specific steps include the absorption of water with TEG in absorber, and the desorption of water from the water-loaded solvent in stripper [51]. However, its regeneration energy consumption is relatively high, and the system operation is complex [52]. In addition to the absorption method, the water in crude SNG can be cooled down and removed in the gas–liquid separator, which can combine with the membrane separation method to remove water in crude SNG to the ppmv level. For example, Chauvy et al. first used a gas–liquid separator to remove 99.99 vol% of water in the raw product, then used a membrane (the commercial Pebax[®]-based membrane) separator to reduce the H₂O content to the ppmv level [53].

2.4. Process Integration of CO₂ Methanation and H₂O/CO₂ Co-Electrolysis

For the PTG process, in addition to methanation reactors, electrolytic cells are another extremely important equipment. The electrolytic cell can efficiently convert steam/water into H₂ and O₂ using surplus renewable energy. According to the principle of water electrolysis, the electrolytic cell can be divided into three types: proton exchange membrane electrolytic cells (PEMECs), alkaline electrolytic cells (AECs), and solid oxide electrolytic cells (SOECs) [54]. Compared with other water electrolytic cells, the significant advantages of SOECs lie in their high-temperature operating nature and high electrolysis efficiency. The SOECs are currently in the pre-commercialization stage [55,56]. Considering the merits

of SOECs, the integration process of CO₂ methanation and H₂O/CO₂ co-electrolysis based on SOECs has been an interesting research area for fuel production in recent years.

From the perspective of energy utilization, the process integration achieves the comprehensive utilization of heat and reduces the dependence of the coupled system on external energy. For instance, Er-rbib et al. designed an integrated process of CO₂ methanation and H₂O/CO₂ co-electrolysis and conducted the process modeling. Moreover, they conducted heat integration to maximize the utilization of reaction heat, which was divided into three parts. The first part was used to heat the stream at the inlet of the SOEC unit, the second part was used to generate electricity through the Rankine cycle, and the last part was used to capture CO₂ and regenerate the solvent. The results presented that the overall power-to-gas energy efficiency reached 67.1% [57]. It is worth noting that H₂O/CO₂ co-electrolysis and CO₂ methanation belong to two independent sections in the integrated process. However, Luo et al. found that coupling H₂O/CO₂ co-electrolysis and methanation into a tubular SOEC reactor has a higher system efficiency. They developed a two-dimensional multiscale electro-thermos tubular SOEC model based on their previous work [58] and realized the direct conversion of CO₂ to CH₄ in a single tubular reactor. Simultaneously, it was found that CO₂ conversion was up to 98.7%, the CH₄ yield was over 50%, and the electricity–gas conversion reached 94.5% [59]. The process breaks the boundary between H₂O/CO₂ co-electrolysis and methanation sections, which are carried out in a single reactor and reduce operational complexity and equipment cost.

2.5. Production Cost Analysis

The CO₂ methane process is relatively mature in technology and has large-scale pilot plants. For example, the largest commercial CO₂ methanation plant worldwide has been built and implemented in Germany [60]. However, economic competitiveness needs to be further improved. Guilera et al. evaluated the economic feasibility of SNG based on the electricity markets of different countries. They found that the production cost currently ranges from 70 to 125 EUR/MWh, which is 2–7 times higher compared with the price of traditional natural gas [61]. To further reduce the production cost of SNG, Blanco et al. proposed specific measures from the economic aspect. Low electricity prices (<10 EUR/MWh), low CAPEX (<1500 EUR), and numerous operating hours (>3000 h) are necessary [62]. Moreover, the operating form of the methanation reactor also significantly impacts the production cost. For example, Aicher et al. investigated the influence of methanation dynamics on production cost and found that, compared with a steady-state operation, the investment of the PTG process can be reduced by 8% in the case of operating the methanation dynamically [63]. In addition to the aforementioned factors, PTG process relies on the sufficient supply of hydrogen. Therefore, the cost of the hydrogen storage vessel is also important [64]. Gorre et al. proposed that the optimal of the hydrogen storage size and the methanation capacity can further reduce the production cost by up to 17% [65]. Overall, SNG is currently not competitive with conventional natural gas. However, Fambri et al. estimated that the levelized cost of SNG could decrease by 36% on average in 2030 due to the reduction in the cost of electrolyzer, hydrogen buffer, and methanation reactor [66]. In the long term, with the improvement of electrolysis efficiency, the expansion of production scale, and the flexible operational strategy of the power grid, the production cost of SNG may drop to 40 EUR/MWh, which is close to the cost of conventional natural gas [61,67].

3. CO₂ Utilization in PTL Processes

3.1. Power-to-Syncrude Process

Power-to-syncrude process mainly aims to convert water and CO₂ into syncrude, in which, CO₂ hydrogenation is a key step. The FTS route is the most effective way to produce C₂₊ products. Compared to petroleum-based products, the obtained products via the FTS route are free of sulfur, nitrogen, aromatics, and other toxic substances, and they can be used directly in subsequent refining processes or commercial consumption [68]. Herein,

the product is mainly hydrocarbons with different carbon-chain lengths, such as gaseous hydrocarbons (C_1 – C_4) and liquid fuels (C_5 – C_{20}), and the product can be upgraded into gasoline, diesel, and jet fuel by subsequent upgrading steps [69]. The power-to-synchrude process can be classified into an indirect one composed of RWGS and Fe/Co-based Fischer–Tropsch synthesis (FTS), and the direct one combined with Fe-based FTS.

3.1.1. Indirect Power-to-Synchrude Process

In the indirect process, the first step is the syngas production via RWGS or H_2O/CO_2 co-electrolysis, and then the syngas is hydrogenated to generate synchrude via FTS. The crucial components are mainly the syngas production unit and the FTS unit, both of which will be the focus in the following sections.

(1) Syngas production via RWGS

The RWGS aims to convert CO_2 and H_2 into syngas (see Equation (2)), and further increase the transforming efficiency of CO_2 [70]. Considering that the RWGS reaction is endothermic, high temperature is beneficial to the RWGS reaction from the perspective of thermodynamic equilibrium and reaction kinetics. However, the temperature is limited by the thermodynamic equilibrium. For example, in the case of Ni-based commercial catalyst and 800 °C, Kaiser et al. found that the CO_2 conversion was almost 80%, and further increasing the temperature had a slight effect on CO_2 conversion (Figure 4) [71]. However, the CO_2 conversion can be further improved by the following ways, such as multiple reactors with interstage condensation devices in series and membrane separation. For example, Meiri et al. employed three RWGS reactors in series and periodically removed water, as shown in Figure 5. The results showed that the CO_2 conversion reached 85% at 320 °C [72]. In addition, some researchers proposed a process integration of RWGS and membrane separation, which removes product steam in situ according to the selective permeability of the membrane. For example, Dzuryk et al. found the CO_2 conversion reached 80–95% in water-permeable packed-bed membrane reactors when the operating temperature is 250 °C [73]. However, Membrane degradation is an unavoidable problem for the membrane separation process. Especially when the operating temperature is above 400 °C, the amorphous membrane and polymer membrane are easy to rupture [74].

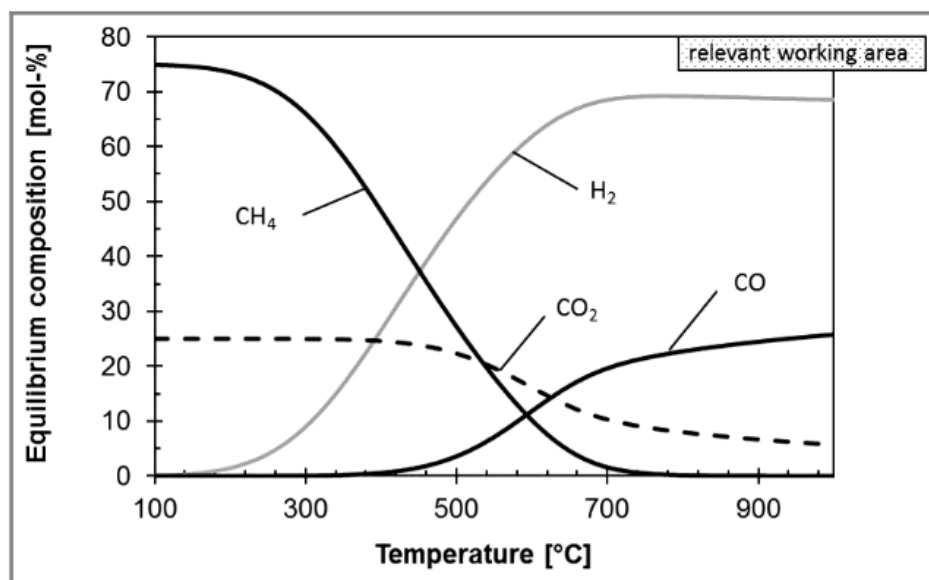


Figure 4. The effect of temperature on equilibrium composition in RWGS reaction. Reprinted with permission from Philipp al. [71]. Copyright (2013) WILEY.

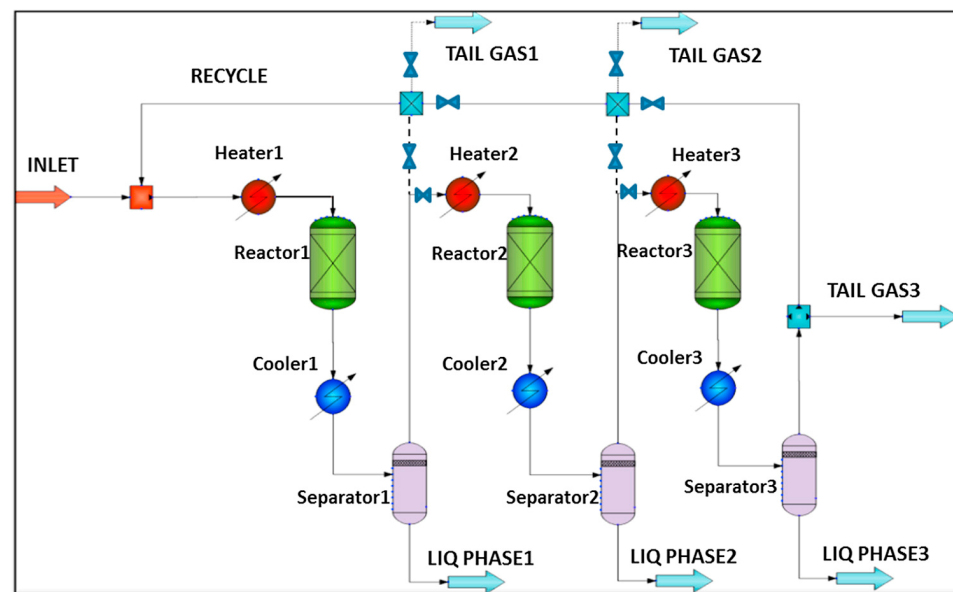


Figure 5. The schematic diagram of RWGS process with interstage condensation devices in series [72]. Copyright (2017) Elsevier.

(2) Syngas production via $\text{H}_2\text{O}/\text{CO}_2$ co-electrolysis

H_2O and CO_2 co-electrolysis process integrates water electrolysis technology and the RWGS process to achieve a comprehensive energy utilization and to reduce the number of reactors and heat exchangers [75,76]. Compared with the traditional CO_2 dry electrolysis, the co-electrolysis process dramatically improves the conversion of CO_2 to CO due to the promoting effect of H_2 [77] and overcomes the soot deposition suffered in the CO_2 dry electrolysis. The schematic diagram is presented in Figure 6. However, the degradation of the cell remains a challenge for commercialization, making a better understanding of the reaction and degradation mechanism as well as further material developments necessary [78].

Considering that H_2O and CO_2 co-electrolysis is endothermic (see Equation (6)), high operating temperatures are beneficial to increase syngas production. In addition, Wang et al. found that high temperatures can enhance electrochemical reactions and reduce electrical energy consumption, making co-electrolysis have better cost benefits and a higher energy efficiency [79]. Like the RWGS process, the co-electrolysis process inevitably has side reactions, such as CO methanation. Samavati et al. found that when the operating temperature and pressure are 900°C and 25 bar, the methane content in the product is up to 5 mol%. Increasing the electrolysis temperature can further decrease the methane content. However, the excessive operating temperatures are impractical due to the temperature limit that the electrode material can tolerate [80]. Recently, the co-electrolysis process has been feasible from the technical aspect [81]. Sunfire GmbH reported that a commercial high-temperature $\text{H}_2\text{O}/\text{CO}_2$ co-electrolysis system had run successfully in Dresden, Germany [82]. However, compared with the relatively mature RWGS process, the co-electrolysis process is still far from large-scale industrial applications.

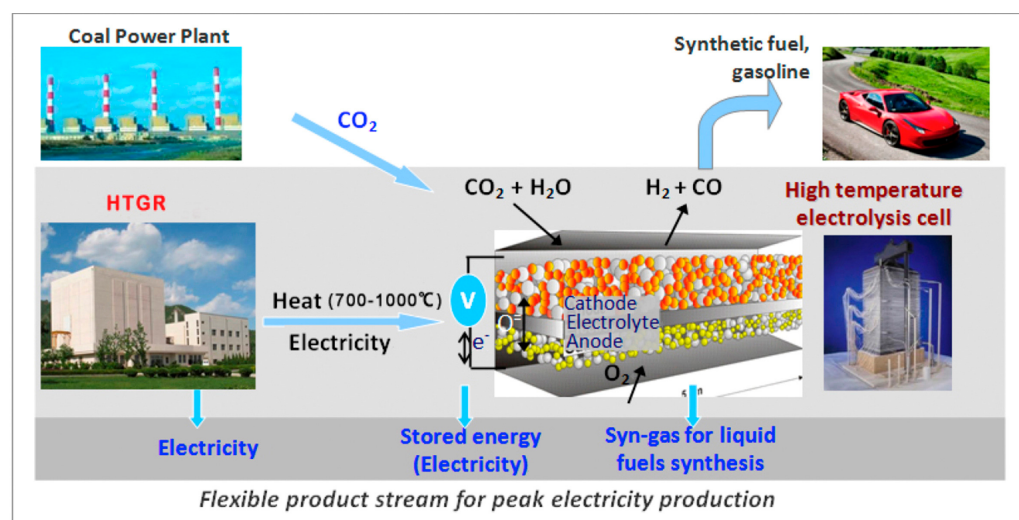


Figure 6. The schematic diagram of co-electrolysis of H_2O and CO_2 . Reprinted with permission from Zhang et al. [83]. Copyright (2017) Elsevier.

(3) Syngas conversion via Fe/Co-based FTS

- Fe-based FTS

Fe-based catalysts show excellent potential in converting syngas into light olefins ($\text{C}_2\text{--C}_4$), in which olefins are mainly α -olefins (see Equation (3)) [84]. The operating temperature is adjusted at a wide range, at 200–350 °C [85]. In addition, Fe-based catalysts have significant water–gas shift (WGS) activity (see Equation (5)), which are widely used for the FTS of syngas with insufficient H_2 [86]. Recently, extensive efforts have been made in Fe-based FTS. For example, Landau et al. developed a system of three packed-bed FTS reactors with interstage cooling in series, which can remove the water and liquid hydrocarbons in the product. It was found that the CO_2 conversion increased from 60% to 89% compared with a single packed-bed FTS reactor [87]. Based on the work by Landau et al., Meiri et al. conducted a comparison of three reactors in series and a single reactor via a recycling process from the aspect of C_{5+} hydrocarbons and light olefins selectivity. The results presented that the single reactor with recycling had a higher C_{5+} hydrocarbons selectivity and a lower light olefins selectivity in the case of the same CO_2 conversion and space velocity [72]. Stempien et al. combined the FTS and $\text{H}_2\text{O}/\text{CO}_2$ co-electrolysis sections and conducted the process modeling. The C_{5+} hydrocarbons selectivity was over 60 wt%, and the efficiency of converting H_2O and CO_2 into synthetic fuels was above 66% [88]. Do et al. proposed a novel process of light hydrocarbons ($\text{C}_2\text{--C}_4$) production through combining heat and power cogeneration and conducted the process modeling. They estimated that the carbon and energy efficiencies were 99.2 and 42.0%, respectively. Moreover, the CO_2 emission was $-1.85 \text{ kg CO}_2/\text{kg}$ of $\text{C}_2\text{--C}_4$ hydrocarbons [89].

- Co-based FTS

Generally, Co-based catalysts are primarily suitable to convert the syngas into long-chain saturate hydrocarbons (see Equation (3)). Compared with Fe-based catalysts, Co-based catalysts have a better chain growth potential [90]. However, Co-based catalysts are prone to methanation side reactions (see Equation (4)) and cause significant changes in the final product distribution at high temperatures [91]. Therefore, the temperature of Co-based FTS is generally controlled at 200–240 °C [92]. At present, significant progress has been made in the Co-based FTS. For example, König et al. implemented a process model of PTL and a comprehensive utilization of energy. It was found that the power-to-liquid efficiency and carbon conversion were 43.3% and 73.7%, respectively [93]. Vázquez et al. proposed a conceptual power-to-syn-crude plant integrated with PEM and direct air capture technologies to produce oil and wax and conducted the process modeling. Its energy and

carbon efficiencies were 47% and 94%, respectively [94]. Zang et al. conducted the technical analysis on a relatively independent power-to-liquid plant production without considering the integration with upstream H_2 and CO_2 production processes. The results showed that the overall energy conversion efficiency was 57.5% [95]. In addition, Herz et al. developed a coupled process of FTS and SOEC sections and compared different methods of heat integration and by-product recirculation. They found that the overall energy efficiency was 62–68% [76]. Kulkarni et al. also designed a similar integrated process and conducted the process modeling. The results showed that the overall energy efficiency was 67% [96].

3.1.2. Direct Power-to-Syncrude Process

In the direct process, CO₂ is hydrogenated directly to generate syncrude via FTS (see Equation (7)). It is well known that CO₂ is a very stable chemical molecule. Hence, more efficient catalysts are necessary to achieve direct CO₂ hydrogenation. At present, some researchers proposed that modified Fe-based catalysts are crucial for direct CO₂ hydrogenation [97]. In addition to the catalysts, it should be noted that the operating temperature of the direct process is generally at 300–350 °C [92].

Kamkeng et al. proposed a novel direct power-to-synchrude process configured with ex situ water removal devices. Compared with the traditional power-to-synchrude process, the application of the ex situ water removal devices further enhances the CO₂ conversion and gasoline yield by 36% and 27%, respectively [98]. Moreover, Zhang et al. proposed a completed PTL/PTG hybrid process based on the direct conversion of CO₂ to synchrude and conducted the process modeling, as shown in Figure 7. They combined the power-to-synchrude process with the Fe-based FTS and methanation process, and achieved the co-production of synchrude and high-calorie SNG. The technical analysis showed that the energy efficiency and the CO₂ reduction rate were 76% and 94%, respectively [99]. Based on the previous work, Gao et al. developed two indirect PTL/PTG hybrid processes combined with RWGS and Fe/Co-based FTS, as presented in Figure 8, and compared direct and indirect processes from the technical aspect. For the indirect hybrid process with Fe-based FTS, the energy efficiency and CO₂ reduction rate were 70% and 88%, respectively. For the indirect hybrid process with Co-based FTS, the energy efficiency and CO₂ reduction rate were 73% and 90%, respectively. Therefore, based on the aforementioned results, the direct process has a higher energy efficiency and CO₂ reduction potential in comparison to the indirect processes [100,101].

3.1.3. Process Integration via the Efficient Utilization of Light Hydrocarbons

The crude product of direct and indirect processes includes unreacted CO, H₂, CO₂, and other C₁–C₄ light hydrocarbons. In the case of a Fe-based catalyst, CO, H₂, and CO₂ can be recycled directly to the FTS unit. In the case of a Co-based catalyst, CO₂ needs to be recycled to the RWGS unit to convert syngas. The specific separation methods are illustrated in Section 2.4. In addition to unreacted gases, numerous reviewers have been preoccupied with the efficient utilization of C₁–C₄ light hydrocarbons. At present, there are three primary integrated processes to achieve the full recovery and utilization of C₁–C₄ light hydrocarbons: reforming, combustion, and the production of high-calorie SNG.

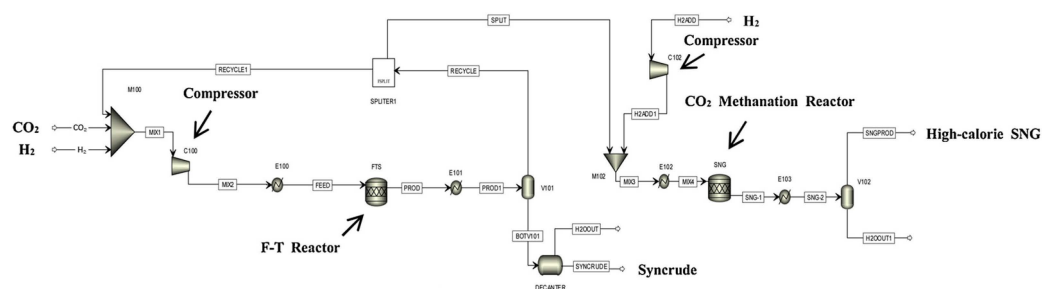


Figure 7. Schematic diagram of the direct PTL/PTG hybrid process [99]. Copyright (2019) Elsevier.

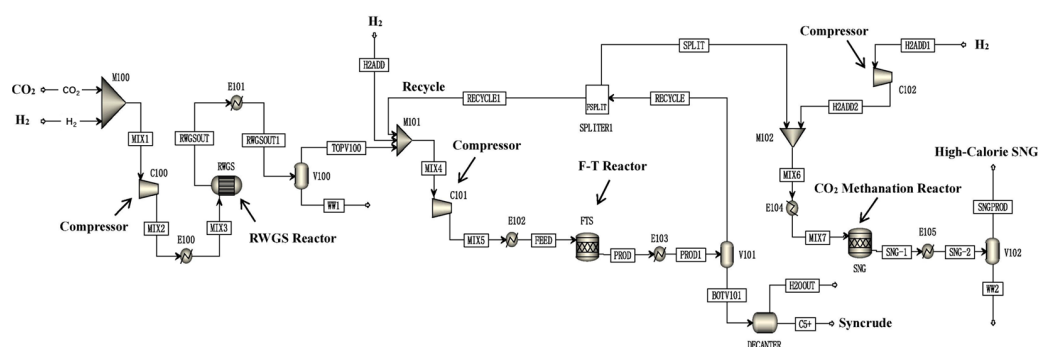


Figure 8. Schematic diagram of the indirect PTL/PTG hybrid process [100]. Copyright (2021) Elsevier.

(1) Syngas production via reforming

Light hydrocarbons are equivalent to inert components and are not conducive to FTS. Generally, C_1 – C_4 light hydrocarbons are reformed into syngas in a reformer or gasification unit, and then recycled to the FTS reactor [100,102]. In addition, some researchers have proposed new integrated processes. For example, Cinti et al. sent C_1 – C_4 light hydrocarbons to the SOEC cell, and they found that the reforming reaction can occur under the operating conditions of SOECs (750 °C, Ni-based catalyst and large amounts of steam) [103]. Although this work reduces the complexity of the system, the electrode material can poison due to carbon deposition.

(2) Heat generation via combustion

This method aims to regard light hydrocarbon as fuel. The heat generated by fuel combustion can be a utility to provide energy for the system. For example, König [93,104] and Adelung [105] et al. used C_1 – C_4 hydrocarbons as fuel and burned them with O_2 from water electrolysis, obtaining steam. It can heat the feedstock of the RWGS unit and provide heat for the RWGS reaction. Although the method reduces the dependence of the operating unit on external energy to some extent, it does not realize the high-value utilization of C_1 – C_4 hydrocarbons.

(3) High-calorie SNG production via process integration

As highlighted above, the significant weakness of the traditional natural gas and SNG is the low energy density and calorific value. However, they can be improved by increasing the composition of C_2 – C_4 hydrocarbons because the energy density of hydrocarbons increases as the carbon number increases [106]. Therefore, the process integration of FTS and methanation is very promising. For example, Zhang et al. proposed a PTL/PTG hybrid process and conducted the process modeling. The process aims to send unreacted CO, CO_2 , H_2 , and C_1 – C_4 hydrocarbons in the crude product to the methanation unit and obtain high-calorie SNG. Compared with the traditional PTL process, the hybrid PTL/PTG process has a higher net CO_2 reduction and lower net CO_2 reduction costs [99].

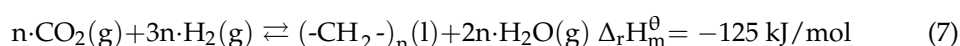
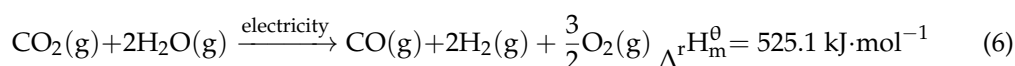
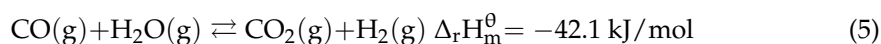
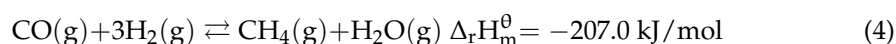
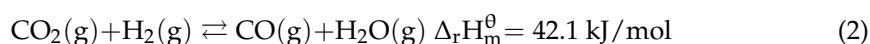
(4) Syncrude production via the olefin oligomerization

The light hydrocarbons generally consist a large portion of C_2 – C_4 olefins, which can be further converted to the high value-added syncrude over the modified HZSM-5 catalyst [107]. With this in mind, Zhang et al. proposed hybrid PTL/PTG processes integrated with FTS and oligomerization technologies, and compared their techno-economic performances with the hybrid PTL/PTG processes with single FTS technology. It was found that the application of the oligomerization reactor significantly improves the syncrude production and techno-economic competitiveness [21,108].

3.1.4. Production Cost Analysis

The power-to-syncrude process is feasible from the technical aspect, but most plants based on the power-to-syncrude process remain on the level of small-scale demonstration. Norsk e-Fuel plans to establish Europe's first commercial power-to-syncrude plant to produce renewable fuels in Norway [109]. From the economic aspect, the product cost of indirect and direct processes is higher than the market price. First, we take the indirect

processes as an example for production cost analysis. Tremel et al. conducted an economic analysis of FTS. They found that the F-T syncrude was not economically viable under the current process conditions. The production cost was 2.01 EUR/kg, which was 3–4 times higher compared with conventional fossil fuels [110]. Moreover, Adelung et al. optimized the operating conditions of the RWGS reactor to further reduce the net production cost of the indirect process. The results indicated that the minimum net production cost was 1.81 EUR/kgC₅₊ hydrocarbons [111]. Cuéllar-Franca et al. found that the main reason for the high cost of F-T fuels is hydrogen production via water electrolysis [112]. Decker et al. also presented a similar conclusion. They found that the H₂ production cost accounts for 70–80% of total production cost [113]. Herz et al. compared the economic performances of the indirect power-to-syncrude processes integrated with different water electrolysis technologies. It was found that the net production cost of the SOEC-based PTL process was lower than that of the PEM-based PTL process by 0.059 EUR₂₀₂₀/kWh_{ch} [109]. With the large-scale deployment of renewable energy and improvements in CO₂ capture and water electrolysis technologies, Drünert et al. estimated that the net fuel production cost of PTL kerosene can be reduced to 1.8–2.6 EUR/L in 2030, and its cost is expected to further reduce to 1.4–2.5 EUR/L_{fuel} in 2050 [114]. For the direct process, Zhang et al. estimated the production cost based on the direct PTL/PTG hybrid process. The total syncrude production cost was 202.58–210.56 USD/bbl [99]. Gao et al. conducted an economic assessment of the indirect processes with Fe/Co-based FTS. For the indirect process with Fe-based FTS, the total syncrude production cost was 225.65–239.12 USD/bbl, while for the indirect process with Co-based FTS, the total syncrude production cost was 215.80–219.18 USD/bbl [100,101]. Moreover, Colelli et al. also compared with the economic performances of the indirect and direct processes. It was found that the product cost of the indirect processes was 460–1435 EUR/bbl, whereas the product cost of the direct processes was 752–2364 EUR/bbl. It should be noted that Colelli et al. did not consider the recovery of the unreacted syngas; therefore, the direct process with lower CO₂ conversions had a relatively higher product cost [115]. In addition, considering the fact that water electrolysis technologies could affect the total production cost, we explored the effect of the different water electrolysis technologies on the total production cost of the hybrid PTL/PTG processes. It was found that the hybrid PTL/PTG process coupled with AEM water electrolysis technology has the lowest total production cost [21,116].



3.2. Power-to-Methanol Process

Power-to-methanol process mainly aims to convert water and CO₂ into methanol, which is an important platform chemical. Based on methanol, organic products such as formaldehyde, formic acid, dimethyl ether, acetic acid, and methyl tert-butyl ether (MTBE) can be produced [117,118]. Although the volumetric energy density of methanol is only

half that of gasoline, the octane number of methanol is higher. Hence, methanol can be mixed with gasoline, improving gasoline quality [78].

3.2.1. Methanol Synthesis via CO₂ Hydrogeneration

For the power-to-methanol process, methanol synthesis is a crucial step. Generally, CO₂ and H₂ can be directly converted into methanol over a commercial Cu/ZnO/Al₂O₃ catalyst (see Equation (8)). The typical operating temperature and pressure are 250–300 °C and 5–10 MPa, respectively [119]. Moreover, the H₂/CO₂ ratio in the feedstock is generally controlled at about 3 [120]. Generally, the per pass CO₂ conversion is about 26% with commercially available catalysts due to the limitation of thermodynamic equilibrium [121]. However, the total CO₂ conversion can be improved by recycling the unreacted gas and multiple reactors in series, which are briefly introduced in the following content.

(1) Enhancement of CO₂ conversion by recycling the unreacted gas

Recycling the unreacted gas is a typical way to improve total CO₂ conversion. For example, in the methanol synthesis process by Pérez-Fortes et al., 99% of unreacted gas mainly composed of H₂ and carbon oxides was recycled to the reactor, and 1% of unreacted gas was purged to avoid the accumulation of inert gases. It was found that the total CO₂ conversion in the process was 94%, while per pass CO₂ conversion was 22% [122]. Leonzio et al. used three different reactor configurations, including a once-through reactor, a reactor with the recycling of unreacted gases after the separation of methanol and water, and a membrane reactor with in situ water removal (See Figure 9). In addition, they compared the effect of different reactors on CO₂ conversion. The results showed that the total CO₂ conversion of the three reactors were 40%, 79%, and 60% at 493 K and 55 bar (recycle ratio = 0.8). The methanol selectivity of the three reactors were 96%, 88%, and 96% at the same operating conditions. Therefore, It should be noted that recycling unreacted gases can improve total CO₂ conversion, but decreases methanol selectivity slightly [123].

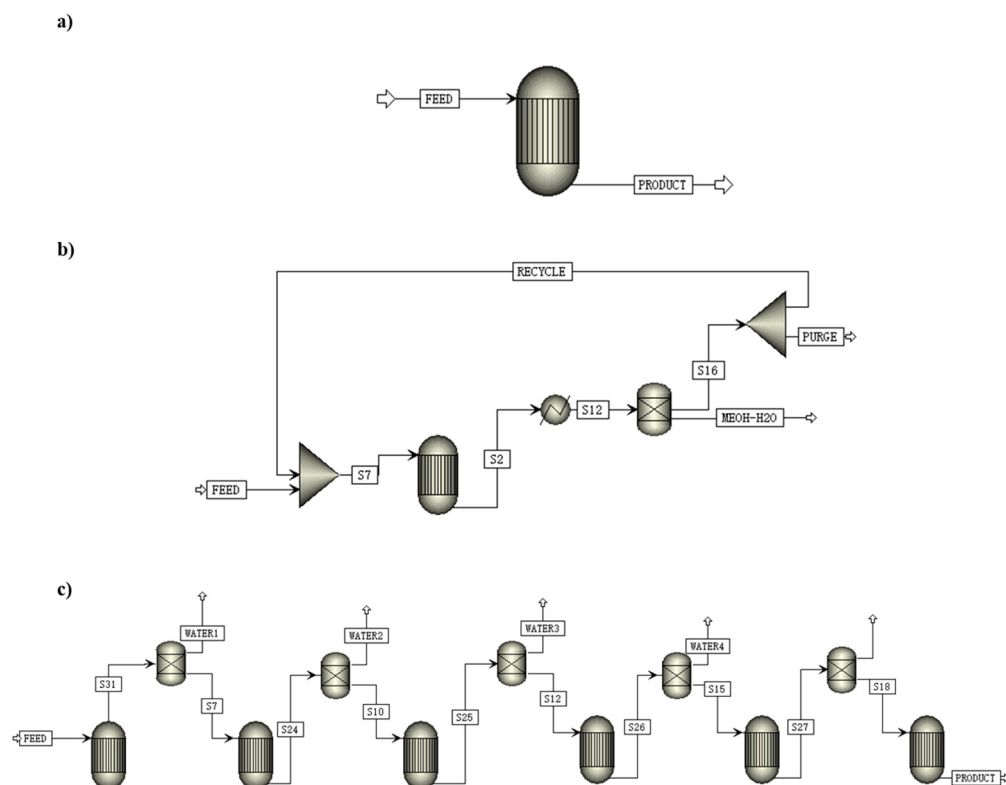


Figure 9. Schematic diagram of the CO₂-to-methanol process with different reactor configurations: (a) once-through equilibrium reactor; (b) equilibrium reactor with recycle of CO-CO₂-H₂ and separation of CH₃OH-H₂O by condensation; (c) membrane reactor with water separation [123]. Copyright (2019) Elsevier.

(2) Enhancement of CO₂ conversion by multiple reactors in series

Wiesberg et al. proposed the methanol synthesis process with two-stage reactors in series and conducted the process modeling. In the first stage, CO₂ is partially converted into methanol at a lower pressure. In the second stage, the unreacted CO₂ is converted into methanol under higher pressure. The total CO₂ conversion was 98.5% [124]. Moiola et al. investigated the influence of the number of stages on the space time yield and methanol yield in the case of selected catalysts, and determined that the optimal number of stages was three [125]. In addition, Samimi et al. used three-stage reactors of water permselective membrane in series for methanol production. They found that compared with a one-stage reactor, the novel reactor configuration caused the CO₂ conversion to increase by about 50% [126].

3.2.2. Process Integration of Methanol Synthesis and H₂O/CO₂ Co-Electrolysis

Process integration of power-to-methanol and H₂O/CO₂ co-electrolysis is a promising technology to achieve the efficient utilization of energy. First, CO₂ and H₂O are converted into syngas via co-electrolysis in the high-temperature SOEC cell, and then the syngas is used as the feedstock of methanol synthesis, as shown in Figure 10. For example, Al-Kalbani et al. compared the integrated process and the direct CO₂ hydrogenation process. They found that the energy efficiency of the integrated process was 41%, which is almost 2 times higher compared with that of the CO₂ hydrogenation process [127]. Hankin et al. evaluated the technical performance of four different methanol production processes. It was found that the methanol production integrated with the high-temperature co-electrolysis of H₂O and CO₂ is the best technology from the aspect of energy consumption and CO₂ conversion [128]. In addition, Zhang et al. developed a complete power-to-methanol process combined with CO₂ and H₂O co-electrolysis technology and conducted the process modeling. Moreover, they burned inert components (methane and ethers) in the boiler, and recovered waste heat in the form of steam. The results showed that the system energy efficiency was 72% [129].

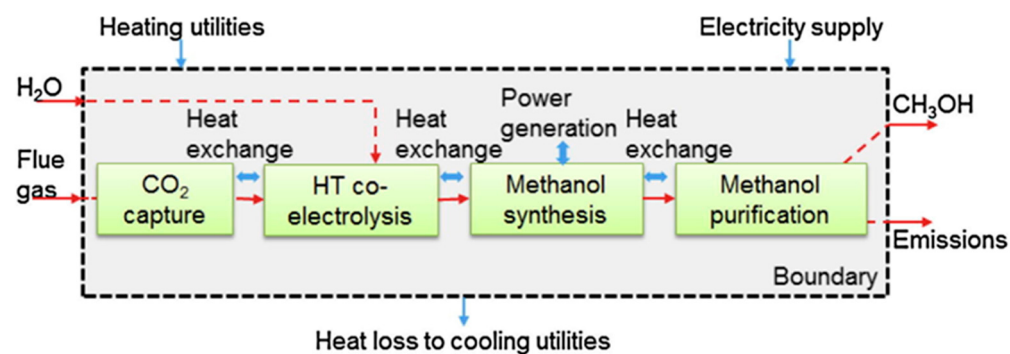


Figure 10. Schematic diagram of power-to-methanol process integrated with H₂O/CO₂ co-electrolysis technology [127]. Copyright (2017) Elsevier.

3.2.3. Product Purification

The crude methanol obtained by power-to-methanol process contains water, dissolved gases, and higher alcohols, and it needs to be further purified and upgraded to meet the requirement of fuel-grade methanol (>99 wt%) [130,131]. Generally, A widely used separation process is the combination of gas–liquid separators and distillation columns. The gas–liquid separators are used to remove most water and dissolved gas, such as CO, CO₂, and H₂. The distillation columns further remove impurities in the crude methanol, such as dimethyl ether (DME), methyl formate, other hydrocarbons, and alcohols [124,132]. However, the traditional distillation technologies are energy-intensive and cost-intensive. Therefore, the emerging membrane distillation technologies and pervaporation technologies have also been developed to achieve the efficient separation of the methanol and water [133]. Nevertheless, the purity of the product obtained via the emerging technologies

still need to be further improved. Meanwhile, these novel technologies still have a long way before achieving large-scale industrialization.

3.2.4. Production Cost Analysis

The power-to-methanol process is feasible from the technical aspect, and some small- and medium-scale demonstration plants are currently in operation. For example, Carbon Recycling International operates a medium-scale demonstration plant in Iceland, and its production capacity is 4000 tons/year [134,135]. However, from an economic aspect, the production cost of methanol via the power-to-methanol process is currently not attractive. For example, Atsonios et al. conducted an economic analysis of the methanol production cost of CO₂ hydrogenation, and found that the methanol cost via power-to-methanol process is 2.5 times compared with that of traditional methanol [136]. Adnan et al. compared three novel power-to-methanol processes from the economic aspect, and the results presented showed that the levelized methanol cost was 860–1585 USD/tons when the electricity price was 0.04 USD/kWh, which was 2–4 times higher than the market prices (300–500 USD/tons) [137]. Sollai et al. conducted a techno-economic assessment of the power-to-methanol processes. As a result, the levelized cost of the methanol was 960 EUR/t, which was two times more than the current methanol price in the international market [138]. Do et al. developed a novel methanol production process based on the sunshine-to-petrol framework and conducted an economic analysis. The results presented that the minimum selling price of methanol was 0.94 USD/kg [139]. Rivera-Tinoco et al. conducted an economic performance analysis of power-to-methanol processes combined with PEM technology and SOEC technology. The results showed that the methanol costs were 891 EUR/tons and 5459 EUR/tons, respectively [140]. Kourkoumpas et al. investigated the methanol production cost of the power-to-methanol process in Greece and Germany. In Greece, the production cost was 421–580 EUR/tons, while in Germany, the production cost was 342 EUR/tons due to lower electricity costs [141]. Cordero-Lanzac et al. suggested that reducing the H₂ price and increasing the carbon taxation could further enhance the economic competitiveness of the methanol production cost. More specifically, when the H₂ price decreased to 1.5 USD/kg and the carbon taxation increased to 300 USD/tons, the power-to-methanol process could be profitable [142].

Nizami et al. conducted an economic analysis of power-to-methanol processes using solar energy, and found that the production cost of methanol was 1040.17 USD/tons [143]. Bos et al. evaluated the methanol production process using 100 MW stand-alone wind power, and found that the production cost of methanol was 750–800 USD/tons [144]. Gu et al. proposed three power-to-methanol processes coupled with wind, solar, and wind–solar energy. The results indicated that their production costs of methanol were 531.4 USD/tons, 889.5 USD/tons MeOH, and 488.5 USD/tons, respectively [145]. Overall, the power-to-methanol process using the solar energy has the highest production cost due to expensive solar panels [146]. The production cost of the power-to-methanol processes using different renewable energy are listed in Table 2.

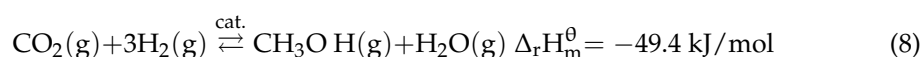


Table 2. Comparison of the production cost of the power-to-methanol processes using different renewable energy.

Type of Renewable Energy	Production Cost	Unit	References
Solar	1040.1	USD/tons	[143]
Wind	750–800	USD/tons	[144]
Wind	3805	USD/tons	
Solar	6369	USD/tons	[145]
Solar–Wind	3498	USD/tons	

3.3. Power-to-Ethers Process

3.3.1. Power-to-DME Process

DME is currently regarded as a clean synthetic fuel. Compared with traditional diesel fuel, DME has a higher cetane number, higher oxygen content, and no C–C bond. Moreover, its combustion generally produces less particulate matter, smoke, and CO [147]. In addition, DME is an important platform chemical, which can be efficiently converted into acetic acid, ethanol, methyl acetate, and aromatics [148]. Generally, the power-to-DME process can be classified into either an indirect or a direct one, which are briefly introduced in the following content.

(1) Indirect power-to-DME process

For the indirect power-to-DME process, CO₂ and H₂ are first converted into methanol, which are further dehydrated to obtain DME over acidic catalysts such as γ -Al₂O₃ and HZSM-5 zeolites and ion exchange resins (see Equation (9)) [149,150]. The operating temperature is 220–250 °C, and the operating pressure is 10–20 bar [148]. The thermodynamic equilibrium limits the methanol conversion, and the crude product likely contains unreacted methanol, which results in subsequent complex separation steps [151]. Hence, the total methanol conversion needs to be further improved by the following ways, such as recycling the unreacted methanol and reactive distillation (RD). For example, Michailos et al. separated the methanol from the crude product via distillation and recycled it to the DME reactor. The results showed that the total methanol conversion reached 99.9%, and the total CO₂ conversion reached 82.3% [152]. In addition, RD based on process intensification principles is becoming an emerging research hotspot. The RD aims to further improve the process performance limited by the equilibrium and reduce energy consumption and economic cost. For instance, Bildea et al. developed a novel reactor-separation-recycle process combined with RD, as shown in Figure 11. The process achieved the complete conversion of methanol. In addition, 6% of the specific energy requirements and 30% of CAPEX were reduced [153].

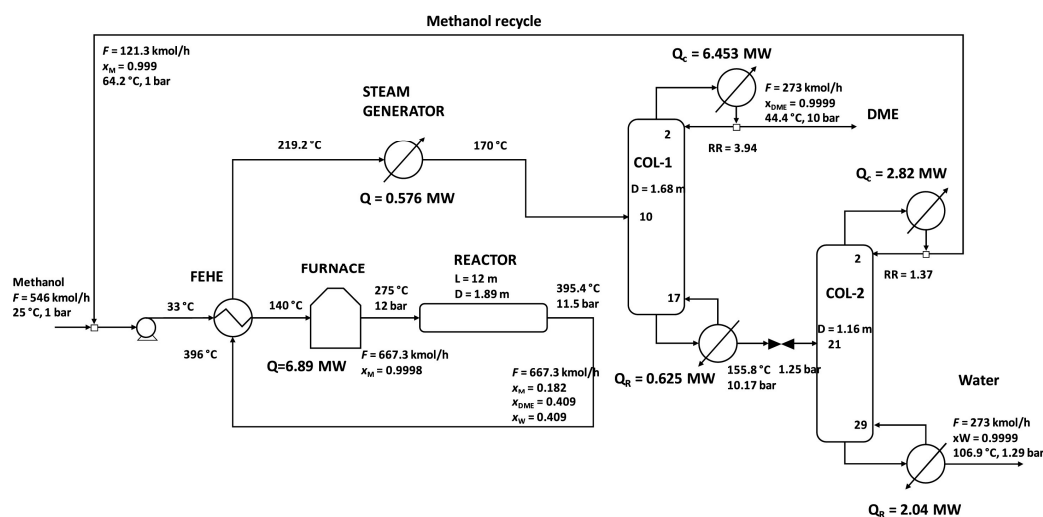


Figure 11. Schematic diagram of power-to-DME process integrated with reactive distillation technology [153]. Copyright (2016) Elsevier.

(2) Direct power-to-DME process

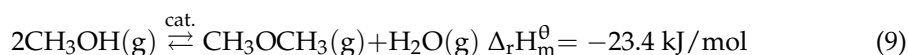
For the direct power-to-DME process, CO₂ is directly hydrogenated to synthesize DME over bifunctional catalysts, such as Cu–Zn–Zr/zeolite (see Equation (10)) [154]. Methanol synthesis and subsequent dehydration steps are conducted in the same reactor, which saves the equipment cost from the economic aspect [155]. In addition, in situ methanol generation and consumption can contribute to breaking the thermodynamic limitation of methanol synthesis, which can be carried out at higher temperatures and lower pressures [148,156]. Chen et al. compared direct and indirect processes from the

thermodynamic perspective, and found that the direct process had a lower thermodynamic limitation than the indirect process and a higher selectivity and yield [157]. Similar to the indirect process, recycling unreacted H₂ and CO₂ can further increase DME production. For example, Kartohardjono et al. compared the effect of the different recycling amounts on DME production. It was found that the DME production increased by 65.1% when the recycling amount increased by 70% [158]. Moreover, Zhang et al. compared the technical performances of the direct and indirect processes. It was found that the direct process had higher energy efficiency, exergy efficiency, and net CO₂ mitigation rate due to the lack of the energy-intensive distillation and evaporation unit [159].

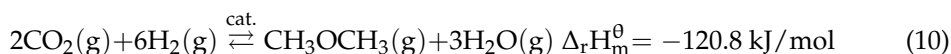
(3) Process performance enhancement

Both the direct and the indirect processes produce a considerable amount of by-product water. Especially for the direct process, the issue is more serious. A small amount of water can attenuate the coke deposition [160], but as the water content increases, the catalyst activity is inhibited, resulting in a decrease in CO₂ conversion and DME yield [161,162]. Hence, it is necessary to remove water to enhance process performance in time. Peinado et al. used 3A zeolite to remove water in situ. The results showed that the DME productivity was 2 times higher than that of the process without 3A zeolite [163]. Kampen et al. used the same adsorbent and developed a sorption enhanced DME synthesis process combined with pressure swing adsorption. It was found that the DME productivity was 4 times higher than the traditional DME process without PSA [164]. Ateka et al. used H₂O permeation selective membranes (H-SOD-type zeolite membranes) to remove H₂O in situ, and the CO₂ conversion and yield reached 70% and 60%, respectively [165]. De Falco et al. designed a staged membrane reactor composed of multiple conventional reactors and selective membrane modules in series [166]. Unlike the aforementioned in situ removal of H₂O, the staged membrane reactor separates the membrane from the reactor and removes H₂O after each reactor. Therefore, the membrane can be prevented from being affected by improper operating conditions.

Indirect process: methanol is obtained through Equation (8).



Direct process:



3.3.2. Power-to-OME_n Process

The oxymethylene ether (OME_n) with the molecular structure of CH₃O(CH₂O)_nCH₃, which is produced by the catalytic conversion of H₂ and CO₂, is attracting increasing interest from academic research and industry [167,168]. Most of the research on OME_n primarily focuses on OME_{3–5}, which are promising oxygenated fuels, and their physicochemical properties performance is similar to traditional diesel. However, the combustion of OME_{3–5} generally produces less soot formation and hazardous exhaust gas than traditional diesel due to an absence of a C–C bond [169,170].

Generally, the synthetic routes of OME_n can be classified into two categories, A and B. In route A, methanol and formaldehyde (FA) undergo condensation reactions (see Equation (14)) over an acidic catalyst such as ion exchange resin, obtaining OME_n [171]. In route B, methanol reacts with FA to produce methylal (MAL) (see Equation (13)), which further reacts with trioxane (TRI) over the zeolite to obtain OME_n (see Equation (15)) [172].

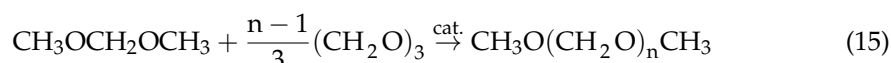
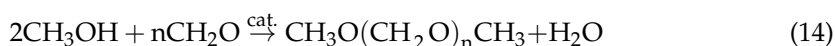
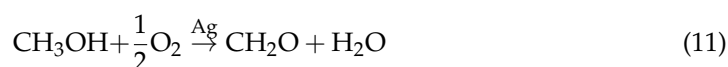
The similarity between the two routes is that intermediate methanol and FA are essential. Methanol is oxidized partially (see Equation (11)) or dehydrogenated directly (see Equation (12)) over a silver catalyst, obtaining FA [173]. Especially for the direct dehydrogenation of methanol, the product H₂ needs to be recycled, thus decreasing the electricity demand of the electrolysis [174].

There are differences between these two routes. Route A generates a large amount of water in comparison with route B, which reduces the selectivity of OME_n. The byprod-

uct water can be removed via membranes, such as zeolite membranes, but it increases equipment investment simultaneously [175,176]. TRI in route B has high production complexity, high energy consumption, low yield, and high price [177,178]. Additionally, route B requires more operating units than route A, which requires a higher capital expenditure. From the aspect of energy efficiency, Held et al. compared route A and route B from the perspective of system efficiency and heat integration. They found that the efficiency of route A was 31.3–36.3%, while the efficiency of route B was 29.2–36.7% [174].

3.3.3. Production Cost Analysis

From the economic aspect, the power-to-ethers process is not feasible under current technical conditions. For example, Michailos et al. conducted an economic assessment of the power-to-DME process, and found that the minimum DME selling price was 1828–2322 EUR/tons, which was 4.5–5.7 times more compared with fossil diesel's gate price [152]. Hepburn et al. estimated that the production cost of DME was 2.74 USD/kg DME, which exceeds the market price (0.66 USD/kg) [179]. In fact, the production cost of DME is related to the production scale. Skorikova et al. estimated that the production cost of DME was about 1.55 USD/kg DME when the DME production rate was 23 kt/year [180]. Martín et al. found that the production cost of DME was 1.4 USD/kg DME when the production scale of DME increased to 197 kt/year [181]. In our previous work, we compared the economic performances of the direct and indirect DME synthesis processes. The results indicated that the direct process had a lower total product cost [159]. For an economic analysis of OME_n, Rodríguez-Vallejo et al. compared the economic performance of different OME_{3–5} production ways, and they found that the total monetized cost of OME_{3–5} fuel is 1.5–3.6 times more compared with that of conventional diesel [182].



4. Conclusions and Prospect

4.1. Conclusions

To mitigate climate change, it is necessary to take measures to reduce CO₂ emissions. PTG and PTL are promising processes that can significantly reduce CO₂ emissions and produce valuable chemical products. In this review, we have critically and comprehensively summarized the recent research progresses of PTG and PTL processes from the technical and economic aspects. Herein, we mainly focus on the power-to-methane process in the case of PTG and the power-to-syn crude, power-to-methanol, and power-to-ethers processes in the case of PTL.

In the power-to-methane processes, we mainly studied the effects of the operating conditions (i.e., operating temperature and operating pressure) and reactor configurations (i.e., fixed-bed, fluidized-bed, three-phase, and structured reactors) on the process performances of CO₂ methanation. Moreover, considering that the CO₂ and water impurities in the crude SNG could cause damage to the transportation equipment, some typical product purification technologies, such as absorption, adsorption, and membrane separation, have been widely applied. Furthermore, the integration process of CO₂ methanation and

H₂O/CO₂ co-electrolysis has become the research emphasis due to the reduction in the dependence of the coupled system on external energy. In addition, it was found that the production cost of SNG is still 2–7 times higher compared with the cost of traditional natural gas.

In the power-to-synchrude processes, the research progress of indirect and direct pathways were summarized. For the indirect pathway, the traditional RWGS and emerging H₂O and CO₂ co-electrolysis technologies have been used to produce the syngas. Moreover, we further illustrated and compared the differences between the Fe-based and Co-based FTS routes to convert the syngas into the synchrude. For the direct pathway, it showed a stronger competitiveness compared to the indirect pathways in terms of energy utilization and carbon mitigation potential. Furthermore, we summarized four technologies to achieve the efficient utilization of the light hydrocarbons in the FTS reaction, namely reforming them to syngas, combusting them to provide heat, converting them to high-calorie SNG, and transforming them to synchrude. Lastly, it was found that the production cost of synchrude is 3–4 times higher compared with conventional fossil fuels. In the power-to-methanol processes, the CO₂ conversion over commercially available catalysts was limited by the thermodynamic equilibrium. Recovering the unreacted syngas and adopting multiple reactors in series can further improve CO₂ conversion. Similar to the production cost of the synchrude, the production cost of the methanol obtained via the power-to-methanol process is also 3–4 times higher compared with that of traditional methanol. In the power-to-ethers processes, DME and OME_n are primary products. For the power-to-DME processes, the differences between the indirect and direct routes are compared in detail. Moreover, the adsorption and membrane separation methods were proposed to remove the byproduct water and enhance the process performance. For the power-to-OME_n processes, we briefly reviewed the relevant production pathways and summarized the differences between these pathways. In addition, the production costs of DME and OME_n were 4–6 times and 1–4 times higher compared with fossil diesel, respectively.

4.2. Prospect

From the technical aspect, the major challenge of PTG and PTL processes is the low system efficiency, which can be improved via heat integration and/or process integration. For instance, the heat released from reaction and/or the combustion of inert compacts can be used to generate the steam required by co-electrolysis. The extra heat can be used to regenerate solvent in the CO₂ capture process or generate power through the Rankine cycle. In addition, the CO₂ conversion, product yield, and selectivity are concerns of academia and industry, which can be improved by the process integration of reaction and in situ product separation, the development of more efficient catalysts, and the investigation of the reaction mechanism.

From the economic aspect, the production cost of green products from PTG and PTL considerably exceeds the cost of conventional fossil fuels. Among the various factors, H₂ production is the primary factor, which can be reduced by the following ways, such as improving electrolysis efficiency and reducing electricity price. First, the electrolysis efficiency can be improved by developing novel water electrolysis technologies with a higher electrolysis efficiency, such as anion exchange membrane and solid oxide water electrolysis technologies. Moreover, increasing the current density, reducing the membrane thickness, and using a more efficient electrode material are also expected to further improve electrolysis efficiency. The deployment scale of renewable energy significantly affects the electricity price. In addition, the carbon tax has a significant effect on the PTG and PTL processes. High carbon tax contributes to improving the economic competitiveness of the PTG and PTL processes. In addition, the government should formulate incentive policies to stimulate more enterprises to produce green commodities effectively.

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