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Review

Assessing the potential of higher alcohols as green fuels for carbon circularity

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ABSTRACT

Excessive fossil fuel use has increased carbon dioxide (CO_2) emissions, driving climate change and ocean acidification. This review evaluates the potential of higher alcohols as fuels for carbon circularity, comparing their properties, energy efficiency, and technology readiness with hydrogen, methane, and methanol. Higher alcohols, produced *via* CO_2 hydrogenation, exhibit advantages such as liquid-phase storage, higher energy density, and safer handling. Additionally, their clean combustion produces fewer pollutants like CO and NO_x. However, CO_2 hydrogenation to higher alcohols faces challenges, including high energy demands, kinetic barriers, and immature production technologies, resulting in lower energy efficiency compared to H_2, methane, and methanol. Higher alcohols, with their superior energy density and safety, hold promise as sustainable fuels, particularly when integrated with CO_2 capture technologies. However, improvements in catalyst performance, process integration, and production scalability are critical for their widespread adoption.

1. Introduction

The rising carbon dioxide (CO_2) emissions due to excessive use of fossil fuels has led to climate change and sea acidification, threatening human being's sustainable development [1,2]. Various strategies have been proposed to incur the continuously increasing CO_2 emissions [3]. Employing the renewable energies, such as solar energy, wind energy, and hydroenergy to produce carbon-free green hydrogen (H_2), which can be used as a fuel or used in various chemical synthesis, represents a promising way to incur CO_2 emissions [4]. However, H_2 has a very low volumetric energy density compared to other fuels, making storage and transport difficult [5]. It requires high-pressure tanks, cryogenic temperatures, or chemical carriers to store it efficiently [6]. Moreover, H_2 is highly flammable and can ignite easily [7]. While it disperses quickly in the atmosphere, leaks in enclosed spaces can pose serious risks. Special materials and protocols are required to handle hydrogen safely, which increases complexity and cost [8].

A solution is to transfer H_2 into liquid fuels such as methanol (CH_3OH) and higher alcohols ($C_{2+}OH$), such as ethanol (C_2H_5OH) and propanol (C_3H_7OH) through reaction with CO_2 [9–12]. The alcohols possess many advantages as a fuel [13–16]. They present in a liquid state at ambient conditions and possess a higher volumetric energy density. Besides, the dispersion of their vapor into atmosphere becomes more difficult. Moreover, compared with gasoline, alcohols have higher octane ratings, which can lead to more efficient combustion and higher engine performance. Also, alcohols burn more cleanly, producing fewer pollutants such as CO, NO_x, and particulate matter. This contributes to improved air quality. Furthermore, alcohols have higher flash points and lower volatility compared to gasoline, making them safer to handle and store.

Alcohols, such as methanol, ethanol, and butanol serve as effective hydrogen storage mediums, offering high energy density and ease of storage at ambient conditions [17–19]. When required,

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hydrogen can be released through catalytic reforming processes like steam reforming, where alcohol molecules are broken down to produce hydrogen gas. This approach provides a practical and renewable solution for on-demand hydrogen production, supporting applications in fuel cells and energy systems. Moreover, higher alcohols are primarily used as solvents, fuel components, and chemicals [20]. A notable downstream product of commercial interest is ethyl *tert*-butyl ether (ETBE), which is commonly used in fuels. Recent commercialization efforts have focused on the production of sustainable polyethylene (PE), polyethylene terephthalate (PET), polyvinyl chloride (PVC), and jet fuels, all derived from olefin chemistry. The conversion of sustainable C_{2-4} olefins creates additional high-volume market opportunities for C_{2-4} alcohols.

By capturing CO_2 from industrial processes or the atmosphere and converting it into alcohol fuels, the carbon is effectively recycled, resulting in a closed carbon loop that can be carbon-neutral or even carbon-negative if combined with carbon capture and storage. Another strategy for carbon circularity, biomass conversion, while valuable, faces challenges related to land-use change, scalability, and feedstock limitations [21,22]. CO_2 captured from industrial processes or the atmosphere is less reliant on land and agricultural resources. Ultimately, CO_2 hydrogenation could play a more pivotal role in achieving a truly circular carbon economy, especially when paired with renewable energy sources for hydrogen production.

However, due to the chemically inert nature of CO_2, the reaction between CO_2 and H_2 needs a high temperature to activate CO_2 and overcome the kinetic barrier. Moreover, CO_2 hydrogenation to alcohols are exothermal reactions [23–26]. Accordingly, the synthesis process needs additional energy input, leading to energy loss and decreasing energy efficiency. This may potentially make the use of CO_2-derived alcohol fuels less competitive compared to use of H_2 directly.

Although higher alcohols have a higher volumetric energy density compared to hydrogen and methanol, which facilitates storage and transport, their use as a fuel may be less energy-efficient. This is due to the more exothermic nature and higher kinetic barrier of CO_2 hydrogenation to higher alcohols compared to methanol. Additionally, the less mature technology for synthesizing higher alcohols from CO_2 hydrogenation and their use in combustion engines or fuel cells could limit their application as fuels for carbon circularity. To evaluate the potential of higher alcohols as fuels for carbon circularity, this perspective analyzes their properties, energy efficiency, and technology readiness, as well as the production costs, market readiness, and potential incentives, comparing them with compressed/liquefied H_2 and CH_4, and methanol.

2. Overview of Properties and Production Methods of Various Green Fuels

Table 1 offers a comparative analysis of various fuels, including hydrogen, methanol, ethanol, propanol, and methane, focusing on their properties, including energy densities, hydrogen content, carbon content, explosive limits, and toxicity, as well as their synthesis/production methods. Natural hydrogen, known as white hydrogen or gold hydrogen [27], has been discovered in various geological environments, including oceanic spreading centers, transform faults, passive margins, convergent margins, and intraplate settings [28]. The primary sources of natural hydrogen are the radiolysis of water, serpentinization, degassing of magma, and reactions of water with surface-free radicals [28]. Natural hydrogen has been identified in various locations around the world, including France, Mali, and the United States [29]. At Bourakebougou in Mali, shallow carbonate reservoirs have been found to contain hydrogen with concentrations as high as 98%. Despite these natural occurrences, molecular hydrogen is not found in large quantities in the Earth's atmosphere because it is light and can easily escape into space [30].

Hydrogen production methods can be categorized by their environmental impact, using color codes such as grey, blue, and green [31]. The primary distinction lies in the source of energy and the handling of CO_2 emissions, with green hydrogen being the cleanest and grey the most carbon-intensive. Grey hydrogen is produced through processes like steam methane reforming (SMR), partial oxidation of methane, coal gasification, and as a byproduct of oil refining or chlor-alkali industry, where fossil resources are used and CO_2 is released into the atmosphere [32–38]. Additionally, water electrolysis using electricity from fossil fuels also produces grey hydrogen due to the indirect CO_2 emissions. Blue hydrogen involves these methods but incorporates carbon capture

Table 1
Synthesis methods and properties of H_2, alcohols, and CH_4.

	Hydrogen	Methanol	Ethanol	Propanol	Methane
MF①	H_2	CH_3OH	C_2H_5OH	C_3H_7OH	CH_4
Synthesis/production methods	Steam methane reforming [36] Partial oxidation of methane [37] Coal/biomass gasification [35] Water electrolysis [33,34] Byproduct of oil refining/chlor-alkali industry [32,38]	Steam methane reforming/partial oxidation of methane/coal gasification/biomass gasification followed by syngas conversion [39] CO_2 hydrogenation [40]	Fermentation of biomass [41] Hydration of ethylene [42] Steam methane reforming/partial oxidation of methane/coal gasification/biomass gasification followed by syngas conversion [43,44] CO_2 hydrogenation [45,46]	Hydroformylation of ethylene [47] Fermentation of biomass [48] Steam methane reforming/partial oxidation of methane/coal gasification/biomass gasification followed by syngas conversion [49,50] CO_2 hydrogenation [45]	Natural gas extraction [51] Biogas production [52] CO_2 methanation [53] Coal/biomass gasification with syngas conversion [54]
EDs②/MJ·kg^{-1}	119.9	21.1	27.7	31.5	50.0
HCs③/mol·kg^{-1}	992.1	124.8	130.2	133.1	249.3
CCs④/mol·kg^{-1}	0	31.2	43.4	49.9 [55]	62.3
EL⑤/%	4.6–73.7 [56]	6.7–36.0 [57]	3.4–18.3 [58]	2.0–12.0 [57]	5.0–15.5 [59]
Toxicity	Non-toxic	Highly toxic	Moderately toxic	Moderately toxic	Non-toxic

① Molecular formular.
② Specific energy density derived from NIST Chemistry WebBook and Ref. [55].
③ Specific H content.
④ Specific C content.
⑤ Explosive limit.

and storage (CCS) technology to capture and store the CO_2, reducing its environmental footprint [31]. Biomass gasification can produce green hydrogen if coupled with CCS, as biomass is renewable and can result in very low or even negative net CO_2 emissions [31]. Green hydrogen is also generated through water electrolysis powered by renewable energy sources such as wind, solar, or hydroelectric power, resulting in zero carbon emissions and representing the most environmentally friendly option [31].

Hydrogen boasts the highest specific energy density (119.9 $MJ \cdot kg^{-1}$) and hydrogen content (992.1 $mol \cdot kg^{-1}$), making it a highly efficient energy carrier. It is non-toxic but has a broad explosive limit range of 4.6% to 73.7%. Hydrogen's potential for zero-emission energy when produced from renewable sources positions it as a pivotal player in the transition to sustainable energy.

Methanol can be synthesized through steam methane reforming, partial oxidation of methane, coal gasification, biomass gasification followed by syngas conversion, and CO_2 hydrogenation [39,40]. It has a specific energy density of 21.1 $MJ \cdot kg^{-1}$ and hydrogen content of 124.8 $mol \cdot kg^{-1}$. Methanol's explosion limits (6.7% to 36.0%) make it relatively safe, though it is highly toxic, posing significant handling and storage challenges [60]. Methanol's production processes, especially from CO_2 hydrogenation or biomass gasification coupled with syngas conversion, are advancing, with the potential to reduce carbon emissions significantly. However, the economic feasibility of these methods varies, with fossil-based methanol production being more mature and cost-effective compared to biomass or CO_2-based methods.

Ethanol produced through fermentation of biomass, hydration of ethylene, and similar processes to methanol [41–46], offers a higher energy density (27.7 $MJ \cdot kg^{-1}$) and hydrogen content (130.2 $mol \cdot kg^{-1}$) compared to methanol. It has explosion limits of 3.4% to 18.3% and is moderately toxic. Ethanol production is well-established, particularly through fermentation, which is cost-effective and renewable [61]. The carbon footprint of ethanol can be minimal when derived from biomass, making it a sustainable fuel option. The production of ethanol through other methods including through biomass gasification followed by syngas conversion and CO_2 hydrogenation also provide low carbon foot print but is less mature.

Propanol can be produced *via* hydroformylation of ethylene, fermentation of biomass, and similar methods to ethanol and methanol [45,47–50]. It possesses the highest energy density among the alcohols (31.5 $MJ \cdot kg^{-1}$) and a relatively high hydrogen content (133.1 $mol \cdot kg^{-1}$). Propanol has explosive limits of 2.0% to 12.0% and is moderately toxic. Propanol's production is less mature compared to ethanol, making it more expensive [62]. Its carbon footprint and economic feasibility are similar to those of ethanol, depending on the production method.

Methane commonly extracted from natural gas or produced *via* biogas production, methanation, or coal/biomass gasification with syngas conversion [51–54], has a higher energy density (50.0 $MJ \cdot kg^{-1}$) and hydrogen content (249.3 $mol \cdot kg^{-1}$) compared with alcohols. Methane is non-toxic, and its explosive limits range from 5.0% to 15.5%, which are much narrower compared to that of hydrogen, making it safer to handle compared with hydrogen [63]. Methane's production methods are well-established and cost-effective, especially for natural gas extraction. However, methane's carbon footprint remains a concern, primarily when sourced from fossil fuels. Methane's advantages include its established infrastructure for extraction, distribution, and utilization, making it a readily available and economically viable fuel [64]. On the downside, methane contributes significantly to greenhouse gas emissions, both from its combustion, which releases CO_2, and from potential leaks during extraction and transportation, as methane itself is a potent greenhouse gas [65]. This environmental impact is a major disadvantage, particularly when compared to cleaner alternatives like hydrogen.

As can be seen, H_2 possesses a higher specific H content and lower specific C content, making it higher energy density and lower carbon emission when used as a fuel compared with other fuels. However, volumetric energy density is another crucial consideration when evaluating fuels because it directly impacts the storage, transportation, and practical application of the fuel. Fuels with high volumetric energy density can store more energy in a given volume, making them more efficient and convenient for various uses, particularly in transportation and portable applications [66]. This efficiency means that vehicles, for example, can travel longer distances without needing to refuel, and storage tanks can be smaller and lighter for the same amount of energy [67]. Additionally, fuels with higher volumetric energy density can reduce the infrastructure costs and complexity associated with their storage and distribution, as fewer refueling stations and less frequent deliveries are needed [68]. Conversely, fuels with low volumetric energy density require larger storage volumes and more robust infrastructure to handle the same energy capacity, leading to higher costs and logistical challenges. Therefore, considering volumetric energy density is essential for optimizing the practical and economic aspects of fuel use.

Table 2 compares the properties of hydrogen, methanol (MeOH), ethanol (EtOH), propanol (PrOH), and methane, across different pressures and states. For hydrogen, the hydrogen content increases from 21.1 $kmol \cdot m^{-3}$ at 30 MPa to 70.2 $kmol \cdot m^{-3}$ in its liquid state, with a corresponding rise in volumetric energy density from 2.56 to 8.5 $MJ \cdot L^{-1}$. Methane shows a similar trend, with hydrogen content increasing from 52.2 $kmol \cdot m^{-3}$ at 30 MPa to 105.3 $kmol \cdot m^{-3}$ in the liquid state, and volumetric energy density rising from 10.47 to 21.10 $MJ \cdot L^{-1}$. Methanol, ethanol, and propanol, examined in their liquid states, exhibit hydrogen contents around

Table 2
Properties of various fuels in their gaseous states at different pressures and in their liquid states.

	H_2					CH_4					MeOH	EtOH	PrOH
	30 MPa	50 MPa	70 MPa	100 MPa	Lq.① H_2 [69]	30 MPa	50 MPa	70 MPa	100 MPa	Lq.① CH_4 [69]			
HC_v②/$kmol \cdot m^{-3}$	21.1	32.1	41.2	50.56	70.2	52.2	68.3	77.9	87.4	105.3	100.5	105.4	107.8
CC_v③/$kmol \cdot m^{-3}$	0	0	0	0	0	13.0	17.1	19.5	21.8	26.3	25.1	35.1	40.4
ED_v④/$MJ \cdot L^{-1}$	2.56	3.88	4.98	6.11	8.50	10.47	13.70	15.62	17.53	21.10	16.98	22.44	25.50
Density⑤/$kg \cdot m^{-3}$	21.31	32.35	41.54	50.96	70.79	209.36	273.82	312.26	350.52	422.5	804.8	808.9	810.1

① Liquid.
② Volumetric hydrogen content.
③ Volumetric carbon content.
④ Volumetric energy density derived from NIST Chemistry WebBook and Ref. [55,69] based on density obtained by Aspen Plus.
⑤ Derived from Aspen Plus.

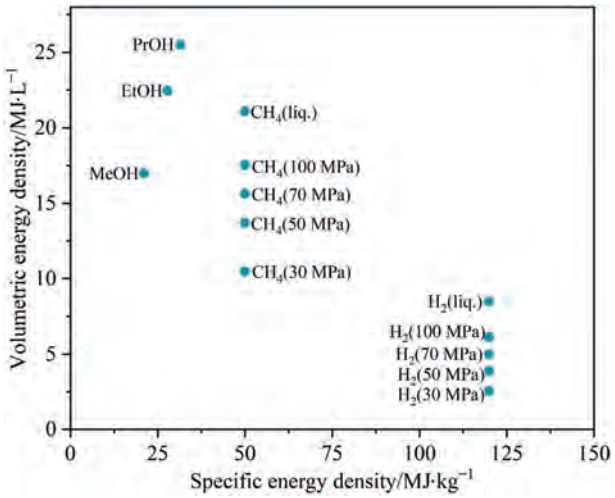

Fig. 1. Correlation between volumetric energy density and specific energy density.

100–108 kmol·m^{-3}, with their carbon content increasing from 25.1 to 40.4 kmol·m^{-3}. The volumetric energy density of these alcohols also rises, from 16.98 MJ·L^{-1} for methanol to 25.50 MJ·L^{-1} for propanol, with densities ranging from 804.8 kg·m^{-3} to 810.1 kg·m^{-3}. A trend is observed where the volumetric energy density decreases as the specific energy density increases (Fig. 1). The volumetric energy density of propanol is about 75% that of gasoline's 34.2 MJ·L^{-1} and is 23.6 times that of lithium-ion batteries (1.08 MJ·L^{-1}) [70,71]. This indicates that higher alcohols offer a significant volumetric energy density advantage over many other fuels.

When comparing these fuels, hydrogen stands out for its high hydrogen content and lower carbon footprint, especially at higher pressures, making it a strong candidate for clean energy applications. However, its volumetric energy density is lower compared to methane and the alcohols, which limits its energy storage capacity. Pressurized/liquid methane and alcohols with higher energy density but also higher carbon content, offers a balance between energy output per unit volume and carbon footprint, making them suitable for applications where storage and transport efficiency are key considerations.

3. Evaluating the Efficiency of Various Green Fuels for Carbon Circularity

Even though pressurized/liquid methane and alcohols possess a higher volumetric energy density compared with H_2, their combustion leads to the formation of CO_2 emission (Table 3). By capturing CO_2 and reacting it with H_2 to produce the methane and alcohol fuels can lead to carbon circularity and carbon neutralization (Fig. 2) [72]. However, the hydrogenation of CO_2 to methane

Table 3
Enthalpy changes for the combustion of various fuels.①

Reaction	ΔH_{298K}②/kJ·mol^{-1}
$H_2 + 1/2\ O_2$=H_2O	−241.8
$CH_3OH + 3/2\ O_2$=$CO_2 + 2H_2O$	−676.1
$1/2C_2H_5OH + 3/2\ O_2$=$CO_2 + 3/2H_2O$	−639.0
$1/3C_3H_7OH + 3/2\ O_2$=$CO_2 + 4/3H_2O$	−636.7
$CH_4 + 2\ O_2$=$CO_2 + 2H_2O$	−802.5

① 25 °C, 101325 Pa.
② Derived from NIST Chemistry WebBook and Ref. [55].

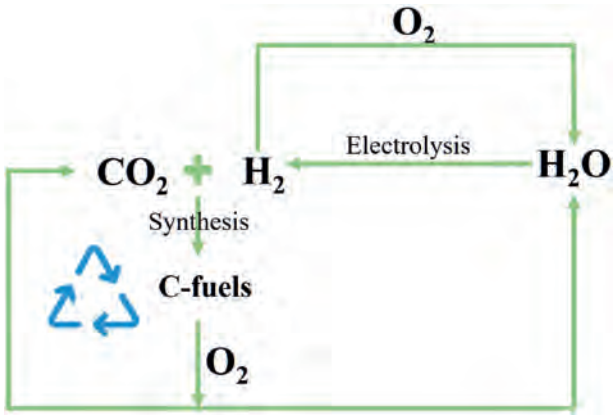

Fig. 2. Schematic representation of direct hydrogen utilization as a fuel and its hydrogenation with CO_2 to produce carbon-containing fuels.

Table 4
Enthalpy changes for CO_2 hydrogenation reactions.①

Reaction	ΔH_{298K}②/kJ·mol^{-1}
$CO_2 + 3H_2$=$CH_3OH + H_2O$	−49.3
$CO_2 + 3H_2 = 1/2C_2H_5OH + 3/2H_2O$	−86.4
$CO_2 + 3H_2 = 1/3C_3H_7OH + 5/3H\ _2O$	−94.7
$CO_2 + 4H_2$=$CH_4 + 2H_2O$	−164.7

① 25 °C, 101325 Pa.
② Derived from NIST Chemistry WebBook and Ref. [55].

and alcohols are exothermal (Table 4), leading to energy loss, which will further reduce the energy efficiency.

We compared the energy efficiency of directly combusting hydrogen versus converting hydrogen into methanol, ethanol, propanol, and methane through CO_2 hydrogenation, assuming no additional energy input is required for the conversion process. Efficiency is defined by Eq. (1),

$$\eta_0 = \frac{E_{\text{fuel}}}{E_{\text{H2}}} \times 100\% \quad (1)$$

where η_0 represents the energy efficiency ignoring the additional energy input required for CO_2 hydrogenation, E_{fuel} (MJ) is the energy released during the combustion of the synthetic fuel, and E_{H2} (MJ) is the energy released during the direct combustion of H_2. E_{fuel} and E_{H2} are derived from NIST Chemistry WebBook and Ref. [55].

As illustrated in Fig. 3, for 1 t of hydrogen, direct combustion releases 119940 MJ heat, serving as the baseline with 100% efficiency. In the hydrogenation pathway, producing methanol (5.30 t) yields 111789 MJ (93.20% efficiency), ethanol (3.81 t) yields 105655 MJ (88.10%), propanol (3.31 t) releases 104277 MJ (86.94%), and methane (1.99 t) yields 99516 MJ (82.97%).

This analysis demonstrates that converting hydrogen into fuels through CO_2 hydrogenation retains a high proportion of energy, though with some efficiency loss compared to direct combustion. The energy loss arises due to the exothermic nature of the reactions between CO_2 and H_2 to produce methanol, ethanol, propanol, and methane. As the reaction enthalpy decreases (Table 4), the energy efficiency of the fuels derived from CO_2 and H_2 decreases in the order: methanol > ethanol > propanol > methane. For the liquid fuels, a trade-off exists between volumetric energy density and energy efficiency. Compared to methanol, ethanol and propanol exhibit 32.16% and 50.18% increases in volumetric energy density, respectively, while only a 5.11% and 6.26% reduction in energy efficiency is observed. Thus, the slight decrease in energy

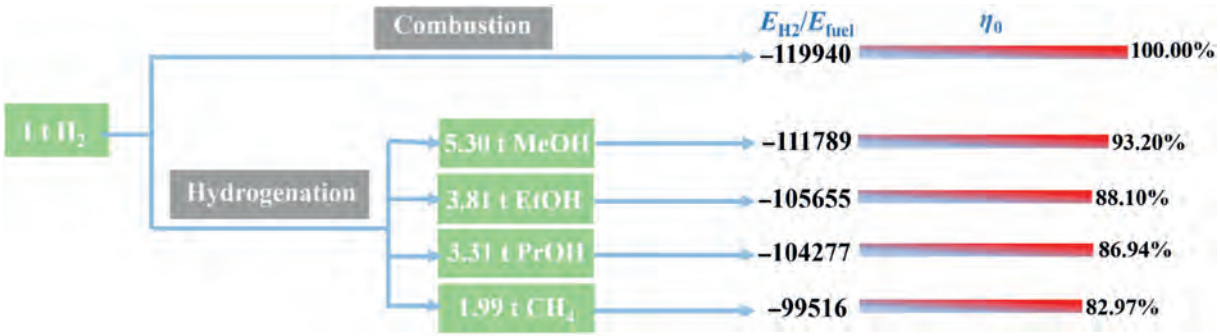

Fig. 3. The energy release and energy efficiency when combusting various fuels, considering that no further energy input is required for the synthesis of alcohols and methane. E_{H2} and E_{fuel} represent the energy released in MJ, and η_0 represents the energy efficiency.

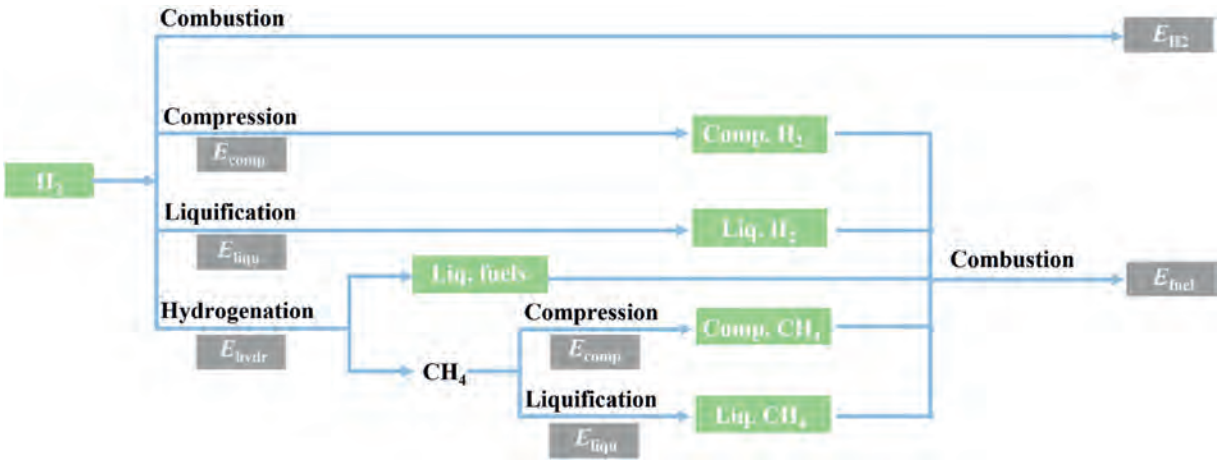

Fig. 4. Schematic representation for calculating the energy efficiency for compressed/liquified H_2/CH_4 and synthetic fuels.

efficiency is an acceptable trade-off for the significant increase in volumetric energy density.

Even when disregarding the additional energy consumption for synthesizing fuels *via* CO_2 hydrogenation, higher alcohols offer the advantages of high volumetric energy density and acceptable energy losses due to the exothermal nature of the reactions. However, the additional energy input for CO_2 hydrogenation is unavoidable because of CO_2's high chemical stability, which necessitates extra energy to overcome the reaction's high energy barrier. Therefore, we further analyze energy efficiency by considering this additional energy input.

To address the high volumetric energy density of liquid fuels, we also examine the energy efficiency of compressed and liquefied H_2 and CH_4. For a fair comparison between compressed H_2/CH_4 and synthetic liquid fuels, the energy consumption for compression, liquefaction, and CO_2 hydrogenation must be considered. These values are obtained through simulations in Aspen Plus using RK-SOAVE property method or from Refs. [73–76]. In this scenario, the energy efficiency is calculated using Eq. (2) (Fig. 4),

$$\eta = \frac{E_{fuel}}{E_{H2} + E_{comp} + E_{liqu} + E_{hydr}} \times 100\% \quad (2)$$

where η (%) represents the energy efficiency, E_{fuel} (MJ) is the energy released during the combustion of the synthetic fuel, E_{H2} (MJ) is the energy released during the direct combustion of H_2, E_{comp} (MJ) is the equivalent heat for compression, E_{liqu} (MJ) is the equivalent heat for liquefaction, and E_{hydr} is the equivalent heat for CO_2 hydrogenation.

Fig. 5 provides a comprehensive comparison of the energy efficiencies for different hydrogen utilization pathways, ranging from direct combustion to hydrogenation and subsequent combustion of synthesized fuels. It is observed 100% baseline efficiency of direct hydrogen combustion, which involves no additional processing energy inputs. However, as hydrogen undergoes compression or liquefaction, the efficiency drops due to the energy required to compress or cool the gas to a denser form. For example, compressing hydrogen to 30 MPa reduces the efficiency to 83.66%, and at 100 MPa, efficiency declines further to 80.89%. Liquefaction incurs even greater losses, with an efficiency of 69.98%. The sharp drop in efficiency illustrates a clear trade-off between energy density and energy efficiency. Compression and liquefaction increase the volumetric energy density of hydrogen, making it more suitable for transportation and storage, but the energy expenditure for these processes reduces the net energy gain.

When considering CO_2 hydrogenation to synthetic fuels like methanol, ethanol, propanol, and methane, additional complexity emerges. Methanol exhibits the highest efficiency among the alcohol products at 80.97%, indicating that its synthesis from CO_2 and H_2 retains a significant portion of the initial energy content of hydrogen. However, ethanol and propanol show lower efficiencies of 66.11% and 67.44%, respectively, primarily due to the higher energy demands of hydrogenating CO_2 to form more complex alcohol molecules. The higher energy demands are ascribed to the relatively low conversion efficiency to higher alcohols compared with methanol [73,76]. Methane, which requires the lowest energy input during hydrogenation compared to alcohols. This is mainly ascribed to the high conversion efficiency for CO_2 methanation

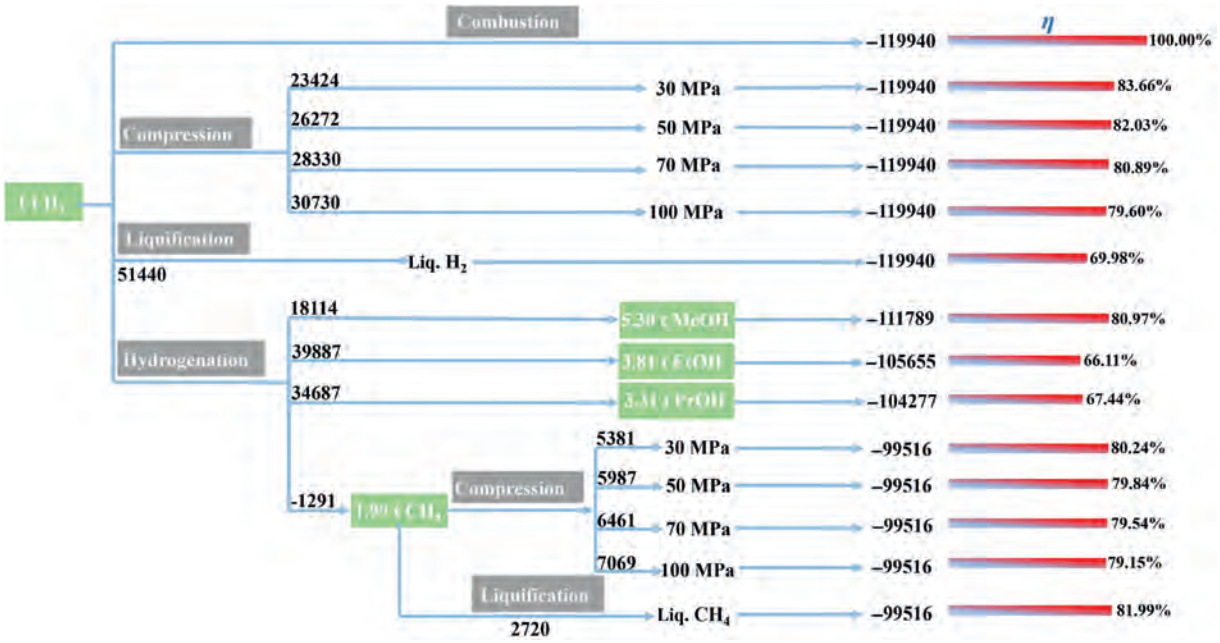

Fig. 5. Energy required for compression, liquification, and hydrogenation in MJ together with the energy efficiency of various fuels.

[74]. It retains an efficiency of around 79.15% if compressed to 100 MPa and 81.99% after liquefaction.

The key trade-off here between the volumetric energy density of these fuels and the energy required to synthesize and store them occurs (Fig. 6). Hydrogen, although highly efficient in direct combustion, suffers from low volumetric energy density, which necessitates compression or liquefaction for practical storage and transport. However, this reduces its overall energy efficiency. Due to high efficiency for CO_2 methanation and relatively low energy required for compressing/liquifying it, compressed/liquified methane represents a promising fuel with both relatively high volumetric energy density and energy efficiency. Moreover, liquid fuels like methanol, ethanol, and propanol offer much higher volumetric energy densities, which are advantageous for long-term storage and easier transportation. Higher alcohols possessing the highest volumetric energy density but lower energy efficiency requires a further improvement in the conversion efficiency during synthesis through CO_2 hydrogenation.

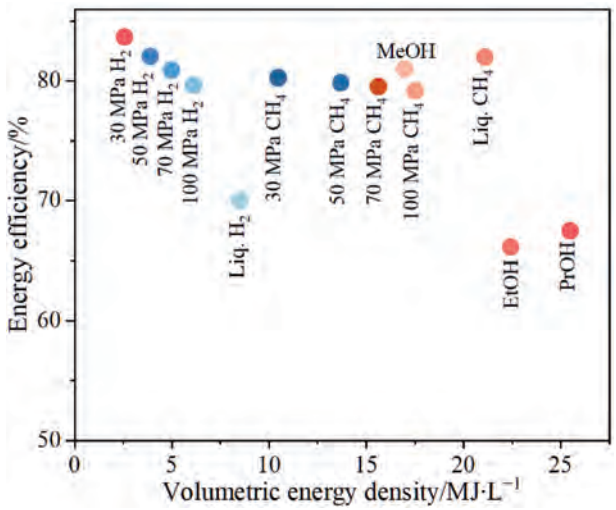

Fig. 6. Tradeoff between volumetric energy density and energy efficiency for various fuels.

4. Assessing the Technology Readiness of Green Fuels for Carbon Circularity

Another aspect to evaluate the potential of higher alcohols as fuel for carbon circularity is to evaluate the technology readiness of CO_2 capture, H_2 production, CO_2 conversion to the higher alcohol fuels and the end use of the alcohols. Technology Readiness Levels (TRL) are a measurement system used to assess the maturity of a particular technology [77]. Each technology project is evaluated against specific criteria for each level and assigned a TRL rating based on its progress. There are nine levels, with TRL 1 representing the lowest and TRL 9 the highest. The TRL of these technologies will be discussed in the following sections.

CO_2 can be obtained from flue gases or air through CO_2 capture technologies such as adsorption, absorption, membrane separation, and cryogenic methods [78]. Absorption, particularly using amines like monoethanolamine (MEA), is the most mature of the CO_2 capture methods. In general, CO_2 capture by absorption leads to about 10% to 30% parasitic energy loss [79], which is one of the main disadvantages of absorption. For example, the SaskPower's Boundary Dam plant (Canada) is one of the world's first commercial carbon capture facilities, utilizing amine-based absorption to capture CO_2 from flue gases [80]. This project captures over one million metric t of CO_2 per year, reflecting a 90% CO_2 capture rate for the 139 MW coal-fired unit, demonstrating a TRL of 8–9. Similarly, the Petra Nova project in Texas, USA, also employs amine absorption to capture CO_2 from a coal-fired power plant at a large scale [81].

Adsorption technologies utilize solid materials to capture CO_2 from exhaust gases. These materials are typically porous, such as activated carbon, zeolites, or emerging metal-organic frameworks (MOFs) [82]. Compared to an aqueous solvent-based process, considerable reduction in the regeneration energy penalty, a wider range of operating temperatures, less waste production during cycling, and easier disposal of spent materials, are advantages of

solid adsorbent-based technology [83]. However, for large-scale CO_2 capture, the high cost of solid adsorbents (*e.g.*, zeolites and MOFs) and adsorbent attrition are examples of the main challenges associated with this technology [83]. One of the leading developers of temperature swing adsorption (TSA) is Svante (ex-Inventys) with their VeloxoTherm capture process, which is an intensified rapid cycle TSA process developed to reach a capture rate of 90% in post-combustion applications [84]. The process consists of structured adsorbents fixed into a rotating frame, which is divided into adsorption and regeneration zones. VeloxoTherm is currently being demonstrated at Husky Energy's Pikes Peak South heavy oil site located in Saskatchewan, Canada, where 30 t of CO_2 is captured per day from a once-through steam generator and utilized in enhanced oil recovery, demonstrating a TRL of 6–7 [84].

In comparison with conventional CO_2 capture plants, membrane systems are a better tool for CCS due to their low capital and operating costs, slow decay in performance, non-reactivity with gases, removal of numerous turn-on and turn-offs of the capture process, adaptability to maintain constant product quality, design efficiency (*i.e.*, integration of several processes into one unit), and facilitated installation and transportation [79]. CO_2 capture by membranes has been successful in the development to pilot and demonstration scales. One example is the facilitated transport membranes (FTMs) developed by the Norwegian University of Science and Technology (NTNU) [85]. Since 2011, pilot or pre-pilot tests based on FTM membranes have been carried out in several testing sites by NTNU with industrial partners (Air Products, *etc.*), including the Sines bituminous coal power station (Sines, Portugal), the Tiller plant (Trondheim, Norway), the Norcem cement factory (Brevik, Norway), and the Colacem cement plant (Gubbio, Italy), illustrating a TRL of 6–7.

The cryogenic distillation process involves condensing gaseous species by reducing temperature. In the case of CO_2, the process needs to be implemented at temperatures below −73.3 °C by using a compressor, a multi-stage heat exchanger, a Joule-Thomson valve, as well as cold traps [79]. For cryogenic carbon capture, two leading technologies are CryoCap by Air Liquide and Cryogenic Carbon Capture (CCC) by Sustainable Energy Solutions (SES) [86]. CryoCap focuses on capturing CO_2 during hydrogen production through a cryogenic distillation process. The feed streams typically contain 40%–50% (mol) CO_2. The Cryocap H_2 installation in Port-Jérôme has an annual capture capacity of 100000 t of CO_2, and Air Liquide's project at the Zeeland Refinery aims to utilize CryoCap technology to capture 800000 t of CO_2 per year [87–89]. Cryogenics is a relatively mature technology with good CO_2 recovery, with TRL levels of 6–7 [90]. However, it is generally applicable at carbon concentrations >90% [79,91]. The high energy demand of cryogenic separation is the main disadvantage of this technology.

Water electrolysis technologies for hydrogen production are represented by three main categories: proton exchange membrane (PEM), solid oxide electrolysis cells (SOEC), and alkaline water electrolysis (AWE) [92]. Each has its own strengths, challenges, and representative technologies in the market. PEM electrolyzers, like Siemens Silyzer and ITM Power PEM systems [93], are at a TRL of 8–9 [94]. These systems use a solid polymer electrolyte that conducts protons while separating hydrogen and oxygen. They offer fast dynamic response, making them ideal for coupling with intermittent renewable energy sources like solar and wind [95]. Siemens Silyzer 300 possess a power demand of 17.5 MW and a production capacity of 335 kg of hydrogen per hour [96]. The key challenge remains the high cost due to the use of precious metals like platinum and iridium. However, ongoing research aims to reduce material costs and improve durability [97].

AWE is mature, with electrolyzers like those from NEL Hydrogen and Thyssenkrupp Uhde Chlorine Engineers [98]. It uses a liquid alkaline electrolyte (KOH or NaOH) and cheaper materials for electrodes compared to PEM. AWE is commercially available and deployed at large scales with a TRL of 8–9, and plants in the megawatt range have been existing for long time [99]. At the current stage, the hydrogen production rate of AWE electrolyzer can be about 1000 $m^3 \cdot h^{-1}$. Thyssenkrupp Uhde Chlorine Engineers, a German company, produces alkaline electrolyzers that could even reach 4000 $m^3 \cdot h^{-1}$ [98]. However, it operates at lower current densities and efficiency, making it less attractive for fast-response energy systems.

SOEC uses solid oxides or ceramic electrolytes that can withstand high temperatures (700–1000 °C), providing significant energy efficiency though it has less developed commercial applications due to more complex system requirements [100]. Representative companies include Sunfire, Fuel Cell Energy and Haldor Topsoe [101]. The current densities in commercial stacks are in the order of 500 to 1000 $mA \cdot cm^{-2}$ [101]. The maturity of the SOEC technology is lower with TRL in the range of 5–6 [102]. It holds promise for future integration with industrial processes where high-temperature waste heat is available. However, material degradation at high temperatures is a key issue still under research [103].

In evaluating the potential of these technologies for carbon circularity, PEM electrolysis stands out as a key technology, as it can produce green hydrogen at scale with renewable electricity. While expensive today, PEM is rapidly advancing and has clear commercial applications. SOEC, though at a lower TRL, has immense potential for improving the energy efficiency of electrolysis through the use of waste heat, making it a future candidate for industrial-scale carbon reduction.

CO_2 hydrogenation technologies convert captured CO_2 into valuable chemicals and fuels, contributing to carbon circularity by reducing emissions and producing drop-in fuels. Methanol synthesis from CO_2 hydrogenation is widely researched. This process typically uses Cu/ZnO-based catalysts [25], to convert CO_2 and H_2 into methanol. A representative example is the Carbon Recycling International plant located in Iceland, which has a production capacity of approximately 5 million liters of methanol per year using local hydrothermal and geothermal energy sources [104]. At TRL 7–9, methanol production *via* CO_2 hydrogenation is already at pilot scale and is close to commercial viability, driven by its potential to integrate with the chemical industry and fuel sector [105]. Several commercial CO_2-to-methanol plants have also been demonstrated in China, Chile, and the United States [104].

Direct ethanol and propanol (or higher alcohols) synthesis via CO_2 hydrogenation is complex and suffers from a low selectivity and conversion [106]. The commercial success of the direct synthesis from H_2/CO_2 is thermodynamically- and kinetically-limited by low yields and selectivity [10,45]. The reaction has already been successfully carried out in a laboratory setting using Rh, Cu, Co, Fe, and Mo based catalysts [10]. For example, the ethanol synthesis by CO_2 hydrogenation over Cu@Na-Beta catalyst achieve a single pass conversion of 14% at 300 °C, 12000 $ml \cdot g^{-1} \cdot h^{-1}$, and 2.1 MPa, corresponding to space-time yield of 398 $mg \cdot g^{-1} \cdot h^{-1}$. As there are no prototype plants, the TRL is between 4 and 5.

Methanation *via* CO_2 hydrogenation, commonly known as the Sabatier process, is already deployed in power-to-gas systems. Companies like Electrochaea and Audi's e-gas project have demonstrated the process at TRL 8–9 [107,108]. Audi e-gas power to methane facility at Werlte, Germany is situated adjacent to a food waste digester which produces biomethane for gas grid injection. The biogenic CO_2 from a food waste digester available is reacted with H_2 from three 2 MW alkaline water electrolysis cells,

ideally using electricity from surplus offshore wind, from the North Sea. The synthetic methane (termed e-gas) is identical to natural gas. The plant produces about 1000 t of methane per year or 1400000 m^3 CH_4 (CH_4 has a density of 0.714 $kg \cdot m^{-3}$) or 14 $TW \cdot h \cdot a^{-1}$ of energy (CH_4 has a volumetric energy density of approximately 10 $kW \cdot h \cdot m^{-3}$). The process is efficient but requires a reliable source of low-cost hydrogen to be economically competitive.

In terms of CO_2 hydrogenation, methanol synthesis is close to commercial viability, offering a viable pathway for creating fuels and chemicals from captured CO_2. Ethanol and propanol production, while promising, still require significant R&D to optimize catalysts and scale up production. Methanation, on the other hand, is already deployed in power-to-gas systems, making it a strong contender for near-term applications in integrating renewable hydrogen with natural gas grids.

The compression or liquefaction of hydrogen and methane are technologically mature but face energy consumption challenges [69,109]. Compression of hydrogen is widely used, with compressors from companies like Howden and Atlas Copco at TRL 9 [110–112]. Compressed hydrogen in carbon-composite tanks at 70 MPa pressure is used in fuel cell cars such as the Toyota Mirai, which has been a production vehicle available since 2014 [113]. While compression technology is mature, the energy requirement for compressing hydrogen is high (about 5% to 20% of the energy content of the gas), reducing the energy efficiency [114]. Hydrogen liquefaction is more energy-intensive than compression, consuming 30% to 40% of the energy content of the hydrogen. A large-scale Linde hydrogen liquefaction plant, installed in Ingolstadt, Germany, has specific energy consumption of 13.58 $kW \cdot h \cdot kg^{-1}$ and capacity of 4.4 $t \cdot d^{-1}$ by applying the Claude process with nitrogen pre-cooling [115,116]. This technology is commercially available with TRL of 8–9 [117].

Methane compression and liquefaction technologies are widely used in natural gas industries. These technologies are mature with TRL of 9. Compressed natural gas (CNG) has been typically utilized in households, plants, factories, and other settings as vehicular fuel [118]. CNG's widely adopted applications can be justified by the fact that it is being used worldwide by increasing numbers of countries that are now using Natural Gas Vehicles (NGV). Among those countries, Iran is one of the highest users of NGV with a total number of 4.07 million NGVs overall, with more than 2500 CNG fuel stations across the country, thus making it the world's third largest country in terms of the highest number of CNG fuel stations [118]. Besides, the global natural gas liquefaction capacity reaches around 483 $Mt \cdot a^{-1}$ as of the end of February 2024 [119]. Further innovations now focused on improving efficiency and reducing carbon emissions in the compression and liquefaction process [120,121].

The compression and liquefaction of hydrogen and methane are crucial technologies for the storage and transportation of these gases. Improving the energy efficiency of hydrogen liquefaction and compression will enhance the practicality of using hydrogen as a widespread energy carrier, while methane compression and liquefaction are already highly advanced, forming a key part of the existing energy infrastructure.

Regarding the end use of various fuels, hydrogen can be used in a range of applications, including hydrogen combustion engines, fuel cells, and hydrogen turbines. Each of these technologies has unique strengths and limitations when it comes to energy conversion [122]. Hydrogen combustion engines are an interesting solution in the field of combustion vehicles, but it was only in the first decade of the 21st century that many commercial vehicles came on the market. The leading manufacturers of hydrogen internal combustion engine vehicles include brands such as Ford, BMW, Mazda, Chevrolet and Toyota [123]. From the point of view of the scale of production, the BMW Hydrogen 7 is particularly noteworthy. It is the first mass-produced hydrogen-powered vehicle. The BMW 7 twelve-cylinder engine is equipped with two separate fuel systems, allowing the vehicle to run on both gasoline and hydrogen. Based on the BMW Hydrogen 7 (bi-fuel), a BMW Hydrogen 7 Mono-Fuel demonstration vehicle with a TRL of 9 was developed, which runs on hydrogen only. A disadvantage of hydrogen engines, however, is the release of nitrogen oxides and, as a result, they require exhaust gas treatment to reduce NO_x emissions [123,124].

Hydrogen fuel cells are commercially available, with technologies such as Toyota's Mirai and Hyundai's Nexo at TRL 8–9 [125,126]. These vehicles use proton exchange membrane (PEM) fuel cells, which combine hydrogen and oxygen to generate electricity, with water as the only by-product. The first-generation Toyota Mirai permitted a 650 km range and quick refueling, which is a huge advantage over battery electric vehicles, plagued by the low range and long battery recharging times. The latest Toyota Mirai travels 1360 km with a full tank of 5.65 kg of hydrogen setting a new world record for fuel cell vehecles [127]. However, the high cost of green hydrogen impacts the overall economics of PEM fuel cells. These cells also degrade over time, reducing efficiency, and rely on expensive platinum catalysts, which raises concerns about cost and supply [128].

Methanol is widely used in the chemical industry as a feedstock, and its application as a fuel is gaining attraction due to its liquid form, which makes it easier to store and transport compared to hydrogen. The TRL of methanol utilization varies by application. Technologies like MAN Energy Solutions' methanol-powered engines are at TRL 8–9, and commercial vessels, including those from Maersk, are set to operate on methanol [129,130]. These new vessels are expected to reduce Maersk's annual greenhouse gas emissions by approximately 450000 tons of CO_2 per year on a full fuel lifecycle basis when powered by green methanol. Methanol as a fuel for ground transportation is currently at TRL 6–7. Companies like Geely in China have been actively promoting methanol-fueled cars, with pilot projects demonstrating its compatibility with combustion engines [131]. Geely's methanol vehicles enable a 70% reduction in CO_2 emissions from well to wheel compared to gasoline models. Direct methanol fuel cells (DMFC), such as those developed by Smart Fuel Cell AG, are at TRL 6–7 [132]. These are primarily used in niche markets, such as portable and backup power systems. While methanol is easier to handle than hydrogen, DMFCs are less efficient than PEM fuel cells, limiting their broader use.

Ethanol is already widely used as a biofuel in the U.S., Brazil, and Europe [133], and it is produced mainly through fermentation of sugarcane or corn and has a well-established production and distribution infrastructure. It can be blended with gasoline or used in modified engines to reduce greenhouse gas emissions. Ethanol in internal combustion engines possess a TRL of 9, as it is extensively used in commercial applications [134]. E10 is a blend of 10% ethanol and 90% gasoline, authorized by the U.S. Environmental Protection Agency (EPA) for use in all conventional gasoline-powered vehicles. In the U.S., most gasoline includes up to 10% ethanol, enhancing octane levels, improving air quality, and meeting Renewable Fuel Standard (RFS) requirements [135]. E85, or flex fuel, is a high-ethanol blend containing 51% to 83% ethanol. With over 4200 public E85 stations across 44 states, these high-ethanol options are accessible to the more than 20.9 million flex-fuel vehicles on U.S. roads [136].

Direct ethanol fuel cells (DEFCs), like those in ongoing research by various institutions, are at TRL 4–5 [137]. The technology is being explored for its potential in portable power and stationary

applications due to ethanol's renewable nature and ease of handling. However, DEFCs are not yet commercially viable due to limitations in catalyst cost-effectiveness and system durability, with precious metals like platinum currently needed to drive the ethanol oxidation reaction efficiently. Research efforts are focused on developing non-precious metal catalysts to enhance affordability and support scalability.

Propanol's use as a fuel is less developed than methanol or ethanol, and its TRL for most applications is still low [62]. Research on propanol as a biofuel is still in the experimental stage, at TRL 4–5. Like ethanol, propanol can potentially be used in fuel cells, particularly in direct alcohol fuel cells (DAFCs). However, this application is still in early research stages, with a TRL of 3–4, as more work is needed to develop efficient catalysts and systems for converting propanol into electricity [138].

Methane, primarily sourced from natural gas, is a highly versatile fuel with applications across transportation, power generation, and industrial sectors. Among alternative fuels, methane boasts the highest technological readiness, with commercial technologies in extensive use. CNG and LNG are the two primary forms of methane. CNG technologies have reached TRL 9, highlighting their maturity and extensive commercial use [139]. Natural Gas Vehicles (NGVs) are well-proven, durable, and already operating on roads worldwide. They offer a cost-effective solution, with significantly lower incremental costs compared to diesel alternatives and much lower costs than electric or hydrogen vehicles [140]. Medium- and heavy-duty natural gas models are readily available and scalable, produced by leading manufacturers like Autocar, Crane Carrier, Ford, Freightliner, Hyliion, Kenworth, Mack, Peterbilt, and Volvo [140].

LNG, with its higher energy density than CNG, is widely used in long-distance transport and heavy-duty applications, particularly in shipping and trucking with a TRL of 9. In maritime transport, vessels like CMA CGM's Jacques Saadé Class and Carnival's AIDAnova cruise ship demonstrate LNG's ability to significantly reduce emissions while covering long-haul routes [141]. In heavy-duty trucking, manufacturers like Volvo and Scania have developed LNG-powered trucks capable of long-range operations, offering a cleaner alternative to diesel without compromising on performance [142,143]. Innovations in LNG are focusing on enhancing the energy efficiency of the liquefaction process, a crucial aspect for lowering the environmental impact and improving overall economic feasibility [144].

Methane is also gaining attraction as a fuel for solid oxide fuel cells (SOFCs), which operate at high temperatures and can directly use methane to generate electricity. Methane-fueled SOFCs have reached TRL 6–7, indicating pilot-level testing and initial commercial interest, though further development is required to improve durability and cost-effectiveness [145]. Representative companies like Bloom Energy have deployed SOFCs for distributed power generation, particularly in areas requiring efficient, low-emission, and reliable energy solutions. It is estimated 70000 household SOFCs currently deployed through Japan's Ene-Farm program [145].

In summary (Fig. 7), mature CO_2 capture technologies like absorption using amines show promising TRL 8–9, with large-scale demonstrations proving effectiveness, despite parasitic energy losses. Membrane and cryogenic methods, while innovative, still face energy efficiency challenges. Water electrolysis technologies for hydrogen, such as PEM and AWE, are commercially mature (TRL 8–9), though high costs persist. CO_2 hydrogenation for methanol synthesis is nearing commercial viability (TRL 7–9), offering a well-integrated path for fuels. However, the direct synthesis of higher alcohols, like ethanol and propanol, remains in lower TRL of 4–5, indicating a need for significant R&D. Storage and transport technologies, like hydrogen compression and

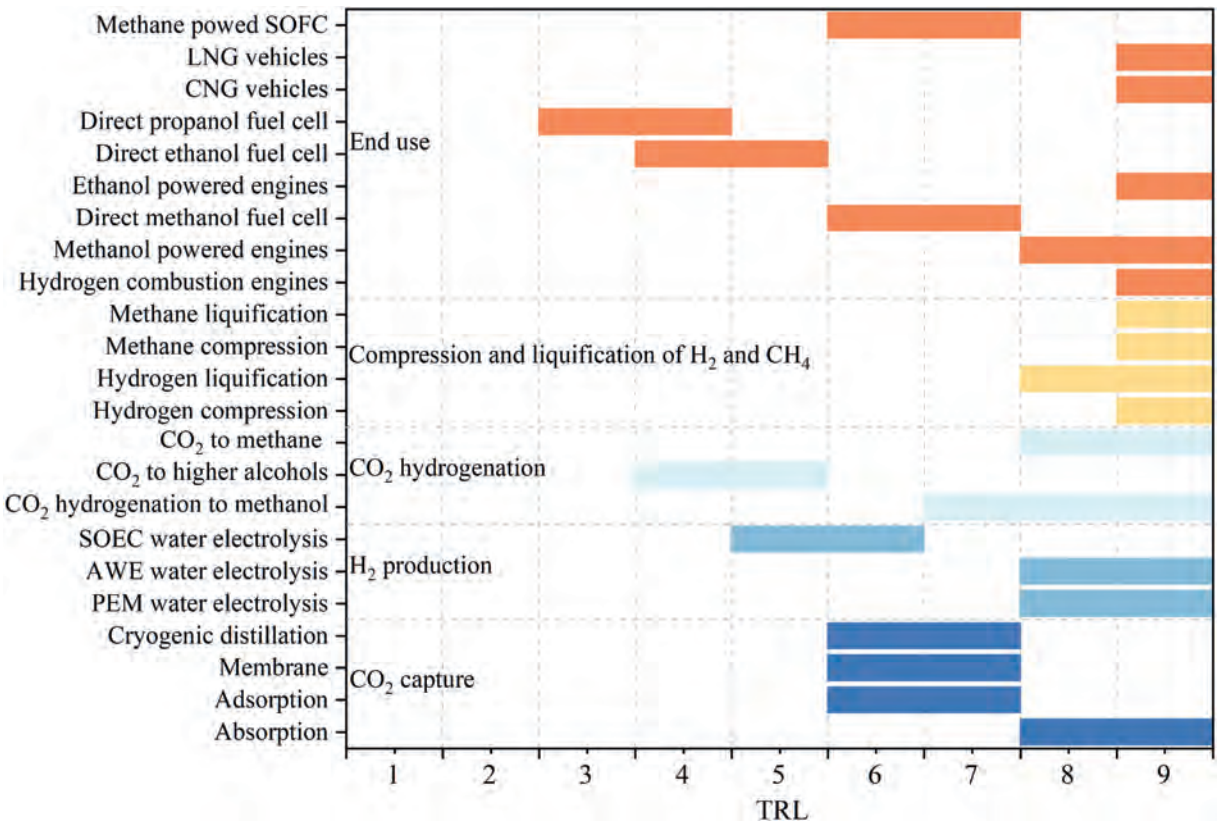

Fig. 7. TRL of technologies associated with the synthesis and end use of various green fuels.

methane liquefaction, are technologically mature, forming the backbone of existing energy systems. While hydrogen applications span combustion engines and fuel cells, they struggle with cost and NO_x emissions. In contrast, methanol and ethanol provide more accessible alternatives due to their liquid state and compatibility with existing infrastructure, demonstrating higher technology readiness for transportation. The potential of higher alcohols as fuels for carbon circularity remains contingent upon advancing catalyst efficiency, scalability, and integration with renewable resources.

5. Production Costs, Market Readiness, and Potential Incentives

The production cost is another key factor influencing the practical application of higher alcohols. The production cost of hydrogen using renewable electricity typically ranges from USD 3.00 to USD 8.00 per kilogram [146]. In contrast, renewable methanol, produced by combining captured CO_2 with green hydrogen, has a lower production cost, ranging from USD 0.80 to USD 1.60 per kilogram for e-methanol derived from renewable sources [147]. The cost of methane produced *via* CO_2 methanation falls within the range of USD 3.25 to USD 4.09 per kilogram when integrated with point-source carbon capture [148]. Meanwhile, the production cost of ethanol from CO_2 hydrogenation ranges from USD 1.73 to USD 2.09 per kilogram [73].

When comparing the costs per unit of energy storage, the figures are as follows: Hydrogen: USD 0.025 to USD 0.067 per MJ; methane: USD 0.065 to USD 0.082 per MJ; methanol: USD 0.038 to USD 0.076 per MJ; and ethanol: USD 0.062 to USD 0.075 per MJ. The per-unit energy cost of ethanol is competitive, falling within a similar range to methanol, hydrogen, and methane. While ethanol may have slightly higher production costs than methanol and hydrogen, it remains a viable and economically competitive energy carrier.

Regarding the market readiness, hydrogen infrastructure remains in the early stages of development, with a limited number of refueling stations and distribution networks, which poses a significant challenge to its widespread adoption [149]. In contrast, methane benefits from a well-established infrastructure, including extensive pipelines and storage facilities, that streamline its distribution and usage [149]. Methanol, too, has a mature infrastructure and a robust market, making it a readily accessible and economically viable option for large-scale deployment [150]. Ethanol, already widely used as a fuel additive, enjoys a substantial market presence, particularly in countries like Brazil and the United States [151]. Its seamless compatibility with existing fuel infrastructure significantly enhances its market readiness, positioning it as a more immediate solution compared to emerging alternatives.

The government has introduced policies to promote ethanol production. In the United States, the Renewable Fuel Standard (RFS), established by the Energy Policy Act of 2005 and expanded under the Energy Independence and Security Act of 2007, mandates the blending of renewable fuels, including ethanol, into the national transportation fuel supply [152]. Similarly, China has set ethanol blending targets, with the national average fuel ethanol blend estimated at 1.8% in 2022 and plans to achieve a nationwide E10 fuel ethanol target [153].

As can be seen, ethanol is a competitive energy carrier with a well-established market and infrastructure, particularly in Brazil and the U.S. Despite slightly higher production costs than methanol and hydrogen, its seamless integration into existing fuel systems and strong policy support make it a viable and readily deployable alternative to emerging renewable fuels.

6. Conclusions

In summary (Fig. 8), hydrogen excels in energy efficiency and technology readiness but is hindered by low energy density and safety concerns, particularly risks associated with leakage and explosion. Methane, with high technology readiness, offers strong energy efficiency and moderate energy density. However, as a potent non-CO_2 greenhouse gas, its potential leakage during use presents a significant drawback. Methanol delivers a well-rounded performance, combining high energy efficiency with moderate energy density and technology readiness.

Higher alcohols, such as ethanol, stand out for their high energy density and safety, making them strong candidates for carbon circularity. Moreover, the per-unit energy cost of ethanol is competitive, comparable to that of methanol, hydrogen, and methane. Nevertheless, their adoption is currently constrained by lower energy efficiency and technology readiness compared to hydrogen, methane, and methanol. These limitations primarily stem from production challenges, including low yields, high energy requirements, and the need for advanced catalysts to enhance conversion efficiency.

Within the broader renewable energy landscape, higher alcohols complement other clean energy carriers, such as batteries and green hydrogen, by providing flexible energy storage solutions and bridging supply gaps caused by the intermittent nature of wind and solar power. They play a crucial role in decarbonizing sectors that are difficult to electrify—such as aviation and heavy-duty transport—where high energy density is essential. Ammonia, on the other hand, has been explored as a carbon-free fuel with its own advantages and challenges. While it can be synthesized through the well-established and widely used Haber-Bosch process, ammonia has several drawbacks, including low flame speed, low flame temperature, unstable combustion characteristics, low reactivity, and high NO_x emissions [154,155]. Although higher alcohols offer superior energy density and compatibility with existing infrastructure, the synthesis of higher alcohols from CO_2 hydrogenation remains in the developmental phase. As renewable energy capacity expands and supportive policies foster advancements in catalyst development and process optimization, higher alcohols are set to become a key component of future energy systems, facilitating a smooth transition toward a circular, low-carbon economy.

To establish higher alcohols as a competitive and sustainable component of carbon circularity, future research must take a holistic approach that integrates advancements in catalysis, process engineering, and scalability. A key focus should be on developing advanced catalysts. Innovations like nanostructured catalysts with

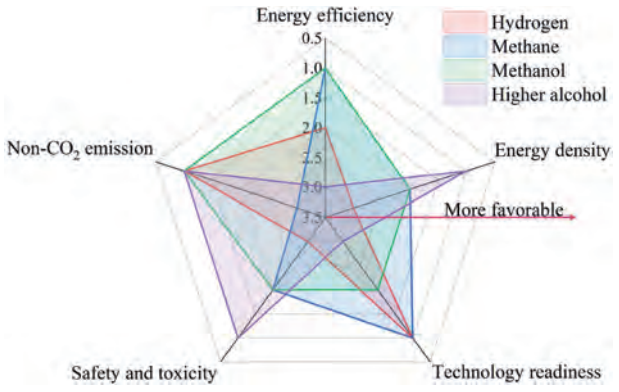

Fig. 8. Comparison of the energy efficiency, energy density, technology readiness, safety and toxicity and non-CO_2 emission of the fuels.

engineered morphologies can improve selectivity and stability during synthesis. Machine learning offers a promising avenue for accelerating catalyst discovery by predicting optimal compositions and structures. Catalysts demonstrating a single-pass conversion greater than 5% [156], a $C_{2+}OH$ selectivity exceeding 95% [157], and a space-time yield surpassing 0.5 $kg \cdot L^{-1} \cdot h^{-1}$ would be of significant interest for industrial applications [12,158].

Process integration should emphasize energy and resource efficiency to minimize the carbon footprint of production. Modular, decentralized systems can utilize captured CO_2, reducing transportation emissions. Combining renewable energy sources such as solar or wind with electrochemical CO_2 reduction can align intermittent power with flexible synthesis processes. Water-efficient purification methods, like advanced membrane separation, can further reduce environmental impact, ensuring the entire production chain aligns with sustainability objectives.

Scaling up higher alcohol production from lab to commercial scale requires establishing pilot and demonstration plants to test process stability, feedstock adaptability, and product quality under real-world conditions. Core infrastructure, including reactors, separation units, and storage, must be developed alongside optimized production processes, such as refining reaction pathways, improving catalyst efficiency, and integrating renewable energy to lower costs and emissions. Meeting regulatory compliance, conducting environmental impact assessments, and implementing safety protocols are crucial. Simultaneously, market integration requires developing supply chains, distribution networks, and educating stakeholders. Addressing these technical, regulatory, and commercial challenges will enable higher alcohols to transition from research to a sustainable energy solution.

Furthermore, efforts to improve combustion efficiency and mitigate emissions during end-use will further cement the role of higher alcohols as a sustainable fuel solution for carbon circularity.

CRediT Authorship Contribution Statement

Xiaolu Xu: Writing – review & editing, Data curation, Formal analysis, Writing – original draft, Conceptualization. Linjun Wang: Writing – review & editing, Writing – original draft. Qingsong Hu: Writing – original draft, Writing – review & editing. Jie Ren: Methodology, Writing – review & editing. Fu Yang: Methodology, Writing – review & editing, Funding acquisition. Ruiyan Sun: Writing – review & editing, Methodology. Zhenchen Tang: Writing – review & editing. Huanhao Chen: Writing – review & editing. Feng Zeng: Writing – review & editing, Funding acquisition, Conceptualization, Methodology, Data curation, Writing – original draft, Formal analysis.

Declaration of Competing Interest

The author is an Editorial Board Member/Editor-in-Chief/Associate Editor/Guest Editor for this journal and was not involved in the editorial review or the decision to publish this article.

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