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Green Methanol—An Important Pathway to Realize Carbon Neutrality

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1. Introduction

The key to reaching China's ambitious "dual-carbon" targets of achieving a carbon peak and carbon neutrality lies in the augmentation of renewable energy generation, particularly in the domain of solar and wind energy. In the context of China, solar energy manifests a periodic availability that is conducive to electricity generation spanning approximately 15%-20% of the annual duration, whereas wind energy exhibits an availability ranging from 20% to 25% on the basis of suitable weather. Regional disparities in China necessitate attention; the duration of solar energy provision diverges between 1100 and 2000 h per year, with merely a handful of regions exceeding the 2000 h threshold. This indicates that solar energy supersedes thermal power in terms of costeffectiveness during the period when solar energy is available, since the price of direct electricity from renewable energy is lower than that of thermal power. Nonetheless, during the remainder of the year, the cost associated with solar energy, along with that of electricity storage, significantly surpasses that of thermal power. Therefore, for the most part, solar energy is not advantageous and is wasted to a great extent. Wind power presents an analogous issue concerning seasonal cost fluctuations; for example, it was reported that the Chinese wind power sector lost about 2.0×10^7 MW-h of electricity from wind curtailment in 2012, due to an unreasonable power source structure and a long-chain power grid network structure [1].

Thus, in order to promote the efficacy of power generation, the development of a commercially viable, large-scale energy-storage technology that can be globally implemented is imperative. In general, battery-based solutions are unsuitable for large-scale energy storage due to their technological immaturity and economic constraints. Moreover, the current production capacity of batteries is insufficient to meet the growing demand for renewable energy. In addition, batteries are primarily suitable for short-term energy-storage demand and cannot be used for large-scale energy-storage, while such as pumped storage, compressed-air energy storage, and gravity energy reservation are limited by geographical constraints [2,3]. Moreover, the efficacy of these energy-storage technologies is significantly limited during periods of reduced rainfall or low wind conditions. Wind resources have been

dwindling in half of the Northern Hemisphere over the past 40 years, exhibiting a decline of over 30%, which can be attributed to climate change. As a result, it is urgent to explore strategies for the large-scale storage of solar and wind energies while concurrently advancing the development and deployment of long-term energy-storage technologies.

Achieving China's dual-carbon goal poses a significant challenge, necessitating a delicate balance between the synergistic development of a dual-carbon pathway and socioeconomic factors. This equilibrium heavily relies on the sustainable utilization of existing and future investments in solar, wind, coal, oil, and natural gas infrastructure and equipment. The financial implications associated with the dual-carbon goal are substantial, making market orientation and steady progress essential for its successful achievement. That is to say, relying solely on financial subsidies is insufficient to attain the desired outcomes. A substantial increase in the proportion of renewable/hydrogen energy within China's total energy structure is anticipated in the future. Nevertheless, the intrinsic intermittence and instability of renewable/hydrogen energy is a critical consideration [4]. Therefore, it is imperative to achieve the reliable, safe, and consistent transportation and storage of renewable energy in order to realize the dual-carbon targets. In particular, there is an urgent academic requirement for the development of large-scale, cost-effective, and practical high-efficiency conversion technologies that enable effective energy storage. At present, most research in energy-storage technology is concentrated on enhancing material energy capacities or discovering novel energy-storage materials [5,6]. However, these efforts mainly remain in the realm of theoretical research and cannot be applied as a large-scale energy-storage technology in the short term. In this work, a green methanol pathway to support the development of a low-carbon society is proposed. Methanol is widely acknowledged as an energy carrier due to its high energy density. By converting intermittent renewable energy in western China into liquid methanol, energy can be effectively stored in a liquid form for long-term preservation. Considering China's geographical features, with high terrain in the west and low terrain in the east, methanol can be transported to coastal cities with an efficiency comparable to that of diesel. This large-scale energy-storage approach aligns well with China's current characteristics.

2. The technical route of green methanol

In China, conventional methanol synthesis primarily relies on coal as a feedstock, as depicted in Fig. 1(a). Coal-based methanol synthesis consists of two main steps: coal gasification (Coal + O₂ + $H_2O \rightarrow H_2 + CO + CO_2$) and methanol synthesis ($2H_2 + CO \rightarrow CH_3OH$), and the synthesis gas employed for methanol synthesis consists of hydrogen (H₂) and carbon monoxide (CO) in a mole ratio of 2:1 H₂/CO. However, the H₂/CO ratio of coal gasification is approximately 1:1; thus, it is necessary to increase the H₂/CO ratio for methanol synthesis via the water-gas shift (WGS) reaction process $(H_2O + CO \rightarrow H_2 + CO_2)$, in order to replenish H_2 and ensure that H_2/CO ratio = 2. Based on the above analysis, the production of one metric ton of methanol in conventional coal-based synthesis consumes approximately two metric tons of carbon dioxide (CO₂). Considering the CO₂ emissions from the combined consumption of electricity, steam, and water for auxiliary equipment, the total CO₂ emissions from traditional coal-based methanol synthesis are greater than two metric tons. The carbon emissions indicated in Fig. 1(a) are estimated based on engineering experience and serve as a reference value.

Kötter et al. [7] and Colbertaldo et al. [8] have investigated the efficiency of power-to-gas storage technology. In the western regions of China, renewable energy presents a cost-effective means to convert water (H_2O) into H_2 and oxygen (O_2) via the promising electrolysis technology. It is envisioned that the H₂ produced in western China can be transported to the eastern regions for use in cars. Although this vision holds considerable promise, H2 is neither easy to store nor easy to transport [4]. For example, the capacity of a tanker to carry H₂ gas is limited due to access restrictions in tunnels. However, methanol is an efficient carrier of hydrogen in liquid form [9,10]. Consequently, the challenges of hydrogen storage and transportation could be addressed if wind and solar energy were stored by means of green methanol [11], which would simultaneously address the fluctuations of wind and solar energy [12]. To enhance the environmental friendliness of methanol production, established coal-chemical industries in western China could receive the electrolysis O2 and H2 from renewable energy sources for utilization in green methanol synthesis.

At present, our research team is engaged in the development of a green methanol synthesis route, illustrated in Fig. 1(b), which pioneers an innovative technique based on the production of methanol from renewable energy. The innovation of the purposed methodology is the elimination of air separation and WGS units from the process, due to the directed generation of electrolyzed green H₂ and green O₂ from renewable energy. According to this methodology, renewable energy is utilized to electrolyze water, obtaining H₂ and O₂; these are then reacted with carbon sources from biomass or municipal waste [13,14], resulting in green methanol synthesis. The entire process relies on renewable energy instead of thermal power, and the carbon used is sourced from biomass or municipal waste; therefore, carbon in methanol originates renewable energy, effectively achieving near-zero carbon emissions. Thus, the distinction from liquid sunshine in other research is that both CO and CO2 are utilized to produce green methanol [15]. In addition, this pathway provides a favorable advantage by facilitating the retrofitting of existing equipment used for the conventional methanol production process, which can be achieved through minor modifications.

Accordingly, green methanol assumes a pivotal role as a carrier in the amalgamation of photovoltaics, wind energy, and geothermal energy for green $\rm H_2$ production. Green methanol can also be generated through biomass gasification and $\rm CO_2$ hydrogeneration (CO₂ + 3H₂ \rightarrow CH₃OH + H₂O), so it provides multiple ways for achieving emission reduction. This route addresses the dilemma of the high carbon emissions associated with conventional methanol synthesis.

3. The expected benefits of green methanol applications

3.1. The cost of green methanol

The above description outlines the green methanol route investigated in this study. To further assess its feasibility, the costs of synthesizing methanol via a coal-based methanol process and a renewable energy-green methanol process were calculated and compared. Table 1 shows the total production cost of these two different processes based on an annual methanol production capacity of 50 000 metric tons. The calculation considers a water-electrolysis electricity price of 0.2 CNY·kW⁻¹·h⁻¹; other costs are based on average price standards in China.

Considering a carbon tax of $100 \text{ CNY} \cdot t^{-1}$ of CO_2 , as well as the consumption and price of raw materials and public works, the

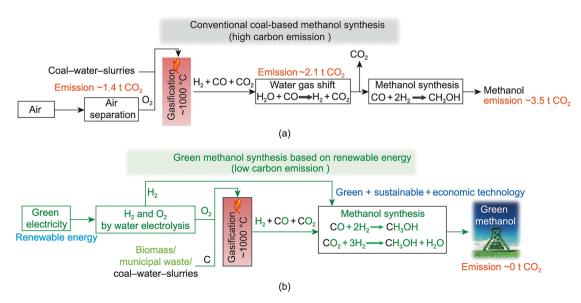


Fig. 1. Schematic diagram of (a) conventional methanol synthesis and (b) green methanol synthesis.

Table 1
Calculation of methanol costs via a conventional route and the green methanol route.

Cost type	Conventional route: coal-based methanol synthesis		Green methanol route: green methanol based on renewable energy		Note/hypothesis
	Consumption	Corresponding cost ^a	Consumption	Corresponding cost ^a	
Coal gasification Hydrogen	1.298 t —	1297,8 CNY·t ⁻¹	0.778 t 1050.6 Nm ³	777.9 CNY·t ⁻¹ 1195.6 CNY·t ⁻¹	Price: 1000 CNY·t ⁻¹ 5 kW·h·Nm ⁻³ > 99.5%, price: 0.2 CNY·kW ⁻¹ ·h ⁻¹
Oxygen Coal Combustion	943.9 Nm³ 0.567 t	_ 340.2 CNY·t ⁻¹	518.6 Nm³ 0.284 t	_ 170.1 CNY·t ^{−1}	By-product from electrolysis > 99.5% Price: 600 CNY·t ⁻¹
Electricity	150.00 kW·h	120.0 CNY·t ⁻¹	60.00 kW⋅h	$48.0~\text{CNY} \cdot \text{t}^{-1}$	10 kV/380 V Price: 0.8 CNY·kW ⁻¹ ·h ⁻¹
Water for reaction	1.9 t	7.6 CNY·t ⁻¹	1.9 t	7.6 CNY·t ⁻¹	0.42 MPa, price: 4 CNY·t ⁻¹
Water for circulating	186 t	14.9 CNY·t ⁻¹	100 t	8.0 CNY⋅t ⁻¹	0.45 MPa, temperature difference: 10 °C
Carbon tax	_	385.2 CNY·t ⁻¹	_	134.1 CNY·t ⁻¹	Price: 100 CNY·t ⁻¹ (CO ₂)
Other cost	_	350.0 CNY·t ⁻¹	_	150.0 CNY·t ⁻¹	Depreciatio, maintenance, catalyst, and labor
Sum	_	2515.7 CNY·t ⁻¹	_	2491.3 CNY·t ⁻¹	_

^a Corresponding cost is based on an annual methanol production capacity of 50 000 metric tons.

estimated production cost of conventional coal-based methanol is approximately 2515.7 CNY·t⁻¹. In contrast, the production cost of green methanol through the proposed route outlined in this study, at the same scale, amounts to around 2491.3 CNY·t⁻¹ (assuming that the renewable energy is stable enough). Consequently, the green methanol process achieves a cost level that is comparable to that of the conventional route while offering the additional benefit of reducing carbon emissions.

3.2. Great impact on China's automotive industry

The geographical characterization of the altitude difference between western and eastern China allows for the automatic flow of liquids, which makes the transportation of liquid fuel convenient. Harnessing this advantage, the abundant and cost-effective renewable energy resources in western China can be effectively utilized. H₂ and O₂ can be generated by electrolyzing H₂O; subsequently, by incorporating a minor carbon source, green methanol can be synthesized, thereby realizing the conversion of solar and wind energy into liquid fuels. The existing infrastructures built for petroleum fuels can be repurposed for the storage and transportation of green methanol, satisfying the requirements of vehicles over various generations.

There are various applications in which green methanol can be utilized as a fuel. Wu et al. [16] proposed a novel methanolutilization technology for power generation based on a hybrid fuel-cell system, which can efficiently and economically convert methanol into electrical energy. Wang et al. [17] proposed a new methanol-electricity cogeneration system, realizing the nearzero-emission resource utilization of medical waste. As for the application of alternative fuels in internal combustion engines, firstly, Geely Auto Group (China) has developed mature technology for methanol internal combustion engines, which has been implemented in various Chinese cities, such as Xi'an and Guiyang. Public transportation vehicles (i.e., buses and taxis) have been equipped with methanol internal combustion engines, demonstrating safe operation in recent years. Secondly, plug-in hybrid electric-methanol vehicles offer the potential to reduce fuel consumption and greenhouse gas emissions, with hybrid power cars such as DM-I by BYD Co., Ltd. (China), achieving fuel consumption rates as low as 5 L per 100 km. Lastly, fuel-cell vehicles can benefit from online H₂ via onboard methanol if fuel cells become cost-effective. Methanol can be used to generate twice the amount of H₂ compared with an equal volume of liquid H₂. In summary, the geographical advantage of liquid transportation in China, along with the versatility of green methanol as a fuel, presents an opportunity for reducing carbon emissions and transitioning toward sustainable energy solutions.

The required construction scale of hydrogen refueling stations significantly surpasses the scale of existing petrol stations. Thus, instead of demolishing the existing refueling stations, it is proposed to retrofit them into green methanol stations. This approach allows for the efficient utilization of current gasoline-filling equipment, accommodating not only internal combustion engines but also plug-in hybrid machinery, fuel cells, and future hydrogen-based technologies. Consequently, the promotion of methanol-based vehicles (e.g., internal-combustion engines, electric vehicles, and fuel-cell vehicles) is advocated.

As an alternative fuel for automobiles, the safety of methanol has always been the most concerned by the public and government departments, methanol vehicle pilot programs have been implemented by the Ministry of Industry and Information Technology of the People's Republic of China in Shanxi, Shaanxi, Gansu, and Guizhou Provinces since 2012. These pilot programs successfully passed tests in 2018, validating the environmental protection, safety, economy, and reliability of methanol-fueled cars. This result alleviates the longstanding safety concerns associated with methanol fuel expressed by both the general public and governmental entities.

3.3. Green methanol used for distributed generation

Methanol steam-reforming processes for $\rm H_2$ production and its subsequent use in fuel cells offer a promising distributed generation technology. The primary applications of methanol-based distributed generation technologies are shown in Fig. 2. One significant application is in powering 5G base stations located in remote, mountainous regions, such as those found in Guangdong Province. These base stations rely on methanol steam-reforming hydrogen power production as their energy supply. The stability of these stations over many years of operation demonstrates the feasibility and reliability of distributed generation method (hydrogen production from methanol steam-reforming for fuel cell generation).

The key advantage of using methanol-based distributed generation is the avoidance of costly energy transmission from cities to remote base stations. For example, by deploying four 2.5 kW



Fig. 2. Primary applications of methanol-based distributed generation technology.

green-methanol-based distributed energy-supply systems, which generate electricity through the reforming of methanol and water, a 5G base station can be adequately powered. Moreover, the power generated through methanol steam-reforming hydrogen fuel cells offers a significant improvement compared with the power from traditional internal combustion engines. The exhaust heat of fuel cells can be efficiently recovered and used for heating in winter and chilling in summer by means of a heat pump. As an example of such potential applications, a single 2.5 kW unit of methanol-reforming hydrogen fuel cells can provide electricity, heating, and cooling for a house. This example highlights the versatility and energy efficiency of this technology for various applications, including both stationary and mobile power systems.

Based on existing technology, two representative hydrogen energy processes have been chosen to calculate the powergeneration efficiency and corresponding costs in Fig. 3.

In the scenario depicted in Fig. 3, cost and efficiency are determined based on certain assumptions. First, it is assumed that hydrogen is consumed at a location approximately 500 km away from the region where it is generated, spanning from western to east–central China. Second, the assumption is made that H_2 is produced using plentiful renewable energy in the west. The percentage values in the figure represent the transfer efficiency of green hydrogen, and the cost of producing and transporting hydrogen is shown at the bottom of each part of the figure. The overall cost of H_2 production can be calculated by dividing the unit

efficiency cost by the final hydrogen volume. When considering the potential cost to make these two routes technologically mature, the combined cost of hydrogen supply can be calculated using a multi-step decomposition evaluation and aggregation calculation. Green methanol reforming for H_2 (41 $CNY \cdot kg^{-1}$ of H_2) is much cheaper than compressed liquid H_2 synthesis (95 $CNY \cdot kg^{-1}$ of H_2). More specifically, green methanol reforming for H_2 offers a cost advantage compared to solar-driven liquid H_2 synthesis due to the following factors:

- (1) **Lower hydrogen-compression costs.** The cost of compressing atmospheric H_2 to high-pressure H_2 (30 MPa) is high. In contrast, the green methanol preparation process utilizes compressed H_2 at a maximum pressure of 10 MPa, significantly reducing operating costs.
- (2) **Improved transportation efficiency.** Transporting liquid H_2 necessitates the use of specialized tankers; however, a certain amount of the liquid H_2 is lost through vaporization during transportation. The rate of loss ranges from 0.5% to 1.0% per day, with longer transportation durations resulting in greater losses. For example, the overall loss can be roughly 3% for a 500 km transit trip. However, the total loss of methanol during transportation (less than 0.5%) is not proportional to distance, and the methanol transport logistics chain is mature and cost-effective. In addition, methanol transfer is much safer than handling liquid H_2 .

Methanol synthesis and hydrogen production are the two essential components of the green methanol reforming process for hydrogen. However, the efficiency of these two components are only 82% and 70%, respectively. Methanol synthesis units only consider one-way efficiency for hydrogen conversion, and the recovery of deflation has not been addressed. Under the current technological scheme, 30% of methanol is consumed as the heat source of the hydrogen reaction unit, without considering the optimization of thermal management. Improving methanol synthesis and hydrogen production units has the potential to significantly enhance the overall efficiency of the process. In comparison, a typical thermal power plant in western China has an overall energy efficiency of approximately 40%. This indicates that, for every 1×10^6 kcal (1 kcal = 4.1868 \times 10³ J) of coal, the power plant can only generate electricity equivalent to 4.0×10^5 kcal. Once energy losses during transportation are considered, only 3.0×10^5 kcal of electricity from the original 1×10^6 kcal of coal is delivered to users in eastern coastal cities. Unlike electricity, heat cannot be efficiently transmitted over long distance via power grids; however, green methanol as a liquid can be transported through pipelines.

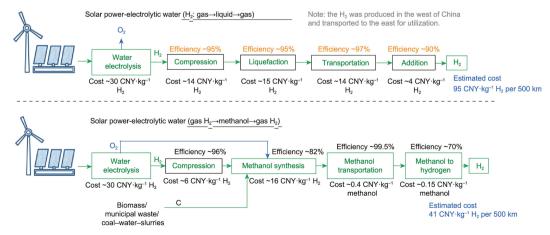


Fig. 3. The cost of hydrogen production: an effectiveness comparison of compressed liquid H₂ synthesis (top) vs green methanol reforming for H₂ (bottom).

3.4. Great effect on reducing oil import dependence

Green methanol can be produced at a reasonable cost by fully utilizing China's renewable energy sources, such as solar and wind power, as well as its abundant biomass, municipal waste (which contains approximately 80% biomass), and low-quality coal. Such utilization will not only dramatically reduce carbon emissions but also progressively replace imported petroleum, thereby reducing the degree of petrodollar monopoly. For the foreseeable future, it is expected that an energy system applying green methanol as a resource can be promoted on a large scale and combined with extensive renewable energy technologies, including power generation, storage, and transmission. The integration of the intelligent power grid and the green methanol network can gradually transform the current coal/oil economy into a green electricity and methanol economy dominated by renewable energy. Green methanol has the potential to meet the energy needs and challenges of China's transportation, electrical, and heating systems. It produces carbon emissions that are only 20% of those from traditional energy sources, effectively addressing both oil scarcity and carbon neutrality.

4. Conclusions and prospects

Renewable energy from western China is a promising alternative to thermal power, given its comparable or potentially lower cost. However, due to its intrinsic intermittence, renewable energy generation operates efficiently for approximately 20% of the year (subject to geographic characteristics), leaving the other 80% or so dependent on energy-storage technologies. Effective energy-storage systems are imperative for the widespread adoption of renewable energy and the displacement of fossil fuels. One cost-effective storage technology for long-cycle energy storage involves converting wind and solar energy into green methanol, thereby benefitting from the superior energy-transport capabilities of liquid substances. Based on the existing liquid infrastructure, green methanol can meet the fuel needs of internal combustion engines, hybrid augmentation vehicles, and fuel cell cars, thereby contributing to the establishment of ecofriendly transportation systems. Furthermore, this methodology exhibits versatility in its application across various distributed generation fields, effectively catering to extra heating and cooling requirements. Finally, realizing carbon neutrality necessitates comprehensive collaboration and support across societal sectors, encompassing innovative social structures and robust industry-academia-government partnerships.

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