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Review

Pathway-Based Review of LCA Studies on Hydrogen, Methane-Based Fuels, Methanol and Ethanol for Internal Combustion Engines

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Abstract

The role of internal combustion engines in future transport systems is expected to remain central, particularly in hard-to-abate sectors such as heavy-duty road transport and maritime applications. However, their decarbonization requires the adoption of low-carbon and renewable fuels. This review examines hydrogen, methane-based fuels, methanol, and ethanol for internal combustion engine applications using a pathway-based approach that integrates life-cycle assessment, technology readiness level, commercial readiness level, and engine-related considerations. The reviewed literature shows that the environmental performance of these fuels varies strongly depending on feedstock, production pathway, process configuration, and energy source. From a Well-to-Tank perspective, hydrogen pathways exhibit particularly large variability, ranging from around 3 gCO_2eq/MJ for wind-based electrolysis to around 230 g CO_2eq/MJ for coal gasification. Methane-based fuels range from around 16 gCO_2eq/MJ for fossil compressed and liquefied natural gas to negative values for waste- and manure-based biomethane. Methanol and ethanol also show substantial variability, with renewable, waste-derived, and bio-based pathways generally offering substantially lower life-cycle greenhouse gas (GHG) emissions than fossil-based routes. In the use phase, Tank-to-Wheel analysis shows that energy demand remains relatively similar across fuels, while differences in direct emissions are mainly related to fuel carbon content and other GHG species such as CH_4 or H_2 slip and combustion-related species such as N_2O. The Well-to-Wheel comparison for heavy-duty applications highlights that upstream fuel production pathways strongly influence overall performance, while use-phase contributions play a secondary role and mainly affect the final ranking when upstream emissions are comparable. Overall, the review shows that pathway selection is more influential than fuel identity itself, highlighting that effective decarbonization strategies should focus on pathway design and upstream fuel production rather than on fuel categories alone, and that renewable and bio-based pathways offer the greatest potential for achieving very low or near-zero life-cycle GHG emissions in internal combustion engine applications.

Keywords: internal combustion engines; alternative fuels; hydrogen; methane-based fuels; methanol; ethanol; life-cycle assessment; well-to-wheel analysis

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1. Introduction

Despite rapid advances in transport electrification, internal combustion engines (ICEs) are expected to remain important in several applications, particularly in heavy-duty (HD) road transport, off-road machinery, and marine propulsion, where energy density, refueling speed, operational flexibility, and existing infrastructure continue to favor combustion-based systems [1–5]. In these sectors, decarbonization strategies consistent with broader climate-mitigation and net-zero objectives cannot rely only on improvements in engine efficiency, but also require fuel options capable of delivering meaningful greenhouse gas (GHG) reductions across the full life cycle.

In this context, hydrogen, methane-based fuels, methanol, and ethanol represent four major fuel families currently considered for ICE decarbonization. However, their environmental performance, understood in terms of life-cycle GHG emissions under Well-to-Tank (WTT) or Well-to-Wheel (WTW) boundaries, cannot be determined from the fuel type alone. Each fuel can be produced through multiple pathways with substantially different feedstocks, conversion processes, and life-cycle emissions, as illustrated by reviews focused on hydrogen [6–9], methane-based and renewable gas pathways [10,11], methanol pathways [12,13], and ethanol systems [14–16]. Although hydrogen combustion produces no direct tailpipe CO_2 emissions, fossil-derived hydrogen may nevertheless be associated with a substantial life-cycle burden [17–20]. A similar consideration applies to natural gas (NG): while engine-out emissions may appear lower than those of gasoline or diesel under some operating conditions, methane leakage and fuel-conditioning requirements can significantly diminish or even offset the expected climate benefit [21–23]. Methanol and ethanol present comparable challenges. Methanol offers the practical advantages of a liquid fuel together with broad feedstock flexibility; however, its environmental performance depends strongly on the production route, including whether it is derived from fossil syngas, biomass, waste streams, or captured CO_2 combined with low-carbon hydrogen [12,13,24–26]. Ethanol is already widely used in transport, but reported environmental outcomes vary considerably depending on whether it is produced through first-generation, lignocellulosic, waste-derived, gas-fermentation, or CO_2-derived pathways [15,16,27–30]. For this reason, a WTW perspective is essential when assessing the decarbonization potential of alternative fuels for ICEs. Another major challenge when evaluating alternative fuels is the comparability of studies. Life-cycle assessment studies differ in their choice of functional unit (FU), system boundaries, treatment of co-products, and assumptions about fuel slip and/or leakage, land-use change, electricity mix, carbon capture and storage (CCS) scope, and carbon-source accounting [1,14,17,24,31–33]. These methodological choices are not minor technical details; they frequently influence the resulting ranking of fuel pathways and represent one of the main sources of variability across the LCA literature on alternative fuels [33]. Beyond methodological comparability, pathway evaluation must also account for technology maturity and practical deployment potential. At the same time, the pathways with the strongest environmental performance are not necessarily those with the highest levels of technological or commercial maturity. Fossil compressed natural gas (CNG) and liquefied natural gas (LNG), conventional methanol, hydrogen produced via steam methane reforming (SMR), and first-generation ethanol remain among the most established options, whereas many lower-carbon alternatives rely more heavily on renewable electricity, sustainable feedstocks, reliable carbon sources, or new supporting infrastructure [19,34–38]. These differences in technology and commercial readiness are also reflected in the current deployment of alternative fuels across transport applications. Natural gas remains one of the most commercially mature alternative fuels for ICE applications, with widespread deployment in urban bus fleets and increasing adoption in HD freight transport. Compressed natural gas is commonly used in urban and regional applications, whereas liquefied natural gas is preferred for long-haul transport due to its higher volumetric energy density and extended driving range [39–41]. Similarly, hydrogen-fuelled ICEs are attracting growing interest in both HD road transport and public transport sectors, with several manufacturers developing dedicated hydrogen-powered buses and trucks [2,42–45]. Although hydrogen engine architectures share similarities with natural gas systems, hydrogen storage typically requires higher pressures and dedicated fuel-system solutions. The application landscape differs for liquid alternative fuels. Ethanol is already used in dedicated HD applications and fuel blends in several markets [46], while methanol is emerging as a promising option for maritime transport due to its liquid-fuel handling characteristics, relatively simple storage requirements, and compatibility with large marine engine platforms [47–49]. These examples illustrate that the deployment of alternative fuels is shaped not only by environmental performance, but also by technological maturity, infrastructure availability, and application-specific requirements. In addition, the deployment of alternative fuels is also strongly influenced by the evolving regulatory context. In road transport, emission standards such as Euro 7 increase the pressure to reduce pollutant emissions from vehicles, while fuel-policy frameworks such as the Renewable Energy Directive III (RED III) define sustainability and GHG criteria for renewable and low-carbon fuels. In maritime transport, the International Maritime Organization (IMO) GHG strategy has further strengthened the long-term decarbonisation direction for shipping. Although these frameworks do not prescribe a single fuel solution, they reinforce the need for transparent life-cycle assessment of alternative fuel pathways and for consistent accounting of both upstream and use-phase emissions.

Although the literature on individual fuel families is already extensive, integrated assessments capable of linking pathway-level environmental performance, technology readiness, and application-specific deployment remain limited. Existing studies often focus on a single fuel family, a specific production route, or a single assessment boundary, making it difficult to compare alternative fuel options within a common decision-making framework. This limitation is particularly relevant for hard-to-abate transport sectors, where fuel selection depends not only on life-cycle GHG performance but also on technology maturity, infrastructure availability, and operational constraints. Against this background, this review aims to examine hydrogen, methane-based fuels, methanol, and ethanol through a common pathway-oriented framework that integrates life-cycle assessment evidence, technology and commercial readiness, and application relevance for ICE systems. Particular attention is given to the role of production pathways in shaping WTT and WTW outcomes, as well as to the trade-offs between environmental performance and deployment readiness that influence decarbonisation strategies in hard-to-abate sectors.

The review begins with the framework used to compare pathways across the four fuels considered, then moves through the pathway-level discussion of hydrogen, methane-based fuels, methanol, and ethanol before turning to engine-related aspects and the WTW comparison that brings together life-cycle performance, maturity, and relevance for ICE applications.

2. Analytical Framework and Methodology

2.1. Pathway Classification Framework

To support a consistent comparison across fuel families, the reviewed literature was organized within a common pathway-based framework that classifies hydrogen, methane-based fuels, methanol, and ethanol according to their production route rather than their fuel label alone. The analysis was limited to studies that reported pathway-level information on fuel production, life-cycle GHG performance, energy demand, and, where relevant, technology and commercial maturity. On this basis, the evidence base includes harmonized assessments of transport fuels, fuel-specific life-cycle reviews, process-level LCA studies, broader system analyses, and selected transport applications in which the end-use context materially influences the interpretation of the upstream pathway [1,6,10–12,14,31]. More

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detailed studies of combustion calibration, injection strategies, and engine optimisation were considered only when they contributed directly to the interpretation of pathway-level performance or clarified the practical relevance of a pathway for ICE applications.

Within this framework, hydrogen pathways were grouped into fossil-based hydrogen, blue hydrogen, renewable electricity-based hydrogen, bio-based hydrogen, and carrier- or import-linked hydrogen [7,17,50]. Methane-based fuels were classified as fossil CNG and LNG, biomethane produced via anaerobic digestion and upgrading, biomass-derived synthetic natural gas (bio-SNG) from gasification and methanation, hydrogen-enriched compressed natural gas (HCNG), and electricity-derived synthetic methane produced via power-to-gas routes (e-methane) [1,10,51,52]. Methanol pathways were grouped into fossil methanol, bio- and waste-derived methanol, and carbon dioxide-based (CO_2-based) or power-to-liquid methanol [12,13,36]. For ethanol, the main pathway structure was discussed first through feedstock generations, distinguishing first-generation crop ethanol from sugar- and starch-based feedstocks and second-generation lignocellulosic ethanol from residues and other non-food biomass. In addition, the review considered fossil-related ethanol as a comparator route, together with waste-derived and integrated systems, gas-fermentation ethanol, and CO_2-derived ethanol as additional pathway categories [1,16,28,29,53]. This structure was adopted because it captures the main sources of environmental variation more effectively than fuel labels alone. Biomethane and fossil methane, for example, share the same end-use molecule but can differ substantially in life-cycle performance depending on feedstock origin and methane accounting. Similar considerations apply across the other fuel families, where production pathway, feedstock, and system boundaries often influence environmental performance more strongly than the fuel identity itself. The pathway classes considered for the four fuel families, together with the main interpretative dimensions used in the comparison, are summarized in Table 1 and provide the conceptual basis for the schematic pathway representations presented in subsequent sections.

Table 1. Pathway classification framework used for cross-fuel comparison in this review.

Fuel	Main Pathway Classes	Main Interpretation Focus
Hydrogen	Fossil-based hydrogen; blue hydrogen; renewable electricity-based hydrogen; bio-based hydrogen; carrier- or import-linked hydrogen	Climate performance depends mainly on electricity source, upstream methane leakage, CO_2 capture rate, and transport or carrier-related logistics.
Methane-based fuels	Fossil CNG/LNG; biomethane from anaerobic digestion and upgrading; bio-SNG; HCNG; electricity-derived synthetic methane (e-methane)	Climate performance depends mainly on methane leakage, feedstock origin, upgrading losses, and the electricity source used in synthetic pathways.
Methanol	Fossil methanol; bio- and waste-derived methanol; CO_2-based methanol (e-methanol/power-to-liquid methanol)	Climate performance depends mainly on the H_2 source, CO_2 source, electricity mix, and the system boundary used in the assessment.
Ethanol	First-generation crop ethanol; second-generation lignocellulosic ethanol; additional pathway cases including fossil-related ethanol, waste-derived/integrated ethanol, gas-fermentation ethanol, and CO_2-derived ethanol	Climate performance depends mainly on feedstock type, land-use treatment, co-product allocation, process heat, and system integration.

Source: authors' elaboration based on the fuel-specific pathway literature reviewed for hydrogen, methane-based fuels, methanol, and ethanol (hydrogen: [6,17,50]; methane-based fuels: [1,10,51,52]; methanol: [12,13,36]; ethanol: [1,16,28,29,53]).

2.2. LCA Approach

The main indicators considered in the literature were WTT, WTW, and cradle-to-gate GHG emissions, together with selected information on energy demand and efficiency, where they were relevant to the interpretation of results. Because the reviewed studies used different FUs, including g CO_2eq/MJ fuel, kg CO_2eq/kg product, t CO_2eq/t product, and g CO_2eq/km, direct comparison was only possible between studies with compatible metrics and system boundaries. Where direct comparison was not possible, the original units were retained and interpreted in context.

A limited set of methodological variables accounts for much of the variation observed across the reviewed literature. The most important of these are electricity carbon intensity, methane leakage, allocation and co-product treatment, land-use change, CCS scope, and carbon-source accounting in carbon capture and utilisation pathways [11,17,21,24,28,54]. These variables do not affect all fuels equally. The electricity mix is particularly decisive for renewable hydrogen, synthetic methane, and e-methanol, whereas methane leakage is especially critical for fossil methane, biomethane, and for natural-gas-based hydrogen pathways, including blue hydrogen. For blue hydrogen, life-cycle performance also depends strongly on capture rate, capture configuration, and the additional energy demand of the CCS system [17,18]. Land-use change, agricultural practices, and co-product allocation are particularly influential in ethanol studies. For this reason, the discussion that follows focuses on pathway classes, representative ranges, and the principal drivers of variation, rather than treating individual point values as universally transferable.

The studies reviewed here differ in scope, assumptions, reporting metrics, and level of detail. Some pathways are described in greater detail than others and reporting is not equally transparent across all studies, making direct comparison more difficult. Therefore, the discussion focuses on pathway classes, representative ranges, and the main sources of variation, rather than on strict numerical harmonization. The main methodological factors affecting cross-study comparability are summarized in Table 2.

Table 2. Key methodological factors affecting comparability across studies of hydrogen, methane-based fuels, methanol, and ethanol.

Fuel	Common Units/Boundaries	Main Sensitivities	Why Rankings Change Across Studies
Hydrogen	kg CO_2eq/ kg H_2; WTT; WTW; cradle-to-gate	Electricity mix, methane leakage, CCS boundary, compression/ liquefaction, logistics	Rankings change depending on assumptions about upstream gas supply, the extent of CO_2 capture, and the electricity source used for electrolysis
Methane-based fuels	g CO_2eq/MJ fuel; g CO_2eq/km; WTT and WTW	Methane leakage, liquefaction/compression, upgrading technology, waste credits, electricity for power-to-gas (PtG)	Fossil methane is highly sensitive to leakage assumptions, whereas biomethane depends strongly on feedstock origin and avoided-emission accounting
Methanol	g CO_2eq/MJ; t CO_2eq/t MeOH; cradle-to-gate, WTT, WTW	H_2 source, CO_2 source, electricity mix, plant-only vs. full-chain boundary, heat integration	E-methanol may appear favourable under plant-level boundaries but less favourable when H_2 production and CO_2 capture are fully included
Ethanol	g CO_2eq/MJ; kg or t CO_2eq per ethanol output; WTW	Allocation method, co-products, land-use change, N_2O, process heat, blend-level use	Ethanol rankings vary strongly with land-use change treatment, residue credits, co-product allocation, and whether production-only or vehicle-use systems are compared

Summary based on [8,14,17,21,24,28,54].

2.3. Technology and Commercial Readiness

In addition to life-cycle indicators, this review considers technology readiness and commercial readiness in order to contextualize the practical deployment potential of the different pathways. Technology readiness level (TRL) is used here to indicate the maturity of a technology from development to near-market application. Commercial readiness level (CRL), by contrast, reflects the extent to which a pathway is established in terms of scale, market uptake, and supporting infrastructure. These dimensions were considered when explicitly reported in the literature or in authoritative synthesis studies and sectoral reports [2,19,35,36,38].

Because TRL and CRL are not always reported in a harmonized way across studies, they are used here as interpretative dimensions rather than as a strict quantitative scoring system. The qualitative positioning adopted in the comparative figures was derived from the consensus emerging across the reviewed literature, sectoral reports, and technology roadmaps, rather than from a formal scoring methodology. Their inclusion is essential because the pathways with the strongest climate performance are not always those most ready for large-scale deployment. Fossil CNG and LNG, conventional methanol, hydrogen from SMR, and first-generation ethanol remain among the most mature and commercially established options, while several lower-carbon alternatives depend more strongly on low-carbon electricity, sustainable feedstocks, reliable carbon sources, or new enabling infrastructure. Based on the information collected from the literature, we highlight a qualitative evaluation of the deployment readiness of the different fuels in ICEs for the hard-to-abate sectors considered in this review. The joint consideration of life-cycle performance, methodological sensitivity, and readiness therefore provides the analytical basis for the comparative discussion developed in the following sections.

2.4. Limitations of the Review

The results discussed in this review should be interpreted in light of several limitations associated with the available literature. First, the reviewed studies differ substantially in terms of functional units, system boundaries, allocation methods, treatment of co-products, methane leakage assumptions, land-use change accounting, carbon-source treatment, and electricity-mix assumptions. As a result, direct numerical comparisons between pathways are not always possible, and the reported values should be interpreted within their original methodological context rather than as fully harmonized results.

Second, the availability and maturity of the literature are not uniform across all fuel families and production pathways. Mature pathways, such as fossil natural gas, conventional methanol, hydrogen produced via steam methane reforming, and first-generation ethanol, are generally supported by a larger body of industrial and life-cycle assessment data. In contrast, emerging pathways such as e-methane, e-methanol, carbon dioxide-derived ethanol, and several bio-based hydrogen routes are less extensively documented and therefore subject to greater uncertainty.

Third, the Tank-to-Wheel (TTW) and integrated WTW comparisons presented in this review are primarily based on HD road transport applications, for which more consistent and comparable datasets are available. Maritime applications are discussed mainly from a qualitative perspective, as harmonized performance and emissions data remain more limited in the literature. The final WTW comparison presented later in the manuscript should therefore be interpreted as an illustrative comparison of representative pathways rather than as a fully harmonized meta-analysis.

Finally, this review focuses primarily on GHG emissions, technology and commercial readiness, and applicability to ICE systems. Other relevant sustainability dimensions, including production costs, water consumption, air-pollutant emissions, land-use impacts, resource availability, and regional infrastructure constraints, are acknowledged but are not assessed in detail. Future studies integrating these aspects within harmonized assessment frameworks would further strengthen cross-pathway comparisons and support more comprehensive decision-making.

3. Pathway-Based Analysis of Alternative Fuels

3.1. Hydrogen Pathways

Hydrogen is not always a low-carbon fuel. Its life-cycle emissions vary widely depending on how it is produced and delivered. The literature shows clear differences between fossil, blue, renewable, bio-based, and imported hydrogen supply chains [6–9,17,18,55,56]. For ICE applications, this means that very low tailpipe CO_2 emissions alone are not sufficient to ensure environmental performance. As also noted by Buffi et al., hydrogen pathways should be assessed based on life-cycle performance, material and energy requirements, and technology readiness rather than by colour labels alone [50]. The overall WTW result also depends on the upstream hydrogen pathway, as well as on engine efficiency and hydrogen use during operation [20,57–60]. Fossil-based hydrogen remains the industrial reference case. SMR is the dominant production route, producing grey hydrogen, while coal gasification continues to play a role in coal-dependent systems [6,34,56,61,62]. Across the literature, these pathways consistently lie at the high-emission end of the hydrogen spectrum. SMR is commonly reported in the range of 8.9–12.9 kg CO_2eq/kg H_2, whereas coal gasification performs substantially worse [6,50]. Patel et al. report 12.3 kg CO_2eq/kg H_2 for grey hydrogen produced from pipeline natural gas and 13.9 kg CO_2eq/kg H_2 for LNG-based grey hydrogen, showing that gas-supply assumptions alone can materially influence the result [17]. Staffell et al. further show that methane leakage and downstream conditioning increase life-cycle burdens, while compression and liquefaction add further energy demand [56]. In the context of ICE applications, fossil hydrogen should therefore be regarded as a high-emission baseline rather than a credible low-carbon option.

Blue hydrogen is hydrogen made from fossil fuels, usually natural gas, with CCS. It has lower emissions than grey hydrogen, but it is still not a fully low-emission option. Patel et al. report 7.6 kg CO_2eq/kg H_2 for pipeline-gas blue hydrogen and 9.3 kg CO_2eq/kg H_2 for LNG-based blue hydrogen at 60% overall capture. When capture increases to 90%, these values fall to 5.1 and 6.7 kg CO_2eq/kg H_2, respectively [17]. Overall, the final result depends on methane leakage, capture rate, gas supply route, and the method used in the assessment. For this reason, blue hydrogen can be seen as an intermediate option, but it is not the same as renewable hydrogen.

Renewable electricity-based hydrogen from electrolysis can be a very low-emission option, but only when the electricity has low-carbon emissions. In the JEC WTT report, hydrogen from electrolysis with the EU electricity mix is reported at 20.98 kg CO_2eq/kg H_2, while wind-based electrolysis is reported at 0.43 kg CO_2eq/kg H_2 [31,50]. Patel et al. similarly report 0.6 kg CO_2eq/kg H_2 for proton exchange membrane (PEM) electrolysis using wind electricity, 1.5 kg CO_2eq/kg H_2 for a mixed wind–solar case, and 2.5 kg CO_2eq/kg H_2 for solar-powered PEM electrolysis [17]. The climate performance of electrolysis therefore depends mainly on the electricity source. Accordingly, the same hydrogen can have high or low life-cycle emissions depending on whether the electricity comes from carbon-intensive or low-carbon power [35,37,63]. In this sense, hydrogen is a clear example of how life-cycle results are driven more by the production pathway than by the fuel molecule itself.

Bio-based hydrogen is not one single pathway. It includes biomass gasification, steam biomethane reforming, pyrolysis, hydrothermal routes, and biological routes such as dark fermentation [37,50,64]. Buffi et al. [50] report that many biomass-based pathways are in the range of 6–11 kg CO_2eq/kg H_2. They also show some better cases, such as wood gasification at about 2.14 kg CO_2eq/kg H_2 and biomethane-based hydrogen at 2.74 kg CO_2eq/kg H_2 [50]. These pathways can be useful when waste or residue feedstocks are available. However, the final result can change a lot with the feedstock, the process, and the technology level. For this reason, bio-based hydrogen should not be treated as one single renewable benchmark.

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The main hydrogen pathway families considered in this review are shown in Figure 1. The figure provides an overview of the main production and supply routes discussed in this section.

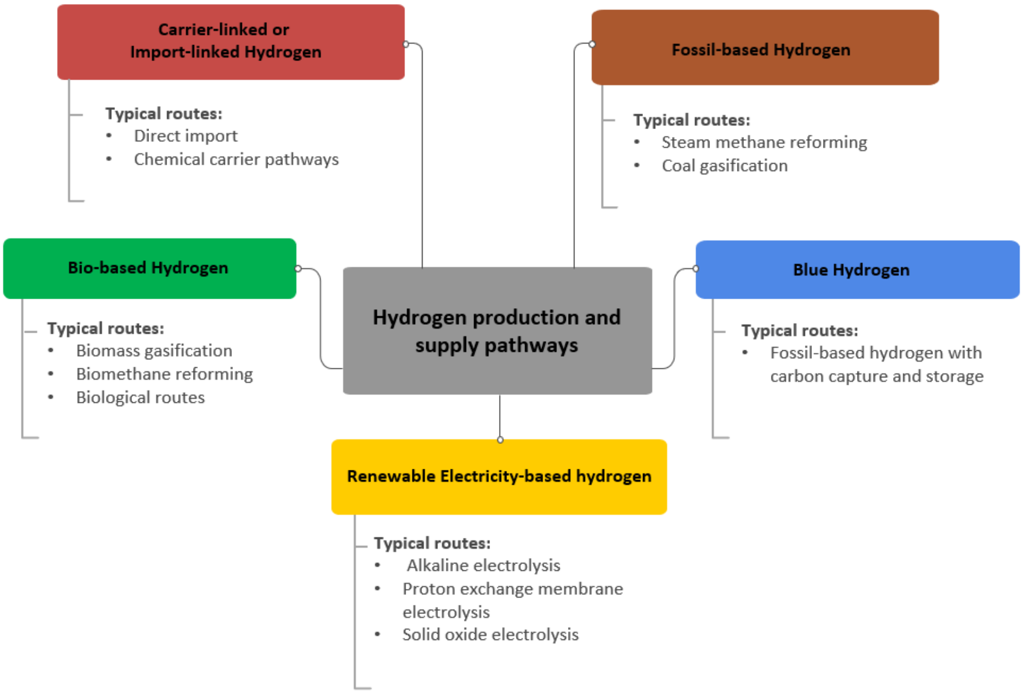

Figure 1. Overview of hydrogen production and supply pathways relevant to ICE applications. Source: [6–9,17,18,34,35,50,55,56,64–66].

Hydrogen is also different from many other fuels because transport and storage are part of the pathway itself. Compression, liquefaction, storage pressure, shipping, and the use of carriers such as ammonia or methanol can all change the final emissions [34,35,65–67]. Sbaffi [65] shows that imported renewable hydrogen can still have relatively low emissions under good conditions, but direct delivery routes usually perform better than carrier-based routes because the extra conversion and reconversion steps add more burden. For H_2-ICE applications, hydrogen should therefore be evaluated as a full supply chain, not only as a fuel with zero-carbon tailpipe emissions.

Hydrogen leakage should also be considered when hydrogen pathways are compared. Hydrogen is not a direct GHG, but it can still affect climate indirectly through atmospheric chemistry. Leakages may occur along the entire supply chain, including storage, transport, distribution, refueling, and during vehicle use. However, as GHG accounting methodology typically refers to IPCC AR5, no GWP is attributed to such hydrogen leakages, while they are accounted at vehicle end-use level. The IPCC explains that higher H_2 emissions may reduce the oxidizing capacity of the atmosphere because hydrogen already uses about 5–10% of the global OH sink. Higher H_2 emissions may also increase water vapour formation. This can support more cirrus clouds in the troposphere and more polar stratospheric clouds, and it can make ozone depletion more efficient [68]. More recent studies report 100-years global warming potential (GWP_{100}) for H_2 of 11 ± 5 and 11.6 ± 2.8, which shows that hydrogen leakage can create a real indirect warming effect [69,70].

Recent work also shows that this effect is fairly stable under most practical conditions. Skeie et al. show that H_2 GWP_{100} changes only a little with leakage size, emission location, or future atmospheric composition, and that the main uncertainty still comes from the hydrogen budget, especially the soil sink [71]. At the life-cycle level, Goita et al. show that adding hydrogen leakage and its indirect warming effect increases total emissions, but usually by less than 0.5 kg CO_2eq/kg H_2 at 2% leakage, while the main differences between pathways still come from the production route, the electricity source, and feedstock-related emissions [72].

This system perspective is shown in Figure 2. The figure shows that the climate and energy performance of H_2-ICE applications depends on the whole hydrogen chain, not only on the engine. The WTT boundary includes hydrogen production, purification, conditioning, storage, and transport/distribution, while the WTW boundary also includes vehicle use. The figure highlights two important points for this review. First, hydrogen pathways can differ a lot because production, conditioning, storage, delivery, and leakage do not have the same energy demand or emissions. Second, some lower-carbon pathways may still need more infrastructure or more energy for compression, liquefaction, storage, transport, or reconversion.

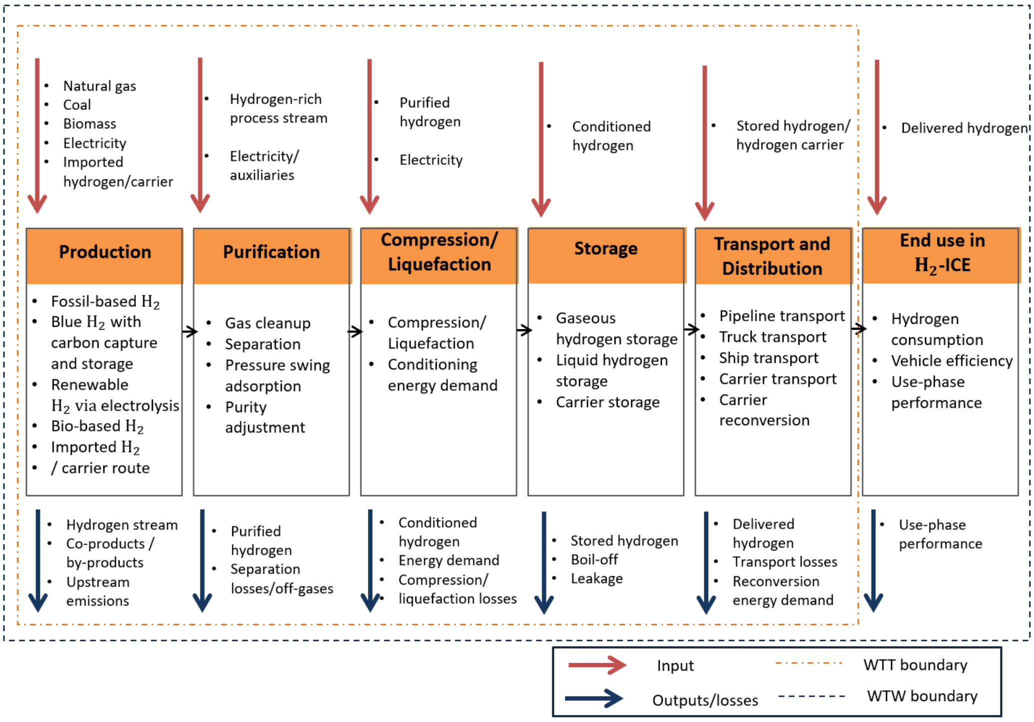

Figure 2. Pathway-dependent hydrogen supply chain and system boundaries for H_2-ICE applications. Source: [1,17,34,35,65,69–72].

Figure 2 also shows that the WTW result depends strongly on upstream choices such as production route, electricity source, storage, transport, and conversion losses. Consequently, supply-chain decisions can increase or reduce the climate benefit seen at the vehicle level.

From a TRL perspective, SMR and coal gasification are still the most mature and widely used production routes, but they perform poorly in climate terms. Blue hydrogen can be seen as a transitional option. Among the lower-carbon routes, alkaline and PEM electrolysis are the most credible today in terms of readiness and scale-up, while solid oxide electrolysis cell (SOEC) and many biological routes are still less mature [2,19,35,37,73]. For this reason, hydrogen can be a realistic fuel for ICEs only when the supply chain is both low-emission and ready for practical use at scale. This contrast between climate performance and readiness is summarized in Figure 3. The figure shows that the lowest-emission pathways are not always the most ready for large-scale deployment. Blue hydrogen routes with CCS are shown as transitional because their emissions still depend strongly on capture rate, upstream methane leakage, gas supply route, and system boundary.

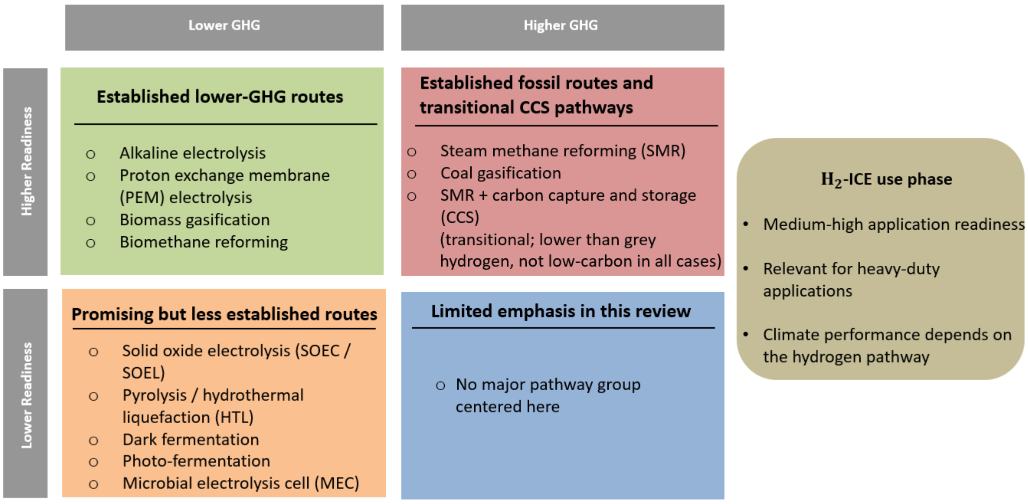

Figure 3. Qualitative trade-off of hydrogen pathways by life-cycle climate performance and readiness. Source: [2,17,35,37,50].

3.2. Methane-Based Fuels

Methane-based fuels provide one of the clearest examples of how the same fuel molecule can arise from very different production pathways and therefore show very different life-cycle results. Fossil CNG and LNG remain the dominant methane routes for ICE applications, but methane-based fuels also include biomethane produced via anaerobic digestion and upgrading, bio-SNG from gasification and methanation, HCNG, and electricity-derived synthetic methane produced via power-to-gas routes (e-methane) [1,11,21,22,31,51,52,54,74]. This diversity is important because methane-based fuels are often treated as broadly cleaner than conventional fuels, while the literature shows that their climate performance depends mainly on methane leakage, feedstock origin, fuel-conditioning requirements, electricity use, and system-boundary assumptions.

Fossil compressed natural gas and LNG are commercially mature, but their climate performance is constrained and highly sensitive to upstream methane losses. Within the JEC framework, fossil CNG is reported at approximately 15.1 g CO_2eq/MJ fuel, while fossil LNG ranges from about 16.6 to 18.3 g CO_2eq/MJ fuel [1]. Curran et al. show that methane leakage during recovery, processing, and transmission remains a major driver of WTW results, while Tong et al. further show that the apparent climate benefit of natural-gas pathways depends strongly on the GWP time horizon chosen for methane [21,54]. Under a 20-year GWP (GWP20), several natural-gas pathways appear significantly less favourable than under a GWP100 because methane becomes more influential in the total balance [21]. For LNG, the burden is not limited to methane leakage alone. Liquefaction energy demand and long-distance transport can materially increase upstream emissions, and comparative studies show that fossil LNG can range from slightly better than diesel to slightly worse depending on assumptions regarding methane slip, transport distance, and engine efficiency [22,74,75]. Fossil methane should therefore be regarded as a mature reference pathway, but not as a consistently low-carbon one.

Renewable methane pathways are centered primarily on biomethane produced through anaerobic digestion and upgrading. In this area, the literature suggests a clear feedstock hierarchy. Crop-based biomethane often performs better than fossil methane, but remains highly variable because cultivation emissions, fertilizer use, digestate treatment, and allocation choices can materially affect the outcome [74,76,77]. Waste- and manure-based biomethane generally performs much more favorably in climate terms, as they often receive avoided-emission credits for methane that would otherwise be released during waste storage or treatment [22,78,79]. Adams and McManus report broad ranges of 26–85 g CO_2eq/MJ for crop biomethane, 11–18 g CO_2eq/MJ for waste biomethane, and −71 to −44 g CO_2eq/MJ for manure biomethane [76]. The JEC results reinforce this pattern, reporting municipal-waste biomethane at 9.5 g CO_2eq/MJ fuel and liquid-manure biomethane at −102.9 g CO_2eq/MJ fuel [1]. These pathways therefore represent some of the strongest near-term methane options for ICE decarbonization.

Upgrading technology is also a critical determinant of performance. Ardolino et al. show that membrane separation, water scrubbing, chemical absorption, and pressure swing adsorption differ sufficiently in methane slip and utility demand to alter pathway ranking [11]. Biomethane should therefore be understood not only as a feedstock-dependent pathway family, but also as one whose performance is shaped by purification design and methane-loss management [78]. In practice, the best-performing biomethane routes are typically associated with waste or residue feedstocks combined with low-loss upgrading systems.

Synthetic methane, or e-methane, is the electricity-based branch of the methane family. Its climate performance depends mainly on the electricity source, hydrogen production, carbon-source treatment, and methanation efficiency [10,80]. Because electricity supply is a major contributor to pathway performance, temporal and geographical variations in renewable electricity availability are often discussed as potential sources of variability. Seasonal and hourly fluctuations can affect electrolyser utilisation, methanation plant operation, and overall fuel production rates. However, for the pathways considered in this review, the resulting impact on reported WTW GHG emissions is expected to be limited, as the underlying studies generally assume compliance with renewable-fuel sustainability criteria and account for renewable electricity using a near-zero carbon intensity. Under these assumptions, temporal variability primarily affects system operation, infrastructure utilisation, and economic performance rather than the reported life-cycle carbon intensity. Under favourable conditions, the JEC framework reports synthetic methane at about 2.4 g CO_2eq/MJ fuel and synthetic LNG at about 6.7 g CO_2eq/MJ fuel [1]. However, Kolb et al. show that PtG methane can become much more emissions-intensive when electricity has high carbon intensity [10]. E-methane can therefore be a low-emission option, but only under specific system conditions.

E-methane should also be treated separately from biomethane in the policy framework. Under RED II and RED III, biomethane belongs to the biomass and biogas framework, while electricity-based synthetic methane belongs to renewable fuels of non-biological origin (RFNBO) [81,82]. The JRC RFNBO report also shows that the climate performance of this pathway depends not only on methanation itself, but also on renewable-electricity sourcing and on conditions already embedded in the RFNBO framework, especially additionality and temporal and geographical correlation under RED II, which RED III continues and further assesses for their impact on costs, GHG savings, and the energy system [81–83]. In the same report, JEC-based values for synthetic methane from renewable electricity and CO_2 from flue gas are reported at about 1.7–3.0 g CO_2eq/MJ, while synthetic LNG from renewable electricity and CO_2 from biogas upgrading is reported at about 6.7 g CO_2eq/MJ [83].

The main methane-based fuel pathways considered in this review are summarized in Figure 4, which provides an overview of the principal production and supply routes discussed in this section.

This system-level perspective is illustrated in Figure 5, which shows the main stages included in methane pathway assessment and clarifies why extraction, upgrading, compression or liquefaction, and vehicle use must be interpreted within clearly defined boundaries.

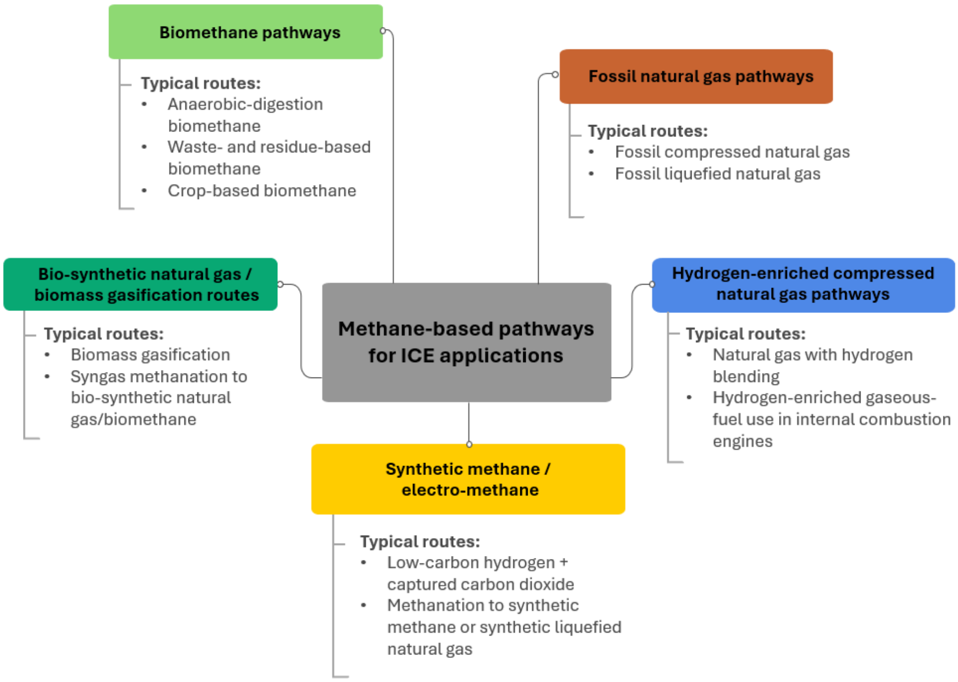

Figure 4. Overview of methane-based fuel pathways relevant to ICE applications, including fossil CNG and LNG, biomethane, bio-SNG, HCNG, and synthetic methane or e-methane. Source: [1,10,11,21,22,50–52,54,74,80,81].

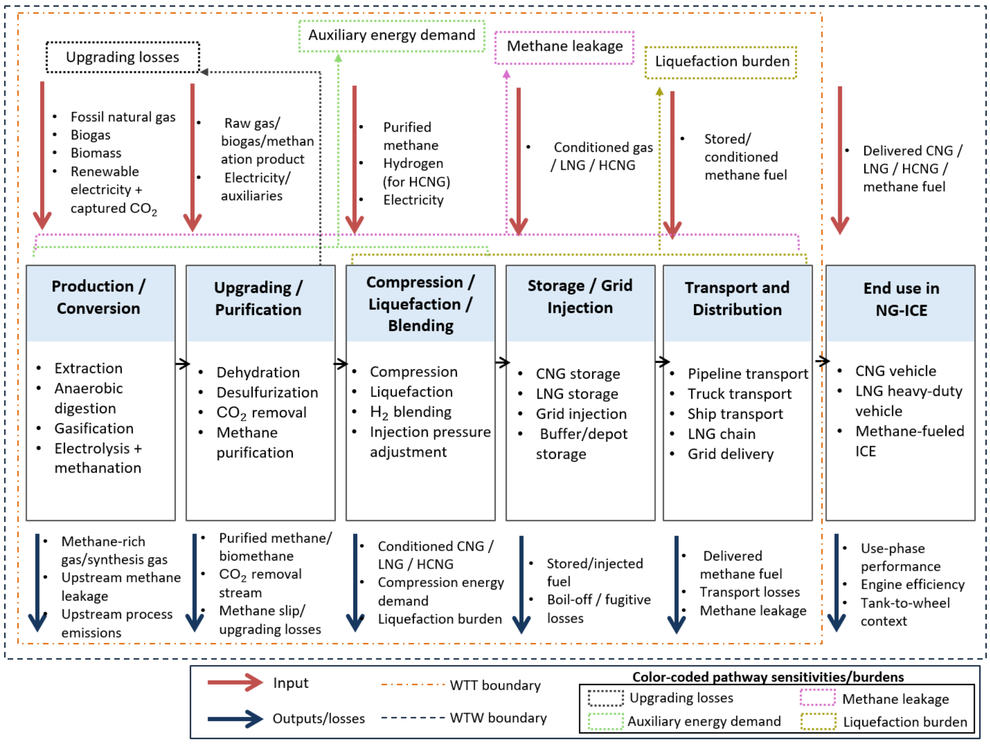

Figure 5. Pathway-dependent supply chain and system boundaries for methane-based fuels in ICE applications. Colored dotted brackets identify the main pathway sensitivities and burdens and show the stages of the chain where they are most relevant. [1,10,11,21,22,50–52,54,74,76,78–81].

From a readiness perspective, methane-based fuels have an important practical advantage. Fossil CNG and LNG are already mature, and biomethane produced via anaerobic digestion is the most established renewable methane pathway. By contrast, bio-SNG and electricity-based synthetic methane (e-methane) remain less mature and depend more strongly on broader changes in the energy system [38–40,84]. This creates a well-known trade-off: the most mature methane pathways are not always the strongest environmentally, while the best-performing waste-based biomethane and e-methane routes remain constrained by feedstock availability, methane management, low-carbon electricity, and scale-up requirements. The contrast between pathway-level climate performance and readiness across the main methane-based fuel routes is summarized in Figure 6.

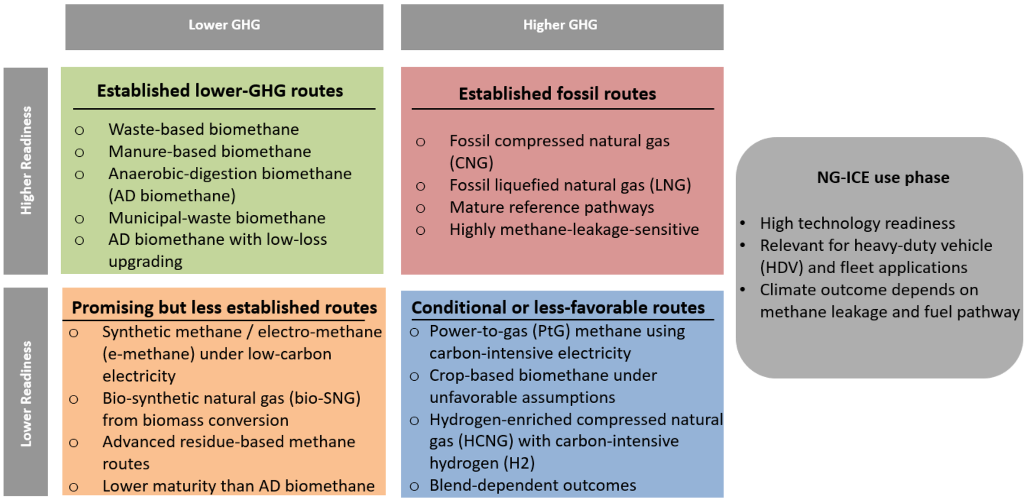

Figure 6. Qualitative trade-off of methane-based fuel pathways by life-cycle climate performance and readiness. Source: [10,11,22,38–40,74,76,80].

3.3. Methanol Pathways

Methanol has a distinctive role among alternative fuels for ICEs. This is due not only to the practical advantages of being a liquid fuel but also to its flexibility within wider energy systems. It can be stored and transported relatively easily, used within existing liquid-fuel infrastructure, and applied not only as a fuel itself but also as an intermediate in broader Power-to-X systems [12,36,85]. For this reason, methanol should not be regarded as a single environmental option. Instead, the literature treats it as a group of pathways, including fossil methanol, bio- and waste-derived methanol, and carbon dioxide-based (CO_2-based) methanol produced with hydrogen, all of which differ significantly in GHG intensity, energy demand, carbon dependence, and commercial maturity [13,24–26,86].

Fossil methanol remains the conventional benchmark against which other pathways are usually compared. In industrial practice, it is typically produced through a syngas route, where the original carbon source is converted into synthesis gas, then into methanol, and finally purified through separation and distillation [12,13,85]. Even within this conventional route, however, performance is not uniform. Natural-gas-based methanol generally performs better than coal-based methanol, although both remain dependent on fossil carbon. Verhelst et al. report about 124.7 g CO_2eq/MJ for coal-based methanol and 28.6 g CO_2eq/MJ for natural-gas-based methanol [12]. Pérez-Fortes et al. report a broader conventional range of 0.5–1.4 t CO_2eq/t methanol, together with a weighted European benchmark of 0.76 t CO_2eq/t methanol and a fossil-energy demand of roughly 33.4–37.15 GJ/t methanol depending on process design [13]. These findings show that fossil methanol is not a single uniform benchmark, although coal-based methanol remains the clearest high-emission reference case.

Bio- and waste-derived methanol pathways often appear more favourable, especially when production is based on residue streams, black liquor, municipal waste, or other non-fossil carbon sources [26,36,87]. Even so, these pathways are not automatically low-emission. Their performance depends on how the feedstock burden is assigned, how far the material must be transported, how intensive the preprocessing and impurity-removal steps are, how co-products are handled, and how the alternative waste-management pathway is defined [26,88]. In practice, these routes range from moderately improved to very low-emission, depending on the feedstock, allocation method, transport assumptions, and treatment of avoided emissions. This is particularly important in comparative assessments because some bio- and waste-derived methanol pathways can perform very well, while others become much less favourable under stricter allocation and boundary assumptions.

Hybrid and transitional methanol routes should also be recognized. IRENA and the Methanol Institute distinguish blue methanol, low-carbon methanol based on co-feeding renewable inputs into existing fossil plants, and combined bio- and e-methanol systems that use excess CO_2 from biomass conversion together with renewable hydrogen [36]. These routes can reduce emissions before fully renewable methanol becomes available at large scale, but they should not be treated as equivalent to fully renewable methanol [12,36].

Carbon dioxide-derived methanol, often referred to as e-methanol or power-to-methanol, has attracted particular interest because it links captured carbon with low-carbon hydrogen and renewable electricity [13,24,86,88]. Its strategic appeal is clear, but its environmental performance depends strongly on system conditions. Across the literature, the main factors are the hydrogen source, the electricity mix, the treatment of the carbon source, and the system boundary used in the assessment [24,89,90]. Pérez-Fortes et al. report plant-level emissions of 0.226 t CO_2/t methanol for a carbon dioxide-based route, compared with 0.768 t CO_2/t methanol for the conventional case [13]. However, this comparison excludes external hydrogen production, carbon dioxide capture, and transport, showing that boundary choice is a central issue in methanol assessment rather than a minor detail. Schreiber et al. and González-Garay et al. likewise show that e-methanol can appear highly favourable when low-carbon electricity and hydrogen are assumed, but much less so when broader fuel-chain conditions are included [24,86]. It is therefore more accurate to describe e-methanol as a conditional low-carbon pathway rather than an inherently carbon-neutral fuel. In the European policy framework, e-methanol is treated as a RFNBO. The JRC RFNBO report shows that its climate performance depends not only on methanol synthesis itself, but also on the source of renewable electricity and on the GHG accounting rules. In the same report, JEC-based values for methanol from renewable electricity and CO_2 from flue gas are reported at about 1.78–1.82 g CO_2eq/MJ [83]. The principal methanol pathway families addressed in this review are illustrated in Figure 7. The figure maps the main methanol production routes discussed in this section, without yet evaluating their relative climate performance or maturity.

For electricity-based methanol pathways, the conversion chain itself represents an important source of environmental burden. Schreiber et al. report a representative power-to-liquid methanol route with a power-to-fuel efficiency of about 52.7–55.4%, depending on the level of heat integration [86]. Gabrielli et al. likewise show that carbon-capture-and-utilisation methanol is highly sensitive to upstream energy assumptions, with total electricity demand of about 10.4–10.9 MWhe/tMeOH and roughly 95% of that demand linked to hydrogen production [90]. For ICE applications, methanol therefore remains a technically credible option, but its environmental value depends mainly on the upstream supply of carbon, hydrogen, and electricity, together with the system boundary used in the assessment. This system-level perspective is illustrated in Figure 8, which emphasizes that methanol assessment depends on how feedstock and carbon inputs, methanol conversion, co-product handling, distribution, and vehicle use are included within the selected boundary. Across methanol pathways, the main interpretative variables include feedstock origin, hydrogen source, electricity supply, carbon-source treatment, co-product handling, heat integration, and boundary definition.

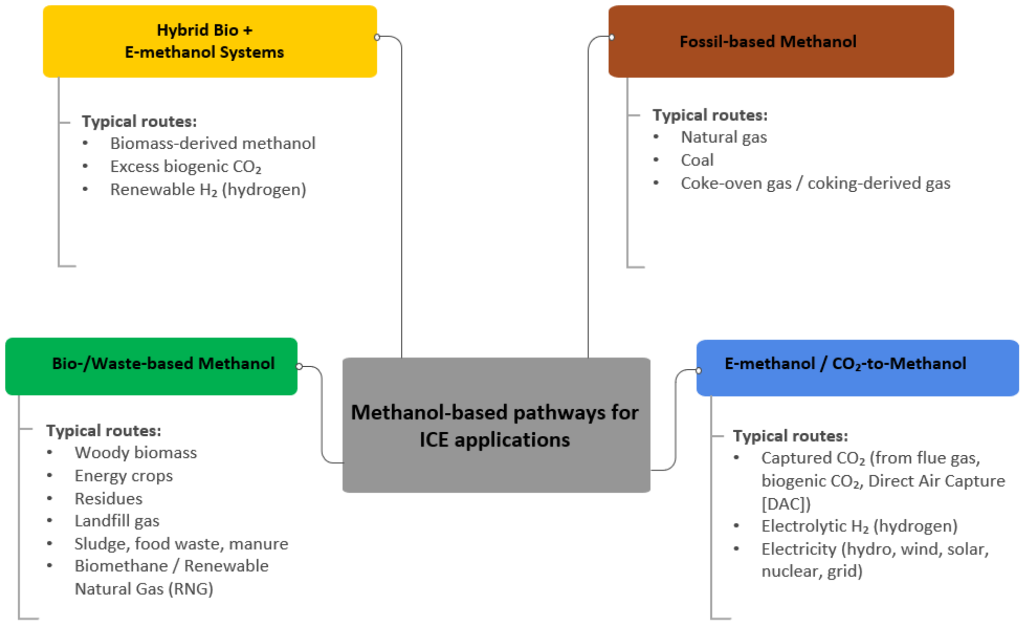

Figure 7. Overview of methanol production pathways relevant to ICE applications, including fossil-based, bio- and waste-based, e-methanol, and hybrid pathways. Source: [12,13,24–26,36,85–89,91].

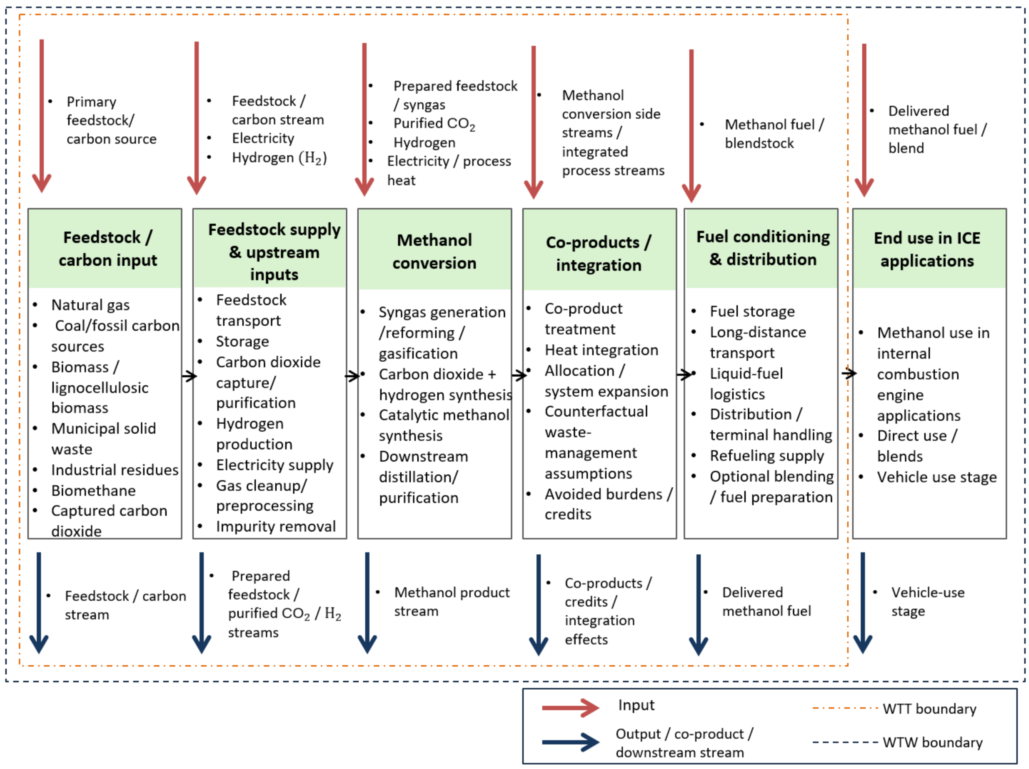

Figure 8. Pathway-dependent supply chain and system boundaries for methanol in ICE applications, including feedstock and carbon inputs, upstream processing, methanol conversion, co-product handling, distribution, and vehicle use across WTT and WTW perspectives. Source: [12,13,24–26,36,85–89].

Methanol is also distinctive in terms of maturity. The molecule itself is already fully commercial and widely traded, whereas the lower-carbon pathways are still much less developed at an industrial scale. Conventional fossil methanol is an established global commodity, while renewable and carbon dioxide-based methanol are still found mainly in pilot projects and early stages of commercial deployment, although activity in this area is increasing [13,36,91,92]. Methanol is therefore best understood as a flexible transition fuel whose long-term role in lower-emission ICE systems will depend not simply on the molecule itself, but on whether lower-carbon production routes can expand under realistic constraints on electricity supply, carbon sourcing, and infrastructure. Figure 9 summarizes the trade-off between pathway-level climate performance and readiness across the main methanol routes.

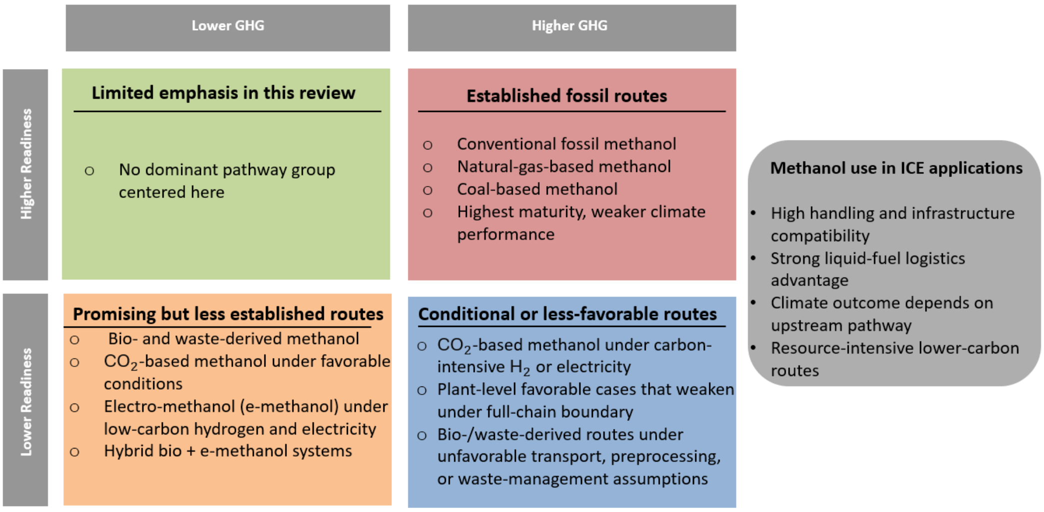

Figure 9. Qualitative trade-off of methanol pathways by life-cycle climate performance and readiness. Source: [12,13,24–26,36,85,86,91].

3.4. Ethanol Pathways

Ethanol is one of the most established alternative liquid fuels for ICEs, but it is also one of the most difficult fuels to generalize in life-cycle terms [14,28,53]. This is particularly important in an ICE applications because ethanol is used not only as a low-level gasoline blend component, but also in higher blends and dedicated formulations, so the upstream production route cannot be separated from the way ethanol is actually used in vehicles [1,93]. The literature covers many ethanol pathways. The main difference is between first-generation crop ethanol and second-generation lignocellulosic ethanol. Other pathway cases include fossil-related ethanol, waste-derived and integrated ethanol, gas-fermentation ethanol, and carbon dioxide-derived ethanol [1,16,28,29,53]. These studies do not identify a single environmental profile. Instead, they show a pathway family shaped by feedstock origin, land-use effects, co-product structure, process integration, utility supply, blend-level use, and technological maturity. Ethanol is therefore better understood as a pathway family than as a single renewable fuel with a fixed environmental profile.

Fossil-related or non-biogenic ethanol pathways remain relevant mainly as comparator routes rather than as plausible decarbonization options. More broadly, the literature shows that these pathways occupy the high-carbon end of the range, while bio-based and more advanced routes can perform much more favorably under suitable assumptions. Coal-based fuel ethanol provides another non-biogenic comparator. Li et al. report a GWP of 8.37 kg CO_2eq/kg ethanol for coal-based fuel ethanol, compared with -1.34 kg CO_2eq/kg ethanol for first-generation fuel bioethanol and -3.12 kg CO_2eq/kg ethanol for second-generation fuel bioethanol in their cradle-to-gate assessment [94]. These values position coal-based ethanol mainly as a high-carbon benchmark rather than as a plausible decarbonization pathway. Even so, pathway rankings remain sensitive to the assessment boundary and to the treatment of end use, which makes it especially important not to interpret ethanol through a single representative value [1,14]. These comparator pathways are primary useful because they illustrate that the environmental case for ethanol depends on pathway design and feedstock origin, not on the product name alone.

The most mature route remains first-generation ethanol, produced mainly from sugar- and starch-based feedstocks such as sugar cane, sugar beet, corn, wheat, cassava, and sweet sorghum [53,95]. Even this commercially familiar category, however, shows substantial environmental variation. Within the JEC framework, integrated sugar-beet ethanol is reported at 11.3 g CO_2eq/MJ fuel, whereas wheat ethanol reaches 64.5 g CO_2eq/MJ fuel when produced with a conventional natural-gas boiler and 33.8 g CO_2eq/MJ fuel when distillers dried grains with solubles (DDGS) are valorized through biogas integration [1]. Sugar-cane ethanol is often presented as one of the strongest first-generation cases, but its performance still depends heavily on land-use treatment, co-product accounting, and process-energy supply [96]. Liu et al. report a baseline carbon intensity of 35.2 g CO_2eq/MJ for Brazilian sugar-cane ethanol and show that this value changes substantially under different allocation and land-use assumptions [27]. Studies of U.S. corn ethanol show the same pattern. The results change when process-energy supply, and future technology improvements are treated differently [97,98]. First-generation ethanol may therefore perform favourably relative to gasoline, but it should not be treated as a single, environmentally consistent pathway.

Second-generation lignocellulosic ethanol is generally more attractive in climate terms because it uses residues, woody biomass, grasses, and other non-food feedstocks [28,99,100]. Within the JEC framework, ethanol from waste residual wood is reported at about 29.0 g CO_2eq/MJ fuel, while wheat-straw ethanol is reported at 17.8 g CO_2eq/MJ fuel [1]. Pretreatment chemistry, enzyme demand, wastewater management, internal heat recovery, and the handling of lignin and other side streams can all materially affect pathway performance [101–104]. For this reason, a favourable feedstock alone does not guarantee favourable life-cycle performance. Conversion design, utility supply, and residue handling still play a major role.

Waste-derived and integrated ethanol systems provide a clear example. Their best results usually come not only from low-burden feedstocks, but also from strong plant integration and residue valorisation. Xu et al. show this in a cassava-based ethanol system combined with anaerobic digestion and combined heat and power (CHP), where greater recovery of internal residues improves climate performance [105]. Similar conclusions are reported in cellulosic biorefinery studies, where lignin, stillage, and related streams are used for heat, power, or biogas [103,106]. Pathway performance therefore depends as much on plant integration, residue valorisation, and internal energy management as on the feedstock category itself.

Additional advanced routes include gas-fermentation ethanol and carbon dioxide-derived ethanol. Handler et al. report very low values for some gas-fermentation routes, including 1.5 g CO_2eq/MJ ethanol for forest-residue gas fermentation and 31.4 g CO_2eq/MJ ethanol for basic oxygen furnace (BOF)-gas ethanol [16]. However, these results still depend on methane control, utility assumptions, and internal energy configuration. Carbon dioxide-derived ethanol is more dependent on upstream conditions. Park et al. and Rojas Sánchez et al. show that these pathways become attractive only when both hydrogen and electricity are very low-carbon [29,107]. Figure 10 summarizes the main ethanol pathway families considered in this review.

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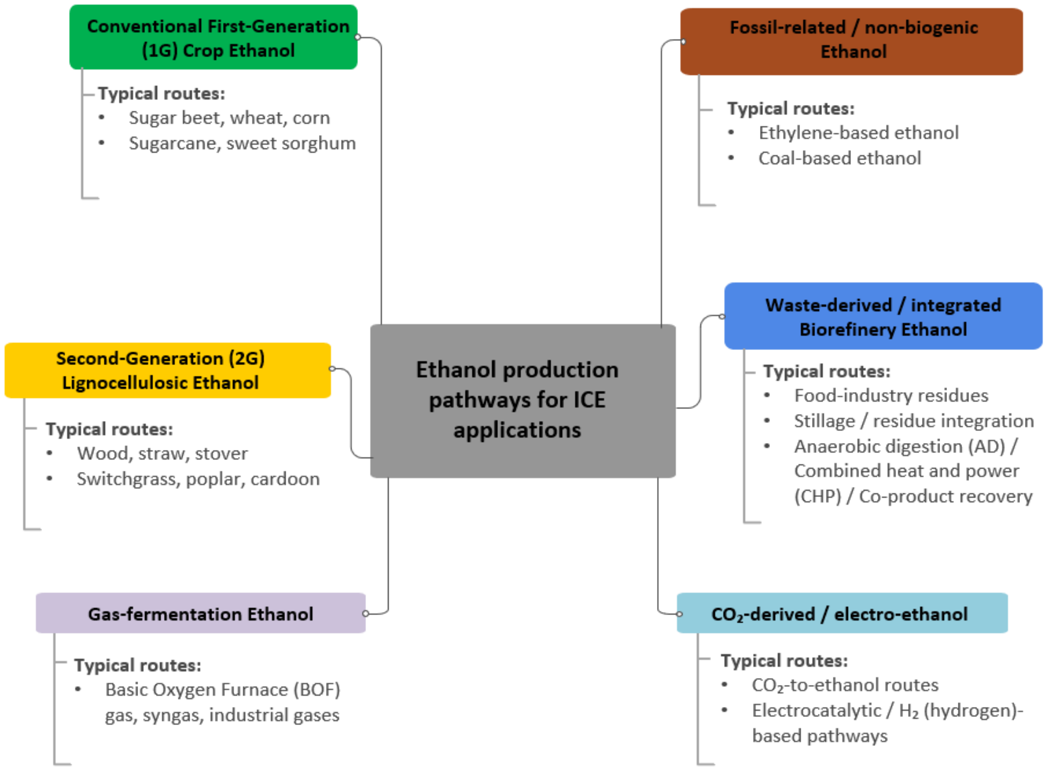

Figure 10. Overview of ethanol production pathways relevant to ICE applications, including fossil-related, first-generation crop, second-generation lignocellulosic, waste-derived/ integrated biorefinery, gas-fermentation, and CO_2-derived/electro-ethanol pathways. Source: [1,14–16,28,29,53,95,99–107].

For ethanol, methodological choices can affect the result as much as the technology itself. Allocation method, co-product treatment, land-use change, nitrous oxide (N_2O) assumptions, process heat source, and the treatment of end-use blends can all affect the reported outcome [14,32,108,109]. Differences in FU, system boundary, and data maturity can further amplify these variations across studies. For ICE applications, ethanol is therefore best assessed through a pathway-resolved LCA framework that connects production, formulation, and use, rather than through isolated headline values. This is especially important because ethanol is used in multiple blends and formulations, meaning that a pathway that performs well at the production stage does not necessarily deliver the same WTW benefit once vehicle use is included [93,110]. The JEC framework shows this clearly by including ED95 (95% ethanol fuel blend for compression-ignition applications) as a diesel-engine ethanol formulation instead of neat ethanol, with a selected WTT value of 17.6 g CO_2eq/MJ fuel for a straw-based route that includes fossil i-butanol [1,31]. In the same transport comparison, JEC reports that ethanol pathways can deliver about 30% to 90% WTW GHG savings relative to conventional gasoline, depending on feedstock and process design, with waste-wood and straw routes among the most favourable cases [1]. This system-level perspective is illustrated in Figure 11, which shows how feedstock supply, upstream inputs, conversion, co-product integration, formulation, and distribution, and vehicle use interact within ethanol pathway assessment. Across ethanol pathways, the main interpretative variables include feedstock type and land-use treatment, process design and heat source, co-product treatment and allocation, and blend-level end-use context. In some cases, these methodological differences do not merely shift the magnitude of reported results, but change which ethanol pathway appears preferable.

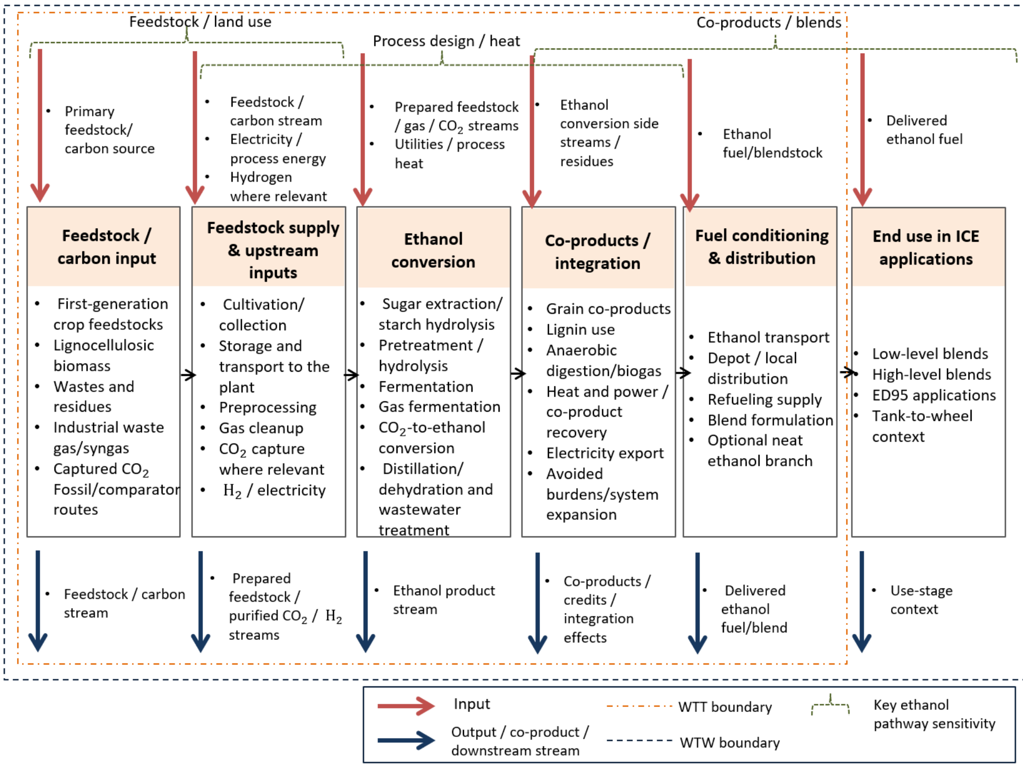

Figure 11. Pathway-dependent supply chain and system boundaries for ethanol in ICE applications, linking feedstock supply, upstream inputs, conversion, co-product integration, fuel conditioning and distribution, and vehicle use across WTT, TTW, and WTW perspectives. Dotted brackets indicate the main pathway sensitivities, including feedstock type and land-use treatment, process design and heat source, and the role of co-products and blend-level end use. Source: [1,14,16,28,93,95,100–103,106–109].

From a readiness perspective, ethanol pathways are easier to classify than to rank in terms of environmental performance. First-generation ethanol remains the most commercially established renewable liquid fuel and is already embedded in major fuel markets [27,53,95]. Second-generation lignocellulosic ethanol is less mature but growing in importance, while waste-derived and integrated routes often appear environmentally promising but remain highly dependent on design choices [28,103,111]. Gas-fermentation ethanol is emerging, and carbon dioxide-derived ethanol remains the least mature of the main routes, with strong dependence on future access to low-carbon hydrogen and electricity [16,29,107]. Taken together, the literature shows a clear pathway pattern. Fossil-related ethanol acts mainly as a high-carbon comparator, with coal-based ethanol as a clear example [94]. First-generation ethanol is mature but highly variable. Second-generation ethanol is often stronger in climate terms, but it is also more sensitive to process design. The best waste-derived, integrated, and gas-fermentation routes depend strongly on internal energy recovery, co-product treatment, and methane management. The relationship between pathway-level climate performance and readiness for the main ethanol routes is summarized in Figure 12. Overall, the main lesson is that the final LCA result depends on pathway design, methodological choices, and end-use context.

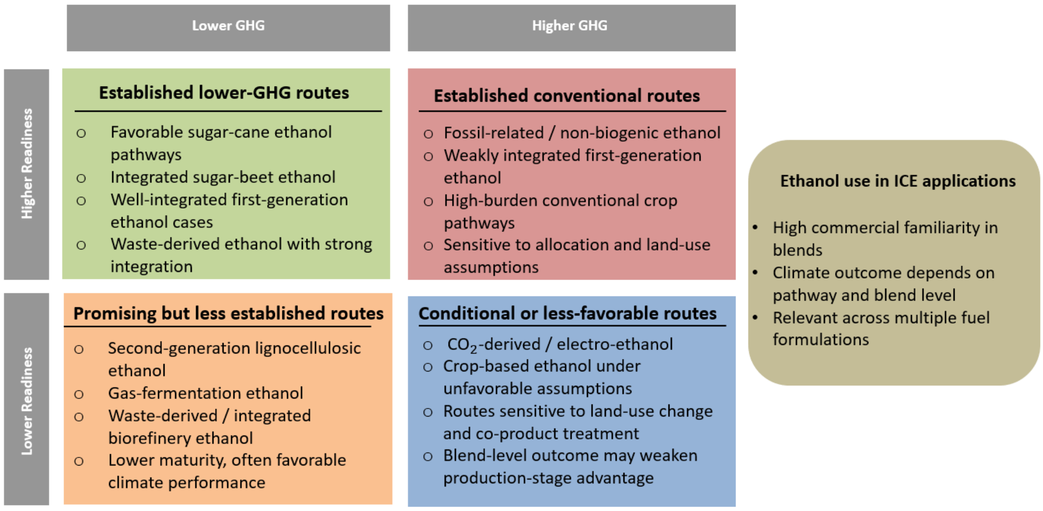

Figure 12. Qualitative trade-off of ethanol pathways by life-cycle climate performance and readiness. Source: [14,16,28,29,53,95,103,107,111].

4. Combustion Concepts for Alternative Fuels in Hard-to-Abate Sectors

The integration of alternative fuels into ICEs is primarily driven by the interaction between fuel properties and application-specific constraints. IN this context, the TTW phase remains relevant in shaping overall WTW outcomes, as it captures differences in both efficiency and direct GHG emissions. The use phase is characterized by significant variations in direct emissions, ranging from zero CO_2 emissions at the point of use for hydrogen to carbon-containing fuels such as methane, methanol, and ethanol, whose impact depends on both fuel composition and engine operation. In practical applications, the interaction between fuel characteristics and engine design becomes critical in hard-to-abate sectors such as HD transport, off-road machinery, and maritime applications, where operational requirements limit the range of viable solutions. In these contexts, ICEs are being adapted to accommodate alternative fuels through both fuel-specific design approaches and more flexible architectures. Recent developments highlight two complementary trends. On one hand, fuel-specific engine concepts are being developed to fully exploit the characteristics of individual fuels, particularly in demanding applications where efficiency and performance are critical [43,112]. On the other hand, flexible engine platforms derived from a common base architecture are emerging as a strategy to enable the use of multiple fuels with limited hardware modifications, improving scalability and facilitating industrial deployment [42,113]. These approaches reflect a trade-off between fuel-specific optimisation and system flexibility, which is closely linked to both technological maturity and application constraints.

This section first examines the main fuel properties relevant for ICE operation, and then discusses representative application cases in hard-to-abate sectors, highlighting the deployment readiness of the different fuels in ICEs for the analyzed sectors.

4.1. Fuel-Specific Challenges and Opportunities

The behavior of alternative fuels in ICEs is governed by a limited set of key physico-chemical properties, together with fuel-dependent combustion characteristics, as shown in Table 3. Methane properties refer to the CH_4 molecule and are therefore representative of both CNG and LNG.

Hydrogen is characterized by a very high gravimetric energy content, wide flammability limits, and fast flame propagation. These features enable efficient lean-burn operation, but also require careful control of mixture formation and combustion to avoid abnormal combustion phenomena and to manage NOx emissions [4], while recent engine developments confirm the feasibility of high-efficiency operation under controlled conditions [42]. However, compressed hydrogen typically exhibits a volumetric energy density of only about 5–8 MJ/L at 350–700 bar, substantially lower than that of conventional liquid fuels. As a result, HD vehicles require larger onboard storage systems and high-pressure tanks, potentially affecting vehicle packaging, payload capacity, and achievable driving range in long-haul applications.

Table 3. Fuel properties relevant for ICEs applications. Source: [4,12,14,21,22,42].

Property	Unit	Hydrogen	Methane	Methanol	Ethanol
Ambient state	[-]	Gas	Gas	Liquid	Liquid
LHV	[MJ/kg]	120	50	20	27
AFR_{st}	[-]	34.3	17.2	6.5	9
Laminar flame speed	[cm/s]	∼170	∼25	∼35	∼30
Ignition limits λ-range	[-]	∼0.13–10	∼0.9–2	∼0.25–2	∼0.3–2
Advantages		High efficiency potential; lean-burn capability; no CO_2 at combustion	Mature technology; stable combustion; existing infrastructure	Good knock resistance; flexible feedstock; easier storage than gases	High knock resistance; widely used in blends
Challenges		Pre-ignition, H_2 leakages, NO_x formation, complex air handling	Methane slip; lower flame speed	Low energy density, cold-start issues, material compatibility	Very low energy density, cold-start issues, aldehyde emissions

Methane-based fuels offer a more balanced combination of properties, including relatively high energy density compared to hydrogen and strong resistance to knock. These characteristics support stable combustion and have enabled widespread adoption in HD applications. However, the lower flame speed and the occurrence of methane slip introduce limitations in terms of efficiency and overall GHG performance, particularly due to the high GWP of methane emissions [21,22].

Methanol and ethanol share several characteristics typical of oxygenated fuels, including high octane number and strong charge-cooling effects, which enhance knock resistance and allow efficient spark-ignition (SI) operation. At the same time, cold-start and fuel handling issues may affect real-world performance [12,14]. For methanol, the relatively low volumetric energy density (approximately 16 MJ/L, compared with about 35–36 MJ/L for diesel fuel) generally requires larger fuel tanks to achieve equivalent driving ranges. Nevertheless, methanol retains the practical advantages of liquid-fuel storage, reducing some of the infrastructure and packaging constraints associated with gaseous fuels.

Overall, the comparison highlights that no single fuel provides optimal performance across all properties. Instead, each fuel introduces specific trade-offs between reactivity, stability, efficiency, and operability. These differences directly influence engine design choices and operating strategies, and ultimately determine the suitability of each fuel for specific applications and combustion concepts, as can be seen in the next section.

4.2. Application Case Studies in Hard-to-Abate Sectors

In HD road transport, ICEs remain a dominant solution due to their robustness and ability to operate under sustained high-load conditions, as also reflected in their continued use in applications requiring high energy density, operational flexibility, and rapid refueling [41]. Methane-based fuels represent the most mature alternative in this sector, with widespread deployment in commercial vehicles and well-established engine technologies. For example, modern natural gas engines, such as 10 L HD platforms, have achieved brake thermal efficiency values around 41% through optimized combustion and air-handling strategies [113]. From a TTW perspective, methane combustion results in direct CO_2 emissions proportional to its carbon content, typically around 55–56 gCO_2/MJ, which is lower than liquid fuels due to its higher hydrogen-to-carbon ratio. However, methane slip during combustion introduces an additional GHG contribution that can significantly affect overall climate performance (i.e., methane GWP100 is around 28–30) [21,41]. Hydrogen ICEs are emerging as a promising option for HD applications, particularly as a complement to fuel cell systems. Recent developments include medium- and HD engines such as the 6.7 L hydrogen SI engine developed by Cummins and larger platforms such as 15–17 L engines for long-haul applications, with reported brake thermal efficiencies in the range of 40–45%, comparable to modern diesel engines [42,43]. Recent demonstrations of hydrogen ICE trucks indicate fuel consumption values on the order of 9–12 $kgH_2/100$ km for HD long-haul applications [2,44]. When converted on an energy basis, these values correspond to approximately 9–14 MJ/km depending on vehicle configuration and operating conditions, remaining broadly comparable to other HD ICE fuels [45]. These values are consistent with the typical energy demand range observed for other fuels in HD transport and confirm that TTW energy demand remains broadly comparable across fuels, with hydrogen showing slightly lower values under favourable operating conditions due to its high efficiency potential. From an emissions perspective, hydrogen combustion produces no direct CO_2 emissions (i.e., 0 gCO_2/MJ), representing a key advantage in decarbonization strategies. However, the possibility of hydrogen leakage should be considered when assessing the overall TTW and WTW performance. Although hydrogen is not a direct GHG, it has an indirect warming effect through atmospheric chemistry, with a GWP100 of approximately 11. While leakage rates during vehicle operation are generally low, this contribution may become relevant at the system level and should be consistently accounted for in comparative assessments [69–71]. In addition, the formation of nitrogen-related species such as N_2O under specific conditions may contribute to the overall GHG balance, although at significantly lower levels compared to carbon-based fuels (i.e., N_2O GWP100 is around 273 [68]). Other fuels, such as ethanol and methanol, play a more limited but still relevant role in HD applications. Ethanol has been successfully applied in dedicated compression-ignition (CI) engines, such as the Scania ED95 platform, demonstrating diesel-like performance together with reduced emissions [46]. At the use-phase level, ethanol combustion results in direct CO_2 emissions of approximately 70–71 gCO_2/MJ, consistent with its carbon content. Methanol, while technically feasible, is currently less widespread in HD road transport and is mainly considered in niche or emerging applications. From a TTW perspective, methanol combustion produces direct CO_2 emissions on the order of 67–69 gCO_2/MJ, with efficiency constraints primarily related to its lower energy density compared to conventional fuels. As mentioned, HD engine design is increasingly moving toward flexible multi-fuel architectures based on a common base engine. These platforms allow the use of different fuels through targeted modifications of subsystems such as injection, air handling, and combustion chamber design, while maintaining a high degree of hardware commonality. Examples include fuel-agnostic engine families where engines derived from a shared architecture can be configured for different fuels, achieving efficiency levels exceeding 40% across hydrogen and natural gas applications [42,113]. From an operational perspective, this approach supports a gradual transition between fuels, although it may limit the extent of fuel-specific optimisation compared to dedicated engine designs.

In maritime applications, the transition toward alternative fuels is driven by the need to reduce emissions while maintaining operational flexibility over long distances.

Methanol is currently one of the most advanced options for ICE applications in this sector. Large marine engines, including dual-fuel systems such as the MAN B&W ME-LGIM platform, have demonstrated reliable operation with significant accumulated service experience, while maintaining performance comparable to conventional fuels [47]. Recent industrial analyses indicate that methanol-fuelled large vessels, such as container ships in the 16,000 TEU class, operate with engine power on the order of 34 MW, confirming the applicability of methanol to large-scale propulsion systems. In these configurations, the main engine operates on methanol, while auxiliary systems often remain based on conventional marine fuels, highlighting that full system integration is not yet achieved in current deployments [49]. In addition, retrofit solutions and medium-speed engines have been developed for existing vessels, further supporting the adoption of methanol in shipping [48]. From a TTW perspective, methanol combustion produces direct CO_2 emissions, but with lower carbon intensity per unit of energy compared to conventional marine fuels. Methane-based fuels, particularly in the form of LNG, are also widely used in maritime transport and represent a transitional solution due to their technological maturity and existing infrastructure. In addition, dual-fuel engines operating on LNG are well established in several vessel categories. In these systems, combustion is typically initiated by a small quantity of pilot fuel, usually marine diesel, which contributes to the overall TTW GHG emissions and must therefore be considered when evaluating the environmental performance of the complete fuel-engine system. Finally, from a TTW perspective, methane slip remains a critical issue, as unburned methane emissions can significantly affect the overall GHG balance [21]. Hydrogen and hydrogen-based fuels are at an earlier stage of development in maritime applications. Current studies focus on their use in specific segments, such as short-sea shipping and port operations, where storage constraints are less critical. From a TTW perspective, hydrogen combustion offers the advantage of zero direct CO_2 emissions, but practical deployment remains limited by fuel storage, infrastructure, and system integration challenges [3]. In practice, current hydrogen-based propulsion concepts remain largely confined to pilot and demonstration projects, with limited large-scale deployment compared to methane and methanol systems. In addition, emerging concepts based on ammonia-fuelled ICEs are under development, particularly for large-scale maritime applications, although they remain at an early stage of deployment [66].

Figure 13 provides a qualitative comparison of alternative fuels for ICE applications in HD and maritime sectors, based on deployment readiness and TTW carbon footprint, considering both CO_2 emissions from fuel combustion and other GHG emissions (i.e., N_2O, CH_4 slip). The positioning along the horizontal axis reflects the current level of technological and commercial deployment observed in the application cases discussed in Section 4.2. Methane-based fuels are located at the highest maturity levels in both sectors, consistent with their widespread adoption in HD transport and maritime applications and the availability of well-established engine technologies and infrastructure [41]. Methanol shows a higher level of deployment in maritime applications compared to HD transport, reflecting the introduction of dual-fuel large marine engines and increasing industrial uptake, while remaining less developed in road transport [49]. Hydrogen ICEs are positioned at intermediate maturity in HD applications and lower maturity in maritime applications, where their use is currently limited to pilot and demonstration projects [3,42]. Ethanol appears at lower deployment levels in maritime sectors, while in HD transport its application is emerging in specific solutions such as ED95 engines [46]. From a TTW perspective, direct CO_2 emissions from combustion primarily scale with the carbon content of the fuel under stoichiometric conditions, resulting in comparable emission levels for carbon-based fuels on an energy basis and near-zero CO_2 emissions for hydrogen. However, the figure reflects GHG emissions in CO_2-equivalent terms, which include also contributions from other species (e.g., fuel leakages, methane slip, or N_2O generated during combustion). In particular, methane-based fuels may exhibit higher TTW GHG emissions due to methane slip during combustion, which has a significantly higher GWP than CO_2 and can influence the overall emission profile [21]. For hydrogen systems, although direct CO_2 emissions are absent, the formation of NOX and, under specific conditions, secondary species such as N_2O may contribute to the overall climate impact [112], together with H_2 slip.

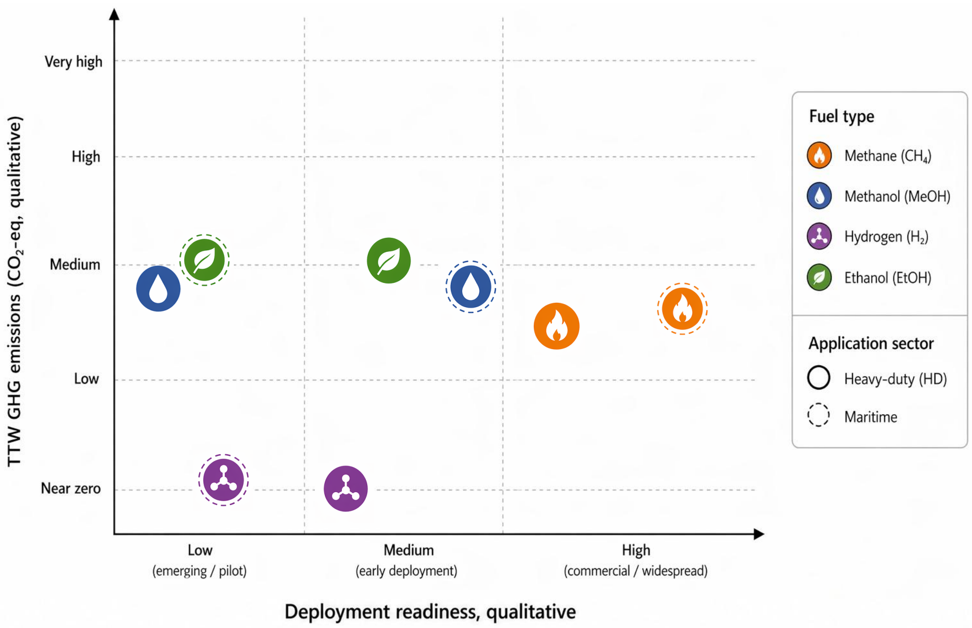

Figure 13. Qualitative positioning of alternative fuels for ICEs applications in HD and maritime sectors, based on deployment readiness and TTW GHG emissions (CO_2-equivalent). Source: [3,21,41,42,45,46,49,112].

It is worth mentioning that deployment readiness is influenced also by regulatory frameworks that promote transport decarbonisation through emission standards, renewable-fuel targets, and sector-specific climate policies. This application dependence is particularly evident for alcohol fuels, where ethanol has reached a high level of deployment maturity in road transport, while methanol is currently experiencing its most significant market uptake in maritime applications, supported by evolving regulatory frameworks and dedicated fuel standards [114].

5. Well-to-Wheel Analysis and Cross-Fuel Comparison

This section brings together the WTT and TTW perspectives discussed in the previous sections to provide an integrated assessment of alternative fuels for ICE applications in hard-to-abate sectors. Due to the variability and limited comparability of the available data in the literature, the WTW assessment is not performed as a fully harmonized life-cycle analysis. Instead, it is developed through a set of representative case studies, selected to illustrate the combined effect of upstream pathways and engine-level performance under consistent assumptions. The analysis is structured in three parts. Section 5.1 reviews WTT emissions across the main fuel pathways, highlighting the dominant role of production routes. Section 5.2 examines TTW performance in representative HD applications, focusing on energy demand and direct emissions. Finally, Section 5.3 combines these elements to discuss the resulting WTW performance and the associated trade-offs between environmental impact, technological maturity, and practical applicability.

5.1. Well-to-Tank Comparison and Pathway-Level Synthesis

This section compares WTT differences across the main fuel pathways and interprets their implications for cross-fuel assessment. Table 4 summarizes the main comparative findings in terms of pathway performance, indicative GHG outcomes, maturity, and deployment constraints across hydrogen, methane-based fuels, methanol, and ethanol. The purpose of the table is not to establish a fixed ranking of fuels, but to highlight the conditions under which different pathways may provide climate benefits or remain associated with high life-cycle emissions. The comparison shows that substantial variability exists within each fuel family. Fossil pathways generally occupy the higher-emission end of the spectrum, whereas many of the lowest-emission cases are associated with waste-based, residue-based, or renewable electricity-based routes. As an example, this variability is particularly evident for methane-based fuels, where fossil pathways and waste-derived biomethane can occupy opposite ends of the emissions spectrum. At the same time, no single pathway ranking remains valid across all methodological assumptions and system configurations, as results are strongly influenced by factors, such as electricity carbon intensity, methane leakage, land-use treatment, co-product allocation, and carbon-source accounting. The table also highlights the trade-off between environmental performance and deployment readiness. Several pathways with the lowest reported GHG emissions remain dependent on low-carbon electricity, sustainable feedstocks, reliable carbon sources, or supporting infrastructure that is not yet widely available. Conversely, some of the most commercially mature pathways continue to play an important role in current transport systems despite offering more limited climate benefits. For ICE applications, particularly in hard-to-abate sectors, pathway evaluation therefore requires the simultaneous consideration of environmental performance, technology maturity, and deployment constraints.

5.2. Tank-to-Wheel Performance Summary on HD Case Study

This section examines TTW performance through an illustrative HD transport case study based on representative fuel-powertrain combinations for which harmonized datasets are available in the literature. The purpose is not to provide a comprehensive TTW comparison of all pathways discussed in this review, but rather to establish a consistent basis for the subsequent WTW assessment. Consequently, the fuels and fuel formulations included reflect current HD applications and data availability rather than the full set of pathways reviewed in previous sections. Methanol is therefore excluded from the comparison, as it is primarily discussed in the context of maritime applications, while maritime transport itself is not included due to the limited availability of harmonized TTW datasets.

The analysis regarding NG and ethanol is based primarily on the JEC TTW framework for HD vehicles [115], which provides a consistent set of results for representative fuel-powertrain combinations under long-haul operating conditions. In particular, the comparison considers SI engines fuelled by methane-based fuels, CI engines operating on ED95, and hydrogen SI engines. The JEC results are reported for a representative HD long-haul truck (group 5, model year 2025) with a weighted payload of approximately 14.3 t. For hydrogen ICEs, recent demonstrations indicate values in the range of approximately 9–14 MJ/km depending on configuration and operating conditions [2,44,45]. Table 5 summarizes the main TTW characteristics of the selected fuel-powertrain combinations. The comparison shows that TTW energy demand remains within a relatively narrow range across fuels, while differences in GHG emissions are primarily associated with fuel carbon content and the contribution of other GHG species, such as methane slip, hydrogen leakages, or combustion-related N_2O emissions.

Table 4. Cross-fuel synthesis of pathway performance, indicative GHG outcomes, maturity (TRL/CRL), and main deployment constraints for hydrogen, methane-based fuels, methanol, and ethanol in ICE applications. GHG values are reported primarily under WTT conditions.

Fuel	Indicative WTT GHG Emissions	Lower-GHG Pathway Examples	Higher-GHG Pathway Examples	Indicative Maturity (TRL/CRL)	Key Interpretation/Deployment Constraint
Hydrogen	SMR: 8.9–12.9 kg CO_2-eq/kg H_2; coal gasification: 28.2 kg CO_2-eq/kg H_2; wind electrolysis: 0.43 kg CO_2-eq/kg H_2	Renewable electrolysis under low-carbon electricity; selected bio-based routes; favourable direct delivery routes	Grey hydrogen; coal gasification; blue hydrogen under low capture rates or high methane leakage	High: SMR, coal gasification; medium–high: alkaline and PEM electrolysis; emerging: SOEC routes and several bio-based routes	Climate outcome is driven by electricity mix, methane leakage, CCS scope, and logistics.
Methane-based fuels	Fossil CNG: 15.1 g CO_2-eq/MJ fuel; fossil LNG: 16.6–18.3 g CO_2-eq/MJ fuel; municipal-waste biomethane: 9.5 g CO_2-eq/MJ fuel; manure biomethane: −102.9 g CO_2-eq/MJ fuel	Waste- and manure-based biomethane; synthetic methane under low-carbon electricity	Fossil LNG under high leakage; fossil CNG under unfavourable methane assumptions; PtG methane using carbon-intensive electricity	High: CNG and LNG; medium–high: anaerobic-digestion biomethane; emerging: bio-SNG and synthetic methane	Climate outcome is driven mainly by methane leakage, feedstock origin, and upgrading losses.
Methanol	Coal methanol: 124.7 g CO_2-eq/MJ; natural-gas-based methanol: 28.6 g CO_2-eq/MJ; CO_2-based methanol: 0.226 t CO_2/t MeOH (plant-level)	Bio- and waste-derived methanol; e-methanol under low-carbon H_2 and electricity	Coal-based methanol; conventional fossil methanol; CO_2-based methanol under carbon-intensive electricity or hydrogen	High: conventional fossil methanol; medium: bio-/waste-derived methanol; emerging: e-methanol and other CO_2-based routes	Lower-carbon routes depend on low-carbon H_2, carbon source, and full-chain boundary definition.
Ethanol	Sugar-beet ethanol: 11.3 g CO_2-eq/MJ fuel; wheat ethanol with natural-gas boiler: 64.5 g CO_2-eq/MJ fuel; BOF-gas ethanol: 31.4 g CO_2-eq/MJ ethanol; forest-residue gas fermentation: 1.5 g CO_2-eq/MJ ethanol	Lignocellulosic, waste-derived, integrated, and gas-fermentation routes; favourable sugar-cane pathways; low land-use change (LUC) cases	Fossil-related ethanol; weakly integrated first-generation ethanol pathways; high-burden conventional pathways under unfavourable allocation or land-use assumptions	High: first-generation ethanol; medium: second-generation lignocellulosic ethanol; emerging: gas-fermentation and CO_2-derived ethanol	Climate outcome depends on feedstock, land-use treatment, co-products, and process integration.

Indicative maturity labels are qualitative and summarised from the reviewed literature: high = commercially established; medium = demonstration to early commercial; emerging = pilot to early scale-up. Indicative GHG values are reported in the units most commonly used for each fuel family and should be interpreted within their own pathway context rather than as directly comparable values across all fuels. Summary based on [1,6,10,12–14,16,17,19,22,26,27,35,36,38,50,76].

Table 5. TTW performance of alternative fuels in HD ICE applications (long-haul).

Parameter	Methane (CNG/LNG)	Ethanol (ED95)	Hydrogen (ICE)
CO_2 emissions from combustion [g/MJfuel]	∼55	∼70	0
TTW energy demand [MJ/tkm]	∼0.82–0.83	∼ 0.66 MJ/tkm	∼0.75–1.0 MJ/tkm *
GHG species (different from CO_2)	CH_4 (methane slip)	N_2O (from combustion)	H_2 leakages, possible N_2O (from combustion)
Relative contribution of other GHG species	∼1–2%	∼3–4%	∼1–2%
Technology considered	SI ICE	CI ICE	SI ICE
Reference conditions	JEC TTW HD vehicle analysis (group 5, 2025, long-haul cycle), weighted payload ∼14.3 t.		
Source	[41,115]	[115]	[2,44,45]

* Derived from reported hydrogen ICE energy consumption values (∼9–14 MJ/km) assuming the same payload conditions as the JEC long-haul case (∼14.3 t).

These data are consistent with the application cases discussed in Section 4.2 and with the qualitative positioning presented in Figure 13. Overall, the comparison indicates that TTW energy demand remains broadly comparable across the selected fuel-powertrain combinations, while differences in direct GHG emissions are primarily driven by fuel carbon content and the contribution of other species, such as methane slip, hydrogen leakages, and combustion-related N_2O emissions. However, the relatively limited variability observed at the TTW stage contrasts with the much larger differences reported for fuel production pathways. As a result, the overall climate performance of alternative fuels can only be fully understood when TTW and WTT contributions are evaluated together within a WTW framework.

5.3. Integrated Well-to-Wheel Assessment

This section integrates the WTT and TTW perspectives discussed in the previous sections to provide an illustrative WTW comparison of alternative fuels for ICE applications in the HD sector. The comparison is not intended as a fully harmonized LCA, but rather as an example of the overall outcome that can be derived from the pathway-level evidence reviewed throughout the manuscript. The selected pathways were chosen based on data availability, relevance to HD transport applications, and consistency of the underlying assumptions. Accordingly, hydrogen, methane-based fuels, and ethanol pathways were included, while methanol was excluded because it is discussed primarily in relation to maritime applications and comparable HD case studies were not considered within the selected framework. WTT values were derived from the representative pathway data discussed in Section 5.1, while TTW contributions were based on the HD applications summarized in Section 5.2. Reported values should therefore be interpreted as indicative pathway examples rather than statistically derived literature averages. For bio-based pathways, biogenic carbon accounting follows the convention adopted in the JEC WTW methodology [1] and in the corresponding literature sources used for pathway definition. Under this approach, the carbon uptake during biomass growth is reflected through pathway-specific biogenic carbon credits already included in the WTT results and subsequently carried forward into the WTW assessment.

Figure 14 presents the resulting WTW comparison of representative alternative-fuel pathways together with a conventional diesel reference pathway, which serves as a benchmark for assessing the relative decarbonisation potential of the alternative fuel options. Hydrogen pathways exhibit the largest variability, ranging from near-zero emissions under low-carbon electrolysis conditions to approximately 110 gCO_2eq/tkm when electricity is supplied by carbon-intensive grids. The average value reported is representative of the average European electricity mix (185 gCO_2/kWh according to [116]). SMR-based hydrogen remains at intermediate levels around 70 gCO_2eq/tkm, illustrating how upstream emissions can outweigh the benefit of zero tailpipe CO_2 emissions. Methane-based fuels occupy an intermediate position. Fossil CNG and LNG pathways result in WTW emissions around 59–60 gCO_2eq/tkm, whereas waste-derived biomethane benefits from favourable carbon accounting and can reach values close to 9 gCO_2eq/tkm. Ethanol pathways show substantial variability depending on feedstock and production route. The pathways considered in this comparison range from approximately 9 to 24 gCO_2eq/tkm, with second-generation and integrated pathways generally performing more favorably than conventional first-generation alternatives. Compared with the conventional diesel reference (approximately 62 gCO_2eq/tkm), all renewable methane and ethanol pathways considered in the comparison achieve substantial GHG reductions, while the performance of hydrogen remains strongly dependent on the upstream production route and electricity source.

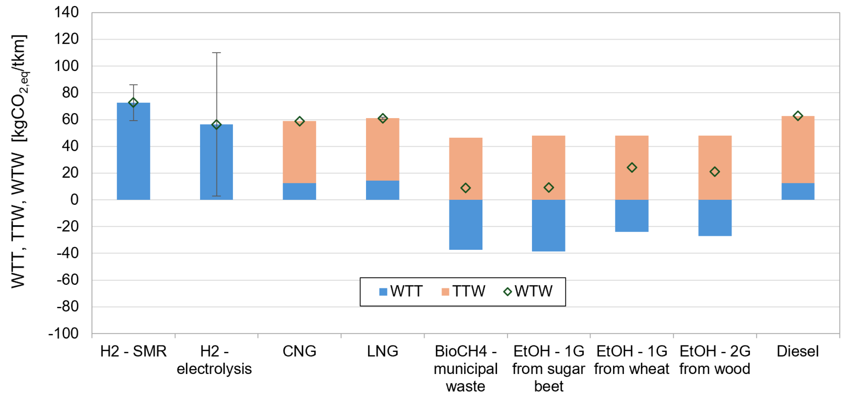

Figure 14. WTW contribution of different alternative fuels (H_2, CH_4, EtOH) for long-haul group 5 applications, benchmarked against a conventional diesel powertrain.

Overall, the comparison highlights that substantial GHG reductions can be achieved through multiple fuel pathways relative to the conventional diesel reference, although the magnitude of the benefit varies considerably across pathways. The results also show that similar fuels may lead to markedly different WTW outcomes depending on feedstock origin, production route, and carbon-accounting assumptions, as illustrated by the variability observed among ethanol pathways. At the same time, the comparison reinforces the trade-off between environmental performance and deployment readiness identified in Figure 13. Mature options such as conventional CNG and LNG benefit from established infrastructure and widespread deployment, whereas several lower-emission pathways, including biomethane and renewable hydrogen, remain more dependent on low-carbon energy supply, sustainable feedstocks, and further technological scale-up. These findings highlight the importance of considering environmental performance, methodological assumptions, and deployment constraints simultaneously when evaluating alternative fuels for ICE applications.

6. Conclusions

This review shows that hydrogen, methane-based fuels, methanol, and ethanol are better understood as pathway families rather than as single fuel categories. Across all fuel types, life-cycle greenhouse gas (GHG) performance depends primarily on the production pathway, with fossil-based routes generally representing the highest-emission cases and renewable or waste-based pathways offering the greatest potential for emission reductions. At the same time, pathway rankings are highly sensitive to methodological assumptions, including electricity carbon intensity, methane leakage, land-use treatment, co-product allocation, and system boundaries. As a result, consistent comparison requires a pathway-based interpretation rather than reliance on single representative values. In addition, the analysis of ICE applications in hard-to-abate sectors confirms that the Tank-to-Wheel (TTW) phase remains relevant, particularly in relation to engine efficiency and other GHG emissions (e.g., methane slip, hydrogen leakages, NO_x from combustion). However, differences in TTW performance are generally smaller than those observed across upstream pathways. In HD applications, energy demand is broadly comparable across fuels, while differences in direct emissions are mainly driven by fuel composition and combustion-related effects. The integrated Well-to-Wheel (WTW) comparison developed in this work highlights the combined influence of upstream emissions, engine performance, and the inclusion of biofuels in the comparison. Hydrogen pathways show the largest variability, ranging from near-zero emissions under low-carbon electrolysis to high values for fossil-based production. Methane-based fuels become competitive when production from waste is considered. Ethanol-based fuels exhibit low GHG values, varying also the generation of considered ethanol. Biogenic carbon credit, related to the captured CO_2 during feedstock growth is explicitly accounted for biofuels, obtaining bio-based pathways can achieve near-zero WTW emissions.

For hard-to-abate transport sectors, these findings highlight the importance of adopting a WTW perspective when assessing decarbonisation strategies. While direct emissions at the point of use remain relevant, the overall GHG performance is largely determined by upstream fuel production pathways. As illustrated by the WTW comparison, pathways based on renewable electricity, sustainable biomass, or waste-derived feedstocks can achieve substantial reductions relative to conventional diesel, whereas fuels produced through carbon-intensive routes may provide only limited climate benefits despite similar end-use characteristics. From a system perspective, these results highlight the presence of trade-offs between environmental performance, technological maturity, and practical deployment. The most mature pathways are not always those with the lowest emissions, while several low-emission options depend on low-carbon electricity, sustainable feedstocks, and supporting infrastructure. Taken together, the reviewed evidence suggests that no single fuel pathway can be identified as universally optimal across all hard-to-abate transport applications. Instead, future decarbonisation strategies are likely to rely on a portfolio of fuel solutions whose suitability depends on pathway design, infrastructure availability, feedstock and energy resources, and sector-specific operational requirements. Consequently, robust pathway-level assessment remains essential for supporting both technology development and policy decisions in ICE-based transport systems.

Future research should focus on improving the harmonization of LCA methodologies, particularly with respect to functional units, system boundaries, co-product allocation, methane and hydrogen leakage accounting, and biogenic carbon treatment. Additional efforts are also needed to strengthen the integration between pathway-level and engine-level analyses, expand the availability of harmonized datasets for maritime and other hard-to-abate sectors, and improve the assessment of emerging pathways such as e-methane, e-methanol, carbon dioxide-derived fuels, and advanced bio-based routes. Furthermore, future studies should increasingly incorporate broader sustainability dimensions, including economic performance, resource consumption, infrastructure requirements, and regional deployment constraints, alongside GHG emissions.

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Abbreviations

The following abbreviations are used in this manuscript:

1G	First-generation
2G	Second-generation
AFR_{st}	Stoichiometric Air–Fuel Ratio
BOF	Basic oxygen furnace
CCS	Carbon capture and storage
CHP	Combined heat and power
CI	Compression Ignition
CNG	Compressed natural gas
CRL	Commercial readiness level
DDGS	Distillers dried grains with solubles
ED95	95% ethanol fuel blend for compression-ignition applications
FU	Functional unit
GHG	Greenhouse gas
GWP	Global warming potential
GWP_{20}	Global warming potential over 20 years
GWP_{100}	Global warming potential over 100 years
HCNG	Hydrogen-enriched compressed natural gas
HD	Heavy-duty
ICE	Internal combustion engine
JEC	JRC-EUCAR-CONCAWE well-to-wheels framework/report
LCA	Life-cycle assessment
LHV	Lower heating value
LNG	Liquefied natural gas
LUC	Land-use change
MeOH	Methanol
N_2O	Nitrous oxide
NG	Natural gas
NO_x	Nitrogen oxides
PEM	Proton exchange membrane
PtG	Power-to-gas
RED	Renewable Energy Directive
RFNBO	Renewable fuels of non-biological origin
SI	Spark Ignition
SMR	Steam methane reforming
SNG	Synthetic natural gas
SOEC	Solid oxide electrolysis cell
TRL	Technology readiness level
TTW	Tank-to-wheel
WTT	Well-to-tank
WTW	Well-to-wheel

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