Direct combustion of recyclable metal fuels for zero-carbon heat and power

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HIGHLIGHTS

- Metals are promising high-energy density, low-emission, recyclable energy carriers.
- Metal fuels can be burned with air to produce heat for many applications.
- A novel combustor that can burn metal fuels is proposed.
- Metal-oxide combustion products can be captured and recycled.
- Use of clean power sources to recycle metals enables low-net-carbon emissions.

GRAPHICAL ABSTRACT

Concept drawing of a metal-fuelled combustor and its possible applications at a range of power-generation scales.
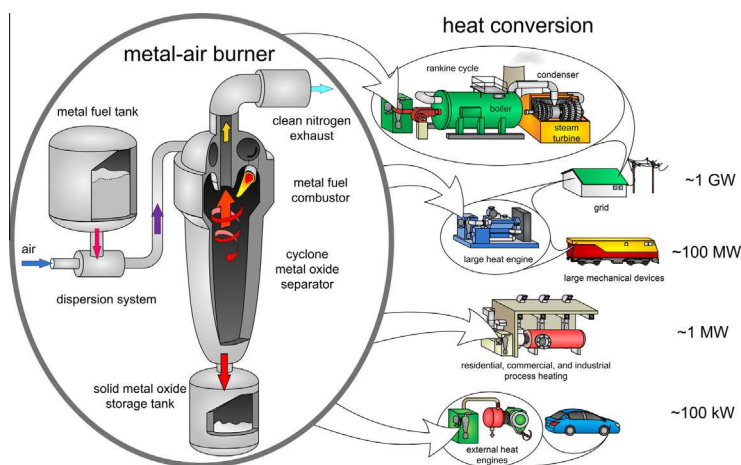
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ABSTRACT

It is becoming widely recognized that our society must transition to low-carbon energy systems to combat global climate change, and renewable energy sources are needed to provide energy security in a world with limited fossil-fuel resources. While many clean power-generation solutions have been proposed and are being developed, our ability to transition to a low-carbon society is prevented by the present lack of clean and renewable energy carriers that can replace the crucial roles that fossil fuels play, due to their abundance, convenience and performance, in global energy trade and transportation. Any future low-carbon energy carriers that aim to displace or supplement fossil fuels must have high energy densities for convenient trade and storage, and should be consumable within efficient high-power-density engines for transportation, heavy machinery, and other off-grid energy applications.

Hydrogen and batteries have been widely studied but they are not suitable for use as international energy-trading commodities and they cannot provide the energy density and safety demanded by society. Metal fuels, produced using low-carbon recycling systems powered by clean primary energy, such as solar and wind, promise energy densities that are competitive to fossil fuels with low, or even negative, net carbon dioxide emissions. To date, however, few practical high-power-density end-use devices for generating heat or power from metal fuels have been proposed.

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This paper proposes a novel concept for power generation in which metal fuels are burned with air in a combustor to provide clean, high-grade heat. The metal-fuel combustion heat can be used directly for industrial or residential heating and can also power external-combustion engines, operating on the Rankine or Stirling cycles, or thermo-electric generators over a wide range of power levels. A design concept is proposed for a metal-fuelled combustor that is based upon extensive experimental and theoretical studies of stabilized and propagating metal flames performed at McGill University. This paper also reviews the fundamental and applied aspects of metal-fuel combustion in order to provide the framework needed to assess any potential metal engine technologies. The energy and power densities of the proposed metal-fuelled zero-carbon heat engines are predicted to be close to current fossil-fuelled internal-combustion engines, making them an attractive technology for a future low-carbon society.

1. Introduction

1.1. The need for clean recyclable fuels

To mitigate global climate change, our energy and transportation systems must transition away from fossil-fuel sources to zero-carbon clean and renewable energy sources [1,2]. Alternatives must also be found to offset future constraints on our global economic growth that are associated with finite fossil-fuel reserves [3,4]. Biofuels are one widely-discussed option [5,6], but estimates indicate that bioenergy alone cannot fully displace fossil fuels in a future low-carbon society [1,7–9] due, primarily, to the low effective energy and power densities associated with photosynthesis [7,10]. Harnessing hydro, solar, wind, geothermal and, eventually, clean thermonuclear power [11] can, in principle, completely eliminate fossil fuels from electricity production [7,12,13].

More difficult, however, is to replace the other essential roles of fossil fuels, including their use as energy-trading commodities and transportation fuels. Indeed, even if electricity is produced with clean energy sources it cannot be stored, transported or traded as easily as hydrocarbons. Therefore, clean and renewable energy carriers are needed that can be transported and stored, which would enable the separation of the primary energy production and end-use consumption in both space and time. To date, batteries and hydrogen are the most-commonly proposed energy carriers for a future low-carbon society [1,7,13–15].

High-power-density, internal-combustion engines (ICEs) burning convenient high-energy–density hydrocarbon (fossil) fuels are essential components of modern society that are difficult to replace [16,17]. These combustion engines power everything from automobiles to locomotives and ships to passenger jets. Thus, it is imperative to have a clean energy carrier, and associated power system, that has energy and power densities on par with hydrocarbon fuels and ICEs so that they can be used in a similar manner. To date, the handful of solutions that have been proposed are, in most cases, inferior to hydrocarbon-fuelled ICEs in terms of fuel energy density and engine power density. Society requires more energy carrier options that can provide high energy and power densities for a range of applications that fossil fuels are dominant in today.

1.2. Batteries

In transportation, the fact that batteries have an energy density that is more than an order of magnitude lower than fossil fuels leads to them being barely sufficient for small passenger cars [18], and not at all suitable for high-power vehicles and machinery, such as trucks, construction equipment, military vehicles, locomotives, or ships. The volumetric power density, P/V [kW/m^3], of a power system fuelled by chemical energy can be estimated using dimensional analysis as:

$$\frac{P}{V} \sim \eta q_\mathrm{m} \rho_\mathrm{m} \, \dot{\omega} \tag{1}$$

where η is the efficiency of the power system, q_m [kJ/kg] and ρ_m [kg/m^3] are the specific energy and density of the chemical reactants, respectively, and $\dot{\omega}$ [1/s] is the characteristic chemical-reaction rate. Traditional batteries must contain both fuel and oxidizer, reducing the energy density of the fuel system, $q_\mathrm{m}\rho_\mathrm{m}$ [kJ/m^3]. Furthermore, chemical reactions in batteries proceed at room temperature, resulting in slow reaction rates, $\dot{\omega}$, and low power densities.

In contrast, fossil-fuelled ICEs burn fuels with air at high temperatures leading to high reaction rates and, together with the high pressures that maximize the air–fuel mixture density, produce high power densities. The combustion of fuels with air leads to system energy densities that are much higher than traditional batteries since the air supplies the oxidizer for "free", which is why airplanes are powered by air-breathing gas-turbine (jet) engines instead of rockets.

Indeed, metal–air batteries, using aluminum, zinc, iron or lithium anodes, make use of the oxygen available within air, as well as the high energy density of metals, in order to improve their energy and power densities [18–24]. Unfortunately, the low temperature of the oxygen-reduction reaction at the cathode leads to slow kinetic rates and requires expensive catalysts and large catalyst surface area, as well as the inert catalyst-support matrix and electrolyte, all of which results in the low power densities of available metal–air batteries [18,25]. The requirement for an oxygen-reduction catalyst, and its associated support materials, also limits the power density achievable by fuel cells [18]. In order to maximize performance, the power system must contain a minimum of inert support materials, or *dead weight*, and react or combust fuels with air at high energy-conversion, or heat-release, rates.

1.3. Hydrogen

For the past few decades, hydrogen, produced using clean electrical power, has been widely assumed to be the universal carbon-free energy commodity of the future that will be used for energy storage and transportation [1,14,15]. Hydrogen promises good energetic performance due to its high specific energy, its high reactivity, and its ability to be used in a variety of energy-conversion devices ranging from ICEs and gas-turbine engines to fuel cells, while producing nearly zero pollutant emissions [26–28].

The hydrogen economy, however, has not yet materialized due to two major obstacles that are difficult to overcome: the low density of the compressed hydrogen gas and the inherent fire and explosion hazards associated with hydrogen storage and refueling [15,29]. Even as a cryogenic liquid, the energy density of hydrogen is more than an order of magnitude lower than that of gasoline or other hydrocarbon fuels [30]. Compression and liquefaction of

hydrogen also consumes additional energy, and bulky insulated Dewar-type storage tanks for liquid hydrogen cannot prevent its boil-off during long-term storage, reducing the energy-cycle efficiency [14,18]. None of the other proposed methods to store hydrogen, including metal or organic hydrides, carbon nano-tube matrices, or porous metal–organic frameworks, have yet achieved the U.S. Department of Energy's target of 7.5 mass% of hydrogen at ambient temperature [31–33]. These methods do not achieve higher hydrogen capacities because they require carrying additional chemically-inert materials, to either chemically bond, adsorb, or physically encapsulate the hydrogen, that do not take part in the oxidation reaction and act as dead weight. Increases in hydrogen-storage density above that of liquid hydrogen do not appear to be within reach.

1.4. Solar hydrocarbon fuels

More recently, the direct synthesis of hydrocarbon fuels, or *solar fuels*, from atmospheric carbon dioxide and hydrogen, using clean primary electricity or solar energy as the energy inputs, has been proposed [34–40]. Synthetic hydrocarbon fuels, along with biofuels, are attractive since they would fit into our current extensive energy-trade and transportation infrastructure [5,38,40]. The key limitation of synthetic-hydrocarbon solar fuels, and also of biofuels, is the dilute nature of the carbon dioxide in the atmosphere (~400 ppm) [40]. For both biofuels and synthetic-hydrocarbon fuels, the atmosphere is used as both a sink, after combustion of the fuel, and source of carbon, as a fuel feedstock. For solar hydrocarbon fuels, this means that carbon dioxide must be concentrated from its dilute concentration in the atmosphere before it can be recycled to produce significant fuel volumes, which requires infrastructure and energy that increase costs [39,40]. The inefficiency in the carbon recycling process sets a limit on the energy-cycle efficiency of solar hydrocarbon fuels.

Such solar fuels can become more economical if flue gases from a fossil-fuelled power station are used as the source of the carbon dioxide [38–40], but the subsequent combustion of the solar hydrocarbon fuel in an engine would simply release the fossil-derived carbon dioxide captured from the flue gases and, as such, cannot be considered to be a low-net-carbon energy carrier [39]. It may also be difficult to achieve net zero or negative carbon dioxide emissions from any energy system that inherently involves emitting carbon dioxide into the atmosphere at the point of fuel consumption, even if the atmosphere is used as the source of carbon dioxide.

Zero-carbon, or low-net-carbon, fuels that can be easily and cheaply recycled are desirable to lower fuel costs and improve the efficiency and sustainability of the energy/fuel cycle. The term *fuel* refers to any reduced material that can be oxidized, typically by oxygen in the air, to produce energy [34], but any such fuel produced from low-carbon primary energy is, in reality, a secondary energy carrier or energy vector. Any new fuel option must be superior to the current battery or hydrogen options in energy and power density to meet the needs of society. These considerations suggest that a non-carbon-based fuel that produces solid combustion products, which can be directly captured for subsequent recycling, should be sought out.

1.5. Metals as recyclable fuels and commodities for energy trade

There are few chemical elements or carbon-free chemical compounds that can compete with hydrocarbons based on their mass and volumetric energy densities. Metals, and specifically metal powders, are a promising, yet largely-overlooked, zero-carbon recyclable-fuel option [25,46–54]. Metals are the most promising zero-carbon fuel choice because they react energetically with the

oxygen in air to form stable, nontoxic solid-oxide combustion or reaction products that can be collected, relatively easily, for recycling, as discussed in this paper.

As shown in Fig.1, many metal fuels have higher volumetric energy densities than gasoline or other fossil fuels when burned with air and some, such as boron, even have higher specific energy (per unit mass). Boron has an extremely high energy density, which is why it has long been considered as a potential fuel additive in propellants and explosives [55–57] and, more recently, as a recyclable solar fuel [58]. Beryllium is a very energetic fuel [59]; however, the toxicity of beryllium oxide precludes its consideration as a fuel option for widespread use [60]. Aluminum, magnesium, silicon and iron are all relatively abundant metals and show high energy densities and good specific energies, making them candidates for use as metal fuels, or as battery anodes, as discussed further below. Metal fuels also boast energy densities superior to biomass (e.g. wood chips or pellets), coal, and compressed or liquefied natural gas, all of which are currently shipped globally for energy trade.

1.6. Metals as fuels within batteries or without

It is their high energy density that makes metals attractive as the anodes, or the fuel, within batteries. Lithium is the main fuel within Li-ion batteries [18], and recently lithium–air batteries [18,61]. Lithium powder has also been proposed as a potential fuel for space propulsion [62,63] or as recyclable fuel [64,65], but may not be suitable as a standalone fuel due to safety concerns resulting from its high reactivity with air and water [66]. Aluminum and magnesium are widely studied for use as anodes in metal–air batteries [19,22,24,25], and have been considered as recyclable fuels that carry clean energy [25,53,54,67,68]. Iron has been considered both as an inexpensive anode material [23] and a recyclable energy carrier [49,50].

Slow metal oxidation reactions within an electrochemical battery can lead to high efficiencies, at the cost of low power densities due to the dead weight of the oxygen-reduction catalyst and electrolyte. If higher power densities are desired, then the metal fuels should be consumed at higher rates, as shown in Eq. (1), which motivates their direct combustion, in powder form, with air to power heat engines.
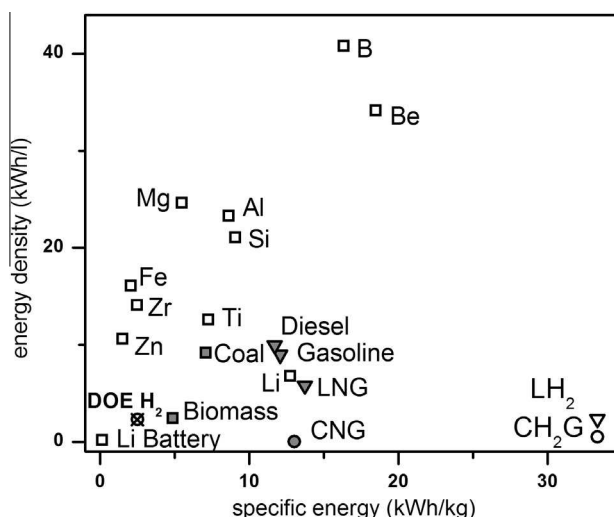

Fig. 1. Volumetric and gravimetric energy density for various metal fuels [41] compared to batteries [42], hydrogen [43], bio-derived fuels [44], and fossil fuels [43–45] (1 kW h = 3.6×10^6 J). Abbreviations used: compressed natural gas (CNG), liquefied natural gas (LNG), compressed hydrogen gas (CH_2G) and liquid hydrogen (LH_2). Gaseous fuels are indicated by ($\bigcirc$), liquid fuels by ($\bigtriangledown$) and solid fuels by ($\square$). Open symbols indicate potential zero-carbon fuels. The energy density goal for hydrogen storage materials set by the DOE is shown for comparison (DOE H_2) [33].

2. Metal fuel cycle

Our vision for a metal-fuel energy cycle is depicted Fig. 2. Metal-powder fuels would be produced in regions with excess clean primary energy and then be traded globally. The metal fuels would be consumed in power-generation devices, such as the metal-fuelled combustor and heat engine proposed in this paper, for a variety of transportation and power-generation applications. The resulting metal-oxide reaction products would be collected and recycled using existing metal smelters or novel technological processes powered by green power sources [25,67,69–73], enabling an energy cycle with zero associated carbon dioxide emissions. While there have been accidents caused by ignition of metal-powder clouds [74,75], metal powders can be transported and stored with similar safety to liquid hydrocarbon fuels and improved safety compared to hydrogen. Metal fuels can have an effectively indefinite shelf life if protected from humidity and the ambient atmosphere in hermetically-sealed containers [25,52], allowing them to be used as part of energy stockpiles or strategic reserves. The bottleneck to implementing a zero-carbon energy system based on metal fuels is the current lack of an end-use device that can efficiently convert the chemical energy within the metal at high rates to achieve high power densities.

2.1. Metal–water reactions for producing hydrogen and heat

In addition to the metal–air batteries that are under active investigation as discussed above, the reaction of metal fuels with water to produce hydrogen and heat is another possible means of achieving the zero-carbon metal-fuel cycle that has been widely studied by many researchers [25,58,67,68,76–79], including by our group [80,81]. The metal–water reaction produces solid metal oxides and hydroxides that are easy to collect for recycling, along with hot hydrogen mixed with steam. The ability to produce hydrogen on demand using metal–water reactors can enable the benefits of hydrogen, as an efficient and reactive fuel for ICEs, gas-turbine engines or fuel cells [26–28], to be realized while overcoming the inherent safety and low-storage-density limitations associated with hydrogen.

Although a very promising solution for many applications, the metal–water energy-conversion cycle has its own deficiencies. Due to the relatively slow metal–water reaction at low to moderate temperatures and pressures (up to $T = 500$ K and $p = 20$ atm) [80,81], an estimated power density, using Eq. (1), of typical metal–water reactors is much lower than that of combustion-powered devices, such as ICEs. Engines burn fuels at flame temperatures well above 2000 K and, in accordance with the basic exponential Arrhenius reaction-rate law, result in fuel consumption rates and engine power densities that are several orders of magnitude greater than for low-temperature reactors. As a result, the low-temperature metal–water power cycle is unlikely to be suitable for compact high-power applications, such as high-load trucks, autonomous robotic systems, or heavy machinery.

2.2. Harnessing the chemical energy of metal fuels through direct combustion

In this paper, we propose an alternative route for harnessing the chemical energy within metals: direct combustion of metal-powder fuels with air to generate high-grade heat that can be used directly or that can drive an external-combustion heat engine. Although metal–air combustion engines are more technically challenging to develop than low-temperature metal–water reactors, they should provide superior performance in high-power-density and high-specific-power applications, especially for ground transportation where the weight and volume of the water required for the metal–water cycle reduces system performance. As discussed in this review, the direct combustion of metal fuels can lead to power systems that match the power density of hydrocarbon-fuelled engines. Direct combustion can also enable metals that cannot be used in the low to moderate temperature metal–water cycle, such as iron [81], to be used as recyclable fuels. This is important because the optimal metal fuel for a given application will depend not only on its chemical reactivity and combustion or reaction properties, but also on its cost, the ease of collection of its metal-oxide combustion products, and the economics and life-cycle impacts of the fuel production and recycling systems.
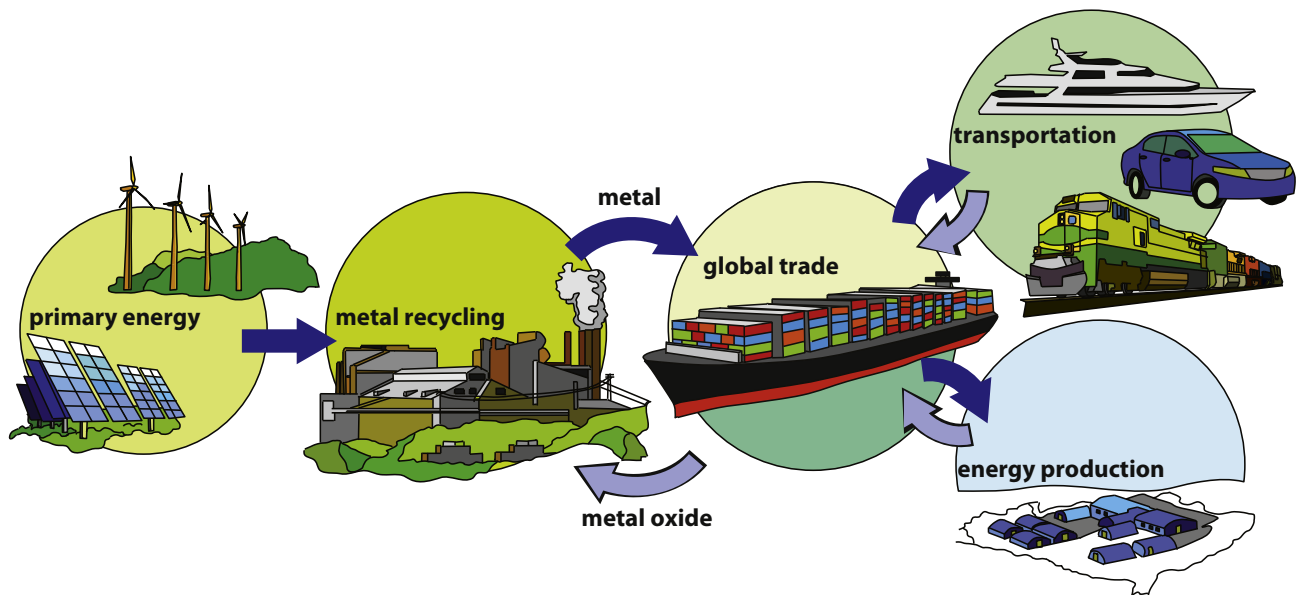
Fig. 2. The metal-fuel cycle. Metal fuels can be used as energy-trading commodities and transportation fuels. Clean primary energy is used to reduce metal oxides into metal fuels, which are then transported and sold for transportation and energy production. The metal oxides can be collected and recycled back into metal fuels, closing the energy cycle.

Preliminary life-cycle and economic assessments have been performed for some potential metal fuels [25,51,82,83], with the results generally indicating that metal fuels can be competitive options to either metal–air batteries or hydrogen on the basis of their costs and energy-cycle efficiencies [25,48,76,83]. Metal–air batteries require high-purity metals for their anodes to prevent the parasitic corrosion reactions, leading to high costs, with metal–water reactions taking advantage of these same parasitic corrosion reactions [48]. Metals are also widely used as energy carriers within chemical-looping combustion systems, suggesting that they can be economical as part of power systems [84–86]. As for metal–air batteries, the most abundant metals/metalloids, such as iron, aluminum and silicon, will be promising metal fuels on a cost basis. Other metal fuels may be more desirable for high-performance applications, where cost may be a secondary concern. Additional studies on life-cycle emissions and economic performance of various possible metal fuels, specifically for the cheap micron-sized industrial metal powders identified as important possible fuel candidates in the present review, are needed to identify the most promising metal fuels and their optimal low-carbon and high-efficiency recycling processes. While the economics and life-cycle emissions of available recycling technologies are important issues that must be addressed in future studies for metals to become widely-adopted fuels, such system-level assessments must be based upon a fundamental understanding of metal-fuel combustion science in order to find a solution that works first technically and then economically.

The present paper will, therefore, only focus on the scientific and technical aspects of metal-fuel combustion that will determine the resulting performance of any high-power-density energy technology based on the direct combustion of metal fuels with air. Metals have some unique combustion properties, compared to our traditional gaseous and liquid hydrocarbon fuels, that must be considered in any combustor design for future metal-fuelled engine technologies. Indeed, our current technologies developed for hydrocarbon fuels cannot be directly fuelled by metal powders without some redesign or retrofitting, specifically to disperse the powder fuel, stabilize its combustion, and then enable capture of the resulting solid metal-oxide combustion products. The solid metal-oxide combustion products will be easier to collect if the combustion process produces large particle sizes, and the achievable power density and stability of the flame will be determined by the rate of the combustion reaction, $\dot{\omega}$. The combustion rate and the size of the resulting metal oxides are determined by the physics of the metal-fuel combustion process, which are overviewed in this paper in order to identify promising metal fuels for direct combustion with air.

The combustion of single metal-fuel particles is discussed next, followed by the burning, within flames, of metal-powder fuel clouds suspended in air. A design for a novel high-performance metal-fuel combustor is then proposed that could provide high-grade thermal energy for a variety of power applications. The paper then discusses potential fuel options that have combustion properties suitable for these metal engines, and the potential performance of metal-fuelled engines compared to existing systems is discussed.

3. Combustion modes of single metal particles and metal fuel thermodynamics

The ability of metals to burn in air, and within combustion products, has been known for centuries, and metal powders have long been added to propellants, for commercial or military applications, or to pyrotechnics used in fireworks demonstrations. In addition, the combustion of bulk metals by oxygen is a serious safety concern for oxygen piping and storage tanks. Combustion of metals

using an oxygen flow or jet is also commonly used to cut and process iron and steel, while grinding can produce metal chips and particles that burn as sparks through the air. Only from the middle of the last century did scientific research into metal-combustion phenomena begin in earnest when, due to their exceptionally high energy density, metal powders began to be used as energetic fuel additives in solid rocket motors [87–91], liquid-hydrocarbon slurry fuels [92–94], explosives [95,96], and other energetic materials [97–99].

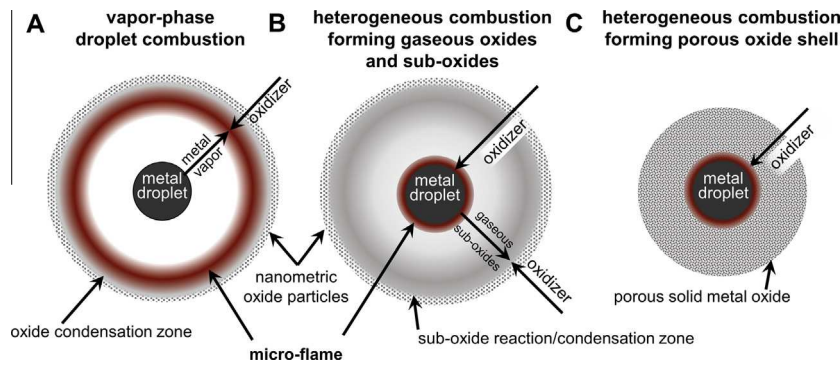### 3.1. Metal-particle combustion modes

The description of metal-fuel combustion processes typically begins at the level of single, isolated metal particles, which can burn in a variety of combustion modes (see Fig. 3). The kinetic rates of metal gas-phase reactions with oxygen are extremely fast even at low temperatures, because they typically have low to zero activation energies [100], such that reactions can proceed after a small number of molecular collisions. This means that physical processes, such as the metal and oxide vaporization properties and the molecular diffusion rates of the oxidizer and thermal energy, have a much stronger influence, compared to chemical processes, over the combustion properties of single metal particles or metal-powder suspensions. As a result, the combustion mode is primarily determined by the flame temperature, at a stoichiometric ratio of the metal fuel with the oxidizing-gas mixture, relative to the boiling point of the associated metal, as explained by Glassman and coworkers [101]. Glassman also realized that the flame temperature of metals that form refractory oxides is limited by the evaporation or dissociation point of the oxide combustion products, since the oxide-dissociation reactions, or oxide volatilization process, would absorb any additional heat release and prevent the flame temperature from increasing.

For a metal whose oxide-volatilization point and flame temperature are above its boiling point, the metal droplet can be heated to boiling and then be burned by a micro-diffusion flame enveloping it, as illustrated in Fig. 3A [103]. The micro-flame structure of a metal droplet burning in Mode A is quite similar to the micro-flames that form around isolated hydrocarbon-fuel droplets [101]. The chemical and physical condensation of the oxide combustion products can form a cloud or halo of nanometer-size oxide particles away from the droplet surface [102].

If the oxide-volatilization or dissociation point, and thereby flame temperature, is below the boiling point of the pure metal, the metal cannot rapidly evaporate and the particle must burn heterogeneously through a multi-phase surface reaction. This heterogeneous combustion process can proceed in one of two modes. In the first, gaseous metal oxides or sub-oxides form on the metal droplet surface, which then diffuse away from the droplet (see Fig. 3B), while in the second mode a condensed metal oxide forms and encases the metal droplet (see Fig. 3C). In Mode B, nano-oxides are again formed in the reaction and condensation zone away from the particle surface. In contrast, the oxide combustion product is formed directly on the metal droplet surface for particles burning in Mode C, leading to a final metal-oxide particle size that is larger than the initial metal particle. It should be noted that these combustion modes are strictly valid for small metal particles, burning within the small Biot number regime [101].

3.2. Metal-fuel combustion thermodynamics

A more rigorous prediction of the metal-particle combustion mode can be made using thermodynamic equilibrium solvers, which allow the effect of changing the metal fuel and oxygen concentrations within the mixture to be estimated. The ratios of the calculated equilibrium flame temperatures, T_f, relative to the

Fig. 3. Modes of particle combustion in the small Biot number regime. The oxidizer is typically oxygen from the air. Modes A and B produce nanometric solid metal-oxide combustion products in a halo around the droplet [102], while Mode C produces micron-sized oxides.
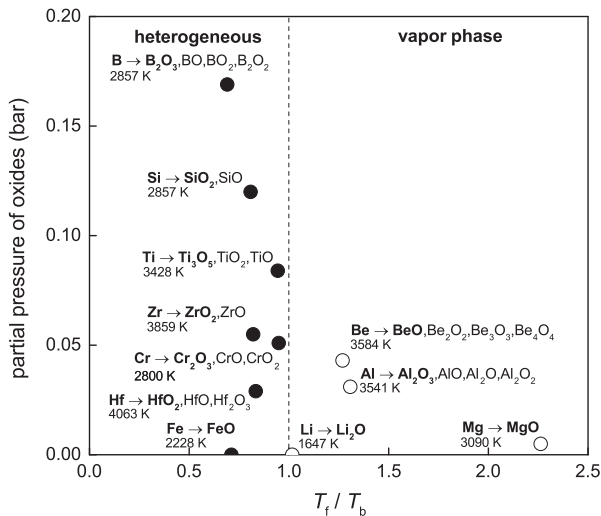
Fig. 4. Classification of metal particle combustion mode based on thermodynamic calculations. Particles with $T_f/T_b > 1$ burn in the vapor phase similarly to hydrocarbon-fuel droplets (Mode A), while those with $T_f/T_b < 1$ burn heterogeneously. The partial pressure of oxides determines if the heterogeneous combustion is likely to occur in Mode B, forming gaseous oxides and sub-oxides, or in the purely-heterogeneous Mode C, where heterogeneous reaction leads to solid oxide formation directly on the particle surface. Only iron is predicted to burn in Mode C at stoichiometric conditions with air, assuming complete oxidation of the metal to the stable product shown in bold. Flame temperatures, T_f, are indicated following the metal and its oxides.

boiling point, T_b, for eleven potential metal fuels burning in air at atmospheric pressure is shown in Fig. 4. Equilibrium calculations were performed with the Thermo thermodynamic software [104] at stoichiometric concentrations of metal in air, assuming the complete oxidation of the metal to the stable metal oxide indicated in bold in Fig. 4. The flame temperatures of many metal fuels with air exceed that of hydrocarbon fuels ($\approx$2300 K), testifying to their high energy content and the stability of the resulting oxides. The ratios of flame temperature relative to the metal boiling temperature allows the determination of whether or not the particle will burn in the vapor phase as a droplet (Mode A for $T_f/T_b > 1$), or heterogeneously (Modes B or C for $T_f/T_b < 1$). It should be cautioned that the boiling point of a small micron-size metal droplet has been estimated to be several hundred degrees higher than the values used in Fig. 4, which apply to a flat metal surface, due to the strong surface tension of some liquid metals [105].

3.3. Formation of volatile oxides and classification into Modes A−C

As discussed further below, formation of volatile oxides or sub-oxides, as occurs in either particle-combustion Modes A or B, is

detrimental to the separation of the metal-oxide combustion products from the exhaust for subsequent recycling. The tendency for a given metal fuel to form volatile oxides and sub-oxides at stoichiometric combustion conditions with air should correlate with the partial pressure of gaseous oxide species formed at equilibrium conditions. To this end, the total partial pressure of gaseous oxides and sub-oxides predicted by the equilibrium solver for each metal fuel is also shown in Fig. 4 and provides a means to determine if a metal whose flame temperature is lower than its boiling point, $T_f/T_b < 1$, will burn in Mode B or C. In this paper, particles are classified as burning in Mode C if the partial pressure of oxides is below 10^{-4} bar, such that iron is the only metal predicted to burn in Mode C under stoichiometric conditions with air at ambient conditions.

As can be seen from the data in Fig. 4, magnesium is a candidate for vapor-phase droplet combustion (Mode A), because its flame temperature exceeds its boiling point by almost 1700 K [102]. Other metals likely to burn in Mode A are beryllium and aluminum. Lithium has been observed to burn with both an envelope flame, or through a heterogeneous surface combustion mode, depending on the particle size and oxidizing atmosphere [64,65].

In contrast, the boiling point of boron is more than 1000 K higher than its flame temperature, resulting in heterogeneous combustion. Boron is known to react through a series of slow reactions involving the formation of gaseous oxides/sub-oxides on the surface of the metal droplet and its oxide coating [55,56,101,103], such that it burns in Mode B. While boron is the best fuel on an energetic basis [101], as shown in Fig. 1, the slow kinetic rates of boron oxidation and the formation of sub-oxides, which trap some of the chemical energy [55] and could lead to a coating of borate glass throughout the combustor, may prevent boron from being a practical fuel for direct combustion with air. Other metals likely to burn in Mode B are silicon (which, along with boron, is actually a metalloid), zirconium and hafnium.

The only metal predicted to burn in combustion Mode C with air at ambient pressure and temperature conditions is iron. The flame temperature of iron is below both its boiling point and the boiling/decomposition point of its associated metal oxide [106], such that solid iron oxide is formed on the surface of the burning metal droplet during combustion (see Fig. 3C). Iron oxide (i.e., rust) has a lower density than iron and is, therefore, porous, in accordance with the Pilling–Bedworth law [107]. The porous iron-oxide shell provides little resistance to oxygen diffusion toward the metal surface, potentially enabling oxidation of the entire metal particle under appropriate combustion conditions.

3.4. Flame temperature control through varying oxidizing-gas conditions

It is important to note at this point that the realization of any of the combustion Modes A−C discussed above depends not only on

the physical and chemical properties of the metal fuel, but also on the combustor operating parameters, including the combustor initial/inlet temperature, pressure, and the local concentrations of metal and oxidizer in the combustion zone [88,103]. While the Glassman criterion indicates that aluminum will burn in air in the vapor phase, since the flame temperature exceeds the boiling point of aluminum (see Fig. 4), thermodynamic calculations indicate that the flame temperature will drop below the boiling point of aluminum if the oxygen concentration in the flow is decreased below 10%. Thus, in flows with depleted local oxygen concentrations, obtained by mixing of fresh air with combustion products as discussed below, the aluminum might burn heterogeneously. In this case, it is likely that liquid aluminum oxide would be formed on the surface of the metal droplet. As direct experimental observations have demonstrated [103], the molten oxide forms a cap on the aluminum droplet that does not significantly obstruct the heterogeneous reaction of molten aluminum with oxygen. This suggests that it should be possible to control the particle combustion mode, and the resulting oxide-product size distribution, through combustor engineering and design.

3.5. Combustion of metal-powder suspensions versus single-particle combustion

The classification of metal-particle combustion into Modes A–C is based on the implicit assumption that effective combustion is possible only if the particle ignites and undergoes a transition to one of the diffusion-controlled combustion modes described above. Particle ignition refers to the process whereby a micro-diffusion flame, or micro-flame, is formed around the fuel particle or droplet, as shown in Fig. 3, that sustains the local gas and solid combustion-product temperatures at values higher than the bulk temperature of the surrounding gas [103,108–110]. Although particle ignition is indeed a pre-requisite for efficient combustion of a single isolated particle in a relatively-cold oxidizing environment, it is not necessary in high-temperature oxidizing flows. At high gas temperatures, particles can also react efficiently in a kinetic regime without undergoing ignition [111], which means that the particle temperature remains close to the gas temperature and no micro-flames are formed [88,103,108,110]. High gas temperatures can be realized in self-propagating flame fronts that can be formed in relatively-dense suspensions of metal-powder fuels burning in air and other oxidizers [112,113].

4. Flames burning metal fuels

It is not widely appreciated that a flame can be stabilized in a flow of combustible metal powders of small particle sizes (<20 µm) suspended in air at sufficient metal concentrations. Fig. 5 shows some metal-fuel flames stabilized on our custom-built Bunsen burner, along with a methane–air Bunsen flame familiar from chemistry labs. The McGill metal-powder Bunsen burner lofts particles between 1 and 20 µm in size into a flow of air or other oxidizing gases [113–115]. The resulting metal-fuel suspension exits the Bunsen burner, where the flame is stabilized through heat loss to the burner rim [101,116], as illustrated in Fig. 6. Laminar metal-powder flames were first stabilized by Cassell in the 1960s [112], but have largely been forgotten and have only been investigated in detail relatively recently at McGill [113–115,117–121], along with several other laboratories [122,123]. Metal flames appear quite similar to flames of either gaseous or liquid hydrocarbon fuels in air, as seen in Fig. 5, and share some properties.

4.1. Metal flame properties

Laminar flames stabilized within a suspension of metal powders in air have a thickness close to that of flames burning in either gaseous or liquid hydrocarbon fuels [113]. This implies that the particle combustion process is fast and is self-sustained by the molecular diffusion of heat from the hot reaction zone upstream to the fresh, unburned reactants, through a similar propagation mechanism to that of gas-phase flames [124]. Laminar flames are reaction–diffusion waves whose flame speeds, or laminar burning velocities, S_f, are controlled by both the heat-release rate, $\dot{\omega}$ [1/s], and the diffusion rate of thermal energy, α [m^2/s], such that $S_f \sim \sqrt{\alpha\dot{\omega}}$ [101,116].

4.2. Particle combustion modes within metal flames

The particles within the metal-powder suspension can burn either by igniting and forming a micro-flame enveloping them, as in Modes A–C, or through a kinetically-limited combustion process where the particle temperature stays close to the gas temperature and the reaction is not limited by the oxidizer diffusivity [103,108]. In either case, the nature of the solid metal-oxide combustion products is dictated by the volatility of the metal and its oxides under the flame conditions, as shown in Fig. 4. All of the particle-combustion modes lead to similar laminar flame structures, as illustrated in Figs. 5 and 6, with differences in reactivity and combustion time, i.e. $\dot{\omega}$, leading to differences in the laminar burning velocity and flame thickness. The diffusion-limited combustion Modes A–C result in a combustion process where micro-flames are formed around individual particles while a coherent thermal wave, or flame front, is stabilized in the gas, such that some of the (macroscopic) flames observable in Fig. 5 are filled with many individual micro-flames enveloping and burning the micron-sized particles within the suspension – i.e., there are _flames within a flame_ [106], as illustrated in Fig. 6.

4.3. Control of oxide product morphology through combustion engineering

Particles burning in diffusion-limited combustion Modes A and B produce nano-oxides through chemical condensation away from the particle surface. The kinetic combustion of the same particles in a coherent flame front might be limited by the rate of heterogeneous reactions on the particle surface or by the kinetics of metal evaporation [119]. In either case, oxides could form on or very near the particle surface and the flame temperature could be lower than it is in the diffusion-limited regime, reducing oxide volatility. If the thermodynamics dictates the formation of a condensed oxide at the designated flame temperature, it could remain attached to the particle surface [102], forming oxide products in a size range close to the sizes of the initial metal particles that makes them easier to collect for recycling. Particles that react in combustion Mode C will produce solid-oxide combustion-product particles that are larger and heavier than the initial metal-fuel particles, due to the additional mass and volume of oxygen gained during oxidation, regardless of whether the particle is reacting in the diffusion-limited or kinetically-limited regime, making them the simplest to capture and recycle.

4.4. Particle combustion rates compared to hydrocarbon fuels

During the combustion of hydrocarbon fuels, the fuel and oxidizer mix within the flame at a molecular level; therefore, the fuel combustion rate is often limited only by the net kinetic rate of the overall chemical-reaction pathway. The kinetic rates of gas-phase
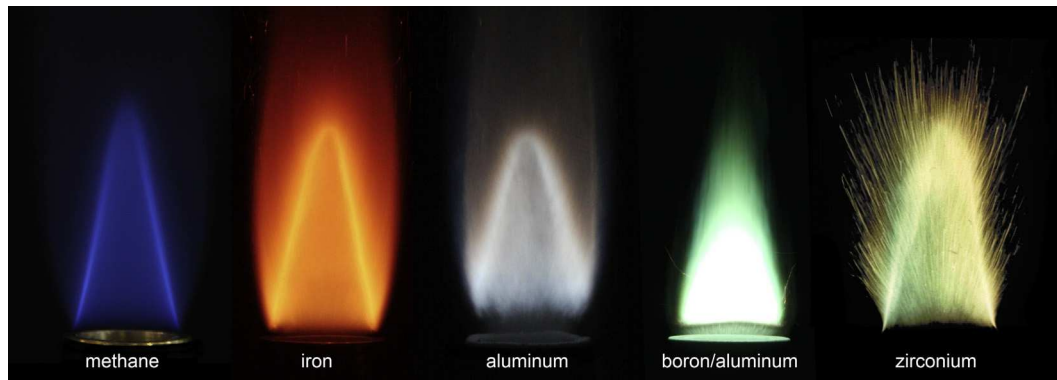
Fig. 5. Stabilized flames of various metal fuels with air compared to a methane–air flame. Flames are stabilized using a custom-built Bunsen burner as shown in Fig. 6.
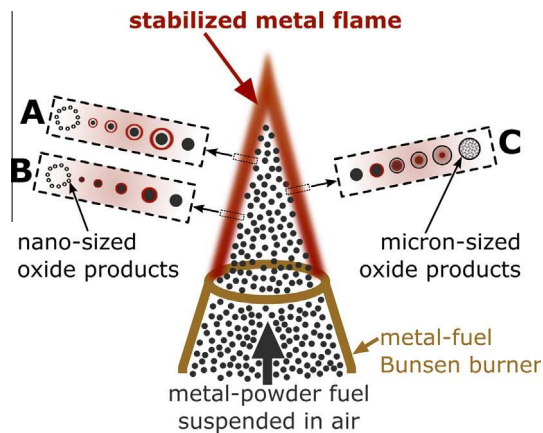

Fig. 6. Sketch of a metal–air flame stabilized on the McGill metal-fuel Bunsen burner. Metal powders are suspended into a flow of air and a metal flame is stabilized by heat loss to the solid burner rim. Particles can be burned either by micro-flames enveloping them or by bulk combustion with the air within the stabilized metal flame. Combustion Modes A and B tend to produce large amounts of vapor-phase oxides or suboxides that can lead to formation of a halo of nanometric oxide particles [102], while those that react completely heterogeneously, such as in Mode C, can produce larger micron-sized oxide particles.

chemical reactions of metals and oxygen are, however, so fast even at low temperatures, because they usually are non-activated [100], that it implies that the formation of a premixed metal-vapor/oxidizing-gas mixture is effectively impossible. Thus, in contrast to hydrocarbon fuels, surface reactions and evaporation or diffusion rates define the rate of metal combustion, such that $\dot{\omega}$ may actually be the inverse of a diffusion or evaporation timescale, rather than a chemical-reaction rate [119,125]. As discussed for isolated particles, metal-combustion processes are strongly dependent on diffusion and evaporation rates, such that they may be considered to generally be limited by physical processes rather than by chemical processes.

It may appear at first that metals should burn slowly, causing them to be inferior to hydrocarbon fuels. However, as can be seen from the experimental data presented below, metals can exhibit high reactivity with air for sufficiently-high reaction surface area, i.e., within a suspension of fine micron-size powders at sufficient metal concentrations.

4.5. Burning velocities of metal-fuel suspensions

When estimating the energy and power density for combustion systems operating with stabilized flames of either metal–air or hydrocarbon–air mixtures, the specific energy of the mixture increases to that of the pure fuel, due to the ability to take advantage of the oxygen from the air. This is the reason why air-breathing engines have higher performance than rockets or traditional batteries, both of which must carry their oxidizer with them. The reaction rate is scaled by $\dot{\omega} \sim S_f/\delta_f$, where δ_f [m] is the characteristic flame thickness and S_f [m/s] is the characteristic flame burning speed. The flame thicknesses, δ_f, of metal flames have been shown to be proportional to the square-root of the molecular diffusivity and are close to those of hydrocarbon flames, $\delta_f \sim \sqrt{\alpha/\dot{\omega}}$ [124]. The flame speed, S_f, is proportional to the laminar burning velocity of the mixture, which is the most important parameter from flame theory and which characterizes the "intensity" of combustion for a particular fuel-oxidizer mixture. The laminar burning velocity for traditional gaseous fuels is the speed with which a one-dimensional reaction–diffusion wave will propagate through a well-mixed quiescent fuel–air mixture with no heat loss. More-reactive fuels burn with faster flame speeds since $S_f \sim \sqrt{\alpha\dot{\omega}}$.

While the burning velocity is a well-established concept that scales the turbulent flame speeds of gaseous and low-boiling-point liquid fuels [116,126,127], it is not completely clear yet if this concept can be applied in the same way to metal-fuel flames of all scales and turbulence intensities. Our recent experiments have demonstrated that the flame speeds of both laboratory-scale metal flames, including stabilized and propagating flames, and large-scale metal flames studied during field trials are indeed scalable using the burning velocity concept [128]. These promising results suggest that burning velocities of metal flames derived from laboratory experiments can be used as a first approximation in designing turbulent metal-fuel combustors required for transportation and industrial applications.

Fig. 7 shows a compilation of the published burning velocity measurements for suspensions of micron-sized metal powders at stoichiometric conditions in different oxygen–nitrogen mixtures. Aluminum, magnesium and iron all have been demonstrated to have burning velocities with air at atmospheric pressure in the range of 20–30 cm/s, just slightly lower than that of hydrocarbon fuels, such as methane. The burning velocities of metal fuels, at least under some conditions [133], scales with the oxygen concentration in the flow in a similar manner to methane flames but with a lower sensitivity [112,113]. Smaller particles have higher surface-to-volume ratios and, thus, higher reaction rates, $\dot{\omega}$, and burning velocities [134]. The fact that flames of metal fuels, with particle sizes in the range from 1 to 20 μm, have burning velocities comparable to hydrocarbon fuels indicates, through Eq. (1), that metal fuels can be efficiently burned within similar combustion devices to those for hydrocarbon fuels at similar power densities.

Fig. 7 also highlights a general lack of accurate data for the flame propagation rates of different possible metal fuels for
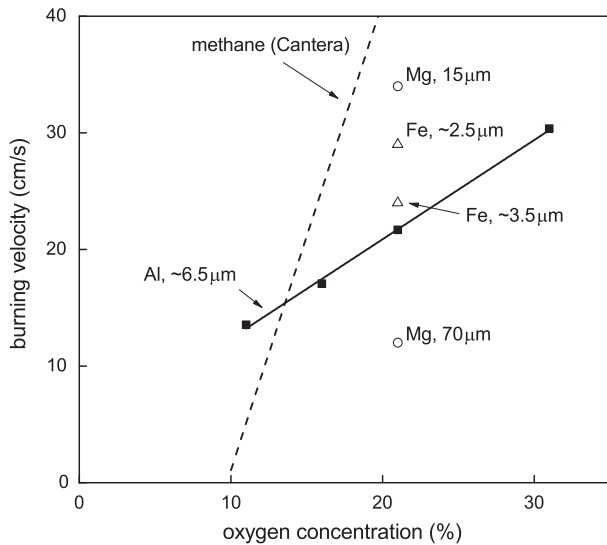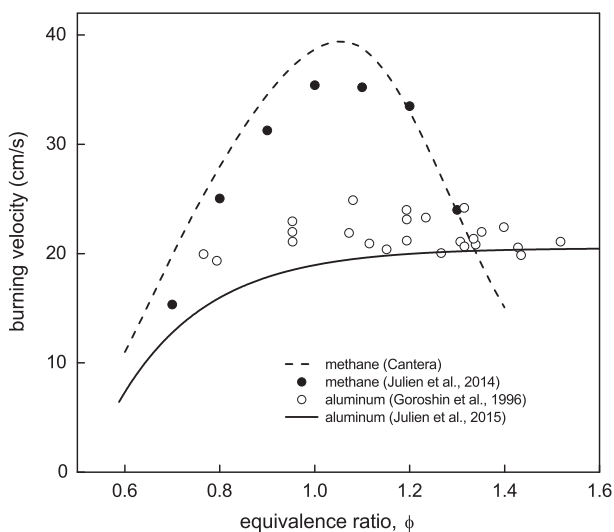
Fig. 7. Laminar burning velocities of suspensions of methane, aluminum [113], iron [129], and magnesium [130] fuels in "air" with variable oxygen concentrations. Methane laminar burning velocities calculated using the Cantera software package [131] and the GRI-Mech 3.0 chemical-kinetics mechanism [132].

different particle sizes and size distributions. More fundamental research into the flame propagation and stabilization properties of a variety of possible metal fuel options is needed and should be the focus of future efforts.

4.6. Effect of fuel concentration on metal flames

Although similar in both appearance and propagation mechanism to flames of liquid or gaseous fuels, flames in metal–air suspensions have some distinct features that must be taken into account to design effective combustion devices. For example, as shown in Fig. 8, the dependence of the burning velocity on fuel concentration has a very long plateau for fuel-rich mixtures, in contrast to a nearly symmetrical bell-shaped dependence of burning velocity on fuel/oxygen equivalence ratio for hydrocarbon fuel/air mixtures. The sharp drop of the burning velocity for hydrocarbon flames on both sides of the stoichiometric value is due to the dilution of the fuel–air mixture with the excess air or fuel, which lowers flame temperatures and reaction rates and, thereby, lowers flame burning velocity.

The insensitivity of the burning velocity to metal-fuel concentration in fuel-rich mixtures is due, first of all, to a diffusion-limited particle-combustion regime that establishes after particle ignition [113]. The formation of a micro-diffusion flame around each particle (see Figs. 3 and 6) makes the combustion quite insensitive to the average temperature of the gas [106,113,135,136]. Furthermore, the drop of the adiabatic flame temperature with increasing metal-fuel concentration is offset by the increase in the reaction surface area resulting from the greater number of particles in the suspension. In contrast with hydrocarbon flames, the addition of more metal fuel does not significantly displace air, due to the much higher density of the solid fuel compared to air, such that the use of rich metal-fuel mixtures does not dilute the oxygen concentration [113,118]. The net result of these effects is that the reaction rates and burning velocities remain relatively constant for fuel-rich flames of metal fuels.

4.7. Stabilizing flames of metal fuels in combustion systems and controlling emissions

The reduced sensitivity of burning velocity, and flame speed, on particle concentration for rich metal flames indicates that metal fuels can be more easily stabilized using a fuel-rich pre-burner, as previously suggested by Goroshin et al. for a metal-fuelled ramjet combustor [124]. Use of fuel-rich mixtures will ensure stable combustion during the inherent fluctuations of the particle-seeding density typical of multi-phase flows [118]. High combustion efficiency, or complete metal combustion, can be achieved by addition of excess air to the burning flow downstream of the primary region, with diffusively-burning particles providing resistance to flame quenching due to cooling from the excess air.

The high flame temperatures possible in some metal flames leads to a concern that metal-fuelled combustors could produce high nitric oxide, or NO_x, pollutant emissions through the thermal mechanism [5,137,138]. Use of fuel-rich combustion to starve the flame of oxygen could mitigate NO_x formation, since the thermal NO_x formation mechanism requires excess oxygen and is enhanced by higher temperatures [5,137,138]. To mitigate NO_x formation, Rich–Quench–Lean gas-turbine combustors often use a fuel-*rich* primary combustion zone followed by a relatively cool mixing and *quenching* zone, where excess air is added suddenly to temporarily halt the combustion until mixing is sufficient, which then leads to a fuel-*lean* dilution and oxidation zone where combustion is completed [5,139,140].

As a rule, purely fuel-rich combustion is avoided for hydrocarbon fuels because it leads to increased emissions of soot, unburned hydrocarbons, aldehydes, and carbon-monoxide pollutants [5], none of which are possible products of metal flames. For metal flames, fuel-rich combustion will improve combustion stability while reducing, or possibly eliminating, nitrogen oxide emissions. More research into NO_x formation within metal flames is needed.

4.8. Controlling particle combustion mode and burning rates through combustion engineering

In a flame within a metal-fuel suspension, the combustion rate, overall flame temperature, and particle combustion mode can be controlled by varying the turbulence level, the preheat temperature, and the level of dilution of the air with exhaust gases (hot

Fig. 8. Burning velocity in suspensions of 6 μm aluminum particles in air at different fuel/oxygen equivalence ratios compared to that for methane/air mixtures. The equivalence ratio is the ratio of the fuel–air mixture to that needed for complete oxidation of the fuel to its associated stable, fully-oxidized combustion products. Methane data from our laboratory [75] compared to simulations using Cantera and GRI-Mech [131,132]. Aluminum curve obtained by fits to recent data obtained in our laboratory [128] and previously-published data is plotted for comparison [113].

nitrogen) to control the percentage of oxygen in the oxidizing gas mixture. Similar combustion techniques are now successfully employed in advanced low-emissions gas-turbine engines [139] or internal combustion engines [5,141] and in low-emissions boilers and furnaces [142]. Reduction in oxidizer concentration reduces burning velocity for some metal flames, as shown in Fig. 7. The reduced sensitivity of metal flames to the oxidizer concentration, compared to hydrocarbon fuels, is important as it means that flames of metal fuels can be stabilized under conditions of depleted oxygen concentration in order to control the particle combustion mode and potentially mitigate NO_x pollutant formation. More research is needed to identify the effect of oxygen concentration on the flame propagation speeds, flame temperatures, and NO_x emissions for a variety of possible metal fuels of different particle sizes.

Limited data are available in the literature on the effect of preheat temperature on metal-fuel flames, but past measurements have shown that the burning velocity can be increased through preheating of the metal-fuel/air mixture [124], as occurs in hydrocarbon–air flames [116]. In addition, our recent results studying flames of metal fuels stabilized in the combustion products of a primary hydrocarbon–air flame show a considerable increase of the metal flame burning velocity with high preheat temperatures, above 2000 K, even though they were burning in combustion products with greatly reduced oxygen concentrations [115,119–121]. Stabilized flames of iron powders burning in the combustion products of methane flames show similar flame propagation speeds for iron particles burning in either the diffusion-limited combustion Mode C, or in a kinetically-limited combustion mode obtained when the flame was starved of oxygen [120]. This is important evidence that preheat and oxygen starvation are important mechanisms to control the particle combustion mode and reaction rate, but more research is needed into how these mechanisms influence the metal flame properties and emissions.

Almost all combustion systems employ turbulent flows in order to increase the flame burning rates [139,143,144], and such techniques would need to be used to improve the power density of metal-fuelled combustors. Little data on the effect of turbulence on the flame speed of metal fuels is available [122], but our recent measurements show a large increase in burning rate for large-scale flames in field tests that contain some residual turbulence created during the required metal-fuel dispersal process [75,128]. Turbulent combustion of traditional fuels remains a challenging area of active research [126,127] and, therefore, much remains to be learned about turbulent metal flames.

While more research is needed to characterize metal flame properties under a range of combustor conditions, the available flame speed and burning velocity data, along with the energy densities of metal fuels shown in Fig. 1, indicate, through Eq. (1), that metal fuels can be burned in power devices at nearly-equivalent power densities to modern hydrocarbon-fuelled systems.

5. Heat engines powered by metal–air combustion

This review has demonstrated that metal powders can be burned with air and other oxidizing gases at rates similar to hydrocarbon fuels and that the particle combustion mode can be controlled through changes in the oxidizing gas composition and temperature in order to achieve a desired combustion rate and, potentially, adjust the particle size distribution of the oxide products. As discussed below, the intense heat generated by these metal fuels can be used directly for industrial and residential heating applications, or can also drive a heat engine for producing mechanical and electrical power. Any metal-fuelled engine system must be designed to achieve both efficient combustion of the metal

fuels and efficient collection of the resulting metal-oxide combustion products. The design of an effective metal-fuelled engine must take into account the physical and combustion properties of metal fuels and their solid oxide products.

5.1. Burning metals in internal-combustion engines (ICEs)

The combustion of metal fuels within ICEs has been proposed by several authors [49,53,54]. Unfortunately, the properties of metal powders are not well-suited for fuelling ICEs. The solid and abrasive metal-oxide combustion products formed during metal combustion are incompatible with ICE design and operation and cause wear [49], which was previously identified as a serious issue during the development of compression–ignition ICEs to burn coal and biomass slurries [145].

To achieve the rapid combustion rates necessary within ICEs, several authors have proposed the use of metal nano-powders [49,53,54]. The study of nano-powder combustion for propulsion applications has demonstrated that the high reactive surface area of nano-particles does not necessarily translate into a proportional increase in their reactivity [146,147]. This poor combustion performance can be explained by the strong tendency of nano-powders to agglomerate during dispersal [56,90,94,147–149]. The combustion of the resulting large particle agglomerates, consisting of hundreds or even thousands of nano-particles, is then equivalent to the combustion of large solid-metal particles of an approximately equivalent size, because the large internal surface area of the agglomerate is irrelevant for a particle burning in a diffusion-limited combustion mode with a micro-flame enveloping it [150]. Nano-particles will also produce nano-oxide combustion products that are difficult to capture for recycling, as discussed below. Both the nano-particle fuels and their resulting nano-oxides can pose health risks [53] that should be avoided by using metal fuels that produce larger-sized oxide combustion products.

Industrially-available metal powders are typically in the micron-size range, are produced in large quantities annually for various applications, and bulk metal prices are currently cost effective compared to hydrocarbon fuels on an energy basis [83]. Micron-sized metal powders are easily transportable, are safer and more stable to handle than nano-particles or gaseous and liquid fuels, and have a practically unlimited shelf life when protected from humidity in hermetically-sealed containers [25,52]. The extensive existing infrastructure for producing metals and micron-size metal powders can be used for recycling of the metal combustion products with little or no modifications. The energy consumption for producing industrial powders in the micron-size range is close to the energy intensity of the primary metal production [25], suggesting that they will have much lower costs and better energy-cycle efficiencies compared to metal–air batteries, which require expensive high-purity anodes, or metal-fuel combustors/reactors burning expensive nano-powders. These micron-sized industrial metal powders can be burned with air in stabilized flames, as shown in Section 4, but are not compatible with ICEs.

5.2. External-combustion engines (ECEs)

Since the combustion of metal-powder fuels is not realistic in ICEs, external-combustion engines (ECEs) must be considered. ECEs based on the Rankine cycle have been used ubiquitously for stationary power generation at a wide range of power levels, fuelled by fossil fuels, geothermal energy, nuclear or solar power [151,152]. These systems can be adapted or retro-fitted for operation with metal fuels, as discussed further below.

For transportation applications, the efficiency of modern compact ECEs has been vastly improved in comparison to their coal-fired steam predecessors of the industrial revolution era and now

even surpass the efficiency and power density of ICEs [153–155]. ECEs also promise good performance as part of hybrid-electric powertrains, enabling range extension while maintaining the benefits of regenerative braking, elimination of engine idle, and operation of the engine at its optimum set-point [5]. Demonstration programs from several decades ago have shown that Stirling engines can provide enough torque for efficient direct vehicle propulsion without needing hybrid-electric powertrains [153], if elimination of the batteries from the vehicle or machine should prove optimal from an economic, life-cycle, or an energy-density standpoint.

5.3. Metal-fuelled combustors and power systems

The design elements of the proposed metal-fuel combustor are illustrated in the left side of Fig. 9 and include a metal-fuel tank and powder-dispersion system, a metal-fuel combustor combined with a cyclonic solid-combustion-product separator, and a storage tank for the metal-oxide combustion products. Metal fuels can be burned as a suspension at high power densities within turbulent burners. These metal-fuel combustors would convert, at high reaction rates, the chemical energy within the metal fuels into clean, high-grade thermal energy that can be used for a wide variety of high-power applications, as illustrated in Fig. 9.

The clean high-grade thermal power produced from metal-fuel combustion can be directly used for industrial and residential heating applications, similarly to how biomass pellets are used today [44,156]. Alternatively, these metal-fuel combustors can be coupled to Rankine-cycle steam engines, Stirling ECEs, or thermoelectric generators for power generation at a range of scales. Unlike in ICEs, ECE combustors are easily scalable by simply adding additional burners to increase the power of heat delivery. The similarity between the physical properties of industrial metal powders and pulverized coal [47] suggests that such powders could be used in retro-fitted coal power stations, or those fuelled by biomass, to

exploit existing infrastructure for zero-carbon power generation at grid-level scales, reducing the cost associated with a transition to a low-carbon energy system [52].

As discussed in Section 3, metal-fuel laminar flames have thicknesses and burning velocities on par with laminar flames of hydrocarbon fuels, which means that the power density of metal combustors can achieve values similar to those of modern combustors burning hydrocarbon fuels (see Eq. (1)). Therefore, the proposed metal engines will be suitable for various transportation applications, including automobiles, locomotives and ships. For aviation and some transportation applications, biofuels are likely to be the best option [5], but are unlikely to fully displace fossil fuels due to limited biomass resources. For the storage and global trade of clean primary power, from solar, wind or nuclear resources, metal fuels, along with metal-fuelled combustors and heat engines, will provide much higher performance than other energy carriers, such as hydrogen, traditional batteries, or metal–air batteries. The proposed metal-fuelled combustion and power systems achieve high performance through the high energy density of metal fuels, the minimization of any dead weight within the power system, and the fast reaction rates that result from burning the metal fuels within high-temperature flames.

5.4. Capture of metal-oxide combustion products

The key requirement for zero-emission metal combustion, and efficient recycling of the metal fuel, is the complete capture of all metal oxides from the combustion exhaust, a task made possible by the solid nature of the metal-oxide combustion products. Unfortunately, efficient collection of the nanometric metal-oxide particles that often form during combustion of light metals, such as aluminum and magnesium, burning in Mode A would require using fine, HEPA-type or/and electrostatic filters. The separation of particles from the filter materials is energy intensive and such filters are technically difficult to implement within high flow rate,
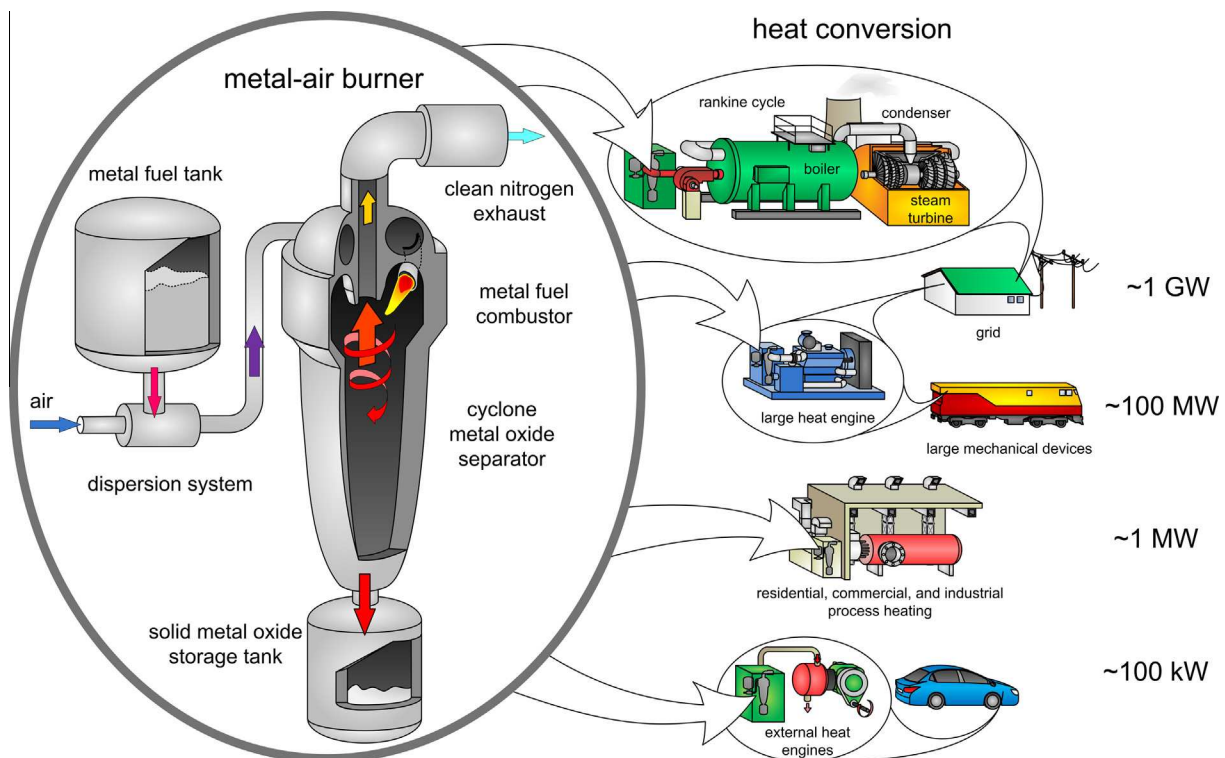

Fig. 9. Concept drawing of a metal-fuelled combustor and its possible applications at a range of power-generation scales.

compact power devices [53]. On the other hand, modern cyclone phase-separation technology has a very high efficiency for particle sizes greater than several microns [157], suggesting that production of metal-oxide particles of this size could enable energy-efficient and practically 100% effective collection of the solid combustion products. Therefore, one of the central considerations in identifying potential metal fuels for power generation via direct combustion with air should be whether they can form relatively-large oxide particles compatible with cyclone-type phase-separation technology. In order to allow recycling of the metal fuel, the overall energy system actually increases in mass, due to the oxidation of the metal powders from oxygen in the air, during operation. This is not a concern for stationary applications but does reduce the performance of metal fuels for transportation systems.

6. Fuel options for direct metal–air combustors and engines

The production of relatively-large micron sized oxide particles during the metal-fuel combustion process with air is critical to enable effective capture and recycling of the metal fuel. The size of the oxides formed during combustion depends directly on the particle combustion mode within the combustor. The metal-fuel combustion Modes A and B, shown in Fig. 3, produce nano-sized or sub-micron oxide particles, via a combination of physical and chemical condensation of vapor-phase oxides and sub-oxides, such that they are not optimal for metal-fuelled combustors. The heterogeneous combustion Mode C is the only combustion mode where the formation of the condensed oxide on the particle surface ensures that the metal-oxide particles in the combustion products are similar in size to the initial micron-size metal-fuel particles. Selection of the appropriate metal fuel and starvation of the combustion zone of oxygen can be used to ensure that the metal combustion occurs in Mode C. Further studies on the combustion efficiency and solid-oxide combustion-product size and morphology under various combustion conditions are needed to guide the design of metal-fuelled combustors.

6.1. Iron as a recyclable metal fuel

The primary candidate fuel that can be burned in combustion Mode C is iron due to its moderate combustion temperature, ≈ 2200 K, which is similar to that of hydrocarbon fuels and is below both the boiling point of the metal and the decomposition points of iron oxides (see Fig. 4). Millions of tons of iron powders are currently produced world-wide for the powder metallurgy, chemical and electronic industries. Iron–air batteries are being developed for economic reasons due to the abundance and low cost of iron resources [23].

An important property of iron is that it is readily recyclable with well-established technologies. Iron can be reduced from iron-oxide powders by reacting them with hydrogen or syngas at moderate temperatures below 1000 °C [50,84,158], enabling the reduction of iron using hydrogen produced from clean sources, such as the artificial leaf [159,160].

The combustion of iron with air, followed by reduction of iron oxides with hydrocarbon fuels, is also at the core of chemical-looping reactor technologies. Chemical looping reactors enable the separation of carbon dioxide, produced when burning hydrocarbons for power generation, and its subsequent sequestration [84–86]. The combustion of the reduced iron powders within the proposed metal-fuel combustors could improve the performance of the metal-oxidation step within chemical-looping power plants, compared to the relatively-slow oxidation of large iron particles within the fluidized-bed reactors currently employed. This would not only permit a drastic reduction in the size of the iron-oxidation reactors, but would also allow chemical-looping power plants to be reprocessing centers of iron-oxide powders collected from a clean-energy distribution network based on iron fuels. Significantly, if biomass or waste streams provide the energy input to the metal-fuel recycling system, using a chemical-looping reactor to enable sequestration of the resulting carbon dioxide emissions, then the metal-fuel cycle can actually have overall carbon-dioxide emissions that are negative [36].

6.2. Silicon – future fuel option?

The other attractive candidate metal (metalloid) fuel is silicon [47,52], provided that it can be burned in Mode C without the formation of submicron silicon oxides using advanced combustion techniques. Because of the widespread availability of relatively pure silica sand that is used to manufacture silicon, the captured silicon-oxide combustion products, which are a main ingredient in glass and are environmentally benign, could simply be recycled within the established systems for household waste. This would avoid additional collection and shipping costs associated with a dedicated metal-fuel recycling infrastructure. Silicon production via solar metallurgy has already been singled out as an efficient way to store and deliver clean solar energy [52]. Ferrosilicon, a combination of iron and silicon, is another potential low-cost metal fuel that has long been used to generate hydrogen on demand for military balloon applications [161]. To the authors' knowledge, no information is available on the flame propagation or stabilization properties of silicon or ferrosilicon with air.

7. Conclusion

Society requires a variety of high performance chemical fuels, or energy carriers, that enable the storage and global trade of clean primary energy. Such recyclable or renewable fuels enable the separation of energy consumption, in both space and time, from primary energy production. To date, batteries and hydrogen are the most widely considered energy carriers, but neither are appropriate for long-distance energy trade. So-called solar fuels, synthetic hydrocarbons produced using clean primary energy and carbon dioxide, do not appear to have favorable life-cycle energy and carbon balances.

An ideal energy carrier would be burned to produce power on demand at high power densities while avoiding carbon dioxide emissions. A fuel whose combustion products can be captured for recycling would likely have improved energy-cycle efficiency, better economics, and reduced life-cycle impacts. Metal powders are the most promising recyclable, and potentially zero-carbon, fuels proposed to date due to their high energy densities and the high collection and recycling efficiencies enabled by the solid combustion products. Recycling of metal fuels with clean energy inputs, or using fossil or biomass sources as part of open-loop chemical-looping processes along with carbon sequestration, could enable the metal fuel cycle to achieve near zero, or even negative, net carbon dioxide emissions. Metal fuels would also eliminate a host of other pollutant emissions created during the combustion of hydrocarbon fuels that impact human and environmental health, including carbon monoxide, unburned hydrocarbons and particulate matter, or soot.

The bottleneck for utilization of metal fuels in a clean energy-distribution network is the current absence of a device that can efficiently convert the chemical energy stored in metal fuels at fast rates to produce mechanical power or electricity at consumption points, such as passenger and cargo vehicles, households, locomotives, ships, and remote power generators. Metal–air batteries are widely being investigated but fail to provide the necessary power

density for some applications. Generation of hydrogen and heat by reacting water with active metals, such as aluminum and magnesium, has also been widely discussed and investigated in the literature as one of the possible energy-conversion routes.

Alternatively, this paper proposes the direct combustion of metal-fuels with air in turbulent combustors to achieve higher power densities. The high-grade heat produced through metal-fuel combustion could be used directly for clean heating, or be used to drive Rankine or Stirling ECEs, as well as thermo-electric generators. While our understanding of metal combustion processes and flames is not as advanced as that for the hydrocarbon fuels that we have relied upon for over a century, our current knowledge, as reviewed in detail in this paper, is sufficient to conclude that the use of metal fuels with heat engines is technically feasible, although an effective metal engine has yet to be demonstrated. The high potential performance of the metal-fuelled combustors and heat engines proposed in this paper motivates further study of, and investment in, this promising technology for a future low-carbon society.

Acknowledgments

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