Firing of Liquid Bio-Derived Fuels for Decarbonization of High Temperature Industrial Heating Processes

Brandon Cerminara – Development Engineer
Dave Schalles – VP-Technical Services
Bloom Engineering Company, Inc.

Abstract

Recent commitments to CO_2/Green-House Gas emissions reductions by governmental, NGO and industrial corporations require that new energy sources be found to replace fossil fuels. While some are envisioning 'The Electrification of Everything,' High temperature industrial heating processes have been identified as one of the key technologies that are difficult to electrify.

Much of the recent discussion on this subject has focused on gaseous Hydrogen as a potential 'energy-carrier' for such processes, as it has the potential to be produced directly from 'low-carbon' energy sources and can be delivered in large quantities via pipeline. However, as mentioned in our 2021 AFRC paper on alternative low-carbon fuels, Hydrogen currently remains one of the higher-cost options.

In addition to Hydrogen compatible equipment, Bloom has developed burners and combustion systems, over the last several years, capable of firing a variety of liquid bio-derived fuels, which could also be viable fossil fuel alternatives. Some of these fuels are alcohols (ethanol and methanol for example), BioOil from cellulosic pyrolysis, as well as glycerin and biodiesel.

We will provide a discussion of combustion characteristics, emissions, safety, and applicability of these various fuels based on our project experience as well as laboratory testing data.

Clearly there remains a significant gap between the needs of industrial users and the cost and availability of 'low-carbon' fuel options. In our opinion, industrial equipment will often need to be designed for fuel-flexible operation. In the upcoming transition period, as fuel production and delivery systems are developed, availability will likely vary according to local and regional conditions. Fuel flexible combustion equipment will reduce risk to users by allowing them to choose from a variety of suitable fuels.

Introduction and Background

Decarbonization has gradually become a focal point across various industries and scientific disciplines. Motivation for businesses to invest in technology related to decarbonization lies in commitments to CO_2 and other greenhouse gas (GHG) emission reductions by governmental bodies. An example of such a commitment can be found in the United States' official "Long-Term Strategy" for net-zero GHG emissions by 2050 [1]. Other countries around the world have adopted reduction policies, many of which are very similar to the United States' policy or are more aggressive. Withholding from comprehensive details of those commitments for the time being, the point to accentuate is a collective drive toward more sustainable requirements for industrial processes.

Societal pressure further contributes to the sustainability mantra adopted by governments as a wave of individuals continue to support policies that demand lower GHG emissions. As will be expounded upon later in this paper, businesses will continue to see rising demands for sustainable solutions and practices as the world pushes toward its net zero goals, largely driven by the Paris Agreement established in 2016.

Many non-governmental organizations (NGO's) and corporations have adopted their own GHG reduction strategies reflective of the Paris Agreement. A natural consequence of these commitments is the need for an alternative fuel source to fossil fuels. Several sources have been identified as leading alternatives, each with its own depth of scientific research and development. "Electrification" serves as the solution for several major industries – the automotive for one. However, as will be discussed later in this paper, electrification in many steel and aluminum treatment processes is not realistic.

Another alternative that has gained substantial momentum in the last decade is hydrogen gas. An appealing solution due to its emission of purely water, hydrogen has been embraced by numerous industries and businesses as the long-term solution to GHG reduction. Similar to electrification, there is an array of benefits and drawbacks to hydrogen usage as a combustion fuel.

One option – the subject of this paper – shows significant potential as an alternative for fossil fuels: Liquid bio-derived fuels (LBF's). These are fuels which are extracted from natural, organic sources such as corn, sugarcane, and various plant oils, as a few examples. In reality, there are numerous products and byproducts of industrial processes from which bio-derived fuels can be obtained. One factor which favors LBF's is that the system components and designs previously developed for Fuel Oil firing are often suitable for handling LBF's, with minor modifications.

These three alternative fuel sources will be discussed and compared in subsequent sections. The systems and burners that will be described in the discussion sections mainly focus on applications in the aluminum and steel industries. Typical process temperatures one can expect range from 1800 to 2400°F. A few examples of furnaces that may use liquid fuels (possibly in addition to natural gas and hydrogen) include aluminum melters, aluminum holders, and reheat furnaces for the steel industry.

Connected capacity for those furnaces can be as low as 5-50 MMBtu in aluminum applications or as high as several hundred million Btu firing rates in the steel industry. Multiple burner technologies are used in these applications such as regenerative burners, low profile flat flame roof burners and typical horizontally fired wall burners.

Other applications where liquid bio-fuels or hydrogen may be used include heat treating furnaces and coating lines that utilize indirect heating via radiant tubes. All of these burner designs are normally flex-fuel capable via fuel nozzle adaptation, addition of atomizing lances or multi-nozzle burner technology. Due to the gross energy intensity and high temperature requirements of these applications, as well as corrosivity some of the off-gases, electrification may be difficult as well as capital and maintenance intensive.

Discussion of Two Popular Options for Fossil Fuel Alternatives

As mentioned previously, several sources have been adapted as fits for fossil fuel alternatives (FFA's). Two of those listed, electrification and hydrogen, are to be discussed here.

Electrification

The transition to all-electric process heating presents an appealing pursuit for several major industries. Side-stepping the need to burn fuel in a process prevents emission of any combustion products, which produces a short-sighted notion that the process would then have much lower, or zero, GHG emissions. A primary shortcoming of electrification emerges in consideration of its demand on the current power grid.

The EIA states that 38% of the US power grid was powered by natural gas in 2021, and roughly 22% was powered by coal under the same year [2]. Despite a steady rise in renewable energy generation sources, most of the grid continues to rely on fossil fuels. Intuitively, power generation is tremendously limited in its conversion efficiency from thermal energy. Most modern gas turbines are only capable of 25-30% efficiency; however, some advanced gas turbines are able to reach up to 60% efficiency [3]. Such a low efficiency leads to the scenario where an electrical demand equivalent to the heat output necessary for a given process may, then, result in higher GHG emissions than if the process were kept in its fossil fuel burning state in the first place. Fuel types used in power generation is, of course, highly dependent on regional power plants and grid demands.

Electrification has been proposed to hold a use in industries primarily where consistency of temperature is crucial to the process. Uniformity of temperature output can be readily obtained in low-temperature applications, but high temperature processes that require constant heat input are not as readily adapted to all-electric heating. Fluctuating grid demands and power station outages pose two examples of major risks for a process that requires accurate temperature moderation with high energy demand. While the "electrification of everything" has become a slogan for some organizations, practical dispatch and operation of that concept is not feasible given current technology and grid capability.

Hydrogen

The use of hydrogen as an FFA has rapidly become an appeasement of sustainability demands in industry. An enticing property of hydrogen is its high calorific value for combustion, which will be explained in further detail, below. The number of generation sources for hydrogen have increased notably as technology in the subject improves. Budding methodologies for its production have led to classification of strategies through a color spectrum, and each generation method has its own benefits and drawbacks.

Green hydrogen is perhaps the most sought-after form of generation presently. For it to be green, the production must come via excess energy off a renewable power generation source (such as wind or solar) which is used to electrolytically split water to make H_2 gas. This form makes up a small fraction of current production methods, primarily due to upfront expenses. The power grid would require a much greater percentage of renewable energy generation for green hydrogen production to be feasible on the scales necessary for continuous operation in industrial processes.

The dominant modern method of generating hydrogen is through steam methane reformation. CO_2 is a natural byproduct of this process, which leads to two different types of H_2 "colors." If the carbon dioxide produced during the process is sequestered via some sort of carbon capture, the resulting hydrogen is referred to as "blue". Grey hydrogen results if the CO_2 is simply vented to the atmosphere [4]. A majority of the hydrogen supplied and used in industrial processes – especially high temperature applications – is grey. The technology necessary to capture the CO_2 resulting from large demands of hydrogen production is simply not in place.

There are various other "colors" of hydrogen, and more continue to be classified as production technology improves and expands. These types will not be mentioned here as they are not as relevant to the discussion. What should be noted, however, is that the form of hydrogen generation used varies widely with regional demands, geographic factors, and economies.

Usage of hydrogen has garnered such attention because of the lack of carbon dioxide produced during its combustion. Absence of carbon in a fuel intuitively results in an absence of CO_2 in the product stream. The notion of sustainable operation of the process at hand is shared with an all-electric system in that no GHG's are emitted as a direct result from operation. However, as one can gather from the previous discussion of hydrogen generation types, indirect production of GHG's is almost guaranteed when considering modern technology.

Nonetheless, hydrogen continues to serve as an attainable means toward decarbonizing industries that require combustion technology. Increased demand placed on hydrogen supply capability should continue to advance the technology required to produce the gas. As discussed in the introduction, further interest in hydrogen use will be driven by demand of companies to pursue sustainable options for use in their processes.

Practical usage of pure hydrogen on existing combustion systems has been extensively studied and verified through testing. Bloom has completed a number of tests on several of its burners using hydrogen and natural gas mixes as well as pure hydrogen itself. Details of this analysis will not be discussed here but instead can be found in Bloom's AFRC paper from 2021 – "CO_2 Reduction Options for High Temperature Industrial Combustion" [5]. The information from that paper can be abridged to emphasize the point here that hydrogen is readily capable of firing on many of the systems previously fired on natural gas, so long as the equipment being used is rated for the required flows and is made of compatible material. This makes the transition to its use more alluring for steel and aluminum companies, specifically, that have mainly natural gas systems in place already.

Other challenges for hydrogen use that arise as a result of both technological and infrastructure limitations are its transport and storage. To date, there are only roughly 1600 miles of pipelines dedicated to hydrogen transport, and most of them are located near and contained within petroleum refineries and chemical plants. Transport via high-pressure tube trailers can be expensive and is typically limited to 200 miles or less [6]. The development of a few other transport methods has commenced, with some currently available, but all pose a significant cost hike. The relatively short transportation range requires production of H_2 gas to occur in a regional setting where the customers who require it are accessible.

Additional concerns arise in consideration of operational hazards for hydrogen combustion. Primary hazards come from it being an invisible, odorless gas, which requires sensors and equipment to determine any unknown leaks in a system. The potential for leaks to go undetected raises further hazards as hydrogen is flammable over a very wide ignition range. Mitigation or elimination of these dangers demands extensive planning and safeguards, which can increase operating costs substantially. Another point worth mentioning when burning H_2 gas regards a flame that does not emit much – if any – light in the visible spectrum. Therefore, operation can be dangerous if there is a rogue flame which plant personnel are unable to see.

Liquid Biofuels as Fossil Fuel Alternatives

An intriguing solution to decarbonization could lie in a source that had long been used in various industries – liquid fuel. While it may seem counterproductive to burn a heavier hydrocarbon fuel than natural gas, an argument could be made in favor of LBF's. By utilizing a liquid fuel derived from a biological source, there is significant potential to minimize natural gas and other fossil fuel usage in the process as well as life cycle carbon emissions via a carbon sink effect. LBF's can be classified under a broad range of definitions, but this paper will focus on fuels such as: Methanol, Ethanol, 'BioOil' derived from cellulosic pyrolysis, glycerin, and various process waste oils. For simplicity, all pricing and fuel properties in this report will be sourced from U.S. data and compared to natural gas.

Methanol

Usage of methanol (CH_3OH), also known as wood alcohol, as a transportation fuel had gathered compelling support in the early 1990's. Today, it is no longer focused on for the purpose of transportation in the U.S. because of its reduced fuel economy in comparison to gasoline. However, it may yet present a valuable opportunity through use as an industrial fuel.

Production of methanol is most commonly performed utilizing a natural gas syngas reaction resulting in methanol and steam product streams. There are several methods of producing methanol as a substrate of other product lines. Methanol is produced as a bio-based fuel through a reaction of glycerin, for

Figure 1 - 100% Methanol flame firing at roughly 15% excess air conditions

example, which itself is a byproduct of biodiesel production. An additional feedstock for methanol production can be sourced from waste streams of the pulp and paper industry. Other sources of production are derived from biomass, waste gas, and organic matter grown specifically for production [7].

Physically, liquid methanol is clear with a low viscosity. The fuel is capable of firing on an oil-tipped burner that utilizes atomization of the liquid feed. Bloom has demonstrated this capability through testing on its 1206 burner, which is traditionally fired on oil. Figure 1, below, displays an image of a pure methanol flame being fired at around fifteen percent excess air. Typical methanol flames look clear-blue, but with adequate mixing in a burner, the flame becomes much more luminous.

Methanol holds a relatively "clean" burning property when compared to other liquid fuels, and complete combustion of the fuel results in very low amounts of particulate matter (PM) generation. Thermal NO_x generation in methanol combustion will vary based on the burner technology being used, but as an example, data was collected during testing on Bloom's 1206 burner, as previously mentioned. Testing indicated a relative NO_x emission decrease of roughly 30% compared to an analogous system firing on natural gas.

Liquid methanol has an energy density (also known as a higher heating value, or HHV) of 9874 Btu/lb.. The US DOE reports the HHV of natural gas on a per-pound basis as 22453 Btu/lb. – note this value is averaged since the makeup of natural gas can vary based on region, time of year, and various other factors [8]. While those values may appear to be strikingly different at first, one must consider that natural gas (in the US) is most commonly supplied in a gaseous state. Therefore, a higher volume of natural gas may be required to meet the same energy output as methanol.

Methanol has a very high volatility compared to other liquid fuels, which leads to potential hazards. The fuel is slightly toxic to humans and its high volatility requires measures to seal and contain any system where it is used. Further danger of methanol use can come from its high flammability. With a flash point of 52°F and an LFL of 6%, there are significant concerns for unintentional combustion and/or explosions to take place without proper care [9]. Methanol's auto-ignition temperature (AIT) – 897°F – is also lower than that of natural gas – around 1000 to 1050°F on average.

Usage of methanol in automotive fuel was largely ruled out by the U.S. because of its miscibility with water. Biodiesel standards require the water content in the fuel to be extremely low at 0.05% by volume [10]. With high distillation costs, it was decidedly uneconomical to continue methanol's expansion for that industry. Industrial combustion processes, however, are not nearly as strict. Water content of fuels such as methanol can be as high as 5% by volume while still maintaining its combustion properties. Of course, some limitation in fuel efficiency will result in a higher water content, but extensive distillation is not necessary.

Ethanol

The stark movement toward biodiesel production allowed ethanol (EtOH or C_2H_5OH) to gain significant traction in commercial and industrial applications. With its production heavily subsidized, it has found widespread usage in blending with other fuels, mainly gasoline. Ethanol continues to be a talking point for political campaigns and lobbying efforts which promotes its leverage as an FFA.

There are several methods in modern practice to develop an ethanol product or byproduct. Most of ethanol's production – almost 90% – is sourced from dry-milling starch-based crops such as corn. This process involves milling corn into flour, followed by a fermentation process that will produce an ethanol product stream. Wet-mill plants focus on creating corn sweeteners with ethanol as a byproduct stream. Another method of "green" generation is via cellulosic operations. Organic products such as grass, wood, and other crop residues are broken down using two methods: Biochemical conversion utilizes plant cell biology to break down the organic matter and eventually produce bioethanol; thermochemical conversion requires heat input to induce ethanol creation. The latter two methods are much more involved and more expensive than dry-mill plants [11].

Many of ethanol's physical and chemical properties are similar to methanol. EtOH has a greater energy density of 12827 Btu/lb., though. Ethanol will burn as a less translucent flame than methanol. Rather than the clear blue flame, a brighter, more yellow flame would be expected due to a higher carbon content than methanol. Further similarities are found when considering NO_x emissions between ethanol and methanol. The fuels' similar chemistries allow one to expect similar emission performance when fired on the same system. However, any alternative fuel should be subjected to suitability testing on the burner or system that it is intended to be applied to.

Like methanol, ethanol has a high volatility compared to other liquid fuels with a flash point of roughly 55°F. Its autoignition temperature is lower than methanol's at 793°F, and an LFL of 3.3% raises concerns of explosive hazards as it can be ignited under almost any ambient temperature condition [12, 13]. Transport, storage, and usage in large scale combustion processes could pose challenges and raise costs through safeguards. Ethanol is harmful if consumed at high concentrations; however, some of the largest consumer industries for ethanol are alcoholic beverages. High exposure to low concentrations of ethanol may still lead to serious health concerns.

A major benefit that ethanol holds as an FFA is that environmental testing has been carried out extensively by many organizations and there is a multitude of data available. Its emphasis as a solution for reducing automotive emissions has allowed widespread manufacturing of the fuel to advance ethanol's infrastructure and technology. Adapting the infrastructure already in place to allow for usage in large-scale industrial applications would encourage a smoother transition from fossil fuels. Contrastively, extensive demand from the automotive industry may compete with demand from industrial combustion processes, causing an increase in EtOH feedstock pricing. This concept will be visited later in the *Economic Considerations* section.

'Bio-Oil'

Bio-oil has recently entered the stage as a candidate for a more organic form of FFA's. The fuel is commonly a liquid, tar-like consistency that contains high oxygen and water contents. As a result, bio-oils are not typically classified as pure hydrocarbons and are immiscible with fossil fuels [14].

The primary method of feedstock decomposition is through the pyrolysis of wood. By subjecting resinous wood to intense heat and pressures, the wood will undergo a process similar to that which results in crude oil underground, but this process will take a much shorter time. The required minimum temperature to induce pyrolysis of wood biomass into liquid products is around 1300°F [15]. One study points out that the energy input required to execute this process is only 15% of the potential output energy, continuing by claiming that modern technology is capable of achieving that efficiency [16]. One drawback of the pyrolysis method, though, is that the biomass feedstock must be processed and dried before converting.

An additional method of bio-oil generation that has been studied is through the use of algae as a feedstock. Algal Hydrothermal Liquefaction (AHL) does not require a low water content in its feedstock. Rather, it converts wet biomass into oil that has a higher energy density than oil produced in wood pyrolysis. Unlike pyrolysis, AHL requires the presence of a catalyst for the conversion process to occur, which raises the cost of the process further. Algae's role in bio-oil production has evoked attention even by some major corporations. The most notably advertised, perhaps, were the efforts established by ExxonMobil™ to advance algae research so they could target 10,000 barrels of bio-oil production per day by 2025 [17].

Bio-oil has a number of unique properties in comparison to other common liquid fuels. Naturally high oxygen contents of the oil result in a high instability when compared to conventional fuel oils, causing it to polymerize and condense. Polymerization leads to an increase in the bio-oil's viscosity and water content over the course of weeks. Pyrolysis-produced bio-oil will contain char from the biomass conversion process, which can catalyze the polymerization process further. However, it has been shown that addition of methanol to bio-oil can drastically reduce the aging factor [18, 19]. Other concerns for bio-oil arise from its high water content and polarity. High water content lowers the energy density of the oil and will

Figure 2 - Bio-Oil testing firing into a radiant tube in Bloom's lab

also reduce the flame temperature. The polarity of bio-oil causes it to absorb water readily, extending concerns toward its combustion.

A study performed on various types of pyrolysis-produced wood oils – oak, to be specific – will be referenced as an example for combustion properties of bio-oil [18]. The bio-oil derived in the study held an energy density of 8125 Btu/lb. which is significantly lower than that of natural gas. While the adiabatic flame temperature of natural gas in air is typically around 3500°F, bio-oil's flame temperature is in a lower range of 2600-3150°F. Causes for this are most likely in regard to the high water and oxygen content of the bio-oil.

Two other challenges to the design of technology that would fire bio-oils for combustion are its viscosity and atomization properties. Oils produced through pyrolysis typically hold very high viscosities due to entrained char particles collected from the feedstock decomposition process. Improvements to char collection and addition of viscosity-reducing agents has shown compelling potential in decreasing viscosity. Atomization of bio-oil is also affected by viscosity, which is crucial for combustion performance of an oil flame. Pumping and piping bio-oil to a process faces challenges if the viscosity is not lowered to a more workable characteristic [18].

Bloom has tested a form of bio-oil in its lab utilizing a burner typically applied to processes that require indirect heating. Testing indicated that the NO_x emissions were analogous to a similar natural gas burner around 1100°F. This data provides an encouraging indication that bio-oil may allow a transition away from fossil fuels while maintaining NO_x performance in comparison to natural gas. Figure 2 displays an image taken while firing the bio-oil into a radiant tube in Bloom's lab.

Unlike petroleum fuel oils, bio-oils are homogenous mixtures of an aqueous and a nonaqueous phase. The presence of water helps to stabilize the fuel while also lowering the heating value. A presence of two different phases could require the oil to be stirred if it sits for a long period of time, complicating its storage and supply. Further, bio-oils have a traceable amount of solid content which puts an increased demand on pumping the fuel. An existing pump system for a lower viscosity fluid likely would not be sufficient for bio-oil without adaptation. Further concerns arise in consideration of Bio-Oils corrosivity. During the testing in Bloom's lab, a cast iron pump was quickly damaged after running the Bio-Oil through it.

Glycerin

Similar to the influx in production of ethanol for the automotive industry, glycerol (commonly referred to as glycerin) has become a widely available by-product of the biodiesel manufacturing process. There are several pathways toward generating glycerol. Common examples of these include processing of propylene, hydrolysis of oils, and transesterification of oil. Glycerol is mostly derived from the transesterification step in the biodiesel production process, where it subsequently forms its own product stream.

Glycerol can be described as a syrupy, viscous liquid that will solidify if left sitting at room temperature for some time. For this reason, it requires low-temperature preheating to convert it to a form that will flow more easily. The energy density of the fuel is around 7756 Btu/lb. [20]. Glycerol flames will burn brighter than a natural gas flame, but not nearly as luminous as an oil flame. The adiabatic flame temperature calculated in one study done by the US DOE for glycerol is around 3500°F, which is comparable to the flame temperature of natural gas mentioned previously [21].

Testing of glycerol on an oil-fired combustion burner has been completed in Bloom's lab. The tested sample was obtained as a waste fraction from Biodiesel production at very low cost. However, this fraction typically contains high levels of salts, which would require particulate capture and would also be harmful to any downstream metallic components such as boiler tubes or recuperators. Further processing to extract the salts would be desirable, but it will raise the cost.

When comparing NO_x emission data to an analogous natural gas system, the thermal NO_x formation was found to be nearly equivalent for each fuel type. A similar NO_x emission rate would aid transition to glycerin's use in combustion systems.

There is concern when firing glycerin for buildup of combustion products and incomplete combustion occurring in a furnace. Analysis of the scale leftover from testing had shown that there was a significant presence of sodium which most likely was used in the production process in catalyst form.

Operational hazards for glycerol combustion are akin to traditional petroleum fuel oils as the two fuels have similar combustion properties. Glycerol has a very low inhalation and ingestion toxicity as it is added in various amounts to a number of consumer products. However, incomplete combustion of glycerol can result in the formation of acrolein, which has an acute toxicity. Therefore, the main challenges for its use in an industrial process would stem from its need for preheating as it will solidify at room temperature, its tendency to form a scale, and the need to avoid acrolein exposure.

Waste Oils

Another FFA comprises displacement of fuels upfront in a process. Many industries have a variety of process oils that are discarded after use, and these "waste oils" can be combustible in their own right. Reclamation and combustion of flammable waste would aid in decreasing upfront fuel usage. Carbon emissions of waste oils may not offset that which would come from natural gas. Rather, the use of these oils would serve more so as an economic incentive.

Bloom has tested a reclaimed mill lubricant on a regenerative burner system. The resulting emissions data showed that NO_x emissions increased by about 13% as compared to natural gas at the same furnace temperature and a similar air preheat temperature. Flame characteristics of the reclaimed oil were found to be similar to #2 and #6 oil, with atomization of the waste oil necessary for efficient combustion.

Summary of LBF's

Each form of liquid biofuel has unique properties that pose both benefits and challenges in a combustion process. Storage of a liquid fuel on site would cover a much smaller footprint than if natural gas supply of the same energy density were stored. There are also ways to generate LBF's on site through processing of waste and biomass feedstocks. A smaller footprint for storage and potential to produce the fuels on site offset some risks and costs that are incurred through transport of other fuels. The US has an extensive natural gas pipeline infrastructure in place, but other "green" fuels like hydrogen are limited in their transport, as mentioned previously. Therefore, avoiding the need for continuous transport is an appealing benefit.

Differences in combustion emissions are observable for each fuel as well. Carbon emissions over the lifecycle of a fuel will be discussed shortly. A summary of the NOx emissions observed in Bloom's testing for the LBF's is shown below.

Fuel	NO_x Emissions Relative to Natural Gas
Methanol/Ethanol	(-) 30%
Bio-Oil	(+) 0-2%
Glycerin	(±) 1%
Waste Oil	(+) 13%

Important to note is that NO_x emission performance is also related to efficiency of the combustion technology used. Changes to a burner design can directly affect the NO_x results reported above. Bloom's fundamental burner design philosophy holds that flame-shaping via combustion air aerodynamics is ideal for flexible-fuel applications, particularly in steel reheating, forging, and aluminum and copper melting.

Fired-combustion remains favorable over alternative heating methods such as electrification or induction because of its flexibility in design and use in high-temperature applications. Reliability challenges and energy demands of high temperature processes hinder practical implementation of "electrified" systems in continuous production settings.

Carbon Emissions and Life Cycle Analysis – An Example Scenario

Consider a forced-air burner that fires at 1 MMBtu/hr nominal capacity. The following analysis will explore the carbon emissions incurred over the lifetime of each fuel type discussed, specifically looking at fuel generation and combustion. For simplicity, fuel transportation CO_2 emissions will not be considered. Potential for a carbon sink effect will not be considered either.

Natural Gas, Electrification, and Hydrogen

Bloom's 2021 AFRC paper, "CO2 Reduction Options for High Temperature Industrial

Combustion” analyzed a similar scenario to the one being evaluated here. Results from the analysis are summarized in the following table for natural gas, electric, and hydrogen CO_2 emissions:

Fuel	CO_2 Emitted Per MMBtu of Fuel Consumed
Natural Gas	120 lbs.
Electricity	284 lbs.
Grey Hydrogen	168 lbs.

Methanol

Conventional production of methanol using natural gas reforming can generate carbon emissions through a variety of steps including extraction and processing. One estimate indicates a rate of 0.7 pounds of carbon dioxide emitted per pound of methanol produced [22]. However, methanol produced from renewable biomass feedstocks can significantly lower that output. One report found that the CO_2 emitted during methanol production sourced from biomass was as low as 11.2 lbs./MMBtu fuel generated [23]. The same report showed that combustion of pure methanol resulted in 153.1 pounds of CO_2 emitted per million Btu of fuel consumed. Combining the production rate with the combustion rate, one obtains the result of around 164 lbs.CO_2/MMBtu of fuel which is drastically lower than if the methanol were produced through the conventional route.

Ethanol

A study by the USDA done on carbon emissions resulting from ethanol production indicated the two main sources are during fermentation and from process heating [24]. Estimates for emissions in that report are around 21 lbs.CO_2/MMBtu of ethanol fuel generated. Combustion of pure ethanol has a yield of around 150 lbs.CO_2/MMBtu of fuel consumed. Combining these two values results in a lifecycle emission rate of 171 pounds of carbon dioxide emitted per million Btu of ethanol consumed.

Bio-Oil

Lifecycle analysis of carbon emissions from bio-oil has been completed for wood pyrolysis [25]. Cradle-to-grave results indicate a generation rate of around 95 lbs.CO_2/MMBtu of oil produced and an output of 340 lbs.CO_2/MMBtu from combustion of the fuel. The combined carbon footprint of bio-oil is thus about 435 pounds of carbon dioxide per million Btu of fuel consumed. This value is substantially higher than the results presented for other fuels, and it has largely been a deterrent for bio-oil’s practical usage. However, ongoing research and advancements into bio-oil production from algae have pointed to a potential penalty much lower than that of wood pyrolysis.

Glycerin

Accurate analysis of CO_2 emissions that result from glycerin production is challenging. Since the fuel is most commonly a by-product of biodiesel production (including ethanol production, in some cases), most lifecycle reports focus on automotive data. Biodiesel and ethanol are derived from similar sources, so the carbon footprint of ethanol and glycerin production will be used in an analogous manner. Recall the emission rate for ethanol production was 21 lbs.CO_2/MMBtu. Evaluating the stoichiometry of glycerin combustion allows one to calculate an emission rate of 186 pounds of carbon dioxide per million Btu of glycerin consumed[1]. These two values can be added to obtain a total of 207 lbs.CO_2/MMBtu of fuel consumed for glycerin.

Summary of Results

The following table summarizes key results that were discussed in the carbon emission lifecycle analyses for each fuel type. It should be made clear that the example calculations in the table *do not* account for the carbon offset or credit potential that arises from growth of bio-based fuel sources. The growth of plant life such as corn or algae will work to offset some, or perhaps eventually all, of the lifetime carbon emissions incurred when burning an LBF. Combustion of natural gas and other fossil fuels results in a strictly "positive" amount of carbon emissions to the environment.

Fuel (Generation Type)	CO_2 Emitted Per MMBtu in Fuel Lifecycle*
Natural Gas	120 lbs.
Electricity (Gas Turbine)	284 lbs.
Hydrogen (Grey)	168 lbs.
Methanol (Biomass)	164 lbs.
Ethanol (Biomass)	171 lbs.
Bio-Oil (Wood Pyrolysis)	435 lbs.
Glycerin (By-Product of Biodiesel)	207 lbs.

It should also be noted that natural gas numbers do not directly account for carbon dioxide released to the atmosphere during extraction, but most extraction processes utilize some of their natural gas product as a fuel. Therefore, the CO_2 lifecycle in natural gas is generally synonymous with having it be burned in an industrial process only.

The analysis in the above sections shows that there is still a CO_2 penalty incurred in the usage of pure biofuel alternatives. However, as technology improves and research into the production process of biofuels continue, the CO_2 penalty will likely fall distinctly. Carbon sequestration as a result of corn and other biomass growth will further aid the reduction of lifetime carbon emissions. Regional government organizations will likely have varying policies regarding carbon offset and crediting.

Economic Considerations

This section will return to the system described in the example scenario previously and evaluate economic concerns. Cost analysis of each fuel discussed in this paper will be explored. To simplify concerns over the volatility of current natural gas prices, a cost of $6/MMBtu will be used as a reference point.

Methanol

Prices for methanol in 2021 were reported as $20.26/MMBtu on average [26]. There is an obvious price increase if a process were to be switched to pure methanol, but a more reasonable approach may be integration of a methanol system in parallel with a natural gas system.

Ethanol

When weighing ethanol's energy density with its 2021 average spot price at roughly $0.364/lb., an energy price of $28.38/MMBtu can be calculated [8, 27]. It should be noted that this sample calculation is in reference to E100, or pure ethanol. There are varying

[1] Glycerin Combustion Equation: $2C_3H_8O_3 + 7O_2 \rightarrow 6CO_2 + 8H_2O$

* Lifecycle does not account for carbon sink, carbon sequestration, offset, or credit

degrees of ethanol purity available. Compare, again, that cost to the same value for natural gas mentioned previously and one can see that pure ethanol has a steeper price.

Bio-Oil

A study conducted on production costs and life cycle analysis of bio-oil estimated a price of $25.74/lb. for fast pyrolysis of wood chips and $13.90/lb. for other forms of biomass such as algae [28]. Additionally, the average specific gravity of bio-oil has been experimentally determined to be 1.2. Therefore, using the energy density listed previously, a cost of $50.44/MMBtu can be calculated for fast pyrolysis of wood chips, and $27.55/MMBtu can be calculated for other biomass sources [29].

Glycerin

The average market price of "crude" glycerin – which has a purity of about 90% – in 2021 was estimated at $0.858/lb. [30]. Converting to an energy cost basis yields the result of $110.62/MMBtu. This is a steep price increase in comparison to natural gas. Reasoning for the large difference in pricing is driven by glycerin's role in a wide variety of consumer products.

Summary

The following table summarizes data that was listed previously in this report for each fuel type discussed. Hydrogen costing data has been sourced from Bloom's 2021 AFRC paper with updates to 2021 prices.

Fuel	Average Cost Per MMBtu
Natural Gas	$6.00
Grey Hydrogen	$14.93
Blue Hydrogen	$17.64
Green Hydrogen	$70.56
'Electrification' (Gas Turbine)	$40.21[2]
Methanol	$20.26
Ethanol	$28.38
Bio-Oil (Pyrolysis/Other)	$50.44/$27.55
Glycerin	$110.62

When evaluating economic differences of each fuel type, it is important to note that prices are highly subject to specific regions, economies, geographic locations, etc. and the listed calculations were completed based on a U.S. national average. Further price volatility may arise as a result of events outside of the production industry's circle of influence, which has been demonstrated several times in the last few years.

Extraction and production methods for LBF's continues to be a growing research and development focus for many industries. While the current costs may appear steep in comparison to natural gas or other fuel sources, future costs will continue to fall as the methodology behind producing the fuels improves.

Outlook for LBF's

There is a great deal of certainty that the push for more sustainable, "greener" solutions will continue to grow in the coming decades. Industries with a high consumption rate of fossil fuels will be challenged with not only finding alternatives for energy sources, but to also incorporate those alternatives into their processes over a relatively short period.

[2] Based on a US national average electricity cost of 13.72¢/kWh

Carbon taxes have also surfaced as governmental incentives toward limiting GHG emissions, especially through the usage of fossil fuels. As of 2019, twenty-five countries have instituted or scheduled a form of carbon tax, and forty-six additional countries have adopted some other form of carbon pricing legislation [31]. While the United States has not instituted a federal form of carbon taxes yet, several states have passed laws that limit GHG emissions such as CO_2.

There is no ideal solution for limiting carbon dioxide emissions as of yet. Further, the transition to technology and practices that limit carbon emissions will not happen overnight. There is a gap between the ideality and reality in this subject, and LBF's may serve as a necessary bridge to cross it. With some infrastructure and technology already in place, these fuels present valuable options for FFA's.

Conclusions and Closing Thoughts

Important to note is that flexibility in combustion technology will be *paramount* to transitioning toward a greener industrial future. The ability to utilize a variety of different fuels – or multiple fuels at once – in a process will allow companies to avoid limitations in fuel availability or other issues that arise from external constraints. Dramatic fluctuations in fuel pricing have occurred over the first half of 2022, pointing to concerns over the world's reliance on fossil fuels.

Utilizing technology that is flexible or adaptable to a variety of fuels will assuage the risk of severe fuel costs incurred. Further, advancements in production capabilities for LBF's will lead to lower upfront fuel costs. Though an increased demand may offset some savings in the future, which is already developing in the consumption and costing of hydrogen. This only reaffirms the need for diverse options in fuel usage. Much of the needed combustion technology for this subject is already available, but the need for lab testing and system design engineering considerations must not be overlooked.

Additional emphasis should be placed on the usage of high-efficiency combustion technology alongside green fuels. Improvements of NO_x emissions and more efficient heat release is a measurable result of this technology, and its usage will ease costs and concerns accrued during the transitional period away from fossil fuels.

References

[1] "The Long-Term Strategy of the United States: Pathways to Net-Zero Greenhouse Gas Emissions by 2050," 2021. [Online]. [Accessed June 2022].

[2] U. E. I. Administration, "Electricity Explained - Electricity in the United States," U.S. Energy Information Administration, 19 April 2022. [Online]. Available: https://www.eia.gov/energyexplained/electricity/electricity-in-the-us.php. [Accessed June 2022].

[3] "How Gas Turbine Power Plants Work," U.S. Office of Fossil Energy and Carbon Management, [Online]. Available: https://www.energy.gov/fecm/how-gas-turbine-power-plants-work#:~:text=A%20simple%20cycle%20gas%20turbine,of%2060%20percent%20or%20more.. [Accessed June 2022].

[4] A. Ivaneko, "A Look at the 'Colors' of Hydrogen That Could Power Our Future," Forbes, 2020.

[5] K. Cokain and M. Cochran, "CO2 Reduction Options for High Temperature Industrial Combustion," Bloom Engineering Company, Inc., 2021.

[6] "Hydrogen Production and Distribution," U.S. Department of Energy, [Online]. Available: https://afdc.energy.gov/fuels/hydrogen_production.html. [Accessed June 2022].

[7] M. Broeren, "Production of Bio-Methanol," International Renewable Energy Agency, 2013.

[8] "Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation (GREET) Model," Argonne National Laboratory, Chicago, IL, 2019.

[9] "Methanol Chemical Data Sheet," Chameo Chemicals, 2022. [Online]. Available: https://cameochemicals.noaa.gov/chemical/3874. [Accessed June 2022].

[10] H. Jääskeläinen, "Biodiesel Standards and Properties," ECOpoint, Inc., 2009. [Online]. Available: https://dieselnet.com/tech/fuel_biodiesel_std.php#water. [Accessed June 2022].

[11] "Ethanol Spot Price," Business Insider, 2022. [Online]. Available: https://markets.businessinsider.com/commodities/ethanol-price. [Accessed June 2022].

[12] J. A. C. J. J. C. A. E. V. C. F. S. C. J. C. S. A. Z. M. Christian J.R. Coronado, "Flammability limits: A review with emphasis on ethanol for aeronautical," *Journal of Hazardous Materials,* Vols. 241-242, pp. 32-54, 2012.

[13] U.S. Department of Energy, January 2021. [Online]. Available: https://afdc.energy.gov/files/u/publication/fuel_comparison_chart.pdf. [Accessed June 2022].

[14] M. Crocker, "Thermochemical Conversion of Biomass to Liquid Fuels and Chemicals," *Royal Society of Chemistry,* no. ISBN 978-1-84973-035-8, p. 283, 2010.

[15] P. Winsley, "Biochar and bioenergy production for climate change mitigation," *New Zealand Science Review,* p. 64, 2007.

[16] M. A. A. T. Dovilė Gimžauskaitė, Recent Advances in Renewable Energy Technologies, M. Jeguirim, Ed., Academic Press, 2022, pp. 155-196.

[17] ExxonMobil, "Advanced biofuels and algae research: targeting the technical capability to produce 10,000 barrels per day by 2025," 2018. [Online]. Available: https://corporate.exxonmobil.com/Climate-solutions/Advanced-biofuels/Advanced-biofuels-and-algae-research. [Accessed June 2022].

[18] C. R. H. D. R. Shaddix, "Combustion Properties of Biomass Flash Pyrolysis Oils: Final Project Report," Sandia National Laboratories, 1999.

[19] J. M. T. C. S. O. A. B. A. C. A. G. S. H. D. a. P. J. Diebold, "Proposed specifications for various grades of pyrolysis oils," *Developments in Thermochemical Biomass Conversion,* pp. 433-447, 1997.

[20] "Hazardous Substances Data Bank (HSDB)," National Library of Medicine, February 2022. [Online]. Available: https://www.nlm.nih.gov/toxnet/index.html. [Accessed June 2022].

[21] "Crude Glycerol as Cost-Effective Fuel for Combined Heat and," 2012.

[22] Carbon Recycling International, "Curbing Carbon Emissions with Green Methanol," December 2019. [Online]. Available: https://www.thechemicalengineer.com/features/curbing-carbon-emissions-with-green-methanol/#:~:text=This%20ranges%20from%200.7%20t,doi.org%2Fddzm).. [Accessed June 2022].

[23] J. J. Corbett and J. J. Winebrake, "Life Cycle Analysis of the Use of Methanol for Marine Transportation," 2018.

[24] J. L. T. H. K. J. K. M. a. J. Rosenfeld, "A Life-Cycle Analysis of the Greenhouse Gas," 2018.

[25] P. Steele, M. E. Puettmann, V. K. Penmetsa and J. E. Cooper, "Life-Cycle Assessment of Pyrolysis Bio-Oil Production," *Forest Products Journal,* vol. 62, no. 4, pp. 326-334, 2012.

[26] "Methanol Price and Supply/Demand," Methanol Institute, May 2022. [Online]. Available: https://www.methanol.org/methanol-price-supply-demand/. [Accessed June 2022].

[27] "Ethanol Production and Distribution," 2022. [Online]. [Accessed June 2022].

[28] A. Ashfaq, T. Rumaisa, W. Ammara, J. Farrukh, A. F. Shams, G. Chaouki, P. Young-Kwon and I. Abrar, "Techno-Economical Evaluation of Bio-Oil Production via Biomass Fast Pyrolysis Process: A Review," 2022.

[29] S. Heidenreich, M. Muller and P. U. Foscolo, Advanced Biomass Gasifcation, Elsevier, Inc., 2016.

[30] A. L. F. F. A. É. B. R. M. d. B. A. a. L. A. M. P. Alisson Dias da Silva Ruy, Biotechnological Applications of Biomass, T. O. B. L. C. B. Thalita Peixoto Basso, Ed., BoD - Books on Demand, 2021.

[31] World Bank Group, "State and Trends of Carbon Pricing 2019," 2019.

[33] T. K. Blank and P. Molly, "Hydrogen's Decarbonization Impact for Industry," 2020.