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Race towards net zero emissions (NZE) by 2050: reviewing a decade of research on hydrogen-fuelled internal combustion engines (ICE)

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Hydrogen fuel offers promising decarbonization pathways for hard-to-electrify transport sectors such as long-haul trucking, international maritime, and aviation. The internal combustion engine (ICE) is and will continue to be important in the transition to net zero emissions (NZE), especially in the transport sector. In this review, the research trend, hotspots, and evolutionary nuances of hydrogen-fuelled ICEs have been investigated. Our analysis reveals that while earlier research primarily focused on the performance and emission characteristics of hydrogen-fuelled ICEs, recent studies are increasingly paying more attention to combustion and emission control strategies. NO_x emissions have received a lot of attention, as it is the most important pollutant from hydrogen engines. Several techniques, namely exhaust gas recirculation (EGR), water injection, and lean combustion, have been predominantly adopted and studied for controlling NO_x emissions. Another major research area in the field has centered on combustion anomalies such as backfiring and knocking, which are key setbacks to the hydrogen-fuelled ICE. Owing to its ability to produce fewer emissions and greater performance than diesel-only operation, hydrogen in diesel engines as dual fuel has also become a major research hotspot in the field within the last decade. Our analysis also showed that there is a strong interest in this field where researchers are focusing on the use of hydrogen with other alternative fuels such as methane, biogas, biodiesel, ammonia, and methanol for optimal operation of the ICE. Finally, we provide some critical challenges and potential solutions related to the use of hydrogen as an ICE fuel. It is anticipated that the results from the present work will pave the way for the continuous development of hydrogen engine research for the ongoing fight to decarbonize the transport sector.

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Introduction

1.1 Renewable energy and net zero emissions

The world must reach net zero emissions to avoid the devastating effects of failing to meet the 1.5–2 °C Paris Agreement target on global warming. According to the Intergovernmental Panel on Climate Change (IPCC), global average temperatures have already risen around 1.1–1.3 °C above pre-industrial levels, 1–3 primarily due to human activities like burning fossil fuels that release greenhouse gases, and the remaining carbon budget to limit warming to 1.5 °C could be exhausted by the late 2020s. 4 While fossil

fuel consumption has declined with increasing renewable energy adoption, conventional fuels still make up around 85% of total global primary energy use.⁵ Achieving net zero emissions is crucial to mitigate further warming and climate change impacts.

To reach the 1.5 °C goal, urgent emission cuts are required to attain global net zero carbon dioxide (CO₂) emissions by mid-century. Net zero emissions (NZE) implies counterbalancing all residual emissions with an equal amount of offsets through carbon removal. For Several countries have committed to carbon neutrality/net zero targets ranging from 2040 to 2070, with more expected to follow. For Reducing emissions through the development and deployment of renewable energy (RE) is crucial for achieving carbon neutrality or net zero emissions. Despite positive trends in RE deployment in recent years, key challenges that hinder 100% RE grid integration include the intermittency of weather-dependent sources like solar and wind, the need for large-scale energy storage to manage variability, and the required upgrades to existing

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power grids. 11,12 Another critical challenge involves decarbonizing hard-to-abate sectors like heavy industry and long-haul transportation that account for around 30% of total emissions^{13,14} and are difficult to electrify directly due to their requirement for high energy-density fuels. 15 To achieve NZE, it is necessary to significantly reduce emissions from these sectors and to find ways to decarbonize them. Some of these potential solutions include the power-to-X concept.

1.2. Power-to-X

Power-to-X (PtX) is an umbrella term that involves a range of technologies aimed at converting electrical energy into various energy carriers or chemical products through various pathways, such as power-to-hydrogen, power-to-ammonia, powerto-chemicals (like methanol or synthetic fuels), power-to-gas synthetic methane), power-to-heat, and power-tomobility^{16–19} (Fig. 1). The primary objective of PtX is to enable efficient storage and utilization of intermittent renewable energy sources like wind and solar power. The PtX concept works by utilizing excess electricity generated from renewable sources to produce energy carriers through processes like electrolysis or chemical synthesis.20 These carriers can then be stored, transported, and utilized as needed, effectively acting as energy buffers and facilitating the integration of renewable energy into various sectors.

Power-to-hydrogen (P2H2) is a specific application of the PtX concept, focusing on producing hydrogen as the energy carrier. In this process, renewable electricity powers an electrolyzer that splits water molecules (H2O) into hydrogen (H2) and oxygen (O₂) through electrolysis. The resulting "green" hydrogen, produced with no carbon emissions, can be compressed or liquefied for efficient storage and transportation. The stored

hydrogen can be utilized in various applications, including fuel cells for electricity generation or transportation (e.g., hydrogen fuel cell vehicles), industrial processes (ammonia production, steel manufacturing), heating and cooling systems, and re-electrification (converting hydrogen back into electricity using fuel cells or turbines). 16-19

One of the pivotal roles of power-to-hydrogen is to store excess renewable electricity, addressing the intermittent nature of wind and solar power generation. 15,21 By utilizing surplus electricity to produce hydrogen, this process enhances the efficiency of renewable energy utilization and mitigates the challenges posed by the variability of renewable sources.²²

The hydrogen from this pathway is critical for achieving the decarbonization of hard-to-abate sectors like chemical, transportation, and industry²⁴⁻²⁶ by providing a fuel with suitable physico-chemical characteristics, and has many potential applications, notably in transport sub-sectors like heavy trucking, maritime, and aviation through internal combustion engines (ICEs) which offer favorable technology readiness, availability, versatility, reliability and relatively low cost compared with alternatives like fuel cells. 27 Also, the huge demand for green hydrogen in the future opens up an opportunity for other carbon-neutral fuels (hydrogen derivatives), such as ammonia and methanol, to be produced and delivered to hard-to-abate sectors for the realization of deep decarbonization targets.22

It is also important to stress that hydrogen could enable more effective large-scale and seasonal storage capacities than alternatives such as batteries and pumped hydro storage.²⁸ Batteries, supercapacitors, and compressed air cannot provide the range and power necessary to overcome seasonal imbalances on their own. On the other hand, pumped hydro storage

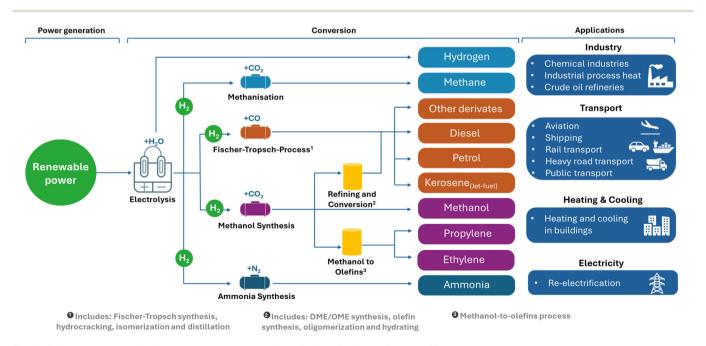


Fig. 1 PtX route and its derivatives and their key sector of application. Re-drawn from ref. 23.

Promote large-scale renewable energy integration, power generation and seasonal storage

Electricity can be produced in high-potential RE regions, converted to H₂, and shipped to low-potential RE regions

Decarbonize hard-to-abate sectors like heavy industry, road trucking, international shipping and aviation

Serve as feedstock for producing other carbon-neutral fuels such as methanol and ammonia for further decarbonization

By coupling the power sector with other sectors, Power-to-H₂ can improve robustness and reliability of grid network

Fig. 2 Role of green hydrogen in a net zero future.

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has the potential to offer long-term and substantial energy storage, but it is constrained geographically for the untapped potential, and its worldwide output capacity of 170 GW is just approximately 2% of the world's installed electrical capacity.²² Fig. 2 summarizes some key roles that may be played by green hydrogen in the NZE future.

As a result, hydrogen has a crucial role to play in enabling the net zero transition by 2050. In 2020, global hydrogen demand was around 90 MMT, with 80% pure hydrogen and the rest used with carbon gases for steel and methanol production.²¹ Under a net zero scenario, hydrogen demand is projected to increase by nearly 500% by 2050 relative to 2020 levels.²⁹ Green hydrogen, produced from renewable electrolysis, currently represents less than 1% of global production but is expected to grow substantially to achieve mid-century net zero goals.²¹ By 2050, green hydrogen and derivatives like ammonia, synthetic methane, and methanol could meet 12-22% of final energy demand (Fig. 3), with green hydrogen and electricity together potentially supplying 63% of final energy consumption. 15,30 The production of these critical net zero fuels fundamentally relies on the availability of green hydrogen.

1.3 Hydrogen-fuelled ICE

ICEs facilitate mobility but rely heavily on polluting fossil fuels such as diesel and gasoline. Adopting hydrogen in ICEs is a leading pathway to achieve complete or near zero carbon transportation in a net zero pathway by mid-century. Compared with fuel cells, hydrogen ICEs could leverage existing industry infrastructure to enable faster hydrogen scale-up. Hydrogen ICEs offer zero carbon emissions and good thermal

efficiency³² and comply with stringent transport emissions rules, with advanced technologies minimizing remaining NO_x emissions,³³ which is one of the main challenges of hydrogen engines. As a result, research interest in hydrogen-fuelled ICEs has grown significantly in the last decade. In the existing literature, there has been a significant number of traditional reviews on hydrogen and its application in ICEs, as summarized in Table 1.

While the existing reviews on the hydrogen ICE provide valuable contributions to existing knowledge, new methods of review such as bibliometric analysis could provide new insights into the key research focus, thematic areas, frontiers, and expected future developmental trends on hydrogen-fuelled ICEs from a quantitative point of view. The use of bibliometric tools is gaining attention in mapping the knowledge landscape of a particular research field. Bibliometric analysis is a method of quantitatively analyzing and evaluating the production, impact, and dissemination of scientific research. 43-47 This method typically involves collecting data on the publication and citation patterns of scientific papers, as well as other indicators of the quality and significance of the research. The essence of bibliometric analysis is to use quantitative data on the publication and citation patterns of scientific papers to assess the performance, quality, and impact of research. 48 Low and MacMillan⁴⁹ argued, "As a body of literature develops, it is useful to stop occasionally, take inventory for the work that has been done, and identify new directions and challenges for the future" (pg. 139). This method can provide valuable insights into the state of a scientific research field, and it can help to identify trends, patterns, and connections between different areas of research.



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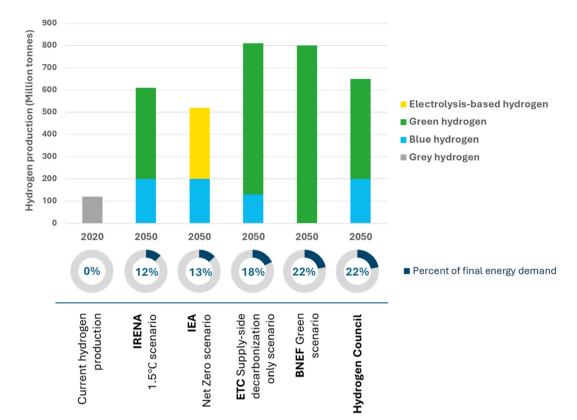


Fig. 3 Relative share of hydrogen production technologies by mid-century. Re-drawn from ref. 15. Here, green hydrogen refers to hydrogen made by electrolysis using electricity from renewable sources; grey hydrogen is derived from natural gas; blue hydrogen is a combination of grey hydrogen with carbon capture and technology; yellow hydrogen refers to electrolytically made hydrogen with solar. Other forms of hydrogen color codes include turquoise hydrogen which splits methane from natural gas into hydrogen and solid "carbon black"; purple/pink/red hydrogen involves hydrogen from the electrolytic process based on nuclear power; energy black/brown refers to hydrogen made from either black or brown coal (lignite).

Original contributions and scope of current study

In the past, researchers have attempted to employ the bibliometric tool to map out the ICE research field, for example, methanol/ethanol in ICEs,50 biodiesel in ICEs,51 diesel engines,⁵² modeling engines,⁵³ and emissions from alcohol/diesel engines.54 To the best of our knowledge, the use of such modern review tools in mapping the knowledge domain on hydrogen in the ICE is scarce. To fill this gap, we employ bibliometric tools to assess the research domain of hydrogen-fuelled ICEs. To uncover internal structures and hidden implications for future development, the research's objective is to quantitatively investigate the research field of hydrogen-fuelled ICEs since 2012 and identify the major research hotspots and emerging and declining research themes. Through keyword analysis, this study systematically identifies the significant areas that need greater focus, offering researchers a thorough understanding and direction for the development of the hydrogen-fuelled ICE. We therefore expect that the outcomes of the current research will open up opportunities for the advancement of hydrogen engine research in the ongoing attempt to decarbonize the transport sector.

Principle of mechanism of hydrogen engines

Hydrogen-powered internal combustion engines (H2-ICEs) operate similarly to traditional gasoline or diesel engines but utilize hydrogen instead of hydrocarbons. The mechanical aspect involves the intake of hydrogen gas into the combustion chamber, where it mixes with air. This mixture is then compressed by the piston, increasing its temperature and pressure. At the top of the compression stroke, a spark ignites the hydrogen-air mixture, leading to a rapid combustion process that generates high-pressure gases. This pressure pushes the piston down, converting the chemical energy into mechanical energy.

From a thermodynamic perspective, the combustion process is governed by the ideal gas law and the principles of thermodynamics. The heat released from the combustion expands the gases, resulting in a power stroke that propels the engine. This thermodynamic cycle characterizes the engine's efficiency, which is crucial for evaluating its performance. The thermodynamic efficiency is influenced by several factors, including combustion temperature, compression ratio, and combustion stability. Hydrogen's wide flammability range allows for operation

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Table 1 Recent reviews on hydrogen in ICEs

Ref.	Key aspect(s) of the study
34	Reviews application of hydrogen-enriched compressed natural gas (HCNG) spark ignition (SI) ICE, focusing on fuel properties through to performance and emission characteristics.
31	Reviews different ignition and injection methods and mechanisms of hydrogen ICE
32	Reviews backfire occurrences and detection, backfire-inducing factors, and control strategies for port hydrogen injection ICE
33	Provides an overview of hydrogen-fuelled ICE alongside its achievements and future challenges
35	Reviews hydrogen fuel blends in ICE. The fuels blended with hydrogen include gasoline, diesel, natural gas, and alcohols. The study focuses on developments in China
36	With a hydrogen-diesel dual-fuel compression-ignition engine, the study reviews the effect of combustion chamber geometry and mixing ratio on engine characteristics
37	Reviews the combustion, performance, and emission analysis of biogas and hydrogen on diesel engines in dual-fuel mode
38	Reviews hydrogen and the fuel's role in future ICE
39	Reviews the advancements made in hydrogen-fuelled ICE, focusing on aspects such as research and development (R&D)
40	In light of the PM-NO _x -BSFC trade-off challenges associated with diesel engines, the study reviews the overarching role played by hydrogen–EGR synergy as a promising solution
41	Reviews the effect of adding hydrogen and natural gas in diesel homogeneous charge compression ignition (HCCI) engines
42	Reviews the R&D of hydrogen-fuelled engines in China
This study	Reviews the prospect and roles of hydrogen in reaching net zero; reveals the evolutionary trends, research hotspots, and key countries/regions in hydrogen in ICE research since 2012 to date; challenges associated with hydrogen engines with potential solutions

under lean conditions, requiring less fuel to achieve complete combustion.⁵⁵ This lean-burn operation reduces the amount of unburned hydrocarbons and carbon monoxide emitted, leading to cleaner exhaust emissions.⁵⁶ Furthermore, hydrogen's high flame speed and low ignition energy enable faster and more efficient combustion than gasoline, resulting in higher thermal efficiencies.⁵⁷ Also, hydrogen's high specific heat capacity helps dissipate heat more effectively, improving engine cooling efficiency and overall thermal management.

The chemical reaction governing H2-ICEs is hydrogen oxidation with oxygen from the air, producing water vapor as the primary combustion product. This can be represented by the following simple chemical equation:

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(g) + energy$$

This reaction is highly exothermic, releasing much energy per unit mass of fuel burned. Unlike hydrocarbon fuels, which produce carbon dioxide and water vapor as combustion byproducts, hydrogen combustion produces only water vapor, making it a clean and environmentally friendly fuel option (Fig. 4). Hydrogen's rapid reaction kinetics result in a faster flame front propagation than hydrocarbon fuels, necessitating precise control over the timing and rate of combustion to prevent engine knock and ensure efficient operation.⁵⁸

Hydrogen possesses key fuel properties that make it suitable for combustion in engines. The research octane number (RON) measures a fuel's resistance to knocking in spark-ignition (SI) engines. While hydrogen combustion does not produce knock in the same way as gasoline, understanding the concept of octane rating is still relevant for comparing the anti-knock properties of different fuels. 60 In the context of hydrogen engines, the absence of knock allows for higher compression ratios, which can improve thermal efficiency and power output. However, excessively high compression ratios can lead to other combustion issues, such as pre-ignition and backfiring, necessitating careful engine design and tuning.61 Brake-specific fuel consumption (BSFC) is the mass

fuel consumption of the engine per unit power output, and it is mainly affected by the lower heating value of a fuel.⁶² The lower heating value of hydrogen of 120 MJ kg⁻¹ would imply that the BSFC of a hydrogen-fuelled ICE would be lower than BSFC in engines fuelled by alternatives such as methane (50 MJ kg⁻¹) and iso-octane. Also, the ratio of the work performed by an engine to the heat supplied to the engine represents the efficiency of the engine, also known as brake thermal efficiency (BTE). In other words, it is the inverse of the product of lower heating value of the fuel and the BSFC.63 As such, a lower BSFC and higher heating content of hydrogen will give a hydrogen-fuelled engine a higher BTE compared with alternatives such as methane and isooctane.

Hydrogen engines and nitrogen oxides emissions

The formation of NO_x during the operation of H2-ICEs is a significant environmental concern, as NO_x are harmful pollutants that contribute to smog and respiratory problems.⁶⁴ Despite hydrogen's clean combustion properties, NO_x formation primarily occurs through thermal NOx, prompt NOx, and potentially fuel NO_x mechanisms. Thermal NO_x is predominant and results from high-temperature reactions between atmospheric nitrogen (N2) and oxygen (O2), described by the Zel'dovich mechanism:65

$$\begin{array}{ll} N_2 + O & \leftrightarrow & NO + N \\ \\ N + O_2 & \leftrightarrow & NO + O \\ \\ N + OH & \leftrightarrow & NO + H \end{array}$$

These reactions are relatively significant at temperatures >1623 K and are common in hydrogen engine operations.⁶⁶ Prompt NO_x, though less relevant in pure hydrogen combustion, can arise from hydrocarbon impurities, while fuel NO_x occurs if

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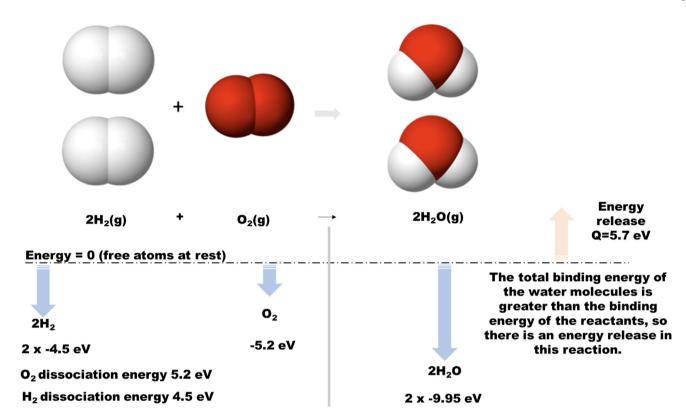


Fig. 4 Chemical process of hydrogen combustion. Re-drawn from ref. 59.

nitrogenous compounds are present in the fuel.⁶⁷ The severity of NO_x emissions is influenced by operational conditions such as combustion temperature, chamber pressure, and fuel purity.

The formation of thermal NO_x increases exponentially with temperature. In hydrogen engines, peak temperatures can be high due to the fast and intense combustion of hydrogen, 65 thus potentially leading to higher NO_x emissions. However, higher pressures in the combustion chamber can also promote NO_x formation by increasing the rate of reactions involved in the NO_x production pathways. 66 Additionally, impurities such as hydrocarbons or nitrogen compounds in the hydrogen fuel can increase NO_x production. Hydrocarbons contribute to prompt NO_x through radical mechanisms, whereas nitrogenous compounds directly add to the NO_x output through fuel NO_x mechanisms. Minimizing NO_x emissions requires careful control of combustion parameters, such as air–fuel ratio and ignition timing, as well as using exhaust gas recirculation (EGR) and selective catalytic reduction (SCR) technologies. 68,69

4. Research methodology

On the 10th of December, 2022, we set out to investigate the evolutionary trends and research hotspots of hydrogen in ICE research in the last decade. In the past, previous authors have used various databases, such as Scopus, Web of Science, PUBMED, CNKI, *etc.*, to retrieve scientific documents for bibliometric analysis. In our study, we have adopted the Web of

Science Core Collection (SCI-EXPANDED) database to collect documents published on hydrogen combustion in ICEs in the last decade. Using a combination of Boolean functions, the following search query was made (TS = (hydrogen AND ("internal combustion engine" OR "compression ignition engine" OR "spark ignition engine" OR "diesel engine" OR "gasoline engine"))) NOT KP = ((hydrogen AND ("internal combustion engine" OR "compression ignition engine" OR "spark ignition engine" OR "diesel engine" OR "gasoline engine"))). The search query was done to retrieve documents based on information from title, abstract, and author keywords and not keyword plus (KP), as previously also done in the work of Sillero et al. 70 The articles were searched to only include those published from 1st January, 2012 to 31st December, 2023. Document types such as reviews, conference proceedings, early access, etc., were excluded, to only include articles. Following this, 1385 articles were retrieved. However, some of these articles were outside the current study's objectives. Articles in which hydrogen has not been experimentally/ numerically/simulated/computationally combusted in an ICE or where the hydrogen-fuelled ICE is not a critical aspect of the analysis were manually deleted. This was done by reading articles' titles and abstracts. Following this, 764 articles remained for the analysis of this study.

To analyze and visualize the study results, the R-Statistical package, Bibliometrix (Biblioshiny), was adopted. Biblioshiny is a tool for creating interactive bibliographies using the Shiny framework in R.⁷¹ The research results obtained from

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Biblioshiny for the present study include research hotspots, topic trends, thematic evolution, and thematic maps. We also reviewed the knowledge domain based on our obtained results alongside that of previously published results to discuss the past, current, and future research development/direction in hydrogen-fuelled engine research. Table 2 summarizes key steps taken to obtain documents relevant to achieving the research objectives.

5. Research hotspots, trends, and frontiers

5.1 Research hotspots

Author keywords serve as key indicators in bibliometric analysis, reflecting the focus of research within a field as illustrated in Fig. 5 through a word cloud. Our results indicate that

the existing research primarily targets the performance, emission, and combustion characteristics of hydrogen in ICEs, crucial for evaluating its potential in decarbonizing transportation. Key areas of past and current research interest include optimizing thermal efficiency, managing fuel consumption, and reducing NO_x emissions. Additionally, researchers have been focused on combustion anomalies like backfire and knocking, alongside strategies for combustion and emission control, such as water injection, lean combustion, and exhaust gas recirculation. Existing studies have also focused on the role played by alternative fuels, including methane, natural gas, biogas, biodiesel, ammonia, and methanol, and explore dual-fuel operation.

In this section, we briefly discuss some of these hotspot areas supported by results from previous studies.

Concerning performance, thermal efficiency and fuel consumption are the two most investigated characteristics.

Table 2 Steps taken to retrieve, analyze, and interpret results

Steps	Comments (selection/strategy)
Database	Web of Science core collection (SCI-EXPANDED)
Topic search strategy	A combination of hydrogen with various synonyms of ICE using Boolean functions (AND/OR). Search was done across topic, abstract, author keywords
Period	1st January, 2012 to 31st December, 2023
Document type	Only primary research articles
Initial documents obtained	1385
Manual refining	Manually excluded articles where hydrogen has not been experimentally/numerically/ simulated/computationally combusted in ICE or where hydrogen-fuelled ICE is not a critical aspect of the analysis
Final documents obtained	764
Data analysis	R statistical package (Biblioshiny)
Key results	Research hotspots, topic trends, thematic maps

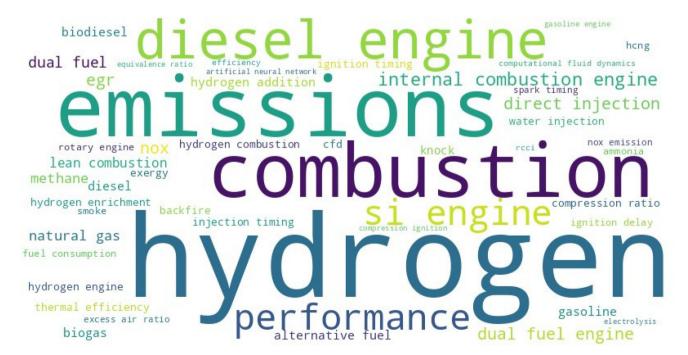


Fig. 5 Research hotspots of hydrogen-ICE in the last decade.

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Thermal efficiency and fuel consumption are important factors in determining the economic performance and overall efficiency of an engine. These can be improved by optimizing the combustion system/mode or the properties of the fuel being used.⁷² Researchers have, in previous studies, shown that the hydrogen-fuelled ICE can achieve higher BTE than a gasoline-fuelled ICE. Shivaprasad et al. 72 report that the BTE of an engine operating with hydrogen enrichment is higher than that of an engine running on pure gasoline at all engine speeds. Additionally, BTE increases significantly as the proportion of hydrogen in the fuel mixture increases. Kahraman et al. 73 also show that the BTE is improved to about 31% with hydrogen-fuelled engines compared with gasoline-fuelled engines. The improvement in BTE is due to the more uniform mixture formation and faster flame speed of hydrogen, which leads to more complete combustion and higher BTE under all load conditions. 74 The concept of hydrogen energy share (HES) quantifies the contribution of hydrogen to the overall energy output of an engine or powertrain system. In a pure hydrogenfuelled engine, the HES is 100%, indicating that all of the energy output is derived from hydrogen combustion. In hybrid systems that use multiple fuel sources, such as hydrogen and gasoline, the HES represents the proportion of energy sourced from hydrogen relative to the total energy output. Understanding the HES is important for evaluating the environmental and economic benefits of hydrogen-powered systems, as well as for optimizing engine performance and efficiency. In the work of Kumar et al., 75 as depicted in Fig. 6, there was a significant increase in BTE due to hydrogen induction when Madhuca longifolia oil (MO) was used as the pilot fuel. The BTE was found to increase with an increasing HES. The highest BTE recorded was 28.5% at a HES of 15%. However, BTE decreased with hydrogen induction when the HES exceeded 15% (which is the maximum efficiency point). The reduction of BTE with hydrogen induction beyond this point is a result of the occurrence of knocking combustion associated with the dual-fuel engine at high HES.

The results have also revealed that the most investigated emission characteristics of hydrogen-fuelled ICEs in the last decade have been NOx emissions. A major disadvantage of hydrogen-powered engines is the high NO_x emissions, which harm the environment. Zel'dovich's original work showed a strong correlation between combustion temperature and the formation of thermal NO during combustion. Put in simple terms, more NO is produced at high combustion temperatures. NO_x formation becomes a concern when the peak combustion temperature exceeds 2200 K. As the proportion of hydrogen in the fuel mixture increases and combustion improves, the temperature also increases, leading to an increase in NOx emissions.⁷⁴ Various strategies are being developed aiming at a solution to this high NO_x-related problem in hydrogenfuelled ICEs. Some of these strategies include using EGR,⁷⁶ addition of inert gases, varying compression ratio, swirl and injection timing,77 water injection,78 lean combustion,79 and so on. It is important to note that in a hydrogen-fuelled ICE, there are significant trade-offs to consider. By using a lean

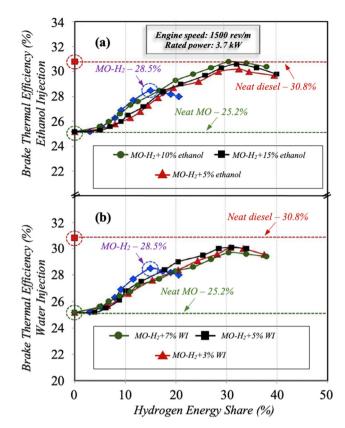
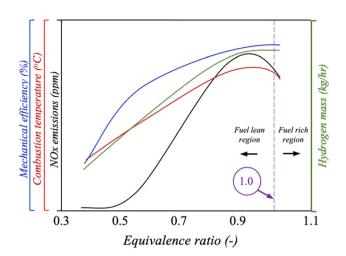


Fig. 6 Variation of BTE with different (a) ethanol injection amounts (b) water injection amounts. MO: Madhuca longifolia oil. Re-drawn from ref. 75.

combustion mode, it is possible to reduce thermal NO, but on the other hand, energy output, which is a reflection of the mechanical power of the ICE, may be reduced. This creates a confusing situation for engine designers, who must choose between either maximizing fuel efficiency and performance of the engine at high NO emissions or controlling NO emissions at a compromised performance level. These trade-offs in the hydrogen-ICE are illustrated in Fig. 7.80

Recent studies have also focused on controlling hydrogen combustion anomalies such as backfire and knock. In hydrogen-fuelled engines, one of the forms of pre-ignition is backfiring, and it occurs during the suction stroke. Backfire is characterized by the combustion of fresh charge in the intake manifold and/or combustion chamber of the engine during the intake (suction) stroke,81 which, when left unattended, can potentially cause significant engine damage. Also, combustion knock can occur during backfiring as a result of the elevated intake temperature in a cycle with backfire.82 Knocking, also known as pre-ignition or detonation, is a phenomenon that occurs in the ICE when the fuel-air mixture in the combustion chamber spontaneously combusts before the spark plug ignition event. With a hydrogen-fueled ICE, knocking combustion can frequently have serious impacts due to the rapid burning speed of the hydrogen mixture.³³ Despite hydrogen's high research octane number (RON) of 140, typically higher



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Fig. 7 Correlation between mechanical efficiency, combustion temperature, and NO_x emissions with respect to the equivalence ratio. Redrawn from ref. 80.

than other fuels, hydrogen's anti-knock performance is low.83 Methane number (MN) is another index for measuring the explosion resistance of gaseous fuels,84 and this value is 0 for hydrogen, explaining the fuel's proneness to knocking.85 Knocking can be harmful to the engine and can lead to reduced engine performance and lifespan. Previous studies have reported various strategies for preventing backfiring and knocking: cold-EGR for reducing the in-cylinder temperature, consequently preventing backfire, 86 water injection leading to a reduction in hotspot and thus avoiding backfire, 87 retarded spark timing and delayed injection timing of the engine, 81 addition of ammonia to increase the ignition delay time of the final blend to control knocking in the hydrogen-fuelled ICE, 85 and so on. In a cycle-based analysis by Dhyani and Subramanian, the authors found that due to backfire, the peak in-cylinder pressure reduces to 25 bar (motoring value). Combustion anomalies were, however, eliminated with the introduction of EGR and water injection (see Fig. 8).⁷⁸

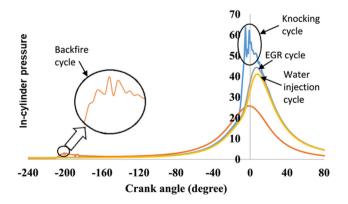


Fig. 8 Control of combustion anomalies with EGR and water injection. Re-drawn from ref. 78.

There has also been ongoing research in recent years involving blends of hydrogen together with other alternative fuels. The overarching objective is to enhance the operation and output of the ICE. Some of the most researched alternative fuels in such cases include methane, natural gas, biogas, biodiesel, ammonia, and methanol. In an engine adapted to run in dual-fuel mode (diesel as the pilot fuel and biogas as the main fuel, respectively), Verma et al.88 demonstrate that the addition of hydrogen (10-20%) improved the dual-fuel engine's performance and emission characteristics. Similar trends in results have been reported in hydrogen-biodiesel,89 hydrogen-methanol/ethanol/butanol, hydrogen-methane. 27 hydrogen-enriched compressed natural gas (HCNG) mixtures, 91 and so on. The studies show that certain limitations associated with alternative fuels can be addressed when they are combusted together with hydrogen. To mention a few, compared with other fuels, biogas, for instance, shows excellent features as an ICE fuel, especially in the areas of life cycle emissions and resource efficiency. 92 However, the low calorific value and flame speed of biogas cause poor performance and emission characteristics when used as an ICE fuel. The addition of a few percentages of hydrogen to the biogas mixture can remedy the situation due to hydrogen's high diffusivity and flame speed, which compensates for that of biogas and promotes the combustion of the resulting blend. 88 Due to its high-octane rating (120-130), natural gas has excellent fuel properties conducive to increasing compression ratios without risk of detonation, resulting in thermal efficiencies similar to those of a gasoline engine. There are, however, some drawbacks with methane as a fuel regarding its relatively low flame propagation velocity, which can result in incomplete combustion, increased cycle-by-cycle variations, and occasional flame failure during lean combustion mode.93 Lower emissions are attainable when hydrogen is added to natural gas, as the blend results in the extension of the lean limit of combustion. Prasad and Kumar⁹⁴ set out to investigate how hydrogen can compensate for the drawbacks of methanol when the two fuels are blended and used in the ICE. Their results revealed improvements in BTE, brake power (BP) and brake-specific energy consumption (BSEC) values (see Fig. 9) due to an increase in hydrogen enrichment. A 20-30% increase in BTE was recorded, but hydrogen addition beyond 12.5% negatively affected volumetric efficiency causing reduction in performance afterwards. Hydrogen enrichment had huge impact on exhaust emissions such as CO, hydrocarbons, and CO2, with reductions between 30-40%. Nonetheless, a slight increase in NO_x emissions was observed as a result of the increase in cylinder temperature due to rapid combustion.

Finally, based on our search strategy and the subsequent results, we speculate that the hydrogen-fuelled diesel engine has received relatively more attention than the hydrogen-fuelled gasoline engine. As mentioned earlier, a key role played by fuels such as hydrogen in the ICE is to help decarbonize transport sectors that are hard to decarbonize *via* direct electrification by battery or grid. Diesel engines are more compatible with long-haul trucking and international shipping/

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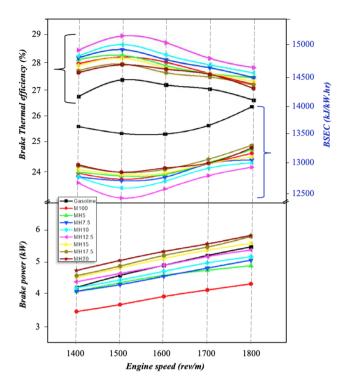


Fig. 9 Effect of engine speed on BP, BTE, and BSEC of various test fuels. Re-drawn from ref. 94.

aviation, and these transportation types require highly dense fuels such as hydrogen. In terms of mass and volume, hydrogen has a significantly higher energy density than batteries. This property allows for hydrogen vehicles to have more storage capacity and better driving range. By extension of these benefits, passenger cars, vans, trucks, buses, and other means

of transport can easily run on hydrogen fuel cells or hydrogenfuelled ICEs. 95 Therefore, it is reasonable for more investigations on the hydrogen ICE to focus on using hydrogen in diesel engines to decarbonize some of these hard-to-abate transport sectors.

5.2 Topic trend and thematic evolution in the last decade

As the name implies, topic trend analysis is a means of putting a chronological characteristic to an ongoing research field. It is also analyzed here with author keywords, but shows the period when a particular term received the 'most' attention from the scientific community (with emphasis on 'most' implying that the term showed some occurrences in other years, albeit not dominant like the captured years). It can be a way of telling between emerging (recent) and declining trends.

In Fig. 10, the topic trend of hydrogen-fuelled ICE research since 2012 is presented. Interesting trends to report on include optimization, injection timing, ignition timing, EGR, dual-fuel engine, NOx, HCNG, and electrolysis.

Recent studies are increasingly paying much attention to optimization in hydrogen-fuelled ICEs. The goal of optimization techniques in engines is to improve the performance and efficiency of the engine while also reducing the emissions, costs and duration of experimental studies. 'Optimization' can also refer to various types of optimization techniques for controlling backfire in hydrogen engines, such as optimizing valve timing, optimizing fuel injection and ignition timing, intake system optimization, and ignition and fuel injection system optimization.³² The following are some of the latest studies on hydrogen-ICE optimization: exhaust emissions, vibration, and noise;⁹⁶ performance and emissions;^{97,98} control of ignition system;99 intake and exhaust phases.100 It also appeared that

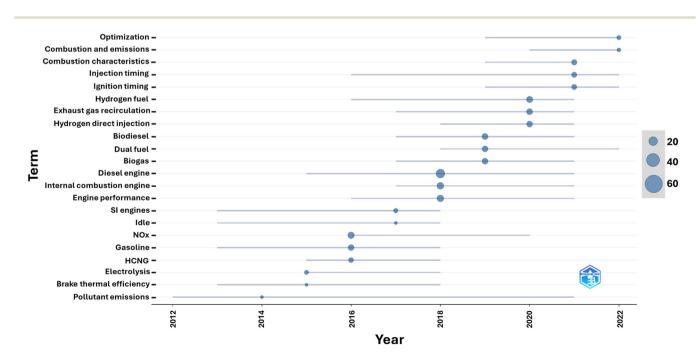


Fig. 10 Trend topics of hydrogen-ICE in the last decade.

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the response surface methodology (RSM) and Taguchi method are the most used optimization techniques in the ongoing studies. Details of optimization techniques in ICE research can be found in the work of Yu et al. 101

In gasoline engines, the ignition timing has a critical influence on the formation of flames, the early stages of combustion, and the emissions produced. 102 To achieve better engine performance, it is important to carefully check and optimize ignition timing when using alternative fuels in engines. 103 The research on the effect of spark timing on the performance of hydrogen engines as investigated by Shi et al. 104 has shown that there is an initial rise followed by a decrease in BTE with the advanced spark ignition angle. NOx, hydrocarbon, and CO emissions tend to decrease when the ignition timing is postponed. In the work of Su et al. 105 on the effect of ignition timing on the performance of the hydrogen-enriched engine under lean combustion, the authors report that as ignition advance increased, the flame propagation period shortened while the flame development period was delayed. Advancing ignition caused cyclic variation to initially weaken, with subsequent deterioration. In addition, by retarding ignition timing, hydrocarbon and NO_x emissions decreased. On the other hand, another parameter that significantly influences the combustion and exhaust emissions of a diesel engine is the injection timing. By varying injection timing, the state of air into which the fuel is injected varies as well, and thus, ignition delay varies accordingly. At an early injection, the initial air temperature and pressure are lower, and this prolongs ignition delay; the reverse occurs at a late injection. Therefore, the variations in maximum pressure and temperature in the engine cylinder due to variations in the injection timing do have a strong influence on the engine performance and exhaust emissions. 106,107 Using numerical simulation, Ye et al. 108 have also studied the relationship between injection timing and knock characteristics in direct injection (DI) engines. They revealed that with an advance in injection timing, both mixture homogeneity and flame speed increase. Also, since early injections help increase knock resistance, they suggest setting it between -108 and -88° after top dead center (ATDC). Also, in their experiment on the influence of hydrogen injection timing on lean combustion in a natural gas/hydrogen dual-fuel injected SI engine, Zhang et al. 109 reported that by delaying the direct injection timing of hydrogen, advanced combustion phase and higher heat release rate were observed which led to an increase in thermal efficiency. The diesel fuel injection timing and HES ratio are closely related to the increase in in-cylinder pressure and the generation of NO_x. There is the likelihood of rapid pressure rise in the combustion chamber and greater formation of NO_x at an early fuel injection. The NO_x emissions can be significantly reduced by retarding the fuel injection close to or after the TDC; however, one should expect a decrease in thermal efficiency with this technique. However, as seen in Fig. 11, the amount of hydrogen fuel also affects the pressure rise and NO_x generation, with greater hydrogen rates producing more NO_r. 110,111

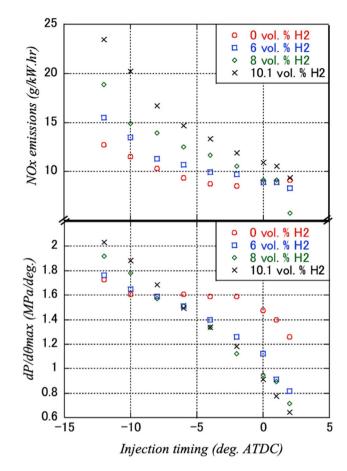


Fig. 11 Variations of NO_x and $dP/d\theta_{max}$ with diesel fuel injection timing for different hydrogen fractions. Re-drawn from ref. 110 and 111.

As has been previously discussed, the sole pollutant of concern released by a hydrogen-fuelled engine is NO_x, 112 and the EGR is one of the well-known and still relevant strategies in reducing NO_x in engines. It works by routing a portion of the exhaust gases back into the engine's intake manifold, where they are mixed with the incoming air-fuel mixture. This means less oxygen reaches the cylinder, and less oxygen implies a lower combustion temperature leading to a significant reduction in NO_x emissions. In gasoline engines, this can also reduce CO2 emissions and fuel consumption. Results on emissions of the hydrogen/diesel dual-fuelled engine with EGR are shown in the work of Nag et al. 113 According to their work, the cumulative decrease for NOx, CO2, CO, total hydrocarbons, and particulate matter was stated to be 38.4%, 27.4%, 33.4%, 32.3%, and 20%, respectively, with a 30% hydrogen share and 10% EGR. Furthermore, Vijayaragavan et al. 114 report that blending diesel-biodiesel with hydrogen led to an 18.13% increase in NO_x emission compared with that of neat diesel. Nonetheless, the addition of EGR guarantees a 19.07% drop in in-cylinder temperature, which significantly lowers NO_x emissions. The simultaneous use of EGR and hydrogen also resulted in a substantial decrease in CO, CO2, and smoke emissions. Mariani et al. conducted a numerical simulation on SI

engine performance fueled with HCNG blends. Based on con-

ditions that reproduce an engine operating in a passenger vehicle over the New European Driving Cycle (NEDC), several simulations were conducted. Due to the higher in-cylinder gas temperatures NO_x emissions increased by about 4%, 11%, and 20% for HCNG 10, HCNG 20, and HCNG 30, respectively. With the introduction of 10% EGR for HCNG blends, NO_x emissions significantly reduced to about 80% compared with the case of no EGR. The inclusion of EGR also showed a positive impact on engine efficiency (see Fig. 12).115

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One of the key approaches for simultaneously achieving high thermal efficiency and lower harmful emissions is dualfuel technology which can combine the benefits of two fuels. The operation of a dual-fuel engine is such that there is a primary fuel and a secondary (pilot) fuel. The primary fuel is injected into the intake manifold and it is typically a gaseous fuel such as hydrogen, syngas or natural gas. On the other hand, the pilot fuel is used to ignite the mixture and it is injected into the combustion chamber. 116 Direct use of hydrogen in diesel engines is limited by the high self-ignition point of hydrogen fuel. It is important to have in place an igniter energy source to deal with the situation. On the other hand, compared with diesel fuel, hydrogen has superior properties such as high flame speed, wide-range ignition limits, narrow flame extinction region and high diffusion coefficient. Hence, as a result of a more homogeneous charge, lower emissions coupled with better performance are achieved using hydrogen in diesel engines as dual fuel. 117 Also, hydrogen as a dual fuel in compression ignition engines offers an in situ solution to performance and emission trade-off challenges associated with traditional diesel combustion in the presence or absence of EGR.40

Compressed natural gas (CNG) is an attractive fuel for use in the ICE due to its lower carbon-to-hydrogen ratio. However, a CNG-fuelled ICE negatively affects vehicle economy and exhaust emissions due to its sluggish combustion characteristics. Gasoline engines fuelled with CNG have low engine

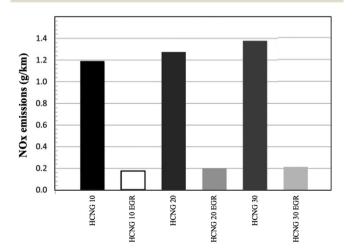


Fig. 12 Influence of no and 10% EGR on NO_x emissions over the NEDC for HCNG blends. Re-drawn from ref. 115.

efficiencies at low load conditions and extreme emissions of HC and CO which can only be solved with costly after-treatment technologies. 118 But due to the excellent combustion characteristics of hydrogen, such as its fast flame propagation speed and wide lean flammability limit, the blends of hydrogen and CNG (HCNG) have an improved combustion phenomenon. 119,120 Several studies have revealed that adding hydrogen to CNG to make HCNG leads to an improved BTE as well as reduced BSFC and cycle-to-cycle variations. Similarly, emission characteristics like CH4, CO, CO2, and total hydrocarbons significantly reduce. Compared with CNG-only operation, engines fuelled with HCNG work at higher compression ratios without any combustion instabilities. For optimum operation of a spark ignition engine, various studies suggest a hydrogen enrichment at 20-30%. 121

Another interesting trend in the last decade in hydrogen-ICE research involves electrolysis. Electrolysis's trend in hydrogen-ICE research can be attributed to two main factors. First of all, though hydrogen is a green fuel, its production can vary depending on the feedstock and technology and as such there is a varying degree of environmental impact associated with each production pathway. Currently, fossil-based hydrogen (coal and natural gas) dominates the market, and to truly achieve net zero targets, green hydrogen production via electrolysis is the way forward. From a well-to-wheel perspective, combusting green hydrogen in the ICE should result in a lower environmental impact than that of brown or grey hydrogen. Thus, researchers in this field are increasingly paying attention to electrolysis to reap the full benefits of transitioning from traditional fuels to hydrogen in ICE applications. More details of such works can be found elsewhere. 122,123 Secondly, through water electrolysis, a carbon-neutral fuel other than hydrogen can also be produced, known as oxy-hydrogen gas (HHO) or brown gas. It has been suggested that this fuel could be a promising complementary fuel to hydrogen, as the current state of green hydrogen production and storage may not be enough for the requirements of a carbon-free transport application. 124 There is also growing interest in this fuel for combustion in engines. Zhao et al. 125 demonstrated how the combination of HHO and EGR with gasoline direct injection may significantly improve an engine's combustion and emission characteristics. It was seen in the work of Subramanian and Thangavel¹²⁶ that when compared with neat diesel operation, using hydrogen and HHO gas in the engine coupled with diesel provides better results in terms of emission reduction. More details of the effect of HHO in the ICE can be found elsewhere. 127-129

Fig. 13 represents the thematic evolution of the research field in the last decade, from 2012-2019 and 2020-2023. It can be seen that some themes have been constant throughout the first seven and last three years. Such themes can be categorized as core research themes in the field, and they are still undergoing development to shape the future of hydrogen in ICE research. Some themes have also evolved to new thematic areas, and such themes can be categorized as 'new' frontiers for the future development of the field. It should be noted that

2012-2019 2020 - 2023

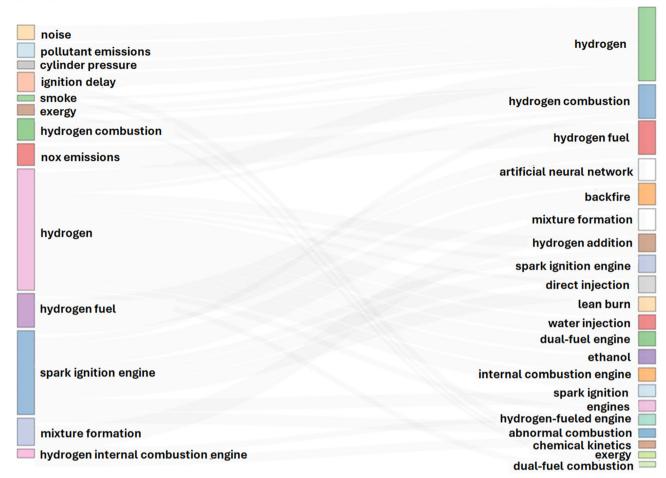


Fig. 13 Thematic evolution of hydrogen-ICE research from 2012-2019 and 2020-2023.

some of these 'new' themes in the last three years might have also featured in earlier studies, albeit with less frequency or attention. Based on the results, we believe that while earlier research primarily focused on performance and emission characteristics of the hydrogen-fuelled ICE, recent studies are increasingly paying more attention to combustion and emission control strategies.

Finally, Fig. 14 represents a thematic map of the field based on the top 100 themes (words). A thematic map is divided into four quadrants, *i.e.*, motor, basic, niche, and emerging or declining themes. More details about these quadrants have been explicitly explained in Cobo *et al.*, ¹³⁰ but briefly, motor themes contain the central and developed themes in the field. Themes in this quadrant are well developed and very relevant to the progress of the field. Basic themes, on the other hand, are similar to motor themes, with the only difference being that the former is relatively less developed; there is more room for themes in this quadrant to continue developing. However, they are very relevant themes upon which the field is advancing. Themes in the niche quadrant are opposite to themes in the motor quadrant, in the sense that niche themes have high

development but their relevance to the field is somewhat marginal, unlike basic and motor themes. The niche themes are basically playing supporting/peripheral roles in shaping the progress of the field. Last but not least, the lower left quadrant represents themes that are either emerging or declining. Themes located in this quadrant have relatively low development and relevance. As the research field progresses, these themes, if emerging, could become critical to the field's advancement. Based on the given information and results plotted in Fig. 14, one can appreciate the role played by each theme in the development of hydrogen-fuelled ICE research in the last decade.

6. Challenges and potential solutions facing hydrogen as a net zero fuel

Hydrogen is poised to play a pivotal role in the global quest to achieve net-zero emissions by mid-century, a crucial target aligned with limiting global warming to 1.5 °C. According to estimates, hydrogen could contribute a substan-

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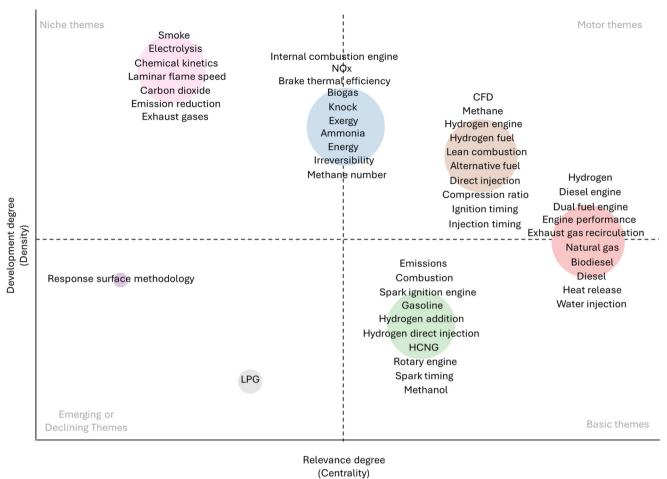


Fig. 14 Thematic map analysis of hydrogen-ICE research in the last decade. Each node represents the major subject/topic areas of the field. From top to down, the development of the thematic areas of the field reduces in terms of the level of development or advancements made in the last decade. From left to right, the relevance of the thematic areas of the field increases in terms of how important and relevant the area is in shaping the direction of advancement in the last decade.

tial 12-22% of the global total final energy demand by 2050, 15,30 primarily in sectors deemed challenging for direct electrification. 26,131,132 The International Renewable Energy Agency (IRENA) has further estimated that around 10% of the mitigation efforts required to deliver the 1.5 °C target by 2100 could be realized through the deployment of hydrogen. 133

However, the successful realization of these ambitious hydrogen targets hinges upon several critical factors. These include the existing policy landscape governing hydrogen, the economic feasibility and cost-competitiveness of hydrogen technologies, market acceptance and adoption rates, and the maturity of the underlying technologies.

6.1 Hydrogen supply chain

The issue of technology maturity for the hydrogen supply chain needs to be addressed in the coming years. Within the supply chain, some essential technologies required for decarbonization have a relatively lower technology readiness level and are not proven at commercial scale. For example, in the maritime trade environment, currently only one prototype

vessel exists that can transport liquid hydrogen. ¹⁵ Additionally, while water electrolysis can provide carbon-free hydrogen, it only accounts for 0.1% of total hydrogen production today. 134 In the next decade, this situation must change through increased research and development funding as well as policy frameworks that could bridge the gap between mature and emerging technologies within the hydrogen value chain.

The urgency to meet global climate targets has prompted several countries to announce ambitious domestic net-zero emission goals. However, a limited number of countries have explicitly incorporated targets for hydrogen deployment within their existing net-zero policies and long-term strategies. As we move forward, it becomes increasingly crucial for more nations to announce concrete plans for integrating hydrogen into their decarbonization strategies. In this regard, the hydrogen strategies put forth by major economies such as China, the European Union, the United States, and India could serve as valuable blueprints for other countries to emulate. 135-139 These comprehensive frameworks outline key objectives, implementation pathways, and supporting mechanisms taiGreen Chemistry Critical Review

lored to each nation's unique circumstances, offering a robust foundation upon which others can devise their own contextualized hydrogen strategies.

Cost remains a limiting factor for net-zero greenhouse gasemitting technologies and fuels such as hydrogen. Currently, high-carbon fuels are still relatively cheaper to consume compared with clean hydrogen, especially green hydrogen. 15 In fact, zero/low-carbon hydrogen variants like green and blue hydrogen are markedly more costly than conventional grey hydrogen. The production cost of green hydrogen ranges from \$2.5 to \$5 per kilogram, while blue hydrogen costs span \$1.50 to \$3.50 per kilogram. In contrast, grey hydrogen has a relatively inexpensive cost of approximately \$1.50 per kilogram. 140 This cost difference is not only limited to production but also applies to costs for transporting, converting, and storing hydrogen. With the rapid decline in costs of renewable energy technologies, 141,142 electrolysis for hydrogen production is expected to become more cost-competitive. Financial support would also be required for the development and scaling of carbon capture and storage (CCS) technologies to aid blue hydrogen production. Before 2030, economy-wide carbon pricing could be an effective approach¹⁴³ to increase the cost of grey and brown hydrogen, making them less economically attractive. With economies of scale, hydrogen technologies could become less costly. Otherwise, a chicken-and-egg problem emerges in building out the necessary infrastructure for hydrogen, i.e., investment may continue to be risky for large and wide-scale hydrogen production that may reduce costs, but the costs of hydrogen technologies will also remain high without economies of scale.¹⁵

Hydrogen storage and transport present significant challenges that must be addressed for widespread adoption of hydrogen as a fuel. Currently, the low volumetric energy density of hydrogen poses difficulties in storing and transporting large quantities efficiently. 144 Liquefaction or compression is necessary, which requires substantial energy inputs and specialized infrastructure. 145 To resolve these challenges, research and development efforts are underway to explore innovative storage solutions, such as solid-state hydrogen storage materials 146,147 and advanced cryogenic tanks for liquefied hydrogen. 145,148,149 Researchers are also investigating innovative materials like metal hydrides, carbon-based substances, metal-organic frameworks (MOFs), and nanomaterials for storing hydrogen more effectively. These materials are designed to improve storage capacity, speed of storage and release, and safety standards. 150 Utilizing the current gas pipeline network for hydrogen transportation is generally unfeasible without infrastructure modifications. Existing physical constraints, such as steel embrittlement, degradation of seals, compressor station reinforcements, and valves, necessitate retrofitting during the conversion process to enable hydrogen distribution, or require the construction of new dedicated pipelines. Alternatively, hydrogen could be transported in liquefied gaseous form or as liquid organic hydrogen carriers like ammonia. Additionally, the development of more efficient liquefaction processes (such as the

Claude cycle and Brayton refrigeration cycle)¹⁵¹ and re-purposed pipelines (with (1) new smooth line pipes, (2) minimized inner surface roughness, (3) moderately lower load capacity, and (4) shortened transport intervals)¹⁵² for hydrogen transport could improve the overall system efficiency and reduce costs.

Once the aforementioned technical challenges are resolved, market acceptance for hydrogen-based solutions could substantially improve. Consumers, industries, and businesses would likely be more willing to embrace these alternative energy carriers as a viable substitute for traditional fossil fuels. However, in countries lacking universal access to electricity, coupled with an absence of refueling infrastructure and negligible experience incorporating hydrogen and its derivatives into the energy mix, convincing the driving populace to adopt fuel cell vehicles will prove difficult. Nonetheless, as cost competitiveness improves, reliability increases, ease of use is enhanced, and other technical hurdles disappear, sales of these vehicles could surge, especially under government policies phasing out or banning fossil fuel-based ICEs. Critically, raising public awareness about the environmental benefits of hydrogen as a fuel, while simultaneously addressing safety concerns, will be paramount in shaping positive perception and driving widespread market adoption of hydrogen technologies.153

6.2 Applying hydrogen as an ICE fuel

Most discussions on hydrogen-fuelled engines focus on the advantages of the fuel and how it could play a key role in decarbonizing the transport sector. However, it is also important to stress that hydrogen as a fuel in the ICE presents certain key setbacks. There are several challenges related to the fuel that need to be overcome to make it the ideal transport fuel for ICE application.

First of all, as discussed previously, combustion anomalies are common characteristics of the hydrogen-ICE. Hydrogen's large flammability range and low ignition energy is a precursor to pre-ignition.³⁸ Pre-ignition is often caused by hot spark plug components, hot exhaust valve head surfaces, hot combustion gases, and combustion that takes place in the crevice volume between the piston and cylinder.³³ To reduce the occurrence of pre-ignition, several combustion techniques have been highlighted by Stępień.³³ The combustion anomalies of knock and backfire of the hydrogen-ICE, when left uncontrolled, could potentially damage the engine's durability and efficiency. The appropriate control measures for dealing with the aforementioned precursors of backfire in hydrogen engines are depicted in Fig. 15.³²

Furthermore, despite certain excellent fuel properties of hydrogen, there are other unfavorable qualities, like low quenching distance, that exacerbate wall thermal losses.³⁸ Hydrogen can also pose safety issues; the fuel can easily ignite and even cause an explosion due to its wide combustion range and low ignition energy.³¹

Today, in the hydrogen ICE, it is difficult to simultaneously achieve high efficiency, low emissions, adequate specific power

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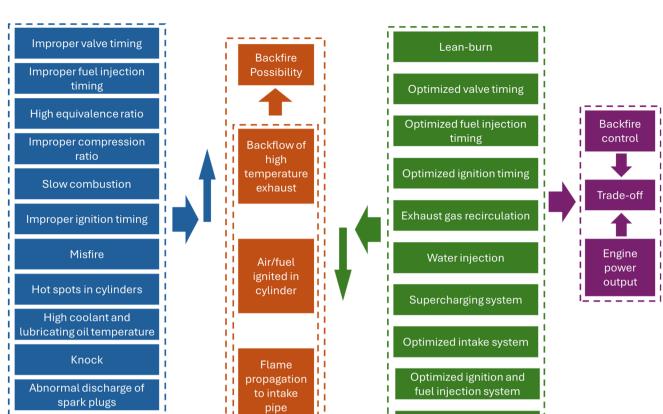


Fig. 15 Control measures for various factors of backfire in hydrogen engines. Re-drawn from ref. 32.

output and durability. Two of the most investigated mixture formation concepts for hydrogen are port fuel injection (PFI) and DI spark-ignited. In PFI, it is possible to simultaneously achieve excellent load efficiency and ultra-low emissions but

Crevices in cylinders

the power output is low. On the other hand, studies have shown that the DI engines are characterized by very high efficiencies and controllable emissions. However, these DI engines require DI injectors, and these injectors have issues

Flame arrester

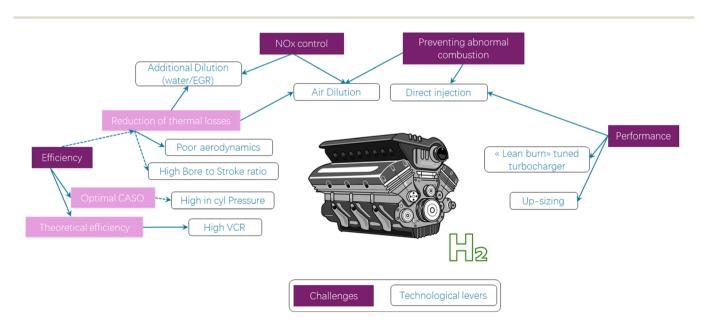


Fig. 16 Technological and control measures for addressing various challenges associated with hydrogen engines. Re-drawn from ref. 61.

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regarding durability. In addition, high injection pressures are needed to attain full freedom in optimizing injection strategies, and this limits on-board hydrogen storage options: either liquid hydrogen is stored in cryogenic tanks, or compressed hydrogen is stored. However, the efficiency advantages of DI engines could be negatively affected with compressed hydrogen on-board.³⁹ In other words, the demand for high-pressure injection can impact on-board hydrogen storage options and introduce additional challenges related to weight, space, and vehicle dynamics. The choice between PFI and DI technologies ultimately depends on the specific requirements of the application, balancing factors such as emissions reduction, power output, efficiency, and practical considerations related to on-board hydrogen storage and vehicle design.

Under optimum conditions, the use of hydrogen in diesel engines leads to a dramatic decrease in the emissions of hydrocarbons, CO, CO₂, and smoke, reaching reduction levels as high as over 50%. An increase in hydrogen addition rates promotes the combustion process, which is characterized by a sharp increase in heat release rate and BTE. However, owing to its high energy content, the combustion of hydrogen causes an increase in in-cylinder temperatures and proceeds to produce more NO_x emissions, especially at high load conditions. To compensate for the increased pressure and heat release rate due to hydrogen enrichment, the EGR is one of the most promising and investigated solutions. The EGR ratio is inversely proportional to the formation of NO_r emission. But this comes with a setback: a smoke, CO, and hydrocarbon emissions penalty is a key feature in an increase in EGR rates, as a result of the reduced levels of oxygen in the cylinder chambers. Nonetheless, when optimum conditions are configured, the hydrogen-fuelled engine together with EGR produces simultaneous reduction of all emissions in contrast to 100% diesel engines.110

To address these challenges, Fig. 16 illustrates several technological solutions that can be adopted to improve the benefits of the hydrogen-ICE while minimizing the challenges associated with it. 38,154

7. Conclusion

Hard-to-abate sectors, also referred to as difficult-to-electrify sectors, account for about 30% of all emissions. They require high-energy-density fuels and, as such, it is difficult to meet this requirement by direct electrification. Heavy trucking, international maritime, and aviation are examples of such sectors, and they require fuels such as hydrogen for deep decarbonization of the transport sector to be achieved. The internal combustion engine will play an essential role in the development and scale-up of hydrogen within the transport sector. As a contribution to the existing reviews on hydrogenfuelled engines, we investigate the research trend, hotspots, and evolutionary nuances of the hydrogen-fuelled ICE. The main conclusions from the present analysis are summarized below.

The analysis reveals that the main focus of researchers in this field in the last decade has been on investigating the performance, emission, and combustion characteristics of the hydrogen-fuelled ICE. In addition, some major research hotspots in the last decade include thermal efficiency, fuel consumption, NO_x emissions, combustion anomalies (such as backfire and knocking), combustion and emissions control strategies (such as water injection, lean combustion, and exhaust gas re-circulation), gaseous and liquid alternative fuels (such as methane, natural gas, biogas, biodiesel, ammonia, and methanol), and dual-fuel operation. Furthermore, the trend of results shows that most of the ongoing research in the last decade has been conducted mostly in diesel engines rather than gasoline engines, as diesel engines are more compatible with hard-to-electrify transport sectors such as longhaul trucking and international shipping/aviation and these transportation types require highly dense fuels such as hydrogen. Similarly, trending topics on hydrogen-fuelled ICEs within the last decade relate to areas such as optimization techniques, injection timing, ignition timing, EGR, dual-fuel engine, NOx, HCNG, and electrolysis. It is also worth noting that while earlier research primarily focused on the performance and emission characteristics of the hydrogen-fuelled ICE, recent studies are increasingly paying more attention to combustion and emission control strategies.

Using low-temperature combustion techniques, it is possible to achieve a high compression ratio which leads to similar or even better efficiency than conventional diesel engine alongside a lower level of emissions at least as good as that of gasoline engines. Researchers are very concerned with the NO_x and knocking of hydrogen engines, and going forward, extensive research is needed to assess whether low-temperature combustion techniques in hydrogen engines can lead to significant reductions in NO_x while improving anti-knocking operation. More studies are also required in the area of combining multiobjective optimizations and machine learning approaches for obtaining suitable multiple control methods that could minimize the penalties caused by backfire control measures. Extensive and in-depth works are also needed regarding the mechanism of hydrogen combustion in order to arrive at an evolutionary period where it is relatively easier and less expensive to fully control hydrogen combustion than the current state.

Data availability

The datasets generated during the current study are available from the authors on reasonable request.

Conflicts of interest

There are no conflicts to declare.

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References

- 1 IPCC, Climate Change 2022: Mitigation of Climate Change. Contribution of Working Group to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change [ed. P.R. Shukla, J. Skea, R. Slade, A. Al Khourdajie, R. van Diemen, D. McCollum, M. Pathak, S. Some, P. Vyas, R. Fradera, M. Belkacemi, A. Hasija, G. Lisboa, S. Luz and J. Malley. Cambridge University Press, Cambridge, UK and New York, NY, USA, 2022.
- 2 M. Laura, Global Temperatures Already 1.2 °C Above Pre-Industrial Levels. BloombergCom 2020.
- 3 NASA, World of Change: Global Temperatures, 2020. https:// earthobservatory.nasa.gov/world-of-change/global-temperatures (accessed August 22, 2023).
- 4 R. D. Lamboll, Z. R. J. Nicholls, C. J. Smith, J. S. Kikstra, E. Byers and J. Rogelj, Assessing the size and uncertainty of remaining carbon budgets, Nat. Clim. Change, 2023, 13,
- 5 N. Sönnichsen, Share of fossil fuels in primary energy consumption worldwide from 1965 to 2020, Statista, 2022.
- 6 J. Fuhrman, C. Bergero, M. Weber, S. Monteith, F. M. Wang, A. F. Clarens, et al., Diverse carbon dioxide removal approaches could reduce impacts on the energywater-land system, Nat. Clim. Change, 2023, 13, 341-350.
- 7 J. D. Ampah, C. Jin, H. Liu, S. Afrane, H. Adun, D. Morrow, et al., Prioritizing Non-Carbon Dioxide Removal Mitigation Strategies Could Reduce the Negative Impacts Associated with Large-Scale Reliance on Negative Emissions, Environ. Sci. Technol., 2024, 58(8), 3755-3765.
- 8 J. D. Ampah, C. Jin, E. B. Agyekum, S. Afrane, Z. Geng, H. Adun, et al., Performance analysis and socio-enviroeconomic feasibility study of a new hybrid energy systembased decarbonization approach for coal mine sites, Sci. Total Environ., 2023, 854, 158820, DOI: 10.1016/j. scitotenv.2022.158820.
- 9 X. Wu, Z. Tian and J. Guo, A review of the theoretical research and practical progress of carbon neutrality, Sustainable Oper. Comput., 2022, 3, 54-66, DOI: 10.1016/j. susoc.2021.10.001.
- 10 CarbonBrief. Will China's new renewable energy plan lead to an early emissions peak? 2022.
- 11 D. Q. Hung, M. R. Shah and N. Mithulananthan, Technical Challenges, Security and Risk in Grid Integration of Renewable Energy, in Smart Power Systems and Renewable Energy System Integration, ed. D. Jayaweera, Springer International Publishing, Cham, 2016, vol. 57, pp. 99-118. DOI: 10.1007/978-3-319-30427-4_6.

- 12 G. M. Shafiullah, M. T. Arif and A. M. T. Oo, Mitigation strategies to minimize potential technical challenges of renewable energy integration, Sustainable Energy Technol. Assess., 2018, 25, 24-42, DOI: 10.1016/ j.seta.2017.10.008.
- 13 World Economic Forum. Zero carbon by 2050 is possible. Here's what we need to do. 2019.
- 14 Strategic Sustainability Consulting. Getting to net-zero for hard-to-abate sectors. 2021.
- 15 IRENA, Geopolitics of the Energy Transformation The Hydrogen Factor, 2022.
- 16 R. Daiyan, I. MacGill and R. Amal, Opportunities and Challenges for Renewable Power-to-X, ACS Energy Lett., 2020, 5, 3843-3847, DOI: 10.1021/acsenergylett.0c02249.
- 17 B. Rego de Vasconcelos and J.-M. Lavoie, Recent Advances in Power-to-X Technology for the Production of Fuels and Chemicals, Front. Chem., 2019, 7, 392.
- 18 A. R. Dahiru, A. Vuokila and M. Huuhtanen, Recent development in Power-to-X: Part I - A review on techno-economic analysis, J. Energy Storage, 2022, 56, 105861, DOI: 10.1016/j.est.2022.105861.
- 19 M. J. Palys and P. Daoutidis, Power-to-X: A review and perspective, Comput. Chem. Eng., 2022, 165, 107948, DOI: 10.1016/j.compchemeng.2022.107948.
- 20 J. Gong, N. J. English, D. Pant, G. R. Patzke, S. Protti and T. Zhang, Power-to-X: Lighting the Path to a Net-Zero-Emission Future, ACS Sustainable Chem. Eng., 2021, 9, 7179-7181, DOI: 10.1021/acssuschemeng.1c03212.
- 21 IEA. Hydrogen, IEA, Paris, 2022.
- 22 H. Liu, J. D. Ampah, Y. Zhao, X. Sun, L. Xu, X. Jiang, et al., A Perspective on the Overarching Role of Hydrogen, Ammonia, and Methanol Carbon-Neutral Fuels towards Net Zero Emission in the Next Three Decades, Energies, 2022, 16, 280, DOI: 10.3390/en16010280.
- 23 R. Viscardi, C. Bassano, G. Nigliaccio and P. Deiana, The potential of E-fuels as future fuels, Energia, Ambiente e Innovazione, 2021. DOI: 10.12910/EAI2021-022.
- 24 H. Liu, J. D. Ampah, S. Afrane, H. Adun, C. Jin and M. Yao, Deployment of hydrogen in hard-to-abate transport sectors under limited carbon dioxide removal (CDR): Implications on global energy-land-water system, Renewable Sustainable Energy Rev., 2023, 184, 113578, DOI: 10.1016/j.rser.2023.113578.
- 25 H. Liu, J. Dankwa Ampah, S. Afrane, H. Adun, C. Jin and M. Yao, Potential benefits and trade-offs associated with hydrogen transition under diverse carbon dioxide removal strategies, Sci. Bull., 2024, 69(1), 34-39.
- 26 X. Yang, C. P. Nielsen, S. Song and M. B. McElroy, Breaking the hard-to-abate bottleneck in China's path to carbon neutrality with clean hydrogen, Nat. Energy, 2022, 7, 955-965, DOI: 10.1038/s41560-022-01114-6.
- 27 P. M. Diéguez, J. C. Urroz, S. Marcelino-Sádaba, A. Pérez-Ezcurdia, M. Benito-Amurrio, D. Sáinz, et al., Experimental study of the performance and emission characteristics of an adapted commercial four-cylinder spark ignition engine running on hydrogen-methane mix-

Green Chemistry

- apenergy.2013.08.063.
- 28 J. A. Faria, Renaissance of ammonia synthesis for sustainable production of energy and fertilizers, Curr. Opin. Green Sustain. Chem., 2021, 29, 100466, DOI: 10.1016/j. cogsc.2021.100466.
- 29 J. Atchison, IEA's latest Global Hydrogen Review includes fuel ammonia, 2021.
- 30 IRENA, World Energy Transition Outlook 1.5° C Pathway,
- 31 Z. Sun, J. Hong, T. Zhang, B. Sun, B. Yang, L. Lu, et al., Hydrogen engine operation strategies: Recent progress, industrialization challenges, and perspectives, Int. J. Hydrogen Energy, 2023, 48, 366-392, DOI: 10.1016/j. ijhydene.2022.09.256.
- 32 J. Gao, X. Wang, P. Song, G. Tian and C. Ma, Review of the backfire occurrences and control strategies for port hydrogen injection internal combustion engines, Fuel, 2022, 307, 121553, DOI: 10.1016/j.fuel.2021.121553.
- 33 Z. Stępień, A Comprehensive Overview of Hydrogen-Fueled Internal Combustion Engines: Achievements and Future Challenges, Energies, 2021, 14, 6504, DOI: 10.3390/ en14206504.
- 34 F. Yan, L. Xu and Y. Wang, Application of hydrogen enriched natural gas in spark ignition IC engines: from fundamental fuel properties to engine performances and emissions, Renewable Sustainable Energy Rev., 2018, 82, 1457-1488, DOI: 10.1016/j.rser.2017.05.227.
- 35 L. Wang, C. Hong, X. Li, Z. Yang, S. Guo and Q. Li, Review on blended hydrogen-fuel internal combustion engines: A case study for China, Energy Rep., 2022, 8, 6480-6498, DOI: 10.1016/j.egyr.2022.04.079.
- 36 N. Gültekin and M. Ciniviz, Examination of the effect of combustion chamber geometry and mixing ratio on engine performance and emissions in a hydrogen-diesel dual-fuel compression-ignition engine, Int. J. Hydrogen Energy, 2023, 48(7), 2801-2820, DOI: 10.1016/j.ijhydene.2022.10.155, S0360319922048509.
- 37 C. Deheri, S. K. Acharya, D. N. Thatoi and A. P. Mohanty, A review on performance of biogas and hydrogen on diesel engine in dual fuel mode, Fuel, 2020, 260, 116337, DOI: 10.1016/j.fuel.2019.116337.
- 38 A. Onorati, R. Payri, B. Vaglieco, A. Agarwal, C. Bae, G. Bruneaux, et al., The role of hydrogen for future internal combustion engines, Int. J. Engine Res., 2022, 23, 529-540, DOI: 10.1177/14680874221081947.
- 39 S. Verhelst, Recent progress in the use of hydrogen as a fuel for internal combustion engines, Int. J. Hydrogen Energy, 2014, 39, 1071-1085, DOI: 10.1016/j.ijhydene.2013.10.102.
- 40 R. Banerjee, S. Roy and P. K. Bose, Hydrogen-EGR synergy as a promising pathway to meet the PM-NOx-BSFC tradeoff contingencies of the diesel engine: A comprehensive review, Int. J. Hydrogen Energy, 2015, 40, 12824-12847, DOI: 10.1016/j.ijhydene.2015.07.098.
- 41 A. A. Hairuddin, T. Yusaf and A. P. Wandel, A review of hydrogen and natural gas addition in diesel HCCI

- engines, Renewable Sustainable Energy Rev., 2014, 32, 739-761, DOI: 10.1016/j.rser.2014.01.018.
- 42 Z. Sun, F.-S. Liu, X. Liu, B. Sun and D.-W. Sun, Research and development of hydrogen fuelled engines in China, Int. J. Hydrogen Energy, 2012, 37, 664-681, DOI: 10.1016/j. ijhydene.2011.09.114.
- 43 H. Hu, W. Xue, P. Jiang and Y. Li, Bibliometric analysis for ocean renewable energy: An comprehensive review for hotspots, frontiers, and emerging trends, Renewable Sustainable Energy Rev., 2022, 167, 112739, DOI: 10.1016/j. rser.2022.112739.
- 44 S. Bhatnagar and D. Sharma, Evolution of green finance and its enablers: A bibliometric analysis, Renewable Sustainable Energy Rev., 2022, 162, 112405, DOI: 10.1016/j. rser.2022.112405.
- 45 M. Bortoluzzi, C. Correia de Souza and M. Furlan, Bibliometric analysis of renewable energy types using key performance indicators and multicriteria decision models, Renewable Sustainable Energy Rev., 2021, 143, 110958, DOI: 10.1016/j.rser.2021.110958.
- 46 A. I. Osman, U. Qasim, F. Jamil, A. H. Al-Muhtaseb, A. A. Jrai, M. Al-Riyami, et al., Bioethanol and biodiesel: Bibliometric mapping, policies and future needs, Renewable Sustainable Energy Rev., 2021, 152, 111677, DOI: 10.1016/j.rser.2021.111677.
- 47 G. Mao, X. Liu, H. Du, J. Zuo and L. Wang, Way forward for alternative energy research: A bibliometric analysis during 1994-2013, Renewable Sustainable Energy Rev., 2015, 48, 276-286, DOI: 10.1016/j.rser.2015.03.094.
- 48 N. Donthu, S. Kumar, D. Mukherjee, N. Pandey and W. M. Lim, How to conduct a bibliometric analysis: An overview and guidelines, J. Bus. Res., 2021, 133, 285-296, DOI: 10.1016/j.jbusres.2021.04.070.
- 49 M. B. Low and I. C. MacMillan, Entrepreneurship: Past Research and Future Challenges, J. Manage., 1988, 14, 139-161, DOI: 10.1177/014920638801400202.
- 50 C. Jin, J. D. Ampah, S. Afrane, Z. Yin, X. Liu, T. Sun, et al., Low-carbon alcohol fuels for decarbonizing the road transportation industry: a bibliometric analysis 2000-2021, Environ. Sci. Pollut. Res., 2022, 29, 5577-5604, DOI: 10.1007/s11356-021-15539-1.
- 51 S. Muji, Y. Dori and D. S. Olusegun, The Concise Latest Report on the Advantages and Disadvantages of Pure Biodiesel (B100) on Engine Performance: Literature Review and Bibliometric Analysis, Indones. J. Sci. Technol., 2021, 6(3), DOI: 10.17509/ijost.v6i3.38430.
- 52 G. E. Valencia, L. G. Obregon and J. E. Duarte, A bibliometric analysis of diesel engine publication from 2007 to 2018, Contemp. Eng. Sci., 2018, 11(56), 2803-2812, DOI: 10.12988/ces.2018.86279.
- 53 G. V. Ochoa, J. D. Forero and L. O. Quinones, A bibliometric analysis of engine modeling research from 2001 to 2016, Contemp. Eng. Sci., 2018, 11(76), 3747-3754, DOI: 10.12988/ces.2018.88388.
- 54 M. D. Redel-Macías, S. Pinzi, M. Babaie, A. Zare, A. Cubero-Atienza and M. P. Dorado, Bibliometric Studies

on Emissions from Diesel Engines Running on Alcohol/Diesel Fuel Blends. A Case Study about Noise Emissions, *Processes*, 2021, **9**, 623, DOI: 10.3390/pr9040623.

Critical Review

- 55 F. Liu, M. Z. Akram and H. Wu, Hydrogen effect on lean flammability limits and burning characteristics of an iso-octane–air mixture, *Fuel*, 2020, 266, 117144, DOI: 10.1016/j.fuel.2020.117144.
- 56 P. Lott, M. Casapu, J.-D. Grunwaldt and O. Deutschmann, A review on exhaust gas after-treatment of lean-burn natural gas engines From fundamentals to application, *Appl. Catal., B*, 2024, **340**, 123241, DOI: **10.1016/j.** apcatb.2023.123241.
- 57 J. M. Ogden, Hydrogen: The Fuel of the Future?, *Phys. Today*, 2002, 55, 69–75, DOI: **10.1063/1.1480785**.
- 58 A. A. Yusuf, F. L. Inambao and A. A. Farooq, Impact of n-butanol-gasoline-hydrogen blends on combustion reactivity, performance and tailpipe emissions using TGDI engine parameters variation, *Sustainable Energy Technol. Assess.*, 2020, 40, 100773, DOI: 10.1016/j.seta.2020.100773.
- 59 Nuclear Power, Combustion of Hydrogen. Nuclear Power n.d. https://www.nuclear-power.com/laws-of-conservation/ law-of-conservation-of-energy/combustion-of-hydrogen/ (accessed May 13, 2024).
- 60 S. T. P. Purayil, M. O. Hamdan, S. A. B. Al-Omari, M. Y. E. Selim and E. Elnajjar, Review of hydrogen-gasoline SI dual fuel engines: Engine performance and emission, *Energy Rep.*, 2023, 9, 4547-4573, DOI: 10.1016/j. egyr.2023.03.054.
- 61 A. Onorati, R. Payri, B. M. Vaglieco, A. K. Agarwal, C. Bae, G. Bruneaux, *et al.*, The role of hydrogen for future internal combustion engines, *Int. J. Engine Res.*, 2022, 23, 529–540, DOI: 10.1177/14680874221081947.
- 62 A. Atmanlı, E. İleri and B. Yüksel, Experimental investigation of engine performance and exhaust emissions of a diesel engine fueled with diesel n -butanol vegetable oil blends, *Energy Convers. Manage.*, 2014, **81**, 312–321, DOI: 10.1016/j.enconman.2014.02.049.
- 63 A. Atmanlı, E. İleri and B. Yüksel, Effects of higher ratios of n-butanol addition to diesel-vegetable oil blends on performance and exhaust emissions of a diesel engine, *J. Energy Inst.*, 2015, 88, 209–220, DOI: 10.1016/j.joei.2014.09.008.
- 64 A. A. Yusuf, J. Dankwa Ampah, M. E. M. Soudagar, I. Veza, U. Kingsley, S. Afrane, et al., Effects of hybrid nanoparticle additives in n-butanol/waste plastic oil/diesel blends on combustion, particulate and gaseous emissions from diesel engine evaluated with entropy-weighted PROMETHEE II and TOPSIS: Environmental and health risks of plastic wa, Energy Convers. Manage., 2022, 264, 115758, DOI: 10.1016/j.enconman.2022.115758.
- 65 M. S. Cellek, The decreasing effect of ammonia enrichment on the combustion emission of hydrogen, methane, and propane fuels, *Int. J. Hydrogen Energy*, 2022, 47, 19916–19934, DOI: 10.1016/j.ijhydene.2021.11.241.
- 66 M. Zajemska, A. Poskart and D. Musiał, The kinetics of nitrogen oxides formation in the flame gas, *Econ. Environ. Stud.*, 2015, **15**, 445–460.

- 67 C. P. Fenimore, Formation of nitric oxide in premixed hydrocarbon flames, Symposium (International) on Combustion, 1971, 13, 373–380. DOI: 10.1016/S0082-0784 (71)80040-1.
- 68 V. Dhana Raju, J. N. Nair, H. Venu, L. Subramani, M. E. Manzoore, M. A. Mujtaba, et al., Combined assessment of injection timing and exhaust gas recirculation strategy on the performance, emission and combustion characteristics of algae biodiesel powered diesel engine, Energy Sources, Part A, 2022, 44, 8554–8571, DOI: 10.1080/15567036.2022.2123068.
- 69 S. Zhang, X. Nie, Y. Bi, J. Yan, S. Liu and Y. Peng, Experimental Study on NOx Reduction of Diesel Engine by EGR Coupled with SCR, ACS Omega, 2024, 9(7), 8308– 8319, DOI: 10.1021/acsomega.3c09052.
- 70 L. Sillero, W. G. Sganzerla, T. Forster-Carneiro, R. Solera and M. Perez, A bibliometric analysis of the hydrogen production from dark fermentation, *Int. J. Hydrogen Energy*, 2022, 47, 27397–27420, DOI: 10.1016/j. ijhydene.2022.06.083.
- 71 M. Aria and C. Cuccurullo, Bibliometrix: An R-tool for comprehensive science mapping analysis, *J. Informetrics*, 2017, 11, 959–975, DOI: 10.1016/j.joi.2017.08.007.
- 72 K. V. Shivaprasad, S. Raviteja, P. Chitragar and G. N. Kumar, Experimental Investigation of the Effect of Hydrogen Addition on Combustion Performance and Emissions Characteristics of a Spark Ignition High Speed Gasoline Engine, *Procedia Technol.*, 2014, 14, 141–148, DOI: 10.1016/j.protcy.2014.08.019.
- 73 E. Kahraman, S. Cihangir Ozcanlı and B. Ozerdem, An experimental study on performance and emission characteristics of a hydrogen fuelled spark ignition engine, *Int. J. Hydrogen Energy*, 2007, 32, 2066–2072, DOI: 10.1016/j.ijhydene.2006.08.023.
- 74 H. Koten, Hydrogen effects on the diesel engine performance and emissions, *Int. J. Hydrogen Energy*, 2018, 43, 10511–10519, DOI: 10.1016/j.ijhydene.2018.04.146.
- 75 M. Senthil Kumar, S. V. Karthic and P. Pradeep, Investigations on the influence of ethanol and water injection techniques on engine's behavior of a hydrogen biofuel based dual fuel engine, *Int. J. Hydrogen Energy*, 2018, 43, 21090–21101, DOI: 10.1016/j. ijhydene.2018.09.145.
- 76 J. Heffel, NOx emission reduction in a hydrogen fueled internal combustion engine at 3000 rpm using exhaust gas recirculation, *Int. J. Hydrogen Energy*, 2003, 28, 1285– 1292, DOI: 10.1016/S0360-3199(02)00289-6.
- 77 S. Syed and M. Renganathan, NOx emission control strategies in hydrogen fuelled automobile engines, *Aust. J. Mech. Eng.*, 2019, 20, 88–110, DOI: 10.1080/14484846.2019.1668214.
- 78 V. Dhyani and K. A. Subramanian, Control of backfire and NOx emission reduction in a hydrogen fueled multi-cylinder spark ignition engine using cooled EGR and water injection strategies, *Int. J. Hydrogen Energy*, 2019, 44, 6287–6298, DOI: 10.1016/j.ijhydene.2019.01.129.

Green Chemistry

Critical Review

79 X Liu H Aliabri M Silva A S AlRamadan M Ben 91 S M V Savar and A K Avarwal Knocking behavior and

- 79 X. Liu, H. Aljabri, M. Silva, A. S. AlRamadan, M. Ben Houidi, E. Cenker, *et al.*, Hydrogen pre-chamber combustion at lean-burn conditions on a heavy-duty diesel engine: A computational study, *Fuel*, 2023, 335, 127042, DOI: 10.1016/j.fuel.2022.127042.
- 80 A. C. Lewis, Optimising air quality co-benefits in a hydrogen economy: a case for hydrogen-specific standards for NOx emissions, *Environ. Sci.: Atmos.*, 2021, 1, 201–207, DOI: 10.1039/D1EA00037C.
- 81 V. Dhyani and K. A. Subramanian, Experimental investigation on effects of knocking on backfire and its control in a hydrogen fueled spark ignition engine, *Int. J. Hydrogen Energy*, 2018, 43, 7169–7178, DOI: 10.1016/j.ijhydene.2018.02.125.
- 82 M. Fischer, S. Sterlepper, S. Pischinger, J. Seibel, U. Kramer and T. Lorenz, Operation principles for hydrogen spark ignited direct injection engines for passenger car applications, *Int. J. Hydrogen Energy*, 2022, 47, 5638– 5649, DOI: 10.1016/j.ijhydene.2021.11.134.
- 83 S. Szwaja and J. D. Naber, Dual nature of hydrogen combustion knock, *Int. J. Hydrogen Energy*, 2013, **38**, 12489–12496, DOI: **10.1016/j.ijhydene.2013.07.036**.
- 84 H. Li, Knock in spark ignition hydrogen engines, *Int. J. Hydrogen Energy*, 2004, **29**, 859–865, DOI: **10.1016/j.** ijhydene.2003.09.013.
- 85 G. Xin, C. Ji, S. Wang, H. Meng, K. Chang and J. Yang, Effect of different volume fractions of ammonia on the combustion and emission characteristics of the hydrogen-fueled engine, *Int. J. Hydrogen Energy*, 2022, 47, 16297–16308, DOI: 10.1016/j.ijhydene.2022.03.103.
- 86 J. Krishnan Unni, D. Bhatia, V. Dutta, L. M. Das, S. Jilakara and G. Subash, Development of Hydrogen Fuelled Low NO x Engine with Exhaust Gas Recirculation and Exhaust after Treatment, SAE Int. J. Engines, 2017, 10, 46–54, DOI: 10.4271/2017-26-0074.
- 87 Z. Yang, L. Wang, Q. Zhang, Y. Meng and P. Pei, Research on optimum method to eliminate backfire of hydrogen internal combustion engines based on combining postponing ignition timing with water injection of intake manifold, *Int. J. Hydrogen Energy*, 2012, 37, 12868–12878, DOI: 10.1016/j.ijhydene.2012.05.082.
- 88 S. Verma, L. M. Das, S. C. Kaushik and S. K. Tyagi, An experimental investigation of exergetic performance and emission characteristics of hydrogen supplemented biogas-diesel dual fuel engine, *Int. J. Hydrogen Energy*, 2018, 43, 2452–2468, DOI: 10.1016/j.ijhydene.2017.12.032.
- 89 M. T. Chaichan, Performance and emission characteristics of CIE using hydrogen, biodiesel, and massive EGR, *Int. J. Hydrogen Energy*, 2018, **43**, 5415–5435, DOI: **10.1016/j.ijhydene.2017.09.072**.
- 90 Z. Tian, Y. Wang, X. Zhen and D. Liu, Numerical comparative analysis on performance and emission characteristics of methanol/hydrogen, ethanol/hydrogen and butanol/hydrogen blends fuels under lean burn conditions in SI engine, *Fuel*, 2022, 313, 123012, DOI: 10.1016/j. fuel.2021.123012.

- 91 S. M. V. Sagar and A. K. Agarwal, Knocking behavior and emission characteristics of a port fuel injected hydrogen enriched compressed natural gas fueled spark ignition engine, *Appl. Therm. Eng.*, 2018, **141**, 42–50, DOI: **10.1016**/j.applthermaleng.2018.05.102.
- 92 P. Börjesson and B. Mattiasson, Biogas as a resource-efficient vehicle fuel, *Trends Biotechnol.*, 2008, **26**, 7–13, DOI: 10.1016/j.tibtech.2007.09.007.
- 93 S. Shrestha and G. A. Karim, Hydrogen as an additive to methane for spark ignition engine applications, *Int. J. Hydrogen Energy*, 1999, 24, 577–586, DOI: 10.1016/S0360-3199(98)00103-7.
- 94 B. S. Nuthan Prasad, J. K. Pandey and G. N. Kumar, Effect of hydrogen enrichment on performance, combustion, and emission of a methanol fueled SI engine, *Int. J. Hydrogen Energy*, 2021, **46**, 25294–25307, DOI: **10.1016/j.ijhydene.2021.05.039**.
- 95 A. Szałek, I. Pielecha and W. Cieslik, Fuel Cell Electric Vehicle (FCEV) Energy Flow Analysis in Real Driving Conditions (RDC), *Energies*, 2021, 14, 5018, DOI: 10.3390/ en14165018.
- 96 E. Uludamar and C. Özgür, Optimization of exhaust emissions, vibration, and noise of a hydrogen enriched fuelled diesel engine, *Int. J. Hydrogen Energy*, 2022, 47, 37090–37105, DOI: 10.1016/j.ijhydene.2022.08.257.
- 97 Z. Liu, J. Luo, Y. Pan, J. Li, L. Li, X. Wei, et al., Multi-objective optimization of the performance and emission characteristics for a dual-fuel engine with hydrogen addition, Fuel, 2023, 332, 126231, DOI: 10.1016/j.fuel.2022.126231.
- 98 D. Tan, Y. Wu, J. Lv, J. Li, X. Ou, Y. Meng, et al., Performance optimization of a diesel engine fueled with hydrogen/biodiesel with water addition based on the response surface methodology, Energy, 2023, 263, 125869, DOI: 10.1016/j.energy.2022.125869.
- 99 J. Dang and L. Wang, Optimization control of hydrogen engine ignition system based on ACO-BP, *Int. J. Hydrogen Energy*, 2021, 46, 38903–38912, DOI: 10.1016/j. ijhydene.2021.09.251.
- 100 H. Wang, C. Ji, C. Shi, J. Yang, Y. Ge, S. Wang, *et al.*, Parametric modeling and optimization of the intake and exhaust phases of a hydrogen Wankel rotary engine using parallel computing optimization platform, *Fuel*, 2022, 324, 124381, DOI: 10.1016/j.fuel.2022.124381.
- 101 X. Yu, L. Zhu, Y. Wang, D. Filev and X. Yao, Internal combustion engine calibration using optimization algorithms, Appl. Energy, 2022, 305, 117894, DOI: 10.1016/j. apenergy.2021.117894.
- 102 C. Gong, Z. Li, Y. Chen, J. Liu, F. Liu and Y. Han, Influence of ignition timing on combustion and emissions of a spark-ignition methanol engine with added hydrogen under lean-burn conditions, *Fuel*, 2019, 235, 227–238, DOI: 10.1016/j.fuel.2018.07.097.
- 103 B. Zhang, C. Ji and S. Wang, Investigation on the lean combustion performance of a hydrogen-enriched n-butanol engine, *Energy Convers. Manage.*, 2017, **136**, 36–43, DOI: **10.1016/j.enconman.2016.12.065**.

104 W. Shi, X. Yu, H. Zhang and H. Li, Effect of spark timing on combustion and emissions of a hydrogen direct injection stratified gasoline engine, *Int. J. Hydrogen Energy*, 2017, 42, 5619–5626, DOI: 10.1016/j.ijhydene.2016.02.060.

Critical Review

- 105 T. Su, C. Ji, S. Wang, L. Shi and X. Cong, Effect of ignition timing on performance of a hydrogen-enriched n-butanol rotary engine at lean condition, *Energy Convers. Manage.*, 2018, **161**, 27–34, DOI: **10.1016/j.enconman.2018.01.072**.
- 106 J. B. Heywood, *Internal combustion engine fundamentals*, McGraw-Hill, New York, 1988.
- 107 C. Sayin and M. Canakci, Effects of injection timing on the engine performance and exhaust emissions of a dualfuel diesel engine, *Energy Convers. Manage.*, 2009, 50, 203– 213, DOI: 10.1016/j.enconman.2008.06.007.
- 108 Y. Ye, W. Gao, Y. Li, P. Zhang and X. Cao, Numerical study of the effect of injection timing on the knock combustion in a direct-injection hydrogen engine, *Int. J. Hydrogen Energy*, 2020, 45, 27904–27919, DOI: 10.1016/j. ijhydene.2020.07.117.
- 109 R. Zhang, L. Chen, H. Wei, J. Pan, J. Li, P. Yang, et al., Optical study on the effects of the hydrogen injection timing on lean combustion characteristics using a natural gas/hydrogen dual-fuel injected spark-ignition engine, Int. J. Hydrogen Energy, 2021, 46, 20777–20789, DOI: 10.1016/j.ijhydene.2021.03.171.
- 110 P. Dimitriou and T. Tsujimura, A review of hydrogen as a compression ignition engine fuel, *Int. J. Hydrogen Energy*, 2017, 42, 24470–24486, DOI: 10.1016/j. ijhydene.2017.07.232.
- 111 T. Miyamoto, H. Hasegawa, M. Mikami, N. Kojima, H. Kabashima and Y. Urata, Effect of hydrogen addition to intake gas on combustion and exhaust emission characteristics of a diesel engine, *Int. J. Hydrogen Energy*, 2011, 36, 13138–13149, DOI: 10.1016/j.ijhydene.2011.06.144.
- 112 L. Das and R. Mathur, Exhaust gas recirculation for Nox control in a multicylinder hydrogen-supplemented S.I. engine, *Int. J. Hydrogen Energy*, 1993, **18**, 1013–1018, DOI: **10.1016/0360-3199(93)90084-N**.
- 113 S. Nag, P. Sharma, A. Gupta and A. Dhar, Experimental study of engine performance and emissions for hydrogen diesel dual fuel engine with exhaust gas recirculation, *Int. J. Hydrogen Energy*, 2019, 44, 12163–12175, DOI: 10.1016/j.ijhydene.2019.03.120.
- 114 M. Vijayaragavan, B. Subramanian, S. Sudhakar and L. Natrayan, Effect of induction on exhaust gas recirculation and hydrogen gas in compression ignition engine with simarouba oil in dual fuel mode, *Int. J. Hydrogen Energy*, 2022, 47, 37635–37647, DOI: 10.1016/j. ijhydene.2021.11.201.
- 115 A. Mariani, B. Morrone and A. Unich, Numerical evaluation of internal combustion spark ignition engines performance fuelled with hydrogen Natural gas blends, *Int. J. Hydrogen Energy*, 2012, 37, 2644–2654, DOI: 10.1016/j.ijhydene.2011.10.082.
- 116 A. Molino, M. Migliori, V. Larocca, T. Marino, A. Figoli and P. Casella, et al., Power Production by Biomass

- Gasification Technologies. Current Trends and Future Developments on (Bio-) Membranes, Elsevier, 2019, pp. 293–318. DOI: 10.1016/B978-0-12-813545-7.00012-X.
- 117 Y. Karagöz, T. Sandalcı, L. Yüksek, A. S. Dalkılıç and S. Wongwises, Effect of hydrogen-diesel dual-fuel usage on performance, emissions and diesel combustion in diesel engines, *Adv. Mech. Eng.*, 2016, 8(8), DOI: 10.1177/ 1687814016664458.
- 118 H. A. Alrazen and K. A. Ahmad, HCNG fueled sparkignition (SI) engine with its effects on performance and emissions, *Renewable Sustainable Energy Rev.*, 2018, **82**, 324–342, DOI: 10.1016/j.rser.2017.09.035.
- 119 S. Chugh, V. A. Posina, K. Sonkar, U. Srivatsava, A. Sharma and G. K. Acharya, Modeling & simulation study to assess the effect of CO2 on performance and emissions characteristics of 18% HCNG blend on a light duty SI engine, *Int. J. Hydrogen Energy*, 2016, 41, 6155–6161, DOI: 10.1016/j.ijhydene.2015.09.138.
- 120 S. Lee, C. Kim, Y. Choi, G. Lim and C. Park, Emissions and fuel consumption characteristics of an HCNG-fueled heavy-duty engine at idle, *Int. J. Hydrogen Energy*, 2014, **39**, 8078–8086, DOI: **10.1016/j.ijhydene.2014.03.079**.
- 121 R. K. Mehra, H. Duan, R. Juknelevičius, F. Ma and J. Li, Progress in hydrogen enriched compressed natural gas (HCNG) internal combustion engines A comprehensive review, *Renewable Sustainable Energy Rev.*, 2017, **80**, 1458–1498, DOI: 10.1016/j.rser.2017.05.061.
- 122 I. Bartolozzi, F. Rizzi and M. Frey, Comparison between hydrogen and electric vehicles by life cycle assessment: A case study in Tuscany, Italy, *Appl. Energy*, 2013, **101**, 103–111, DOI: 10.1016/j.apenergy.2012.03.021.
- 123 Y. Bicer and I. Dincer, Life cycle environmental impact assessments and comparisons of alternative fuels for clean vehicles, *Resour., Conserv. Recycl.*, 2018, **132**, 141–157, DOI: 10.1016/j.resconrec.2018.01.036.
- 124 J. Paparao and S. Murugan, Dual-fuel diesel engine run with injected pilot biodiesel-diesel fuel blend with inducted oxyhydrogen (HHO) gas, *Int. J. Hydrogen Energy*, 2022, 47, 17788–17807, DOI: 10.1016/j.ijhydene.2022.03.235.
- 125 Z. Zhao, Y. Huang, X. Yu, Z. Guo, M. Li and T. Wang, Effect of brown gas (HHO) addition on combustion and emission in gasoline engine with exhaust gas recirculation (EGR) and gasoline direct injection, *J. Cleaner Prod.*, 2022, 360, 132078, DOI: 10.1016/j.jclepro.2022.132078.
- 126 B. Subramanian and V. Thangavel, Experimental investigations on performance, emission and combustion characteristics of Diesel-Hydrogen and Diesel-HHO gas in a Dual fuel CI engine, *Int. J. Hydrogen Energy*, 2020, 45, 25479–25492, DOI: 10.1016/j.ijhydene.2020.06.280.
- 127 J. Paparao and S. Murugan, Oxy-hydrogen gas as an alternative fuel for heat and power generation applications A review, *Int. J. Hydrogen Energy*, 2021, **46**, 37705–37735, DOI: **10.1016/j.ijhydene.2021.09.069**.
- 128 B. Subramanian and S. Ismail, Production and use of HHO gas in IC engines, *Int. J. Hydrogen Energy*, 2018, 43, 7140–7154, DOI: 10.1016/j.ijhydene.2018.02.120.

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- 129 T. B. Arjun, K. P. Atul, A. P. Muraleedharan, P. A. Walton, P. B. Bijinraj and A. A. Raj, A review on analysis of HHO gas in IC engines, Mater. Today: Proc., 2019, 11, 1117-1129, DOI: 10.1016/j.matpr.2018.12.046.
- 130 M. J. Cobo, A. G. López-Herrera, E. Herrera-Viedma and F. Herrera, An approach for detecting, quantifying, and visualizing the evolution of a research field: A practical application to the Fuzzy Sets Theory field, J. Informetrics, 2011, 5, 146-166, DOI: 10.1016/j.joi.2010.10.002.
- 131 A. H. Azadnia, C. McDaid, A. M. Andwari and S. E. Hosseini, Green hydrogen supply chain risk analysis: A european hard-to-abate sectors perspective, Renewable Sustainable Energy Rev., 2023, 182, 113371, DOI: 10.1016/j. rser.2023.113371.
- 132 M. Prussi and D. Chiaramonti, Alternative fuels for hardto-abate sectors: a carbon intensity assessment, J. Phys.: Conf. Ser., 2022, 2385, 012044, DOI: 10.1088/1742-6596/ 2385/1/012044.
- 133 IRENA, Hydrogen, 2022. https://www.irena.org/Energy-Transition/Technology/Hydrogen.
- 134 IEA, Global Hydrogen Review 2023, IEA, Paris, 2023.
- 135 G. Rzayeva, M. Lambert, The Oxford Institute for Energy Studies. What role for hydrogen in Turkey's energy future?,
- 136 J. Nakano, China Unveils its First Long-Term Hydrogen Plan, Center for Strategic and International Studies, 2022.
- 137 World Energy Council, National Hydrogen Energy Strategies, World Energy Council, in collaboration with EPRI and PwC, 2021.
- 138 T. Raksha, U. Bünger, U. Albrecht, J. Michalski and J. Zerhusen, International Hydrogen Strategies A study commissioned by and in cooperation with the World Energy Council Germany, 2020.
- 139 S. Sarkar, India's initiatives on green hydrogen could help global decarbonisation, 2022.
- 140 R. Scita, P. P. Raimondi and M. Noussan, Green Hydrogen: the Holy Grail of Decarbonisation? An Analysis of the Technical and Geopolitical Implications of the Future Hydrogen Economy, Fondazione Eni Enrico Mattei (FEEM), 2020.
- 141 G. Luderer, S. Madeddu, L. Merfort, F. Ueckerdt, M. Pehl, R. Pietzcker, et al., Impact of declining renewable energy costs on electrification in low-emission scenarios, Nat. Energy, 2022, 7, 32-42, DOI: 10.1038/s41560-021-00937-z.
- 142 G. He, J. Lin, F. Sifuentes, X. Liu, N. Abhyankar and A. Phadke, Rapid cost decrease of renewables and storage accelerates the decarbonization of China's power system, Nat. Commun., 2020, 11, 2486, DOI: 10.1038/s41467-020-16184-x.
- 143 A. Finch and J. van den Bergh, Assessing the authenticity of national carbon prices: A comparison of 31 countries,

- Global Environ. Change, 2022, 74, 102525, DOI: 10.1016/j. gloenvcha.2022.102525.
- 144 M. D. Allendorf, V. Stavila, J. L. Snider, M. Witman, M. E. Bowden, K. Brooks, et al., Challenges to developing materials for the transport and storage of hydrogen, Nat. Chem., 2022, 14, 1214-1223, DOI: 10.1038/s41557-022-01056-2.
- 145 T. Zhang, J. Uratani, Y. Huang, L. Xu, S. Griffiths and Y. Ding, Hydrogen liquefaction and storage: Recent progress and perspectives, Renewable Sustainable Energy Rev., 2023, 176, 113204, DOI: 10.1016/j.rser.2023.113204.
- 146 Y. Gao, Z. Li, P. Wang, C. Li, Q. Yue, W.-G. Cui, et al., Solid-State Hydrogen Storage Origin and Design Principles of Carbon-Based Light Metal Single-Atom Materials, Adv. Funct. Mater., 2024, 34, 2316368, DOI: 10.1002/adfm.202316368.
- 147 A. Kumar, P. Muthukumar, P. Sharma and E. A. Kumar, Absorption based solid state hydrogen storage system: A review, Sustainable Energy Technol. Assess., 2022, 52, 102204, DOI: 10.1016/j.seta.2022.102204.
- 148 Z. Abdin, C. Tang, Y. Liu and K. Catchpole, Current state and challenges for hydrogen storage technologies. Towards Hydrogen Infrastructure, Elsevier, 2024, pp. 101-132. DOI: 10.1016/B978-0-323-95553-9.00012-1.
- 149 S. E. Hosseini, Hydrogen storage and delivery challenges. Fundamentals of Hydrogen Production and Utilization in Fuel Cell Systems, Elsevier, 2023, pp. 237-254. DOI: 10.1016/B978-0-323-88671-0.00003-6.
- 150 M. M. Rampai, C. B. Mtshali, N. S. Seroka and L. Khotseng, Hydrogen production, storage, and transportation: recent advances, RSC Adv., 2024, 14, 6699-6718, DOI: 10.1039/D3RA08305E.
- 151 J. Yang, Y. Li and H. Tan, Study on Performance Comparison of Two Hydrogen Liquefaction Processes Based on the Claude Cycle and the Brayton Refrigeration Cycle, Processes, 2023, 11, 932, DOI: 10.3390/pr11030932.
- 152 C. Tsiklios, M. Hermesmann and T. E. Müller, Hydrogen transport in large-scale transmission pipeline networks: Thermodynamic and environmental assessment of repurposed and new pipeline configurations, Appl. Energy, 2022, **327**, 120097, DOI: **10.1016/j.apenergy.2022.120097**.
- 153 J. D. Ampah, C. Jin, I. M. Rizwanul Fattah, I. Appiah-Otoo, S. Afrane, Z. Geng, et al., Investigating the evolutionary trends and key enablers of hydrogen production technologies: A patent-life cycle and econometric analysis, Int. J. Hydrogen Energy, 2023, 48(96), 37674-37707, DOI: 10.1016/j.ijhydene.2022.07.258, S0360319922033912.
- 154 L. Rouleau, F. Duffour, B. Walter, R. Kumar and L. Nowak, Experimental and Numerical Investigation on Hydrogen Internal Combustion Engine, 2021, p. 2021-24-0060. DOI: 10.4271/2021-24-0060.