

## Design Considerations for Carbon-Free Combustion

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### Abstract

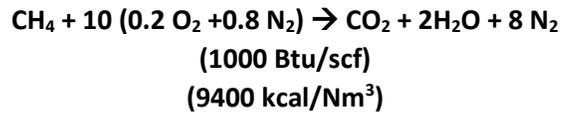
Combustion of a hydrocarbon produces water and carbon dioxide. As consensus continues to build around the contributions of carbon in global climate change, jurisdictions, both internationally as well as domestically, are working towards limiting formation of carbon dioxide. One way to work toward effective decarbonization is through combustion of hydrogen (H<sub>2</sub>) ensuring a source of carbon-free energy, as the only product of combustion of hydrogen is water. However, hydrogen presents several challenges when used as a fuel source. This paper will explore some of the special considerations required to use hydrogen as a fuel both effectively and safely. Because Hydrogen is less dense (at standard temperature and pressure) compared to other fuels, it presents several challenges. For example, compared to denser fuels, flame speeds for hydrogen are much faster, flame temperatures are higher, and diffusion and mixing of fuel and oxygen are faster. Furthermore, the higher flame temperatures, and faster mixing also enhance the production of nitrogen oxides (NO<sub>x</sub>) which are almost universally restricted as known pollutants, requiring creativity to mitigate the formation of these emissions. All of these factors require special consideration in burner and system design.

### Background

Fossil fuels (natural gas, coal, oil, etc.) are the major source of energy for most of the industrialized world. Complete combustion of any hydrocarbon (which are the bulk of the components of fossil fuels) will generate carbon dioxide (CO<sub>2</sub>) in the waste gases. The scientific community generally accepts that atmospheric carbon dioxide contributes to climate change, and jurisdictions, domestic and international, are working towards limiting formation of CO<sub>2</sub>. There is not, however, the same general consensus on the best way to do so. Increased use of renewable sources of energy (wind, solar, geothermal, etc.) are candidates, as well as nuclear fission, or use of biomass as fuel. One other option is simply to use a fuel that does not have any carbon in it, and thus would have no CO<sub>2</sub> in the waste gases. Research is underway on several such fuels, but none have yet proven to be economically viable.

### Review of Combustion

The simplest hydrocarbon (and also one commonly used as a fuel industrially, commercially and in residential applications), is methane (CH<sub>4</sub>). Modeling air as 20% oxygen and 80% nitrogen, complete combustion of methane (**Equation 1**) in air is as follows:



### Equation 1: Canonical Combustion

A few points to remember about the complete combustion of methane is that the only waste gas products (aside from the nitrogen that passes through unchanged) are CO<sub>2</sub> and water (H<sub>2</sub>O). It is possible to generate other molecules such as carbon monoxide, soot, and/or Hydrogen (H<sub>2</sub>) due to incomplete combustion, poor mixing, or other deficiencies in the combustion process, but assuming complete and proper combustion, these incidental components can be neglected. The important point to bear in mind is that combustion of any carbon-bearing fuel will generate CO<sub>2</sub>. Combustion of methane results in 0.120 lb/SCF (2 kg/Nm<sup>3</sup>) CO<sub>2</sub>. The amount of CO<sub>2</sub> formed will vary by the fuel burned.

### Possible Methods of Carbon Mitigation

There has been intense research to find economically viable and sustainable ways to minimize atmospheric carbon dioxide, especially as it relates to combustion. Perhaps the most straightforward way to do so would be simply to burn less fuel either through improvements in combustion efficiency, process efficiency or both. Even though every industry has room to make gains in efficiency, humans have been doing things like smelting ore and firing clay pots for thousands of years, and further efficiency gains in these kinds of industries are probably limited.

Another way to decrease atmospheric carbon dioxide is to remove it from the atmosphere and store it somewhere. By chemically removing the carbon from the waste gas stream, and then later transporting it to a location (generally underground) where it is possible to store it safely away from atmosphere, it is possible to remove up to 90% of the carbon dioxide from the waste gas stream. Unfortunately, there is generally a large expense in both capital dollars and operational dollars. Furthermore, there is an associated “energy penalty” associated with capturing, compressing, transporting and storing the carbon dioxide. This area of research is a fertile one, and progress continues towards a more efficient and cost-effective solution.

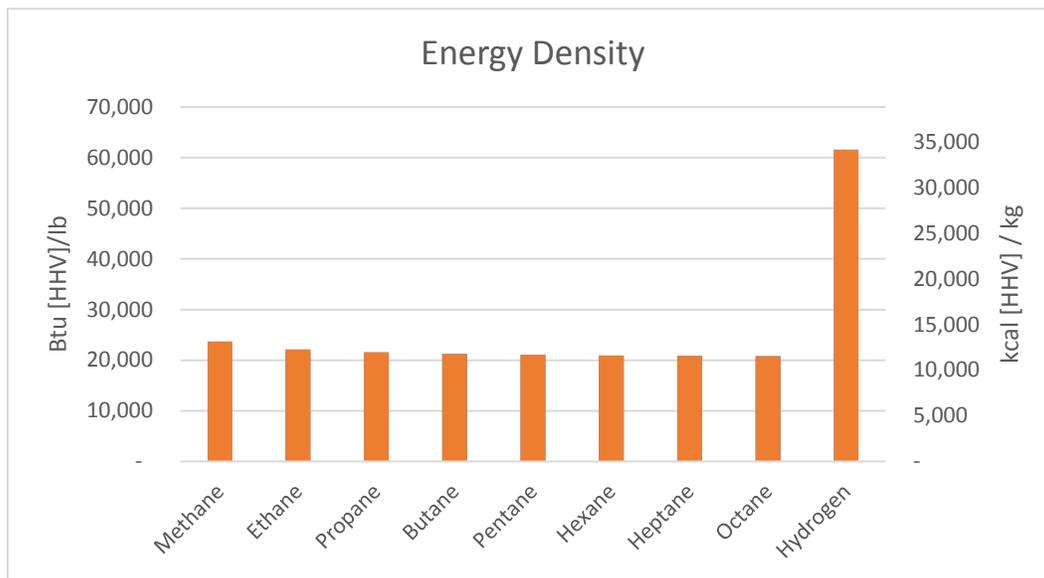
One other option is to choose a fuel that does not have carbon in it at all. If there is no carbon in the fuel, then there cannot be any carbon dioxide in the waste gas. One such fuel that has generated quite a bit of interest over the past 30-40 years is molecular hydrogen (H<sub>2</sub>). There are still many practical and economic hurdles to solve before hydrogen can be a viable option. As decarbonization becomes more of a priority, research on production and transport will continue and a tractable solution will gain more urgency.

Adel Sarofim has made this point since at least 1991: “Advocates of the ‘hydrogen economy’ are correct in identifying this [hydrogen] as the ideal fuel (once it is purchased and delivered to the combustion

chamber). The energy and economic cost of hydrogen manufacture and the problems of storage and transportation systems have made its near and mid-term use of marginal interest in this country.”<sup>1</sup>

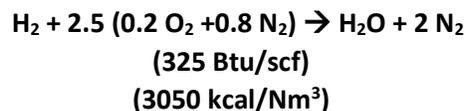
### Comparative Characteristics of Hydrogen

Hydrogen has several characteristics to recommend it as a potential source of fuel. One of which is its high energy density. Energy density is a measure of how much energy is released from complete combustion of that fuel, either on a mass basis, or on a volume basis. Most hydrocarbons have an energy density on a mass basis of between 20,000-25,000 Btu [HHV]/lb. Hydrogen, however, is almost three times as energy dense. **Figure 1** shows the energy density on a mass basis for several fuels.



**Figure 1: Energy Density on a Mass Basis**

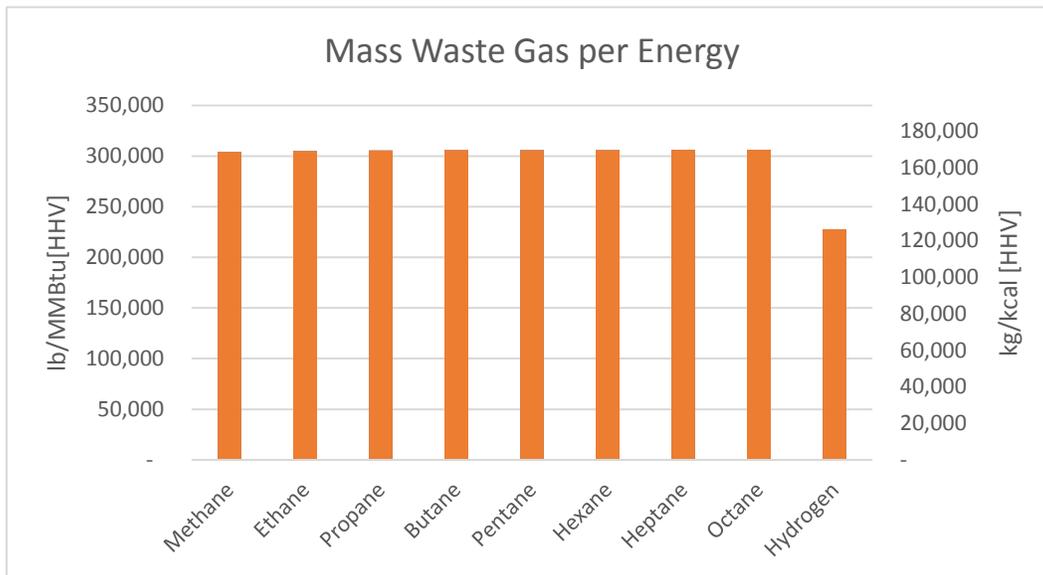
As with the “canonical combustion”, the balanced chemical reaction (**Equation 2**) for combustion of hydrogen is informative.



### Equation 2: Combustion of Hydrogen

It is interesting to compare the mass of waste gas generated per unit of heat from the various fuels. (See **Figure 2**.) That means that there is less mass of waste gas to move through an exhaust system for a given amount of energy. Similarly, about 25% less air (relative to combustion of hydrocarbons) is required per unit of energy, meaning that combustion air delivery systems (fans, blowers, etc.) can be correspondingly smaller.

<sup>1</sup> Adel F. Sarofim, “Interface Between Fuels and Combustion,” in *Fossil Fuel Combustion a Source Book*, ed. William Bartok and Adel Sarofim (New York: John Wiley and Sons, 1991) 10.



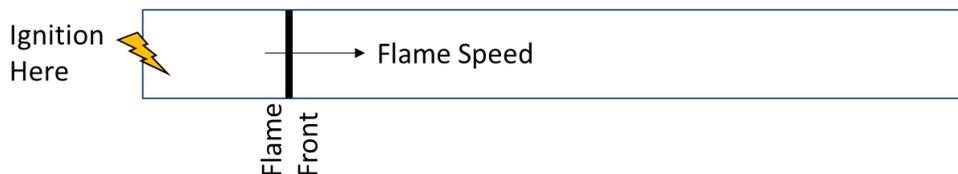
**Figure 2: Mass of Waste Gas per Unit Energy**

Finally, just to repeat what should be clear already, combustion of hydrogen generates no carbon dioxide. Because there is no carbon in the reactants (fuel and air) there can be no carbon in the products (waste gas).

### Special Considerations for Hydrogen Combustion

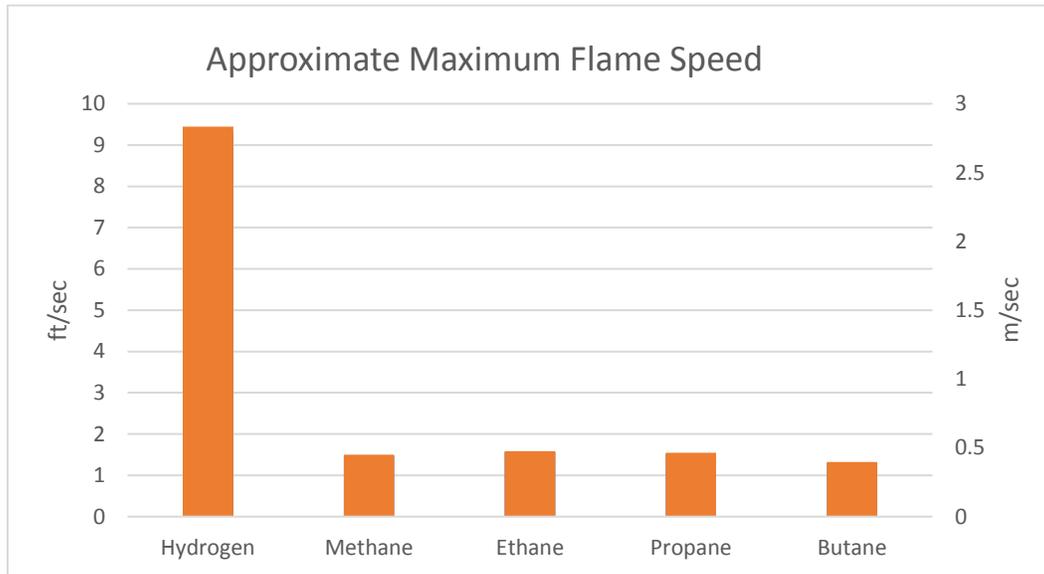
As seen already, hydrogen has thermophysical properties that vary from the patterns seen with hydrocarbons. Other properties of hydrogen (such as flame speed, flammability limits, luminosity, etc.) are sufficiently dissimilar to hydrocarbons as to require special considerations. While it is not a terribly difficult exercise to design a properly functioning combustion system with hydrogen as the fuel, retrofitting an existing system for a conversion to hydrogen fuel is much trickier to do correctly.

One of the more dramatic differences of hydrogen as compared to hydrocarbons is flame speed, that is the speed at which the combustion reaction propagates through space. As a way to conceptualize the flame speed, imagine the arrangement shown in **Figure 3**. This schematic shows a quiescent mixture of air and a fuel in a tube. Providing a source of ignition to the left end of the tube will start the combustion. The chemical reaction will move to the right at a given velocity.



**Figure 3: Flame Speed Schematic**

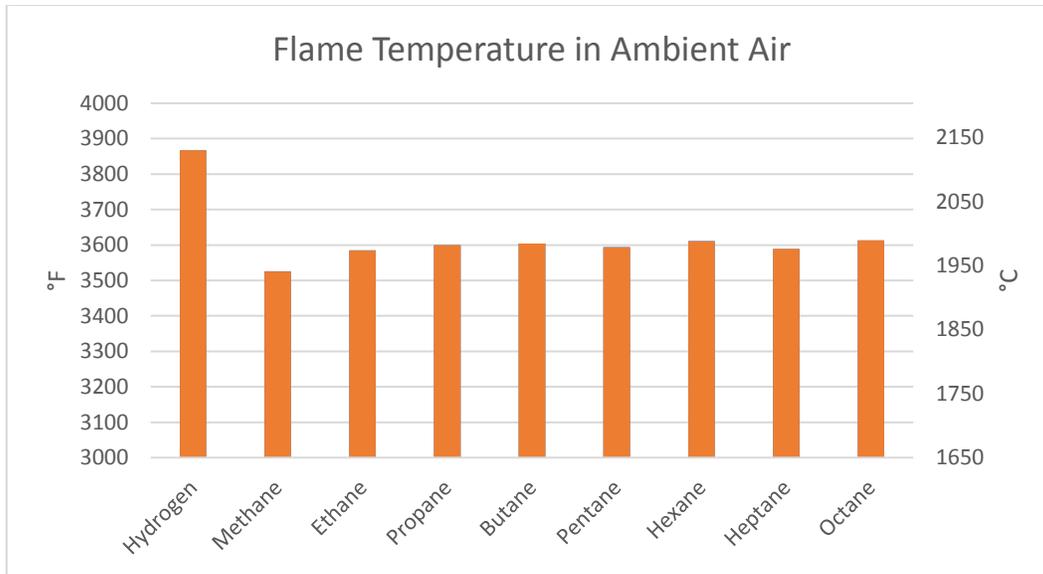
The exact velocity depends on several factors such as temperature, pressure, heat transfer, etc. It is more instructive to consider the relative velocity of the various fuels. (See **Figure 4.**) Hydrogen, here is the clear winner. In round numbers, the flame velocity as compared to hydrocarbons is about ten times. There are several major implications of the much faster velocity.



**Figure 4: Sample Flame Speed for Different Fuels**

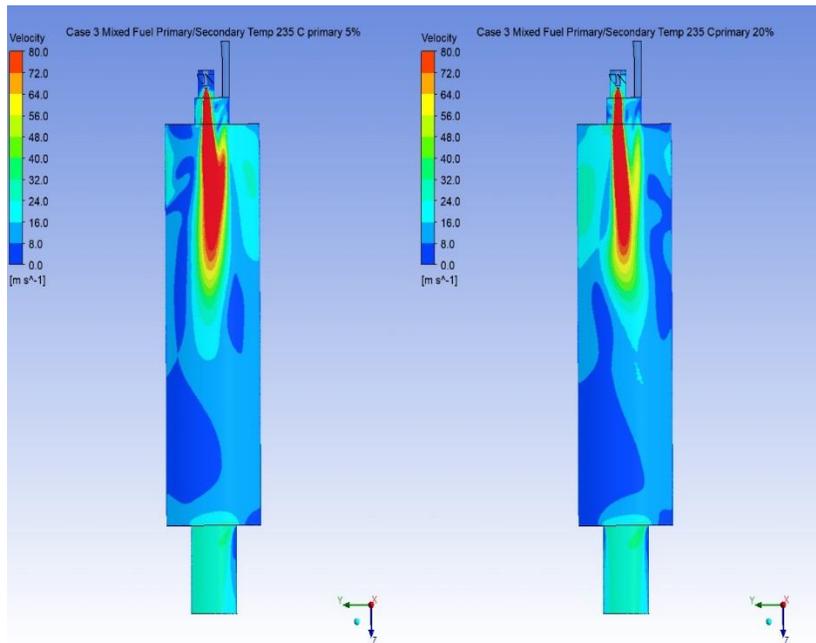
The main function of a properly designed burner is to deliver the fuel and the oxygen (usually in the form of air) in the correct amounts into the chamber where the process heat is required. If the flame is traveling back toward the burner faster than the combustion system is able to push the air and gas into the chamber, then the resulting flame pattern and heat release could be very different. In the case where air and fuel are premixed, then the combustion could travel into the combustion system causing “flashback”. Not only is this situation dangerous, it also delivers the heat to a location that is not useful to the process. Because hydrogen flame speeds are so fast, it is particularly susceptible to flashback and design of the system requires proper attention to it. Retrofit projects with a simple change of fuel in an existing system can be difficult to design properly. Velocity of a fluid is proportional to the square of the pressure drop through a system. Therefore, in order increasing the velocity by a factor of ten requires an increase in pressure drop through the system by a factor of 100! Rarely is such an increase practical or even possible. (There are mitigating factors such as the difference in fuel specific gravity that would reduce this number somewhat, but the resulting pressure increase is still generally not practical to achieve.)

**Figure 5** shows that flame temperature is also noticeably higher for hydrogen flames. It is important to select burner and furnace materials (such as refractories for baffles and port blocks) as well as auxiliary equipment (such as ignitors and flame safety equipment) that can handle higher temperature and more intense flames.



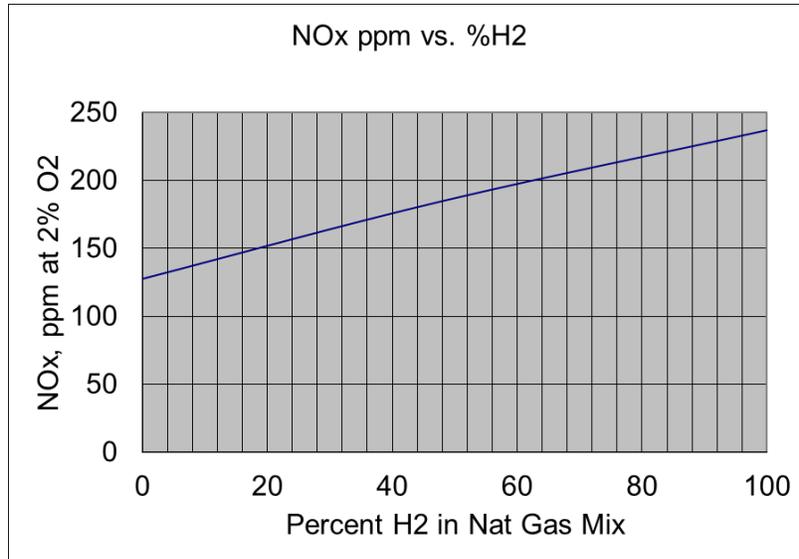
**Figure 5: Maximum Flame Temperature for Different Fuels in Air**

The combination of higher flame temperature and faster flame velocity leads to altered flame geometry and heat release patterns. High velocity flames are generally more compact and more intense, which can lead to uneven heat in the process chamber. It is possible to design a burner with these ideas in mind. Staging a burner, where fuel and/or air are delivered into the flame envelope in different amounts and locations can spread out the heat release, thus lengthening the flame. Testing and/or modeling (as shown in **Figure 6**) is critical for proper design of the burner. In general, hydrogen is not an appropriate fuel for premix systems, primarily because of the flashback discussed earlier.

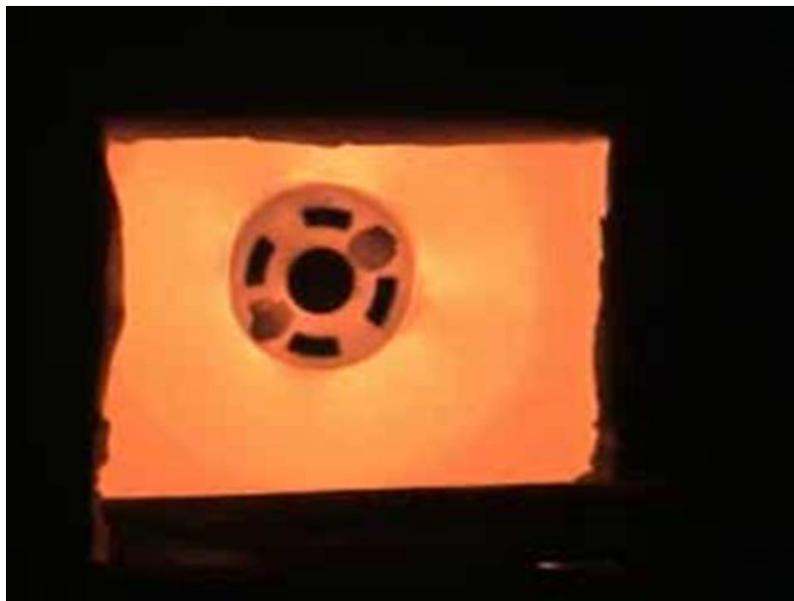


**Figure 6: Sample CFD Model for Hydrogen Burner**

While the primary focus of this paper is emission of carbon dioxide, control of other emissions (nitrogen oxide (NO<sub>x</sub>) being the primary one) is also of interest to the combustion engineer. Generally speaking, the high intensity flame, and the extremely fast mixing causes a relative increase in the formation of NO<sub>x</sub> with hydrogen flame burners. **Figure 7** shows a trend in NO<sub>x</sub> formation as a function of percent hydrogen mixed into methane. As mentioned, proper staging of the burner can reduce the formation of NO<sub>x</sub>, but it requires careful attention. (**Figure 8** shows a sample burner staged for a decrease in NO<sub>x</sub> formation.) In general, higher burner pressure will cause a decrease in NO<sub>x</sub>. The decrease is due to the higher velocity and more entrainment of furnace waste gas into the root of the flame, thus lowering the temperature of the flame and abating its intensity.



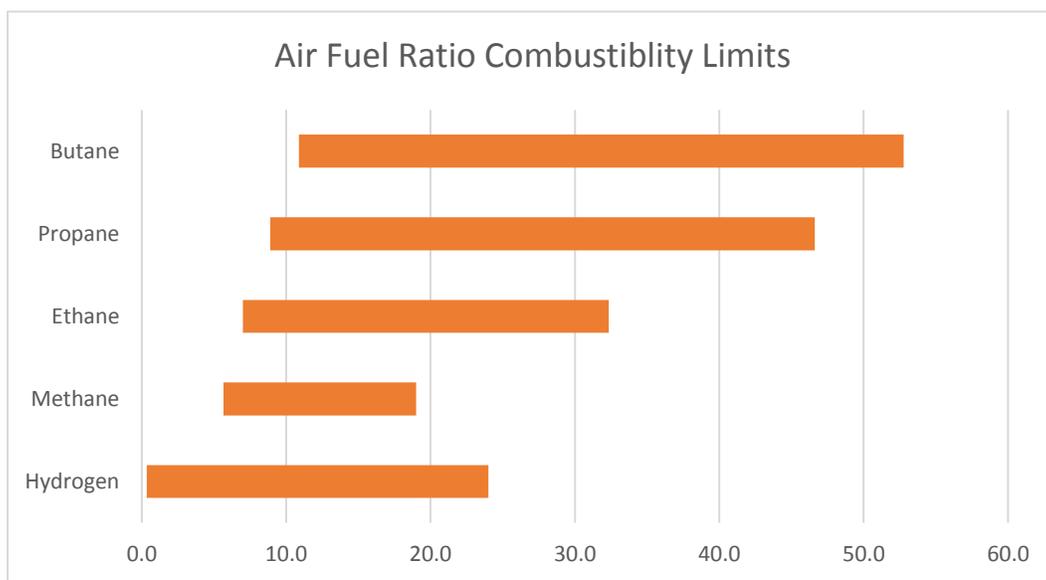
**Figure 7: Sample NO<sub>x</sub> Trend in Increasing Percent Hydrogen (by Volume)**



**Figure 8: Sample Burner Port Showing Staging for NO<sub>x</sub> Reduction**

Without going into the arcana of how to report emissions performance of burners, it is worth pointing out that hydrogen combustion has much less waste gas on a dry basis, so reporting emissions in concentrations (PPM on a volume basis) can be misleading. (Consider combustion of hydrogen in pure oxygen, where the only product of combustion is water, meaning that there is no dry waste gas. It would not even be possible to report the emissions in terms of a concentration!) It is generally better practice to report emissions production in terms of mass per unit heat release (#/MMBtu or mg/MJ).

Hydrogen also has a wide range over which it is flammable in air. Each fuel has a specific range, and **Figure 9** shows these limits for a selection of fuels. Notice that even a slight amount of hydrogen in air is flammable. Extreme caution is required to avoid a combustible mix.



**Figure 9: Flammability Limits for Various Fuels**

### Heat Transfer and Flame Visibility

One side effect of a carbon-free flame is that the luminosity is greatly reduced, meaning that the flame may be invisible to the human eye (in contrast to hydrocarbon flames which are usually visible over normal operational limits). Direct radiation in the visible spectrum decreases, leading to a decrease in radiant heat transfer from the flame. Not all flame radiation occurs in the visible spectrum, though, and the tri-atomic water molecules themselves will provide some level of radiant transfer. Even a small amount (by volume) of hydrocarbons, perhaps 2-3%, can provide enough luminosity to allow both visible flames and enhanced heat transfer from the flame without generating an appreciable amount of carbon dioxide. Intentional introduction through an auxiliary lance is one way of providing these hydrocarbons. **Figure 10** shows a flame with such a hydrocarbon luminosity lance. The flame is obviously visible!



**Figure 10: A Hydrogen Flame Made Visible with the Addition of a Small Amount of Hydrocarbons**

Although direct radiation from the flame might be diminished with hydrogen flames, there are several other ways to enhance process heat with hydrogen flames. The luminosity enhancement lance mentioned above is one such way. Another is use of flat-flame burners to increase radiation to refractory. There are also high emissivity coatings that will increase re-radiation within the furnace. Enhancements of convective heat transfer (especially in lower temperature applications) can also partially mitigate loss of flame radiation.

### **Safety**

All combustion requires caution and a focus on safety. The combination of extremely fast flame speeds and extremely flammable mix, even at very low amounts of hydrogen, require extra caution for this fuel. Furthermore, the higher fuel velocity (to avoid flashback) generally requires higher fuel pressure than would be common for burning hydrocarbons. The combination of high velocity and high pressure can also cause much higher noise levels that might exceed typical OSHA limits. Finally, (in)visibility of the flame could pose hazards to personnel and equipment if it is difficult to determine if combustion is occurring.

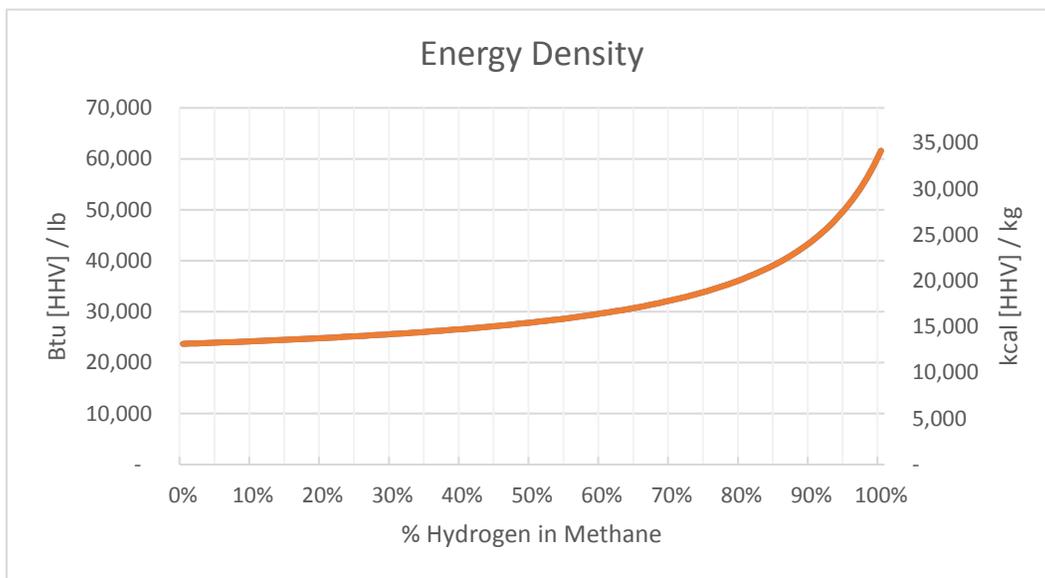
### **Challenges for Natural Draft Burners**

Hydrogen presents unique challenges to natural draft burners in three main ways. First, as discussed above, the high velocity required because of the high flame speeds necessitate a correspondingly higher pressure. For natural draft burners, the fuel usually provides the motive force, and boosting the required pressure enough to generate the required velocity is not always possible. Second, due to both the wide flammability envelope, and the very real risk of flashback due to the extremely high flame speeds, premixing (common in natural draft burners) is neither feasible nor safe. Finally, because of the energy penalty (discussed in detail below), it is crucial to minimize the consumption of hydrogen through improvements in efficiency. One of the most common ways to do so is through preheating the

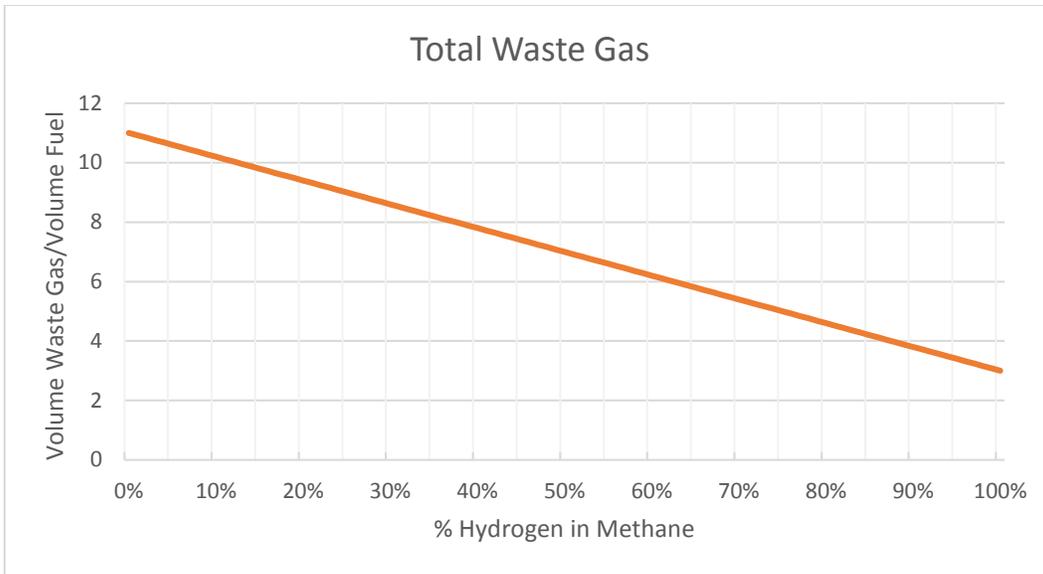
combustion air. Generally, these natural draft burners do not operate very well with variability of air temperature. In general, then, natural draft burners are not good candidates for hydrogen.

### Hydrogen Enrichment

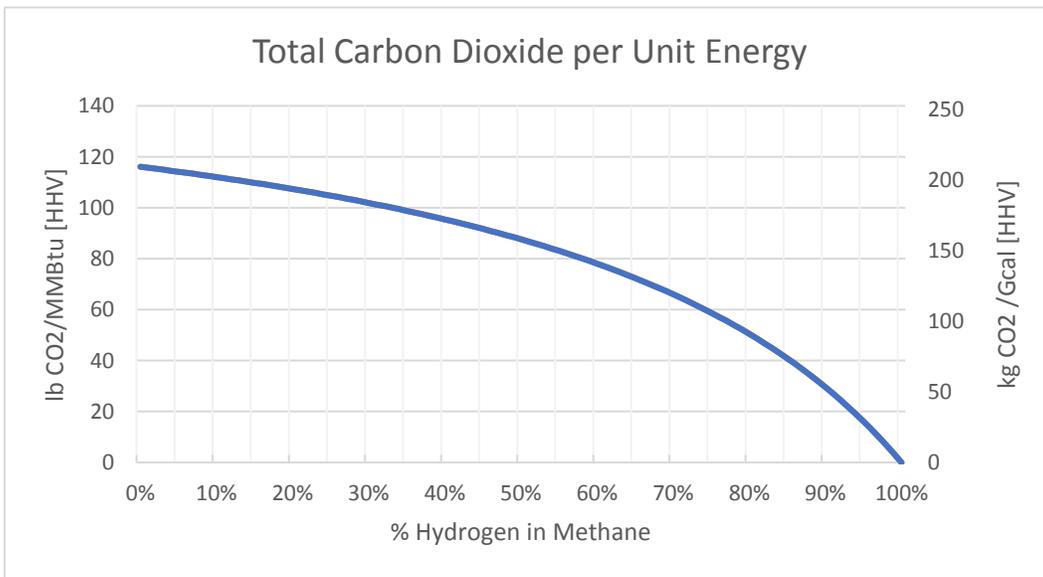
One way to get some of the benefits of hydrogen without accepting all of the challenges is to mix a portion of hydrogen into another fuel. It is possible to do so with any gaseous fuel. As an example, mixing various levels of hydrogen with a hydrocarbon will change the energy density, waste gas volume, carbon release and even the combustion efficiency (and thus amount of gross fuel for net process heat). **Figures 11-14** show sample results for hydrogen enrichment of methane. (The x-axis here is percentage by volume.) It is clear from these charts that there are benefits to enrichment of a hydrocarbon with hydrogen.



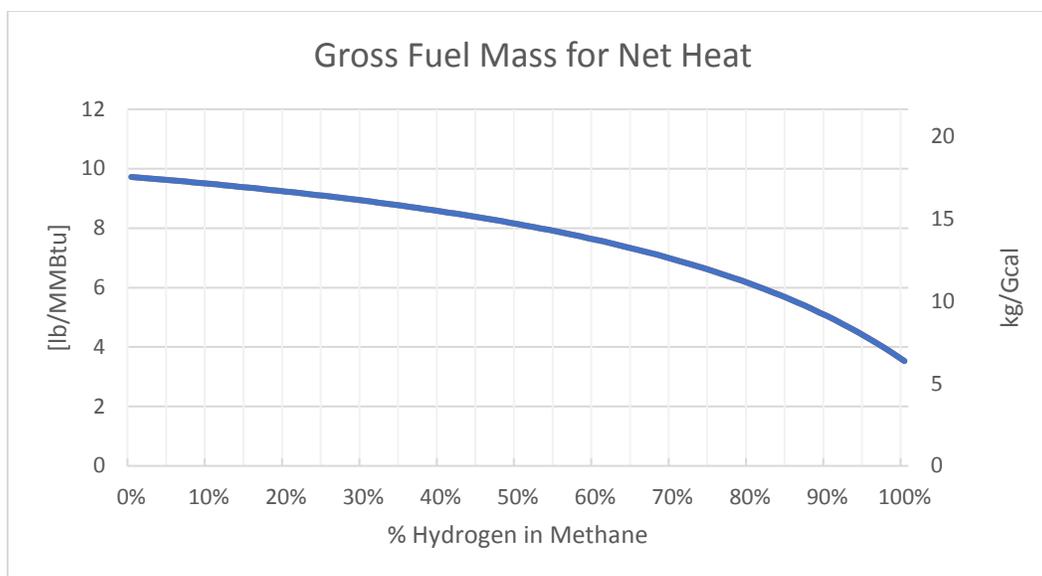
**Figure 11: Energy Density with Enrichment of Methane with Hydrogen**



**Figure 12: Volume of Waste Gas per Volume of Fuel with Enrichment of Methane with Hydrogen**



**Figure 13: Carbon Dioxide per Unit Heat with Enrichment of Methane with Hydrogen**



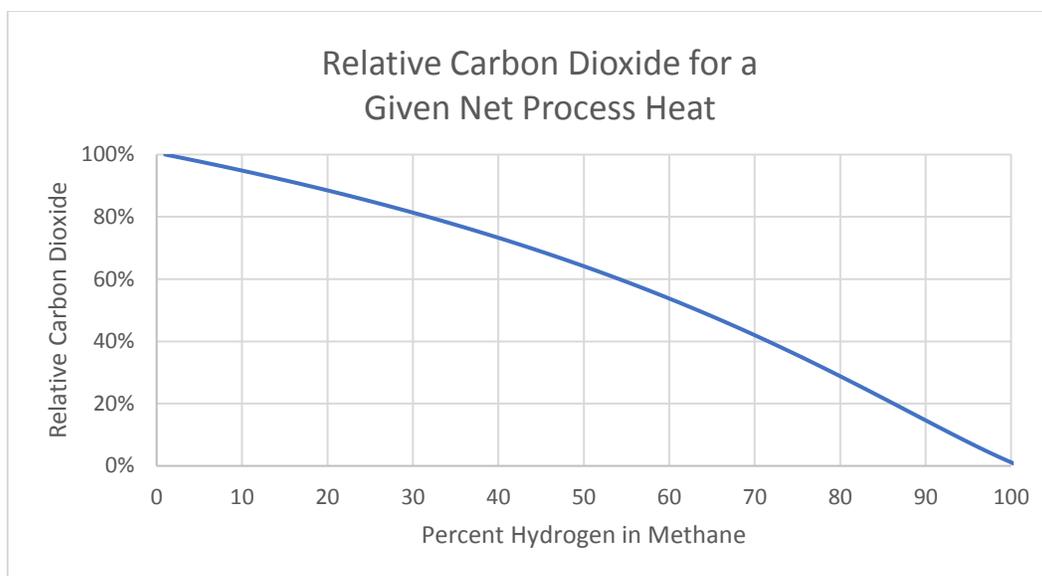
**Figure 14: Gross Heat Required with Enrichment of Methane with Hydrogen (assuming 2000°F [~1100°C] waste gas temperature)**

These fuel mixtures aren't necessarily artificial blends, such hydrogen-enriched fuels occur industrially, as well. One common example is used extensively over the past hundred years or so in the steel industry. Production of steel requires a source of pure carbon. Pyrolysis of coal, which drives off volatile constituents, leaves a form of (nearly) pure carbon known as coke. The pyrolyzed gases form a combustible mixture called coke oven gas (COG). **Table 1** summarizes basic thermophysical properties of COG.

	Lower Value	Upper Value
Hydrogen [% volume]	50	60
Carbon Monoxide [% volume]	5	10
Methane [% volume]	30	35
Calorific Value [HHV] [Btu/scf]	450	550
Calorific Value [HHV] [kcal/Nm <sup>3</sup> ]	4253	5270
Specific Gravity	0.25	0.45
Air to Fuel Ratio	4.5/1	5.5/1

**Table 1: Typical Values Thermophysical Values for Coke Oven Gas**

For illustrative purposes, it is possible to treat the COG as a mixture of hydrogen in methane (see **Figures 13-14**). Focusing on **Figure 13**, at 55-65% enrichment of hydrogen, there is a reduction in carbon dioxide (on a basis of mass per unit heat) of almost a third! Another startling result is that the efficiency gain realized by hydrogen enrichment means that it is actually necessary to burn only about 75% of the fuel (on a mass basis) to get the same net heat to the process. (See **Figure 14**.) Combining these two results, as shown in **Figure 15**, can lead to a reduction in CO<sub>2</sub> of almost half for the same net heat to the process. Of course, the efficiency calculation is for a specific condition, but these trends would be similar for other similar conditions.



**Figure 15: Total Reduction of Carbon Dioxide for a Given Net Process Heat Requirement**

### Carbon Penalty

Although there are many benefits to hydrogen as a source of fuel, it's important to understand that its use in most forms as presently generated, can actually increase the amount of atmospheric carbon dioxide as compared to direct combustion of methane. The majority of hydrogen produced (not just for combustion, but for all commercial and industrial uses) is through combining water in the form of steam and methane in a two-step process to generate carbon dioxide and hydrogen (**Equation 3**).



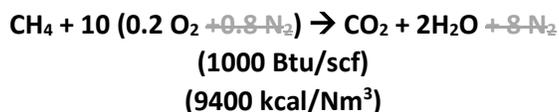
### Equation 3: Hydrogen Generation from Methane

Here, carbon dioxide is a product, and offsets the lack of carbon dioxide in the direct combustion of the resulting hydrogen. Processing and refining the resulting hydrogen, as well as generation of steam require the use of more energy. Assuming that this extra energy required is ultimately from combustion, the final tally against hydrogen as a fuel source shows that there is actually up to a 40% penalty. For example, to generate 47.4 MMBtu [HHV] of heat would require combustion of one ton of methane and would generate 2.75 tons of carbon dioxide. To get the same amount of heat from combustion of hydrogen would require 0.385 tons of hydrogen, but would generate 3.85 tons of CO<sub>2</sub>, which is an increase over combustion of methane of 40%.

This carbon penalty is associated only with the production and formation of hydrogen. If a natural source of hydrogen were available, then the penalty would disappear. Research continues in order to find better ways to generate hydrogen (possibly through electrolysis (decomposition) of water) on an economically viable, environmentally sustainable, and scalable way. In the near future ways might emerge that will reverse the carbon penalty.

## Alternative Ways

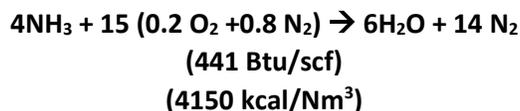
There are other ways, in various stages of development, to do decarbonized combustion. Burning a fuel in pure oxygen will generate only carbon dioxide and water in the waste gas. **Equation 4** shows canonical combustion without the nitrogen:



### Equation 4: Combustion of Methane and Oxygen

After processing the waste gas to condense the water into liquid form, the only remaining component is the carbon dioxide. At that point, sequestration/storage becomes an easier proposition, because no separation of CO<sub>2</sub> and nitrogen is required. This scheme, of course, requires a source of pure oxygen, which itself generally requires energy to form, which itself might increase the carbon footprint of this method.

One recent, and promising, development is the use of ammonia (NH<sub>3</sub>) as a fuel as shown in **Equation 5**:



### Equation 5: Combustion of Ammonia in Air

Obviously, there is no carbon dioxide in this reaction. There are several challenges with ammonia as a fuel, though. In contrast to hydrogen, the flame speed and flammability ranges are very restricted, somewhat limiting the applications. As with hydrogen, there are the concerns with upstream generation of ammonia and the accompanying energy and carbon penalty. However, ammonia is one of the most widely synthesized chemicals in the world, so questions of scale have already been solved. There are some exciting applications of ammonia combustion for use as a jet fuel substitute, and other developments are in the works.

## Conclusion

In light of the growing body of research pointing to the impact of carbon dioxide on global climate change, it is important for us to start exploring ways to minimize the contributions of carbon dioxide from combustion. One of the ways being explored with much interest is the use of hydrogen as a fuel. While hydrogen has many characteristics to recommend it as a fuel, such as high energy density, lower air requirements and less waste gas on a per unit energy basis, it is not necessarily a straightforward exercise to apply hydrogen as a fuel. Due to its high flame speeds, wide range of flammability limits and higher flame temperature, it presents challenges as a fuel. It is possible to overcome these challenges, but it does take careful application. One way to gain some of the benefits of hydrogen while mitigating some of the challenges is to use it as an enrichment for another hydrocarbon. Such a fuel, widely used in integrated steel mills is Coke Oven Gas. While it is true that there is no carbon dioxide formed in the direct combustion of hydrogen, it is important to realize that there is an energy penalty, meaning that

with current technology, isolation of hydrogen usually releases more carbon dioxide than an equivalent hydrocarbon. Other potential methods of carbon free combustion include oxyfuel combustion of hydrocarbons (where isolation of the carbon dioxide is much easier for the purposes of carbon capture and storage) and use of ammonia for fuel. Ongoing research will hopefully produce an economical, sustainable and viable model for one of these methods so that we can achieve carbon free combustion.