

AMMONIA FOR INDUSTRIAL COMBUSTION

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ABSTRACT

Many companies are investigating switching from conventional fossil fuels to “green” fuels such as hydrogen to reduce CO₂ emissions. This assumes hydrogen is made by an environmentally-friendly method such as electrolysis using renewable energy. However, there are concerns with hydrogen. For example, it leaks very easily, is extremely flammable, and is more difficult to transport than other fuels.

A potential solution is to use ammonia as an alternative method of supplying hydrogen to a combustion process, assuming it is made in an environmentally-friendly manner. Like H₂, ammonia also does not produce any carbon-containing pollutants such as carbon monoxide, carbon dioxide, or soot. It has transport properties like propane, so it is easier to contain and transport than hydrogen.

However, there are some concerns with ammonia. It is a caustic and hazardous chemical with a pungent odor so it must be handled accordingly. It has the potential to generate very high levels of NO_x which means a post-treatment system like an SCR may be required. Existing burners may need to be modified or replaced.

While ammonia is a potentially important future green fuel, there are concerns that require attention and further research. This paper compares methane, hydrogen, and ammonia combustion and discusses the advantages and disadvantages of ammonia in particular.

Keywords: ammonia combustion, hydrogen, methane

1. INTRODUCTION

Due to the increased interest in reducing CO₂ emissions, some alternative fuels are getting considerable attention. One of these is hydrogen because no CO₂ is produced when it is combusted [1]. However, considerable CO₂ is generated when hydrogen is produced during steam-methane reforming (SMR) which is used to produce over 90% of the hydrogen made today. Also, large-scale storage of hydrogen as a gas is challenging because it has a very low density and high diffusivity, so it leaks easily. Compressed and cryogenic hydrogen storage, which is particularly necessary for mobile applications such as cars and ships, is a large challenge for the wide-spread use of H₂ [2].

Assuming hydrogen is produced using renewable energy, then the question is what is the best form of hydrogen to use? One possible alternative is ammonia (NH₃) because it is already one of the most commonly produced chemicals, made in a well-established process in large quantities (most of which is used for fertilizers). Ammonia may be a solution for a faster transition to a

hydrogen economy [3]. Figure 1 shows the dramatic rise in ammonia production to help supply food for the rapidly expanding world population.

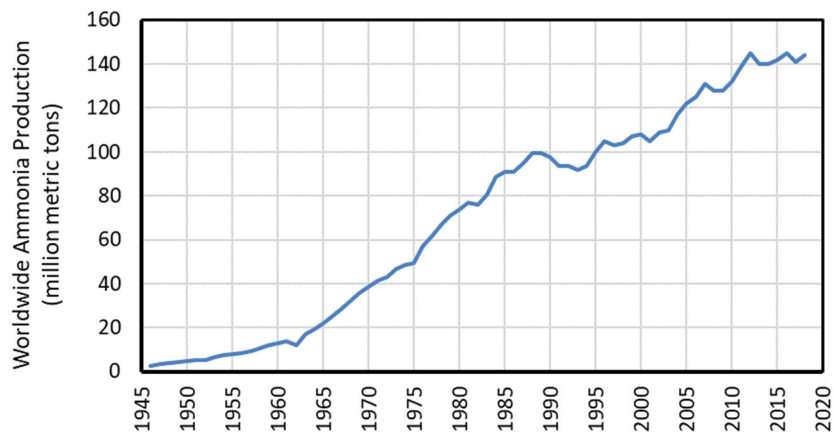


Figure 1: World-wide ammonia production (in million metric tons) from 1945 – 2018 [4].

Ammonia is easier to transport compared to hydrogen and has a very high hydrogen density. Liquid ammonia ($121 \text{ kg-H}_2/\text{m}^3$) can store more H_2 on a volumetric basis than liquid hydrogen ($70.8 \text{ kg-H}_2/\text{m}^3$) [5]. Ammonia's cost per volume of stored energy is significantly less than that of hydrogen [6]. Because it has a relatively high boiling point, it can be easily stored as a liquid at moderate pressures and temperatures and therefore requires much less storage volume compared to many common gaseous fuels. Ammonia is stored similarly to propane. Because of the seasonal nature of fertilizer use which is the primary application for ammonia, there is a large and well-established storage network for ammonia [7]. Unlike hydrogen, ammonia already has an established distribution system [8]. Ammonia has the potential to store larger quantities of energy for longer periods of time compared to many other storage methods such as batteries and flywheels [9]. For these reasons, ammonia is a prominent component of the U.S. Department of Energy's REFUEL (Renewable Energy to Fuels through Utilization of Energy-dense Liquids) program [10].

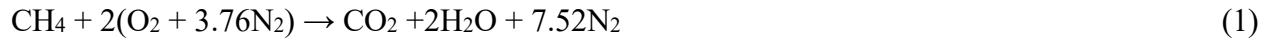
There are also some negative aspects of ammonia including its pungent odor, toxicity, and corrosivity. These can be managed with proper equipment design and procedures. In addition, ammonia has some combustion challenges.

To be considered a green fuel, ammonia is assumed to be made in an environmentally-friendly manner with minimal or no CO_2 generated during the production process. MacFarlane et al. believe this will be via electrochemical conversion where the electricity is generated by renewable energy sources. The most common method for producing large scale quantities of ammonia is through the Haber-Bosch process. Ammonia is typically produced in a steam-methane reformer that produces large quantities of CO_2 . The International Energy Agency (IEA) has written a white paper asking if ammonia is the CO_2 -free fuel of the future [11]. IEA has also written a report considering ammonia as a low-carbon fuel as a source of clean energy in the power sector [12]. While considerable work has been done on using ammonia as a fuel in internal combustion engines and gas turbines, much less has been done on using ammonia in industrial combustion applications. This paper compares methane, hydrogen, and ammonia as industrial fuels, with particular emphasis on ammonia.

2. FUELS COMPARISON

Methane is the largest component in natural gas which is ubiquitous in industrial combustion. High hydrogen fuels are commonly used in certain applications such as ethylene cracking furnaces. There is much less industrial experience using ammonia compared to either methane or hydrogen. The global reactions for the stoichiometric combustion with dry air as (21%O₂+79%N₂) for these three fuels are as follows:

Methane:



Hydrogen:



Ammonia:



Table 1 shows a comparison of some important properties for the three fuels including adiabatic flame computed at 5% EA, 70 Deg F air at 15% humidity without dissociation.

Table 1: Properties for methane, hydrogen, and ammonia [13].

Fuel	Units	CH ₄	H ₂	NH ₃
Molecular weight		16	2	17
Boiling point	°F	-259	-423	-28
LHV/HHV	Btu/scf	909/1010	274/324	359/432
LHV/HHV	1000 Btu/lbm	21.5/23.8	52/61	8.0/9.7
LHV/HHV	1000 Btu/ft ³ liquid	513/569	228/269	341/412
LHV/HHV Wobbe	1000 Btu/scf	1.23/1.36	1.04/1.23	0.46/0.56
Adiabatic flame temperature	°F	3565	3932	3211
Autoignition temperature	°F	1070	930-1060	1200
Flame speed	cm/s	30-40	200-300	6-7
Flammability range	% fuel in fuel/air mixture	4 - 15	4-74	15-28

Figure 2 shows a comparison of the lower heating value (LHV) and the higher heating value (HHV) for H₂, NH₃, CH₄. Both hydrogen and ammonia have low volumetric heating values compared to methane. Because of the large difference in reactivity, hydrogen is very easy to ignite and sustain combustion despite its low heating value. This is not the case for ammonia which is difficult to ignite and sustain combustion compared to most other fuels.

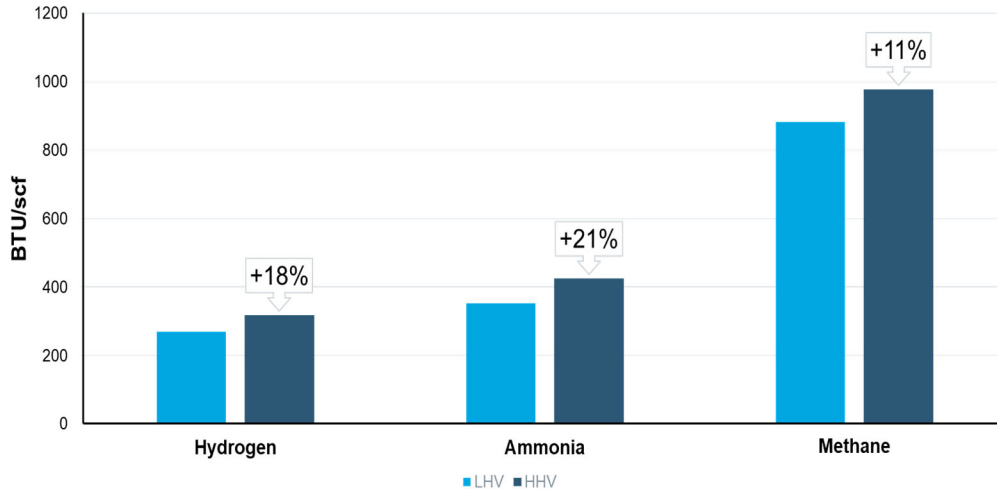


Figure 2: Comparison of LHV and HHV (Btu/scf) for H₂, NH₃, CH₄.

Figure 3 shows the volumetric energy density for different forms of H₂, NH₃, CH₄. Liquid ammonia has a higher volumetric energy density than liquid hydrogen.

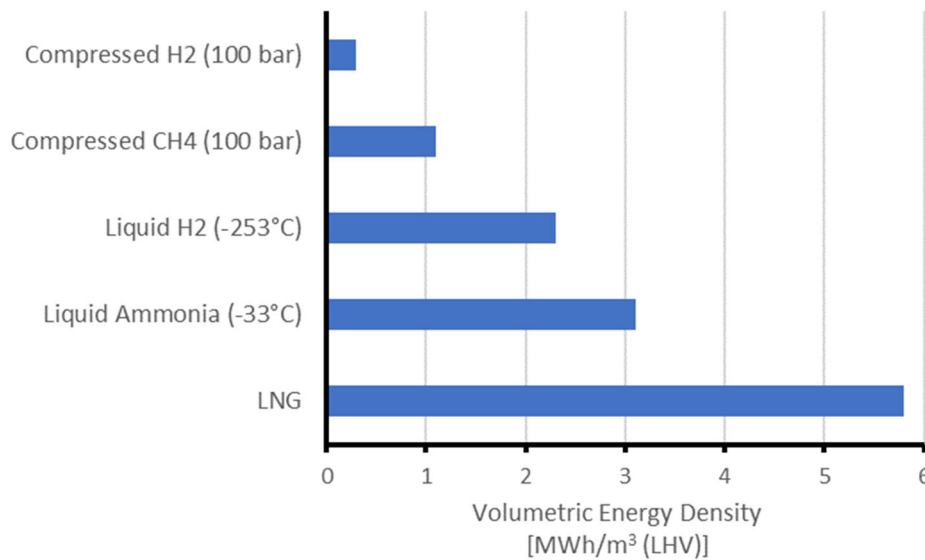


Figure 3: Volumetric energy density [MWh/m³ (LHV)] for various forms of H₂, NH₃, CH₄ (adapted from [14])

Figure 4 shows the normalized fuel and air flow rates (scf/MMBtu_{HHV}) for the stoichiometric combustion of each fuel with air. Hydrogen needs 22% less air and ammonia 13% less air compared to methane.

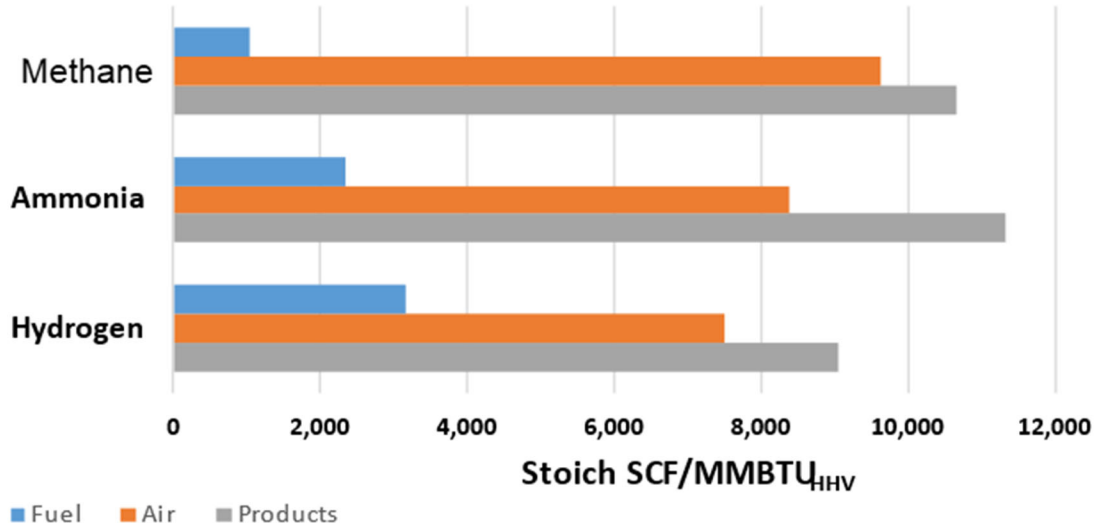


Figure 4: Comparison of fuel and air flow rates for stoichiometric combustion (scf/MMBTuHHV) for H₂, NH₃, CH₄.

Figure 5 shows that about 10-15% more flue gas recirculation (FGR) is needed when using hydrogen compared to methane for a given level of NO_x emissions. This is possible without causing stability issues because of hydrogen’s high reactivity and wide flammability limits. The graph also shows that the pressure drop (dP) across a burner including the FGR to maintain a given level of NO_x is comparable for both fuels.

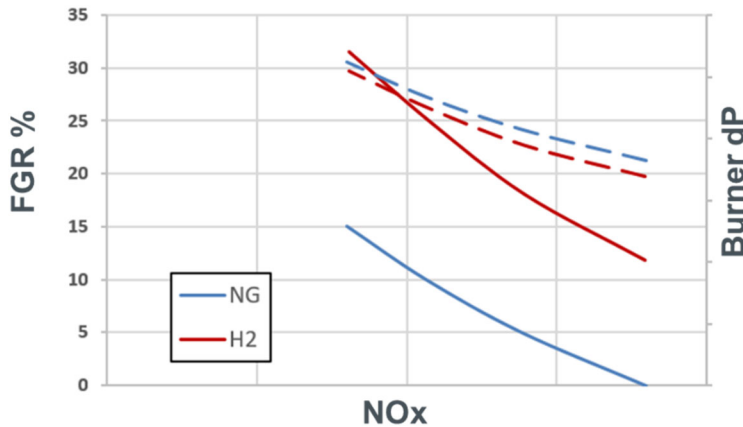


Figure 5: Comparison of flue gas recirculation or FGR (solid lines) and burner pressure drop or dP (dashed lines) needed to maintain a given level of NO_x emissions.

Figure 6 shows the flammability ranges for methane, ammonia, and hydrogen. Methane has the narrowest, hydrogen the widest, and ammonia in-between. A wide range is beneficial for desired combustion, but not for undesired combustion. For example, if hydrogen leaks (which it can do more easily than other fuels because of its low density and high diffusivity), then it will likely combust if it finds an ignition source. One of the advantages of ammonia, which is much

less likely to leak compared to hydrogen, is that it has a pungent odor that can be easily detected if it were to leak.

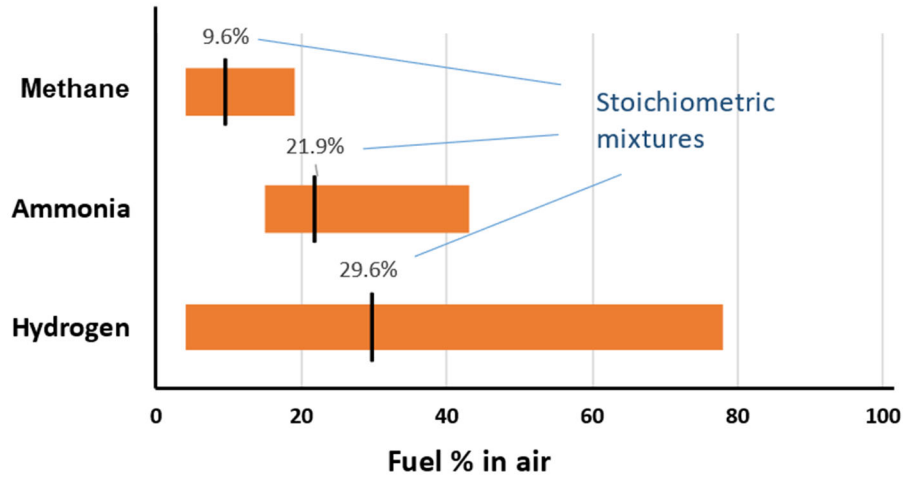


Figure 6: Flammability limits for H₂, NH₃, CH₄.

3. AMMONIA COMBUSTION CHALLENGES

There are some potential combustion challenges using ammonia in industrial burners. An important consideration is possibly very high NO_x emissions through the fuel NO_x mechanism [15]. The primary NO_x mechanism in most industrial combustion applications is thermal NO_x which is highly temperature dependent. When a hydrocarbon reacts with air which consists of about 79% N₂ by volume, very little of the N₂ is converted to NO_x. Unlike N₂ which is a very stable molecule with a triple bond between the N atoms, the N in NH₃ comes apart very easily at higher temperatures and reacts with O₂ to form NO_x. In NH₃ combustion, fuel NO_x dominates thermal NO_x. NH₃ is a reagent used in selective catalytic reduction (SCR) systems to reduce NO_x emissions, but in the presence of a catalyst and within a relatively narrow temperature range which is much lower than typical combustor temperatures. It is possible that some type of post-treatment such as an SCR may be needed if ammonia is used as a fuel.

Figure 7 shows experimental data for the measured NO_x (ppm, corrected to 3% O₂) for a typical radiant wall-fired burner. No attempt was made to minimize NO_x. NO_x peaked for that burner at about 20 vol.% NH₃ in a natural gas mixture consisting primarily of CH₄.

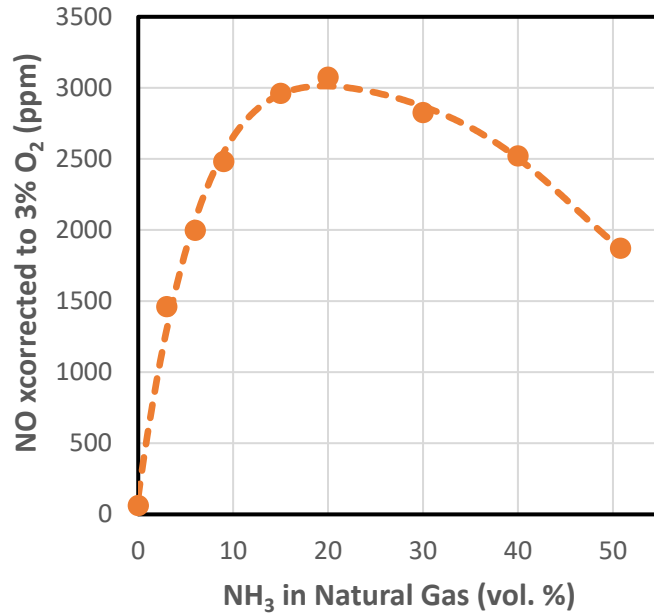


Figure 7: Experimental Data for a typical radiant wall-fired burner.

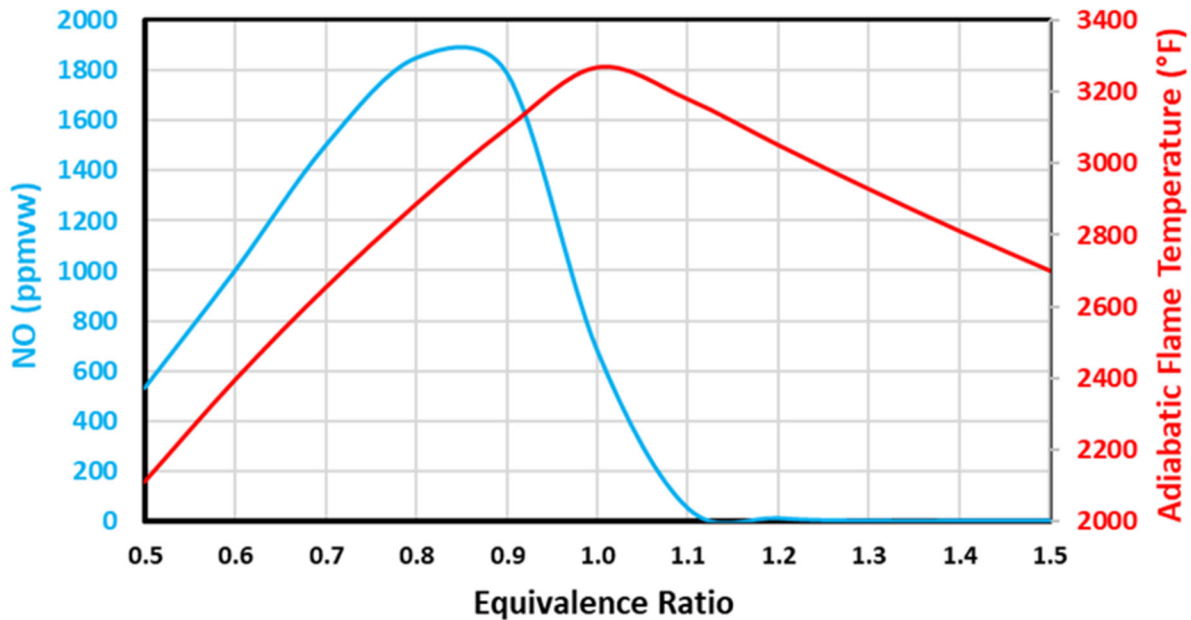


Figure 8: Adiabatic Equilibrium NO_x and Flame Temperature vs. Equivalence Ratio for air/NH₃ combustion (both at 77°F).

Figure 8 shows that predicted NO_x is highly dependent on the equivalence ratio and that high levels are possible under equilibrium and perfectly mixed conditions. The predicted NO_x is lower at very fuel lean and fuel rich conditions with the peak near slightly lean conditions which

is where industrial heaters are typically operated. This graph suggests staging the air or the fuel would be an effective technique for reducing NO_x emissions.

Some type of staging to operate at substoichiometric combustion in the higher temperature section of the combustor is typically needed to mitigate NO_x. This is commonly done by staging the air where the balance of the air needed for combustion is added in the lower temperature section of the combustor.

Another challenge of ammonia as a fuel is that it has a slow flame speed (see Table 1), unlike H₂ which has a very high flame speed. NH₃ also has slow combustion kinetics and a relatively high autoignition temperature which make it more challenging to ignite and sustain compared to other common fuels. In most industrial applications, some type of support fuel such as CH₄ or H₂ may be needed to ensure stable combustion of NH₃ over wide operating conditions including low flows at startup.

A related challenge is that ammonia flames are harder to detect for conventional industrial flame detectors. However, the use of a support fuel mitigates this difficulty.

The impact on heat transfer when replacing a hydrocarbon such as methane with ammonia is more challenging to determine. In terms of radiation, ammonia combustion produces no CO₂ which is a radiating gas and it has a lower flame temperature compared to hydrogen and most hydrocarbons. Figure 9 shows that ammonia has a slightly higher mass flow rate for a given firing rate compared to methane and hydrogen which should mean comparable convection heat transfer between methane and ammonia, assuming other parameters such as gas temperatures are comparable.

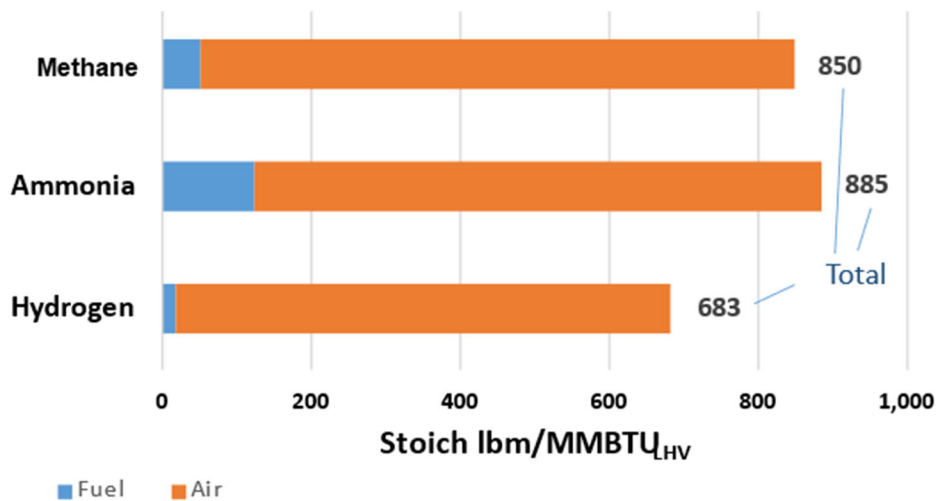


Figure 9: Comparison of normalized mass flow rates (lbm/MMBtu_{LHV}) of fuel + air for stoichiometric combustion for H₂, NH₃, CH₄.

New and larger fuel gas piping and controls are likely needed compared to most hydrocarbons when using pure NH₃ because of its relatively low volumetric heating value as shown in Table 1. There are also some materials issues with elastomers, copper, and zinc when using ammonia, although these can all be handled with proper design and materials selections.

4. COMBUSTION SYSTEM/BURNER DESIGN CONSIDERATIONS

Burner designs can be deceptively simple when considering all the fuel parameters that need to be evaluated. Trial and error methods are not recommended. The following are just a few considerations that need to be considered: near and far field aerodynamics; eddy placement; burner swirl (both local and total); burner multicomponent axial, radial and tangential thrust from both air and fuel flows; laminar and turbulent flame speed; flammability range at ambient temperatures and O₂ levels and elevated temperatures at reduced O₂ levels; chemical kinetics; ignition temperature; and adiabatic flame temperature. A thorough analysis is recommended before using ammonia in an existing combustion system.

5. CONCLUSIONS

While there is the potential to significantly reduce or eliminate CO₂ emissions using ammonia as a fuel, depending on how it is made, there are also some significant challenges to be considered. It is possible existing burners may have to be replaced, rather than retrofitted, depending on how much NH₃ is in the fuel. New and larger fuel gas piping systems would likely be needed if pure NH₃ is used. Because of ammonia's slow flame speed, a support fuel may be needed. Some type of post-treatment system such as an SCR may also be needed due to potentially high NO_x emissions. Ammonia combustion is an active area of research which needs more work to effectively handle these concerns.

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