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Methanol and Ammonia as Green Fuels and Hydrogen Carriers: A Comparative Analysis for Fuel Cell Power Generation

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ABSTRACT

Methanol and ammonia are key energy carriers in a decarbonized society. This study assesses their use in power generation via two pathways: direct utilization as green fuels in fuel cells or as hydrogen carriers. Using these chemicals as hydrogen carriers achieves higher efficiencies (around 40%) due to the maturity of hydrogen fuel cells, resulting in electricity costs around 700 €/MWh compared to 1200 €/MWh for direct utilization. While hydrogen offers lower electricity production costs, efficiency advancements in methanol and ammonia fuel cells could enhance their competitiveness. Additionally, for scenarios involving transportation and power generation, methanol and ammonia prove economically viable, particularly for distances exceeding 3000 km. Consequently, both are crucial for addressing hydrogen-related challenges in the new renewable energy systems.

Keywords: Process Design, Energy Storage, Hydrogen, Fuel Cells, Methanol, Ammonia

INTRODUCTION

The energy sector, responsible for around 75% of greenhouse gas emissions, requires a significant shift to achieve global climate goals. The integration of renewable energy sources, particularly wind and solar, is expected to increase substantially in the coming years. However, these technologies face challenges mainly related to their variability, which could disrupt grid stability. Additionally, sectors like heavy transport, shipping, and industrial heating are difficult to electrify directly. In this context, hydrogen is emerging as a promising solution to address these issues due to its versatility and potential to decarbonize hard-to-abate industries.

According to Bloomberg [1], hydrogen and its derivatives could reduce up to one-third of global emissions, with a projected capacity to meet 24% of global final energy demand by 2050. Hydrogen's challenges, such as low volumetric energy density and complex storage conditions, have led to the exploration of hydrogen-derived products with methanol and ammonia being the most prominent. These chemicals offer easier storage and transport options and are gaining attention for use in energy storage, power generation, and as alternative fuels in sectors such as maritime transport and aviation.

Ammonia and methanol can be used for different applications through two approaches: as green fuels or as hydrogen carriers [2]. When used as green fuels, they are synthesized from green hydrogen and directly utilized in end-use sectors. Alternatively, they can function as hydrogen carriers, simplifying the storage and transport of hydrogen. In this case, methanol and ammonia are first synthesized, then decomposed or reformed to release hydrogen for final applications. In this last option, methanol steam reforming and ammonia decomposition emerge as the key technologies for hydrogen production from these two liquid carriers.

For power generation, methanol and ammonia can be used in two pathways. The thermochemical approach involves combusting methanol or ammonia, mainly, in gas turbines, sometimes requiring co-fuels to stabilize combustion. Alternatively, electrochemical methods employ methanol or ammonia in fuel cells, known as Direct Methanol Fuel Cells (DMFC) and Direct Ammonia Fuel Cells (DAFC). While promising, these technologies face energy efficiency challenges today that require further research.

Another option is using methanol and ammonia as intermediaries to generate hydrogen, which is then used in hydrogen fuel cells. This approach benefits from the higher efficiency of hydrogen fuel cells but introduces added process complexity, energy losses, and costs.

Research has mainly focused on optimizing catalysts and reactor designs for processes like methanol reforming and ammonia decomposition, as well as improving fuel cell materials and configurations. However, there is limited comprehensive analysis from a process system engineering perspective of these X-to-Power alternatives using fuel cells. Therefore, this work addresses the gap by systematically evaluating five process alternatives: direct methanol and ammonia fuel cells, methanol reforming and ammonia decomposition coupled with hydrogen fuel cells, and direct hydrogen use in fuel cells. A technical and economic evaluation is performed, introducing detailed reactor modeling, to provide comprehensive insights into the deployment of this power generation technology.

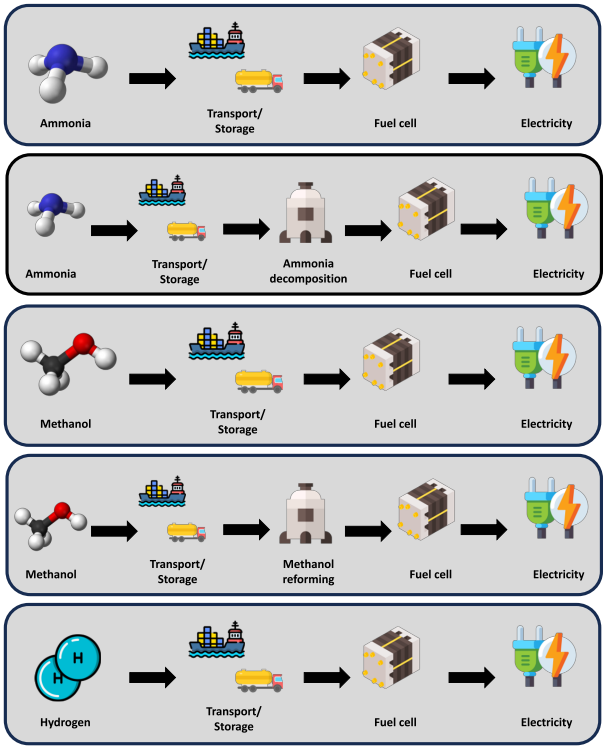

Figure 1: Overview of the analyzed alternatives [3]

PROCESS ALTERNATIVES

This study evaluates two distinct methods for utilizing methanol and ammonia in power generation with fuel cell technology. The first approach directly introduces these compounds into fuel cells, while the second uses them as hydrogen carriers. In the latter option, hydrogen is generated from methanol or ammonia before being fed into a fuel cell. A third alternative is also examined, where hydrogen is directly utilized as a fuel for comparative purposes. A schematic representation of these approaches is provided in Figure 1.

Methanol based alternatives

The first method involves the direct use of methanol in a direct methanol fuel cell (DMFC), which operates with an aqueous methanol solution (1 M) and air. In the DMFC, methanol reacts at the anode to produce carbon dioxide, protons, and electrons, while oxygen at the cathode reacts with protons to form water according to the following reactions.

$$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^- \quad (1)$$

$$6H^+ + 6e^- + \frac{3}{2}O_2 \rightarrow 3H_2O \quad (2)$$

The system operates at a temperature of 333 K under atmospheric pressure. Effluents from the DMFC are processed to separate carbon dioxide, water, and methanol. Gaseous CO_2 can be recycled to methanol synthesis, while water and methanol are reintegrated into the fuel cell feed. The cathode effluent undergoes similar separation to recycle water and adjust methanol composition.

In the second alternative, methanol is reformed to produce hydrogen, which is then fed into a solid oxide fuel cell (SOFC). The reforming process involves steam reforming of methanol in a fixed-bed, adiabatic, catalytic, membrane reactor, producing hydrogen, carbon dioxide, and small amounts of carbon monoxide. $Cu/ZnO/Al_2O_3$ is the selected catalyst due to its favorable catalytic activity, rapid kinetics, high selectivity, and cost-effectiveness. The following reactions are involved in the methanol steam reforming unit:

$$CH_3OH + H_2O \rightleftharpoons CO_2 + 3H_2 \quad (3)$$

$$CO + H_2O \leftrightharpoons CO_2 + H_2 \quad (4)$$

$$CH_3OH \leftrightharpoons CO + 2H_2 \quad (5)$$

The process operates at 600 K and 10 bar with a steam-to-methanol ratio of 1.5. A Pd-Ag membrane separates hydrogen from the reforming mixture, and the remaining stream is further processed. To maintain the endothermic reforming reactions, heat is supplied through intermediate heating stages (interheaters between adiabatic reaction stages). This involves burning a fraction of methanol and utilizing the flue gases for heating.

Hydrogen generated is then introduced into an SOFC, which operates at 800°C. This technology has been selected for its high level of efficiency, exploiting the high temperature of the hydrogen obtained in the reforming stage. The high-temperature outlet gases are used to heat the incoming streams, and the remaining energy is utilized in an organic Rankine cycle (ORC) to maximize energy recovery. Refrigerant R134a is selected as

working fluid in this work. The SOFC has an electrical efficiency of 60%, and its fuel utilization ratio is set at 80%.

Ammonia based alternatives

The first alternative explored with regards to ammonia utilization is the direct ammonia fuel cell (DAFC). In this study, an alkaline membrane fuel cell has been selected since it allows operation at low temperature. Ammonia reacts at the anode to produce nitrogen, water, and electrons, while oxygen reacts at the cathode to form hydroxyl ions. The following reactions take place in the DAFC unit:

$$2NH_3 + 6OH^- \rightarrow N_2 + 6H_2O + 6e^- \quad (6)$$

$$3H_2O + 6e^- + \frac{3}{2}O_2 \rightarrow 6OH^- \quad (7)$$

The process operates at 368 K under ambient pressure, with air at 50% relative humidity. A fraction of the ammonia permeates the anion exchange membrane (referred to as crossover), undergoing oxidation at the cathode to produce nitrogen oxide (NO). A selective catalytic reduction (SCR) unit is used to remove nitrogen oxides from the cathode effluent. The anode effluent, primarily ammonia, water, and nitrogen, is cooled to separate and recycle ammonia.

In the second ammonia-based method, ammonia is decomposed in a fixed bed, adiabatic, catalytic membrane reactor to produce hydrogen, which is then fed into a SOFC. The reaction is endothermic, requiring high temperatures (900 K) and a pressure of 10 bar. Ni/Al_2O_3 is the selected catalyst due to its economic advantages and satisfactory performance. The following reaction is performed in the ammonia decomposition process:

$$2NH_3 \leftrightharpoons N_2 + 3H_2 \quad (6)$$

To enhance the performance of the decomposition reaction, a Pd-Ag membrane separates hydrogen in situ, improving equilibrium conditions. A sequence of four reactors along with their respective heat exchangers has been implemented to supply the required energy for the reaction. A fraction of ammonia is combusted to provide the necessary energy in the decomposition section. Hydrogen produced is heated and introduced into the SOFC, similar to the methanol reforming case. Waste heat from the SOFC is also used in an ORC to improve the energy efficiency of the overall process.

Hydrogen based alternative

In the final alternative, hydrogen is directly fed into a SOFC. The process is similar to the hydrogen utilization stages of methanol and ammonia as hydrogen carriers. Hydrogen is preheated to 800°C, and the high-temperature SOFC exhaust gases are used, in a first stage, to heat the inlet streams and, finally, for energy recovery via an ORC.

Solution Procedure

A detailed 1-D differential equation model is included to evaluate the performance of the reactor units (ammonia decomposition and methanol steam reforming). With this information, all alternatives are modeled using a nonlinear programming (NLP) approach in GAMS, optimizing system operation under an economic objective function. Mass and energy balances, equilibrium conditions, detailed 1-D differential equation models, etc. are used to represent the different units involved. Capital (CAPEX) and operating (OPEX) costs are estimated using established correlations for the chemical industry. For the calculation of the operating cost, the main inlet parameter is the cost of the fuel. For methanol, the baseline price is set to 1200 €/t, for ammonia, 1060 €/t and, for hydrogen, 5 €/kg. All cases are modeled for a fuel cell with a power capacity of 1 MW. In addition, an integrated assessment of the transportation of these chemicals and their subsequent transformation into power (using the proposed alternatives) is performed. To compute the transportation cost for each chemical, an average value is taken from the literature for the different alternatives.

RESULTS AND DISCUSSION

The result section presents the key operating variables for four analyzed alternatives that utilize ammonia and methanol as hydrogen carriers, along with a baseline scenario using hydrogen directly in a fuel cell.

Table 1: Main operating variables for power production using methanol/ammonia as hydrogen carriers.

Variables	Methanol	Ammonia
% inlet fuel to combustion	22.5	25.5
% H_2 recovery in the membrane	78.8	96.1
Final reactor conversion (%)	97.3	97.5
kg H_2 /kg fuel	0.11	0.12
Net power (kW)	1106	1108
Energy efficiency (%)	35.8	42.3
Energy yield (kWh/kg)	2.00	2.18

Both methanol reforming (600 K) and ammonia decomposition (900 K) are endothermic reactions requiring significant heat input. To achieve standalone operation, a fraction of the fuel (20–25%) is combusted to meet these thermal requirements. Ammonia decomposition demands more fuel combustion due to its higher operating temperature (as shown in Table 1). The reactor configuration based on a multibed reactor ensures nearly complete conversion of methanol and ammonia (around 97% in both cases). However, hydrogen recovery varies between processes attributed to differences in permeability and partial pressures in the membrane. Consequently,

the hydrogen yield is 0.11 kg H_2/kg methanol (58% of maximum potential) and 0.12 kg H_2/kg ammonia (67% of maximum). This operating results directly influence the energy efficiency of the process. Methanol-based systems achieve 36% efficiency, while ammonia-based systems reach 42%, mainly due to the better performance in the production of hydrogen from ammonia.

Table 2: Main operating variables for power production using methanol/ammonia/hydrogen as green fuels.

Variables	Methanol	Ammonia	Hydrogen
Net power (kW)	1000	885.7	1000
Energy efficiency (%)	26.5	16.8	52.9
Energy yield (kWh/kg)	1.46	0.86	17.6

Methanol and ammonia can also be used directly in fuel cells. The fuel cell efficiencies achieved are 23.3% for methanol and 15% for ammonia (reaching the global efficiencies of Table 2). These efficiencies are significantly lower than those of hydrogen fuel cells (60% of the selected SOFC). The overall energy efficiency of the process (including other units apart from the fuel cell) is 26% for methanol, 17% for ammonia, and 53% for hydrogen. Therefore, despite the more complex processes in hydrogen carrier alternatives, they remain competitive due to the lower efficiencies of the current DMFC and DAFC technologies.

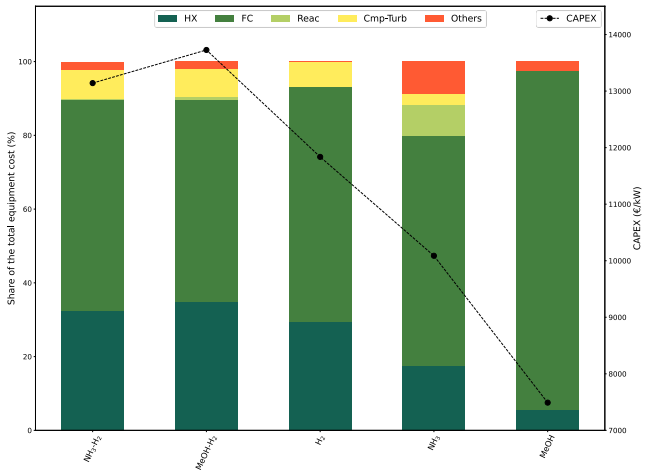

Figure 2. Total CAPEX and its distribution [3]

A systematic economic evaluation of the proposed alternatives has also been performed. The CAPEX for the systems studied ranges from 7,000 to 14,000 €/kW (as shown in Figure 2). Processes employing methanol or ammonia as hydrogen carriers exhibit higher investment costs compared to direct fuel cell technologies, mainly due to the added complexity introduced by methanol reforming or ammonia decomposition. Among these, the DMFC represents the least capital-intensive option, as it operates with minimal additional equipment beyond the fuel cell. However, alternatives with lower CAPEX have reduced energy efficiencies according to Tables 1 and 2, presenting a trade-off that becomes evident in the operating costs, as discussed below. The distribution of CAPEX shows that the fuel cell unit accounts for the majority of the investment, ranging from 55% to 92% of the total cost. Heat exchangers also constitute a significant portion of CAPEX in methanol reforming and ammonia decomposition processes, given their critical role in managing the thermal demands of these systems.

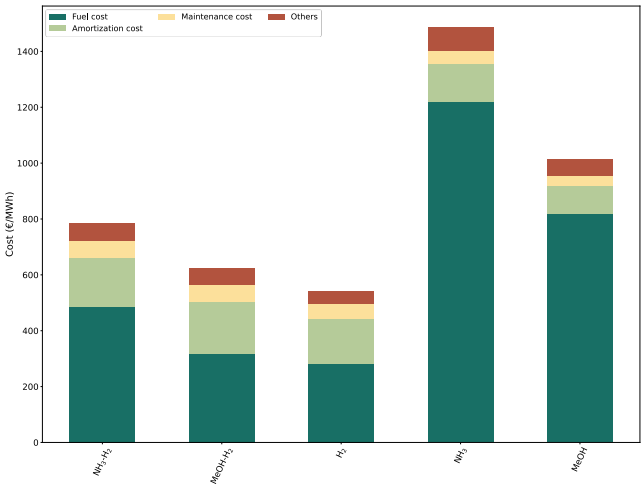

Figure 3. OPEX of the different alternatives with its breakdown [3]

When compared to other power generation technologies, the CAPEX for methanol and ammonia fuel cell systems is considerably higher. For instance, renewable technologies like PV panels (810 €/kW), onshore wind turbines (1178 €/kW), biomass-based systems (1998 €/kW), and concentrated solar power (3950 €/kW), as well as traditional sources like natural gas combined cycle plants (924–1386 €/kW) and nuclear plants (6470–7394 €/kW), all show significantly lower CAPEX. The elevated capital costs of methanol/ammonia fuel cell systems arise from two main factors: the high cost of fuel cells, which are still maturing and expected to become more affordable, and the lack of economies of scale due to their relatively small-scale application (in this study 1 MW capacity).

Figure 3 presents the operational costs for the analyzed alternatives. In contrast to CAPEX, the OPEX of systems using methanol/ammonia as hydrogen carriers is lower than that of direct ammonia or methanol fuel cell systems. For hydrogen carrier-based configurations, the OPEX is approximately 500–800 €/MWh, whereas for direct ammonia or methanol usage, the OPEX ranges from 1000–1500 €/MWh. The higher energy efficiency of

hydrogen carrier alternatives offsets their increased CAPEX, leading to comparatively lower operating costs. Fuel costs dominate the OPEX, especially for systems where methanol or ammonia is directly used as green fuels, contributing over 80% of total operational expenses. Thus, the reduction of the production cost of green methanol and ammonia will be a critical driver for the broader adoption of these power generation pathways.

Compared to current electricity generation costs, methanol and ammonia systems are more expensive. For example, renewable systems such as solar PV (60–100 €/MWh), onshore wind (40–80 €/MWh), and biogas (90–170 €/MWh) are more cost-effective. However, methanol and ammonia are employed as energy carriers/storage systems, involving the chemical production and the back transformation into electricity, which inherently leads to higher costs. When viewed as energy storage options, methanol and ammonia offer competitive costs compared to other storage technologies. For instance, pumped hydro costs range from 185–278 €/MWh for short-term applications but escalate to 2778–3704 €/MWh for seasonal storage. Similarly, battery storage costs range from 370–556 €/MWh for short-term and 37037–41667 €/MWh for seasonal applications [4].

In addition, a sensitivity analysis is performed for two critical parameters: fuel cell energy efficiency and the price of methanol/ammonia. Hydrogen fuel cells currently achieve approximately 60% efficiency, while direct ammonia and methanol fuel cells achieve around 15% and 25%, respectively. These efficiency differences significantly affect economic performance. Hydrogen fuel cells, being more developed, are expected to see moderate improvements (up to around 80%). However, direct methanol/ammonia fuel cells are in earlier stages of development, with potential for significant efficiency gains. The economic performance of the proposed system is analyzed under different energy efficiency scenarios showing the results in Figure 4. For direct methanol fuel cells, achieving an efficiency of 47% would make them competitive with systems based on methanol reforming and hydrogen fuel cells. Similarly, direct ammonia fuel cells would need to reach 43% efficiency.

Fuel cost is a dominant factor in the overall electricity cost, as indicated in Figure 3. Green methanol and ammonia prices vary widely, influenced by production methods. Future projections estimate prices of 231–583 €/t for methanol and 285–350 €/t for ammonia by 2050 [5]. If methanol and ammonia prices drop below 400 €/t, electricity costs could range between 400 and 600 €/MWh, narrowing the gap between direct and hydrogen-based systems. Direct methanol systems, in particular, could become more economically competitive, potentially outperforming hydrogen-based alternatives.

The previous results are circumscribed to the process itself. At this point, hydrogen as such shows the best economic performance with the lowest operating cost. However, the main limitations about the use of hydrogen come from its storage and transport conditions.

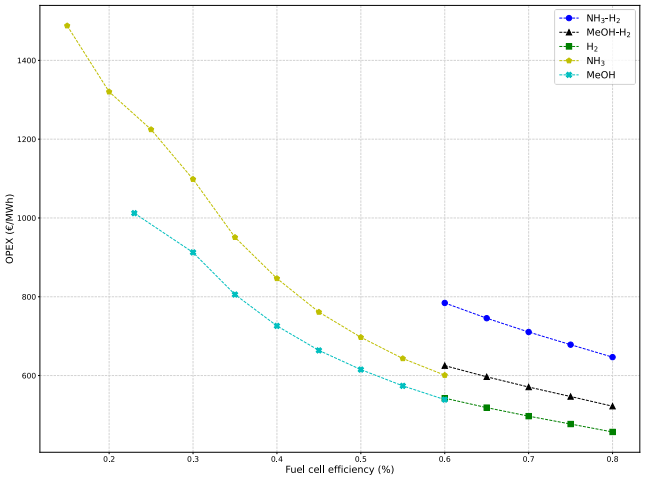

Figure 4. Operating cost versus fuel cell efficiency [3]

For shorter distances, the percentage of the transportation cost in the total cost remains low in all cases. Therefore, as hydrogen shows the best operating cost in the transformation stage, this is the technology with the best global performance. In the case of rail transport or shipping, hydrogen transport is not considered due to the difficulties associated and the lack of data for these alternatives. As distance increases, the transport costs associated with hydrogen experiments notably increase, higher than in the case of methanol or ammonia. For example, when transported by truck over 3000 km, the transportation cost represents around 70% of the total cost for hydrogen. Consequently, the total cost of the system exceeds the cost values associated with ammonia and methanol. In the case of truck transport, the transition point is around 400 km, where the use of methanol as hydrogen carrier is recommended. Regarding pipelines, the hydrogen transportation cost is significantly lower than the case of truck, shifting the transition point to around 3000 km. Hence, methanol and ammonia demonstrate great potential in applications where transportation and/or storage is critical.

CONCLUSIONS

A systematic evaluation compares methanol and ammonia as green fuels or hydrogen carriers for electricity generation via fuel cells. Ammonia and methanol as hydrogen carriers demonstrate superior technical and economic performance today, with overall energy efficiency of 35–40% compared to 15–25% for direct alternatives. This efficiency translates to lower operating costs (600–800 €/MWh). While hydrogen fuel cells

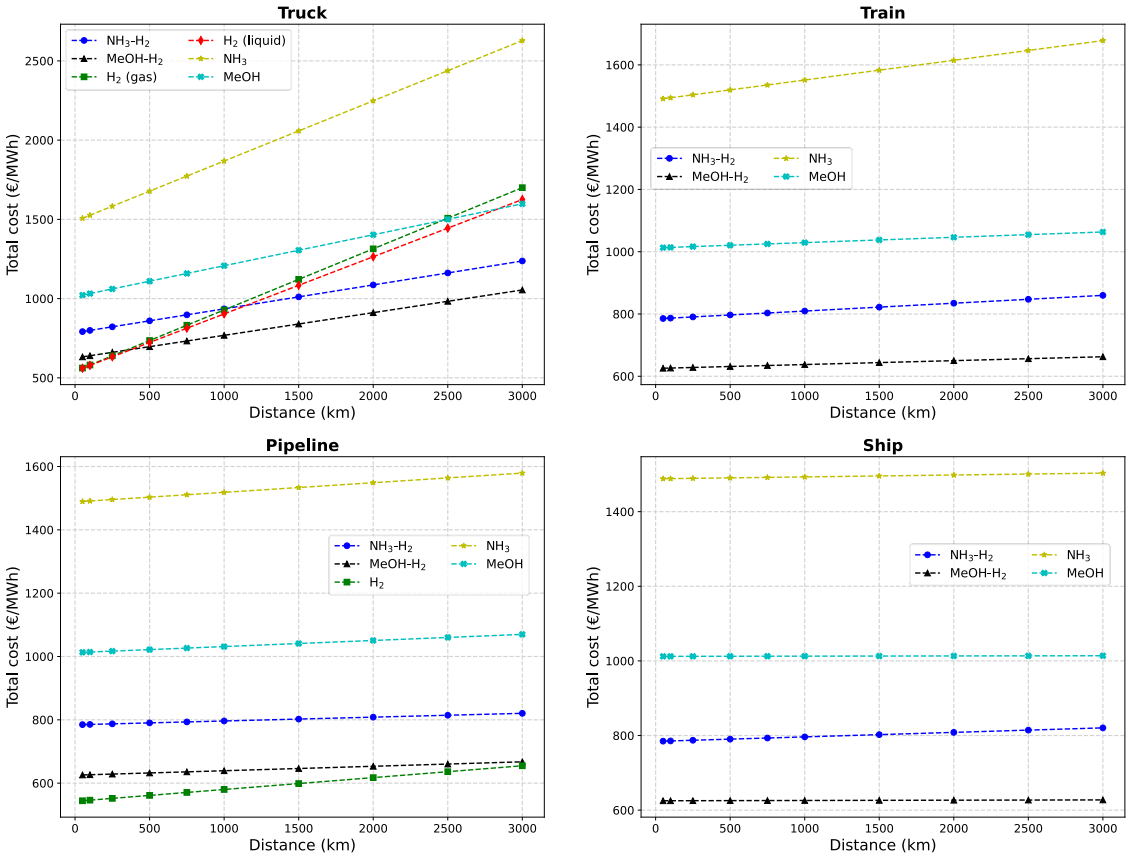

Figure 5: Total cost of transportation and power production [3]

exhibit higher efficiency in power generation, transportation costs favor methanol and ammonia, particularly for long distances. With potential efficiency improvements for direct alternatives, methanol and ammonia are positioned as critical solutions for long-term energy storage and transportation challenges.

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REFERENCES

1. BloombergNEF. Hydrogen economy outlook. 2020, URL: https://about.bnef.com/blog/hydrogen-economy-offers-promising-path-to-decarbonization/.
2. Tawalbeh M, Murtaza SZ, Al-Othman A, Alami AH, Singh K, Olabi AG. Ammonia: A versatile candidate for the use in energy storage systems. Renew Energy 194:955–77 (2022) https://doi.org/10.1016/j.renene.2022.06.015
3. Sánchez A, Blanco EC, Martín M. Comparative assessment of methanol and ammonia: Green fuels vs. hydrogen carriers in fuel cell power generation. Appl Energy 374: 124009 (2024) https://doi.org/10.1016/j.apenergy.2024.124009
4. Schmidt O, Melchior S, Hawkes A, Staffell I. Projecting the future levelized cost of electricity storage technologies. Joule 3(1):81–100 (2019) http://dx.doi.org/10.1016/j.joule.2018.12.008
5. Fasihi M, Weiss R, Savolainen J, Breyer C. Global potential of green ammonia based on hybrid PV-wind power plants. Appl Energy 294:116170 (2021) http://dx.doi.org/10.1016/j.apenergy.2020.116170