# Aluminum-Water Reactions for Hydrogen Production: *An investigation of its implementation in power generation devices*

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# Abstract

An analytical investigation of a novel alternative fuel source, aluminum powder, for its reactive properties upon reaction with water. Extensive research has been performed over the years studying metal-water reactions for their heat generation and in-situ hydrogen production. Both theoretical and experimental studies have focused on determining the effect of parameters such as the type of metal, metal-to-water ratio, activation method, particle size, and temperature of the reaction. However, few have explored the implementation of such fuel in a power generation device. This work explores the use of aluminum-water reactions to power three different Siemens engines of varying power outputs: two industrial engines- RB211 (33 MW) and Trent 60 (66 MW) and one heavy duty gas turbine- SGT5-4000F (329 MW). The thermodynamics cycle is proposed, and analysis is performed to determine the required reactor size. Then, a life cycle carbon emission of aluminum-water fuel is analyzed and evaluated against that of natural gas – the fuel currently used in the three engines.

# Abrégé

Une investigation analytique d'une nouvelle source d'énergie, une alternative au carburant : l'aluminium en poudre, connu pour ses propriétés lorsqu'il est en mis en réaction avec l'eau. Au cours des années, des recherches approfondies on été effectuées pour étudier la réaction entre le métal et l'eau et sa production de chaleur et d'hydrogène. Des études théoriques et expérimentales ont déterminé les effets de différents paramètres tel que le type du métal, le rapport métal-eau, la méthode d'activation, la taille des particules et la température de la réaction. Cependant, peu d'exploration est faite sur l'implémentation du carburant dans un dispositif produisant de l'énergie. Ce document étudie l'utilisation des réactions aluminium-eau pour alimenter trois différents moteurs RB211 (33 MW), Trent 60 (66 MW) et une turbine à gaz haute performance SGT5-4000F (329 MW). Le cycle thermodynamique est introduit et une analyse est effectuée pour déterminer la taille du réacteur requise. Le cycle de vie des émissions du carbone est évalué et comparé à celui du gaz naturel – le carburant qui est couramment utilisé dans ces trois moteurs.

# CHAPTER 1

# Introduction

### 1.1. The Arising Need for Alternative Fuels

Today's society relies heavily on energy and its omnipresent availability. Since the industrial revolution, with fossil fuels as the main source of fuel, the world's economy flourished, working and living conditions improved as technologies developed and urbanization began. Nearly 260 years after the beginning of the industrial revolution, theorists and scientists predict that peak oil has been reached [1]. The rate of consumption of fossil fuels is continuously on the rise [2] –energy needs are expected to double and even triple in the upcoming 40 years [3]; meanwhile, oil

production is expected to decline [4], [5]. This leads to the price of oil to continuously increase [4], [6].

Combustion of fossil fuels release large net carbon emissions which have negatively impacted our environment – leading to climate change. As expressed by Veer, a former CEO of Shell, this can be summarized as the 'three-hard-truths': 1) growing energy demand, 2) depleting gas fields and oil reserves, and c) environmental impact accruing from GHG emissions [7]. It is evident that without alternative fuels, the society will not be able to operate to today's standards for much longer both economically and environmentally.

As a result, a new source of energy, as well as an associated power system, must be developed. In 2014, ~80% of the world energy was fueled by non-renewable fossil fuels [8], the alternative source of energy must be able to satisfy majority, if not all, of this energy demand. These alternatives must produce low to no carbon dioxide emissions, possess high specific energy and power densities, and be a safe energy carrier [9]. Various alternatives such as batteries, biofuels, and hydrogen have been explored; however, they have been deemed insufficient as they do not satisfy all the required criteria, particularly in applications that require high energy density. For instance, due to their low reaction rate, batteries have low power densities; they also have a long turn around time in terms of recharging and/or replacing [10]. Biofuels, upon sustainable production may produce zero net carbon; the CO<sub>2</sub> absorbed throughout the organisms' lifetime is presumed to be equal to the amount that is released when it is burned as biomass [5], [11], [12]. However, there exists an ethical question of food versus fuel; it may affect the economy as it drives

up food prices to impact lower income families and developing countries [13], [14]. Concerns regarding the land resource availabilities for energy plants cultivation are also raised [5]. Its current method of production relies on fossil fuels [4]. In 2014, 10% of the total world energy demand was met by bioenergy and estimates predict that our society will not be able to sustain on biofuels alone [8], [15]. Hydrogen, a more promising energy source, is discussed in the following section.

### 1.2. Hydrogen as an Alternative Fuel

Hydrogen, the most abundant element in the universe, exhibits high specific energy, which represents the energy per unit mass, and reactivity. It can be used as fuel in hydrogen internal combustion engines or generate electricity through fuel cells. It can be rapidly refueled and when combusted in air, its only combustion by-product is water, making it a clean source of fuel. Hydrogen stores 143.0 MJ/kg (39.7 kWh/kg), its specific energy is three times greater than that of gasoline by mass [2]. However, it is not a suitable energy carrier due to its low energy density, which represents the energy per unit volume, of 0.0108 MJ/L (0.003 kWh/L) (more than 3000 times smaller than gasoline) and high range of flammability (4 – 75 vol. % in air) [2], [16], [17]. Despite these challenges, many predict the future of a 'hydrogen economy' powered by fuel cells and/or internal combustion engines. The 'hydrogen economy' is expected to be the solution for all our energy and environmental concerns [18] Figure 1 plots the different fuels' specific energy and energy density values to illustrate their energetic potential.



Figure 1: Volumetric vs. Gravimetric Energy Density of Different Fuels

### 1.2.1. Current Hydrogen Production Methods

Though abundant, due to its high reactivity, hydrogen gas is not found naturally in the environment; it is typically in molecules such as water and hydrocarbons. Current methods of hydrogen production include: thermochemical processes such as natural gas reforming, coal gasification, and electrolytic processes. Electrolytic hydrogen production splits water into its elementary molecules and is one of the most energy intensive way to produce hydrogen [18], [19]. Currently, more than 90% of industrial hydrogen production methods are based on fossil fuels [17]; this is neither sustainable nor clean. However, if the electricity used for the electrolytic process is generated using renewable sources such solar, wind, or geothermal heat, the generation

process will be clean. This carbon-free hydrogen production method has a high energy production cost of ~\$29 CAD/GJ in comparison to that of oil or natural gas at ~\$7CAD/GJ [17].

### 1.2.2. Current Methods of Hydrogen Storage and Transport

Due to its high diffusivity and small size, storage of hydrogen and transportation introduces another challenge. Current storage methods require gasification or liquefication of hydrogen and they must be kept in highly pressurized tanks (~200 – 700 bar) or cryogenic tanks of very low temperature (20 K); both are energetically expensive storage methods [9]. Due to the low energy density of hydrogen, larger tanks will be required, lowering the specific energy of this fuel. The related cost of shipping and storing hydrogen is equivalent to that required to produce hydrogen currently [20]. In fact, sustaining a hydrogen economy will require more energy than today's energy economy [18]. The energy required to produce, package, transport, store and transfer hydrogen can be double the amount of energy it provides [18]. Other means of hydrogen storage have been explored such as in carbon nanotubes and metal hydrides; they have proven to be inefficient and expensive – liquification is the most feasible storage technique if its costs become comparable to gasoline [21]. Though hydrogen exhibits energetic potential, its difficulties production and storage prevent it from being the ideal alternative fuel candidate.

# 1.2.3. Metal-Water Reactions for Hydrogen Production, Storage, and Transport

Metal-water reactions are highly exothermic, and the only products of their reaction are solid metal oxides/hydroxides, heat, and hydrogen. Some metals are abundant, inexpensive, easily transported, and highly energetic when oxidized with water or in air. They can be a zero/low carbon energy source when produced using clean (wind or solar) energy and non-carbon anodes [15]. Upon determination of the right conditions, metal-water reactions can yield fast reaction rates to allow the in-situ, on-demand production of hydrogen. This would eliminate the need to store and transport hydrogen but still allow for its use as a fuel through preserving its high specific energy and power density. The solid products can be recycled in a smelter to produce secondary aluminum product which can be reacted again to form a closed loop reaction cycle. The produced hydrogen can be further combusted in oxygen to produce heat and no pollutants; when reacted with air, the high nitrogen content of air will lead to some NO<sub>x</sub> formation. However, the wide range of flammability of hydrogen, allows for low combustion reaction is H<sub>2</sub>O (g); if well captured, it can be reused to induce the metal-water reaction, again forming a closed loop reaction cycle.

### 1.3. Focus of this Work

This research involves the investigation of the implementation of aluminum-water reactions in power-generation devices of varying scales. To best illustrate, three engines: Industrial RB211, Siemens Industrial Trent 60, SGT5-4000F with power ratings of 33.2 MW, 66 MW, and 329 MW [23], [24], respectively have been chosen as models. A comprehension of the full thermodynamic

power cycle is required, this takes into consideration the path each reactant (metal and water) takes to produce the desired power. Understanding the reactions (metal-water reaction and hydrogen combustion) helps determine the conditions under which the engine components must operate under to achieve the desired efficiency and required power output. It will also illustrate the fraction of power produced from each reaction. Reaction conditions such as reactor and boiler temperatures and pressures will determine the reaction properties such as the reaction rate, total hydrogen yield and heat production.



Figure 2: Industrial 'RB211 (33.2 MW)- Top Left; Heavy Duty SGT5-4000F (329 MW) – Top Right Trent 60 (66 MW)-Bottom

$$\frac{P}{V} = \eta q_m \rho_m \dot{\omega} \tag{1}$$

Equation 1 demonstrates that the power density  $[kW/m^3]$  of a system is a parameter dependent on  $\eta$ , the system efficiency,  $q_m$  [kJ/kg], the specific energy of the fuel;  $\rho_m$   $[kJ/m^3]$ , the energy density of the fuel; and  $\dot{\omega}$  [1/s], the reaction rate. A power-dense system must have high efficiency and reaction rates; it must also be powered by a fuel with high specific energy and energy densities. The latter requirements are determined by the intrinsic properties of the fuel while the efficiency and reaction rates are factors dependent on reactor design and operation conditions.

This work will present the potential of reacting metals with water to produce hydrogen, as well further combusting this hydrogen for power generation. It will explore the different potential metal fuels and the need for reaction activation for the chosen fuel, aluminum. Chapter 3 will then explore metal-water reactions at the application level. It will present the power cycle with the aluminum-water reactor and hydrogen combustor system that replaces the combustor of a typical gas turbine engine. It will then present the metal and water input requirement at different operation conditions and power requirements. Chapter 4 will quantify the feasibility of the implementation of metal-water reactions through a carbon cost analysis in comparison to fossil fuels.

# **CHAPTER 2**

# Hydrogen Production via Metal-Water Reactions

### 2.1. Metal Water Reactions

As previously mentioned, some metals are abundant, inexpensive and highly reactive when reacted with water. To illustrate the reaction in greater detail, a typical metal-water reaction is illustrated in equations 2 and 3.

$$xM + yH_2O \rightarrow M_xO_y + yH_2 + Q_1 \tag{2}$$

$$xM + 2yH_20 \to xM(0H)_{\frac{2y}{x}} + yH_2 + Q_1$$
 (3)

Depending upon reaction conditions and the stoichiometry of the reactants, the product of the reaction will be a solid oxide or solid hydroxide; the reaction will always produce hydrogen and heat. The produced hydrogen can be further combusted with pure oxygen or in air to produce heat; this reaction is given in equation 4.

$$yH_2 + \frac{y}{2}O_2 \to yH_2O + Q_2$$
 (4)

The sum of the two heats of reaction will be the total heat of combustion of a typical metal-water reaction. When using aluminum as the metal fuel, the two heats are of the same order of magnitude and in total, equate to approximately 30 MJ/kg<sub>Al</sub>.

Above metal-water reaction is thermodynamically equivalent to metal-air combustion expressed in equations 5 and 6.

$$xM + \frac{y}{2}O_2 \to M_xO_y + Q_3 \tag{5}$$

$$xM + \frac{y}{2}O_2 + yH_2O \to xM(OH)_{\frac{2y}{x}} + Q_3$$
 (6)

Where the heat of combustion of the metal-air reaction is equivalent to the heat of reaction of the metal-water reaction and the subsequent hydrogen combustion heat.

$$Q_3 = Q_1 + Q_2 \tag{7}$$

However, the products of metal-air reaction are more difficult to capture – particularly light metals such as magnesium and aluminum produce nanometric oxide particles which will be energetically expensive to capture and subsequently filter and recycle [25].

To determine the most suitable metal(s) for this reaction, a comparative study was performed by Y. Yavor with 16 different metal powders [26]. In his experiments, he compares the total hydrogen yield, reaction completeness, and maximum flow rate of each of the metals at four different temperatures: 80°C, 120°C, 150°C, and 200°C. Each of these parameters are important for the following reasons: total yield will determine the total energy that can be harnessed through the hydrogen combustion, reaction completeness is related to reactor efficiency, and the maximum flow rate determines the reaction rate and subsequently the power that can be generated. Figure 3 summarizes the results. Refer to appendix A1 for details on the specific powders used in this experiment.



Figure 3: Comparative Study of 16 Different Metals-Water Reactions [26]

The results illustrate positive trends in all three measure parameters (reaction completeness, total hydrogen yield, and reaction rate) with increasing temperature. Magnesium

and aluminum appear to be the most promising candidates as they produce 50% more hydrogen per unit mass of metal than any other species [26]. Manganese, as well, at 200°C show high volumetric hydrogen yield and reaction completeness; however, due to its toxicity it is eliminated as a candidate. Cost is another important consideration for a potential energy carrier and fuel source. The unit price of aluminum and magnesium in 2017 are \$2.52 CAD/kg (Sept 12) and \$2.75 CAD/kg (May 31), respectively [27].

Dividing this amount by the specific energy density (8.61  $kWh/kg_{Al}$  and 6.86  $MJ/kg_{Mg}$ ), it is evident that aluminum is the cheaper energy source at \$0.29 CAD/kWh, in comparison to magnesium at \$0.40 CAD/kWh. Additionally, aluminum is the most abundant metal in the earth's crust as well as 100% recyclable, making it an ideal candidate [27], [28].

An important characteristic is the nominal diameter of the powder, this is as the aluminumwater reaction is a surface reaction; an increased surface area per weight and volume of aluminum will result in a higher yield [19], [29].

### 2.2. Aluminum-Water Reaction

Metals appear in nature in their lowest energy state as an oxide. Aluminum, in particular, has a low electronegativity; due to this, when exposed to air, a 2-3 nm passivation layer of aluminum oxide ( $Al_2O_3$ ) immediately forms on its surface [9]. This is an intrinsic property of the metal that prevents corrosion and further oxidation in air. The metal-water reaction begins with

the induction phase during which the water attempts to penetrate through the oxide layer. The reaction occurs at the aluminum interface; the oxide layer must be compromised first. The length of the induction phase is a parameter dependent on the pH level and temperature of the water. The aluminum/aluminum oxide is the most reactive in solutions of the pH range 4-9 [30]. Higher temperatures decrease the length of the induction phase [30]. Hydrogen production begins once the water reaches the aluminum surface. The hydrogen production rate increases until it reaches a maximum value then begins to decline (see Figure 4). The production rate reaches zero when the oxide layer becomes too thick and inhibits the water from reaching the unreacted metal core. The reaction is then quenched and there is no hydrogen produced. The thickness of this oxide layer as the reaction stalls is called the penetration thickness [31]. Figure 4 exhibits the described reaction behaviour as illustrated in an experiment performed by V. G. Ivanov [32]; the numerical results are different than Yinon's experiment as they used particles of different nominal diameters, but the general trend of the reaction rate is the same.



Figure 4: Hydrogen Production vs. Time of Aluminum [32]

Metal-water reactions can take one of three paths dependent upon the reaction temperature. Each path reacts different stoichiometric ratios of aluminum to water and results in different solid oxides/hydroxides; this is illustrated in equations 8, 9, and 10. The different solid products are 2Al(OH)<sub>3</sub>, bayerite; AlO(OH), boehmite; and Al<sub>2</sub>O<sub>3</sub>, aluminum oxide; they are each the most stable products at their own temperature ranges [30].

$$2Al + 6H_2O \to 2Al(OH)_3 + 3H_2 + Q_1(871kJ) \quad T < 550K$$
(8)

$$2Al + 4H_20 \rightarrow AlO(OH) + 3H_2 + Q_1(846kJ) \qquad 550K < T < 750K \qquad (9)$$

$$2Al + 3H_20 \rightarrow Al_2O_3 + 3H_2 + Q_1 (817kJ) \quad T > 750K$$
(10)

All reactions produce the same amount of hydrogen, three moles per two moles of aluminum, and release heat of the same order of magnitude,  $15 MJ/kg_{Al}$ . The hydrogen producing capacity of aluminum-water reactions, considering that water is readily available, is approximately 11.2 wt% ( $0.112kg_{H_2}/kg_{Al} = 1.24L_{H_2}/g_{Al}$ ) [32]. The hydrogen produced can be combusted with air to generate more heat following the reaction given in equation 11.

$$H_2 + \frac{1}{2}(O_2 + 3.76N_2) \rightarrow H_2O + 1.88N_2 + Q_2 (241.83kJ/mol)$$
 (11)

The Gibb's energy of the reactions, at stoichiometric ratio is a negative value; this indicates spontaneous reaction even at room temperature. However, the previously mentioned thin layer of aluminum oxide ( $Al_2O_3$ ) that forms on the particle inhibits the reaction from occurring instantaneously. A table summarizing the heat of reaction and Gibbs free energy of aluminum-water reactions at different temperatures can be found in appendix A2.

### 2.2.1. Reaction Activation

Various methods can be used to activate the reaction. The purpose of each activation method is to compromise the oxide layer to allow the water to reach the aluminum surface to induce the reaction. Sodium hydroxide, NaOH has been experimentally proven to induce the reaction [29]. However, NaOH solutions are corrosive and may lead to corrosion of the reactor; this is undesirable. Salt promoters, such as NaCl and KCl compromise the oxide layer through producing localized pitting and rupture, activating the reaction [30]. Another method is through aluminum alloys; for instance, a gallium-aluminum alloy (20% gallium and 80% aluminum – by weight) prevents the oxide layer from initially forming. This allows the reaction to occur spontaneously. The oxide layer can also be mechanically removed through ball milling, grinding, cutting or drilling among other methods [28], [33], [34]. These methods are proven and successful; however, they require additional chemicals and instruments which will complicate the reactor design and increase expenses.

The preferred method to activate reactions is through raising the temperature of the reactor. Previous experiments have shown that at higher temperatures, metal-water reactions have high hydrogen production yield and rate [26]. As illustrated through Arrhenius equation, the reaction rate, k, is a function of temperature, T. In equation 12, *k* is the rate constant, A [1/s] is the frequency factor,  $E_A$  [J/mol] is the activation energy, R [J/K•mol] is the gas constant and T [K] is the temperature. In the following calculations, high temperature is used to activate and control the reaction parameters.

$$k = Ae^{-\frac{E_A}{RT}} \tag{12}$$

# ARRHENIUS KINETICS

Figure 5: Arrhenius Kinetics

As metal-water reaction is a surface reaction, the reaction rate is proportional to the surface area of the particle. Regardless of the size of the aluminum particle, the passivation thickness will be the same – resultantly, with smaller particle sizes, the total reaction time for the given mass will be shorter [35] Thus, it is the total surface area per volume, specific surface area, that determines the total hydrogen production potential. Larger specific surface areas increase the chemical activity of aluminum [36].

# CHAPTER 3

## Implementing Al-Water Reactions for Power Generation

### 3.1. Points of Application

Gas turbine engines today are used for various purposes and points of application. They are widely used in aviation, marine, and land transportation as well as in power generation. Different uses may present varying resources and operation conditions that may affect the efficiency, energy density or specific energy of the given engine. For instance, in marine transportation and stationary power generation, the reaction oxidizer, water, is not required to be carried on-board. This increases the specific energy and energy densities of the fuel; this is illustrated in Figure 1. These values are represented in equations 13 and 14, respectively.

$$\varepsilon_{m.f} = \frac{Q}{m} \left[ \frac{kW}{kg} \right] \tag{13}$$

$$\varepsilon_{v.f} = \frac{Q}{V} \left[ \frac{kW}{L} \right] \tag{14}$$

Q is the heat of reaction, m represents either  $m_{metal}$  or  $m_{mixture} = (m_{metal} + m_{water})$ , and V represents either  $V_{metal}$  or  $V_{mixture} = (V_{metal} + V_{water})$ . The volume, V, is the product of the mass and density,  $\rho$ , of the fuel/mixture.

When the mass/volume of both the metal and water are considered, a decrease in both specific energy and energy density can be observed.

### 3.2. Reaction Parameters

### 3.2.1. Vapour Pressure of Water

The aluminum-water reactor will receive both aluminum and water at a specific feed rate, this will control the mass flow rate of the reactants entering the reactor. The water will be collected from a reservoir and fed into a furnace/boiler via a high-pressure pump. The water reservoir will be kept around 20°C; the high-pressure pump will raise the pressure of the water to the desired level which will be then into a furnace to raise the temperature of the water to the desired reaction temperature. To ensure that the water remains in its liquid phase through its temperature increase, the pressure of the furnace must correspond to the saturation/vapor pressure of water at the given

temperature. The vapour pressure corresponding to different temperatures between 80 and 300°C can be found in appendix A3.

### 3.2.2. Hydrogen Production

Recalling the Arrhenius trend illustrated equation 12, reaction rate is exponentially related to temperature; this is also demonstrated in experiments plotted in Figure 6 below. Also recalling Figure 4, hydrogen production rate was a time dependent value due to the required reaction induction by penetrating through the passivation layer; the reaction rate we refer to here is the maximum hydrogen production rate. The induction time is also a temperature dependent value, decreasing with increasing temperature. As the reactor will have a constant inflow of reactants, it can be assumed to be at 'steady state' with the established outflow of generated hydrogen at the maximum flow rate. Figure 6 first plots the experimental flow rates presented in literature [26]; then, determining the exponential trend of the Arrhenius equation, the flow rates at high temperatures: 250°C, 300°C, and 350° are predicted. The activation energy is obtained through obtaining the slope of the resulting curve plotting the inverse of temperature and natural logarithm of rate as shown in Figure 7: Activation Energy, the activation energy of aluminum is found to be 65.5 kJ/mol. As for the hydrogen yield, there is a maximum theoretical hydrogen yield of 1249  $cm^3/g_{Al}$ ; this is assuming complete reaction and no loss of hydrogen. The trend projects the saturation temperature, the temperature at which 100% reaction completion is achieved, to be 207.1°C for aluminum powder, H-10 produced by Valimet, used in the particular experiment with a mean diameter of 13.3µm and specific surface area of 0.468 m<sup>2</sup>/g [26]. Figure 9 demonstrates increased hydrogen yield with increased temperature until it reaches the maximum value mentioned.



Figure 6: Temperature vs. Maximum Production Rate

This figure shows that the experimental results and projections are consistent with Arrhenius Kinetics



Figure 7: Activation Energy

The linear slope shows again that the results are consistent with Arrhenius Kinetics



Figure 8: Temperature vs. Reaction Time

A decrease in reaction/residency time is observed with increasing temperature. This is due to the increased hydrogen flow rates



Figure 9: Temperature vs. Hydrogen Yield Experimental and Projected

An increasing trend of hydrogen yield is exhibited until a theoretical maximum value is reached

### 3.2.3. Water to Aluminum Ratio

When operating at stoichiometric ratio, if the water boils or evaporates the reaction will never reach completion [34]. Here, it must be considered that operating in too much excess solution will require greater heat to keep the reactor temperature [29] – as well as the initial heat required to raise the water temperature. The water to aluminum ratio (by mass) will also affect the hydrogen production rate as illustrated in Figure 10. This graph corresponds to experiments performed by Rosenband and Gany with activated aluminum; however, similar trends are expected with inactivated reactions. With increasing water to metal ratios, the maximum hydrogen production rate will decrease. Smaller ratios may better employ the heat of the exothermic reaction to raise

the temperature of the water, accelerating the reaction [37]. This refers to Arrhenius kinetics which illustrates the exponential relation of temperature to reaction rate – recall equation 12.



Figure 10: The Effect of Metal-Water Ratio on Hydrogen Production Rate [34]

With increasing water – metal ratio, a decrease in hydrogen production rate can be observed in this figure

A fair balance between ensuring acceptable reaction completion, hydrogen production rate, and energy requirement to keep the reactor temperature must be evaluated for optimal operation. The energy required in operating the reactor – maintaining the desired reactor temperature and pressure, considers several parameters such as the particle size and the amount of solution present. As the metal-water reaction is an exothermic chemical reaction, the heat released may be used to control the reactor temperature and less external energy is required. However, in excess solution, more energy will be required to keep the same temperature [29]. Especially due to the high specific heat capacity of water, 4.182 J(/g K) at 20 °C and 5.65 J(/g K) at 300 °C (see appendix A4 for the

data of temperature dependent specific heat capacity of water), the energy required to raise and maintain the water temperature is extensive in water-rich reactions. At stoichiometric ratio, the heat required in proportion to the heat released by the reaction is only about 4%. There is an approximately linear increase in this ratio with increasing water-metal ratio; at water-metal ratio of 6, the ~27% of the heat released during the reaction is used to maintain the temperature of the reactor – these values can be obtained from the results shown in Figure 11. The calculations assume that the water is retrieved from a reservoir maintained at 20 °C.

Table 1 summarizes data from the NASA CEA code, an online software which evaluates chemical reactions with varying inputs, varying ratios of reactants in this case, to output thermodynamic properties of the reaction. It demonstrates that with increasing water-to-aluminum ratios, the internal energy, and thus, the heat of reaction shows a decreasing trend. The rate of reaction can be controlled through changing the temperature of the reactor in this manner – and a constant rate can be maintained through a controlled system with temperature feedback. It can be summarized that with increasing water-metal ratios, the heat of reaction decreases while the heat required to raise the temperature of the water increases.

H2O – Al Ratio	Internal Energy	Gibbs Free Energy of	Heat of Reaction	Entropy
	(kj/kg)	Reaction (kJ/kg)	(kJ/kg)	(kJ/kgK)
2 (stoichiometric)	-14658.0	-17539.7	-14512.4	6.3983
3	-14157.2	-17649.8	-14157.2	7.3815
4	-14118.7	-17707.8	-13944.0	7.9546
6	-13887.7	-17767.0	-13700.6	8.5943

Table 1: The Effect of Water-Al Ratio on various Thermodynamic Variables at

### 200°C



Figure 11: Water-Al Ratio vs. Heat Released/Required at 210°C with Data from

NASA CEA

### 3.2.4. Reactor Size

To power engines of different sizes, the amount of required aluminum varies. For instance, to power the 66 MW Industrial Trent 60, assuming complete reaction and hydrogen combustion, approximately 2.12 kg of aluminum is need per second. Operating at twice the stoichiometric ratio, to ensure complete reaction, 8.52 kg of water is needed every second. Dependent on the reactor operating temperature, the residence time varies as illustrated in Figure 8; this directly affects the required size of the reactor.

The first investigation sets the reactor operation temperature at 200°C as the reaction parameters under this temperature have been empirically obtained. At this temperature, the residence time is 22.58 seconds with ~92% reaction completeness [26]. Taking this into account, to power the Industrial RB211 engine with power rating of ~33 MW, 1.17 kg<sub>Al</sub>/s and 4.66  $_{\rm H20}$ /s must be input to the engine. This requires the reactor volume of 114,570 cm<sup>3</sup>; if the reactor were perfectly cubic, each side would be approximately 49 cm long.

On the other hand, if the reactor operates at 210°C, 1.07 kg<sub>Al</sub>/s and 4.28 kg<sub>H20</sub>/s are required; at this temperature, 100% reaction completeness is expected. The residence time at 210°C is 19.6 seconds. To power the Industrial RB211, the required reactor volume is 91,360 cm<sup>3</sup>. On the other hand, at the same temperature, to power the 66 MW Industrial Trent 60 and the 329 MW, heavy duty SGT5-4000F, the required reactor volumes are 181,630 cm<sup>3</sup> and 905,390 cm<sup>3</sup>, respectively. On the other hand, to power the SGT5-4000F engine at 350 °C, only 5,620 cm<sup>3</sup> reactor volume is required. The increased temperature decreases the residency time and resultantly, the reactor size (see Figure 12).



Figure 12: Temperature vs. Reactor Size

This figure shows that with decreasing power ratings and increasing reactor operation temperatures, reactor sizes decrease

### 3.3. Thermodynamics Cycle

A comprehensive illustration of the implementation of the aluminum-water reactor in a power generation device is explored. Several important parameters that will allow an understanding of this noble technology include: the type of thermodynamics cycle used and the reactor operation conditions. An aluminum-water reactor and hydrogen combustor will replace the boiler of a typical Brayton cycle; this is the thermodynamic cycle employed in typical gas-turbine engines. The heat of reaction from the aluminum-water reaction as well as the heat of combustion of the hydrogen produced will contribute to the total power output. Reactor operation conditions

include: temperature, pressure, and water and aluminum feed rates. The water will be pumped from a reservoir kept at approximately 20°C. The reactor temperature and pressure must be carefully controlled to ensure that the water, as oxidizer, must remain in its liquid state. For this reason, the reactor will operate at temperature and pressures below the critical point of water (373.95°C and 22,060 kPa). Above the critical point, the phase of water cannot be controlled by temperature or pressure alone. This is as water, and any other molecule, exhibit different properties at different phases; this work focuses on reactions of metal and liquid water. Figure 13 shows the T vs. v and P vs. v diagram of water, the reaction must occur in the region to the left of the vapor dome in the compressed liquid region, on the saturation liquid curve, or in the left part of the dome.



Figure 13: T vs. v & P vs. v Diagram of Water



Figure 14: Typical Brayton Cycle

The schematic of the thermodynamics system is shown in Figure 15, the following steps can be referred to in this figure. The water from the reservoir will be pumped through a high-pressure pump to the required pressure of the aluminum-water reactor. This will be the saturation pressure of water reactor operation temperature. For instance, reactor temperature of 210 °C requires a pressure of 1907 kPa – this is discussed in section 3.2.1. Then, in step 2, together with aluminum powder, the water enters the reactor for the chemical reaction to take place. The reactor is kept at the required reactor temperature. Through a filtration system, the metal oxide/hydroxide is collected for later refinement and potential reuse. The produced hot hydrogen will then enter a hydrogen turbine connected axially to a generator to produce the power resulting from the first reaction. This process is required to control the temperature of the hydrogen entering the hydrogen turbine temperature of approximately 620 °C for safe operation is estimated. The exhaust steam exiting the hydrogen turbine in step 5 will enter a hydrogen combustor together with the precompressed air. The maximum steam turbine temperature limits the hydrogen combustor entrance

temperature at approximately 290 °C. Following the combustion reaction, steam exits the combustor to enter the steam turbine connected axially to the second generator. The turbine exit pressure is equivalent to that of the condenser – in which the exhaust steam is condensed to form a closed cycle. The cycle is analyzed assuming steady operations and that kinetic and potential energies are negligible.

$$\eta_{carnot} = 1 - \frac{T_C}{T_H} \tag{15}$$

Carnot efficiency is the maximum efficiency that a cycle can achieve and is illustrated by equation 15. It indicates that to maximize efficiency, the highest temperature ( $T_6$ ) must be as high as possible and the lowest temperature ( $T_7$ ) must be as low as possible.



Figure 15: Thermodynamics Cycle Implementing Al-Water Reactor

Higher cycle efficiency is achieved as well through higher reactor temperatures. Power cycle analyses were performed at two different temperatures: 210 °C and 350 °C. The temperature and pressures at each of the steps are summarized in Table 2 and Table 3. Hydrogen is treated as an ideal gas in the calculations. Higher reactor temperature, of 350 °C was able to achieve a higher efficiency of 53.8% than a reactor operating at 210 °C – which achieved an efficiency of 40.4%. The analysis assumes the pump and boiler efficiencies of 90% and turbine efficiency of 85%. Both the hydrogen combustor and aluminum-water reactor were assumed to have 100% efficiencies.

Step	Temperature (ºC)	Pressure (kPa)
1	20	2.34
2	20.5	1,907
3	210	1,907
4	971.8	1,907
5	290	4,215.8
6	621	4,215.8
7	20	2.34

Table 2: Cycle temperatures and pressures of reactor operating at 210 °C

Table 3: Cycle temperatures and pressures of reactor operating at 350 °C

Step	Temperature (ºC)	Pressure (kPa)	
1	20	2.34	
2	23.9	16,500	
3	350	16,500	
4	856.4	16,500	
5	290	5 <i>,</i> 587	
6	621.4	5 <i>,</i> 587	
7	20	2.34	

For this analysis, three engines of different power outputs are explored: Siemens Industrial Trent 60 gas turbine (SGT-A65TR), Industrial RB211 (SGT-A35RB) engine, and heavy duty gas turbine SGT5-8000H. Trent 60 has a power rating of 66 MW [23]. It is a three-spool engine comprised of a low, intermediate, and high-pressure compressor - turbine system. The RB211 is a two-spool engine with a maximum power output of 33.2 MW [24] SGT6-5000F, a core component of gas power plants, has a gross power output of 329 MW [38]. Between the compressor and the turbine is a combustor with a fuel intake value - all engines generally use natural gas fuel. In employing the alternative fuel concept, the combustor will be replaced by an aluminum-water reactor, hydrogen turbine, and hydrogen combustor, this is illustrated in Figure 15. In this two-stage power generation scheme, there are two fuels and two oxidizers. In the aluminum-water reactor, the aluminum is the fuel and the water is the oxidizer. The product of this reaction, hydrogen, becomes the fuel in the hydrogen combustor with air as the oxidizer. The reactor will have a filtration and solid oxide collector system to capture the solid products of the metal-water reaction. The captured solid products can be recycled to be reused in an equivalent system.

### 3.3.1. Increasing the Efficiency

Efficiency is the ratio of total power output to total required heat input. Some of the heat generated from the aluminum-water reaction can be used to preheat the water exiting the reservoir as illustrated in Figure 16 to decrease the required heat input in the system. Often, regeneration is used in Rankine cycles to increase the efficiency of the system. The concept shown in Figure 17 adopts a similar concept. The multistage turbine is implemented in the system, a fraction of the flow after the first expansion is routed to a heat exchanger/feedwater heater where it transfers some

of its heat to the water exiting the reservoir. The two streams will later meet in a mixer before entering the cycle together in the furnace. A regenerative cycle is generally able to increase the overall power output by approximately 5% in a steam powerplant – similar results are expected for this cycle.



Figure 16: Aluminum - Water Reactor with Heat Exchanger 1



Figure 17: Aluminum-Water Reactor with Heat Exchanger 2

# CHAPTER 4

# **Comparative Analysis**

One of the three requirements of the alternative fuel is that it must have low carbon emissions. In this section metal-water fuels are weighed against fossil fuels in terms of its carbon emission.

To perform a full analysis, each fuel source is analyzed from the beginning of its production to the end– from extraction to refinement, storage, transportation, and post processing or recycling of the reaction products.

### 4.1. Carbon Cost Analysis

The novel fuel to replace today's fossil fuels must produce low to no carbon emissions. The carbon footprint of aluminum-water fuel is compared to that of fossil fuels. The measure of unit used in this analysis will be  $g_{CO_2e}/kWh$  of energy produced. Carbon dioxide is not the only pollutant involved in obtaining, processing, and utilizing the source of fuel. Other significant emissions include perfluorinated carbon (PFG) emissions -  $CF_4$  and  $C_2F_6$  produced during the smelting process of aluminum – this is a significant greenhouse gas emission contributor - as well as carbon monoxide (CO) and hydrogen fluoride (HF). This comparative analysis evaluates the environmental effects of each fuel source and all different pollutants must be considered – all emissions are represented as CO2 equivalents. This is established through the "global warming potential (GWP)" of each fuel.

### 4.1.1. Carbon Emission of Fossil Fuel Combustion

Coal has been the primary fossil fuel used in power generation stations; however, to reduce carbon emissions, the industry moved toward using 'cleaner fuels' such as natural gas. Natural gas is the primary fuel for all gas turbines explored in this research. As illustrated in Figure 18 and Figure 19, both the energy demand and generation of natural gas is expected to rise while that of most other fuels including oil, and coal is expected to decline. These projections are provided by the National Energy Board based on data collected since 1967 [39]. Consequently, Natural gas provides the baseline for this carbon cost analysis. Natural gas power plants produces 35 - 66% less carbon emissions than coal-fired power plants [40].



Figure 18: Primary Energy Demand 2014 vs. 2040 (Projected)<sup>1</sup>



Figure 19: Past and projected Energy Generations by Fuel

The processes associated with natural gas usage are: natural gas recovery/extraction, processing, transportation, storage and finally combustion [41].

<sup>&</sup>lt;sup>1</sup> https://www.neb-one.gc.ca/nrg/ntgrtd/ftr/2016/index-eng.html#s6

Conventional natural gas can be extracted through drilling vertical wells and allowing the natural gas to rise to the surface. Unconventional natural gas such as shale gas, tight gas sandstone and coalbed methane are extracted rather through horizontal wells or hydraulic fracturing. Tight gas sandstone production is expected to provide 76% of the total natural gas production by 2040 as illustrated in Figure 20 [39]. This is the extraction method used in this analysis.



Figure 20: Natural Gas Production by Type

The carbon cost associated with the upstream processes using Tight Gas extraction is  $0.032 kg_{CO_2e}/kWh$ ; this involves all processes from extraction to delivery of the fuel to the power generation station, prior to combustion [42]. The contribution of each step is illustrated in Figure 21: Natural Gas  $CO_2e$  Emissions.



Figure 21: Natural Gas CO<sub>2</sub>e Emissions

Significant emissions from the extraction process is associated with well construction, completion, and workovers as well as valve fugitive emissions. Notable carbon costs in the processing step involves acid gas (hydrogen Sulfide) removal and compressors usage. Natural gas is largely composed of methane which has a high GWP (100 year) of 25. Venting and flaring also emits significant amounts of methane in both the extraction and processing steps of natural gas production. Natural gas is transported through a large network of pipelines and emissions associated with this step include pipeline construction, fugitive emissions (leakage) as well as natural gas compressors. The most significant GHG contribution is from the energy conversion process at  $0.683 kg_{C0_2e}/kWh$  [42] – this is the average emission of a single cycle gas turbine power plant. The total carbon emissions related with natural gas-powered power plants is  $0.715 kg_{C0_2e}/kWh$  - this analysis was performed on a single cycle gas turbine with the power output of 360 MW (similar rating as the SGT5-4000F used in our model).

### 4.1.2. Carbon Cost of Aluminum Fuel

The upstream values involved with utilizing primary aluminum fuel involve extraction and refinement of bauxite to alumina through the Bayer process. Following, using the energy and carbon intensive Hall-Héroult method, alumina is electrolytically reduced to aluminum. Molten aluminum is then casted into ingots. The ingots are then atomized into micro powders using the commercial inert gas atomization (CIGA) method. Transportation of bauxite from the mine to the refinery and that of the ingots from the smelter to the atomization plant are also involved in the upstream carbon emission. The total carbon emissions of primary aluminum fuel usage is summarized in Figure 22.

Rio Tinto Alcan, a Montreal based company, is a world leader of aluminum mining and production. The company owns various Bauxite mines in countries like Australia, Brazil, and Jamaica. The mining process emits 0.085 kg<sub>CO2e</sub>/kg<sub>Al</sub> [43]. This analysis assumes bauxite is imported from Australia and refined in Quebec. The mineral is mined in Weipa, located just 19 km of railway away from the port. From the Weipa port, the freight is shipped approximately 15,000 km to Sept-Îles Port. From the port, bauxite is transported via Rio Tinto operated railway to the refinery located 39 km away. The total transportation cost is approximately 0.825 kg<sub>CO2e</sub>/kg<sub>Al</sub>. The large transportation emission is due to the great distance the bauxite must be travel – additionally, 5.10 kg of Bauxite is required to produce 1 kg of aluminum, adding significant weight to the freight. The transportation emissions are calculated using an online GHG calculator provided by CN [44].



Figure 22: Carbon Emissions Associated with Aluminum-Water Fuel

Aluminum Alouette, located in Sept-Îles, Quebec, is the leading aluminum manufacturer of the Americas – here Bauxite, then alumina are refined to produce primary aluminum, the refinement process produces 1.626 kg<sub>CO2e</sub>/kg<sub>Al</sub> contributing to 90.4% of the total emissions. The Hall-Héroult process requires a great amount of electricity, 5.38 kg<sub>CO2e</sub>/kg<sub>Al</sub> is emitted in generating this electricity [43]. This assumes 64% of the electrical power utilized to be hydroelectricity [43]. This is an extrinsic emission, the high carbon cost is due to today's high carbon economy. If the smelters were to operate using electricity generated from clean sources such as wind, solar, water, the refinement process can be significantly reduced. Primary aluminum is first casted into ingots emitting 0.238 kg<sub>CO2e</sub>/kg<sub>Al</sub> [43], this is also an extrinsic emission.

Primary casted ingot can then be transported to Toyal, an Alcan partner located in Illinois, to be atomized into powder form - this process emits about 5.7  $kg_{CO2e}/kg_{Al}$  [45].

The aluminum-water reaction only produces water, heat, and hydrogen; there are no carbon emissions associated with this step. The hydrogen combustion in air; however, produces Nitrous oxide -this greenhouse gas has a GWP of 298. Combustion with pure oxygen yield only water as its by-product – making this a zero-emission process, this analysis assumes pure oxygen combustion.

Primary aluminum production contributes a high amount of carbon emission due to the energy intensive as well as the high carbon emitting Hall-Héroult process. However, aluminum is an infinitely recyclable material. Approximately 33% of the annual aluminum production is from recycled aluminum [10]. In using secondary aluminum, the Bayer process to refine bauxite and

the Hall-Héroult method can be eliminated. The carbon emissions in producing secondary aluminum is only 5% in comparison to that of primary aluminum [43]. Secondary ingot casting emits 0.58 kg<sub>CO2e</sub>/kg<sub>Al</sub>, this value accounts for the melting, refining, and recasting of the recycled aluminum. This is an extrinsic carbon emission resulting from the electrical energy requirement. The life cycle emissions of aluminum-water fuel using secondary aluminum is 43% of that of the emission when using primary aluminum; this is illustrated in Figure 23.

In 2014, 55% of Canada's energy demand was met by hydro/wave/tidal electricity [39]. In reactor operation, assuming 55% of the required energy is be met by hydroelectricity and the remaining 45% from a coal powerplant. The carbon emission due to reactor operation would be  $0.559 \text{ kg}_{\text{CO2e}}/\text{kg}_{\text{Al}}$ . If operated using clean energy, this can be a zero carbon emitting step.

Figure 23 also demonstrates the effect of reactor temperature on the total carbon dioxide equivalent emission of aluminum-water fuel. This is the result of reaction completion, or otherwise efficiency, of the reactor; at temperatures greater than 210 °C, the reactor is estimated to operate with 100 % efficiency, requiring less metal for the same amount of power produced as a reactor operating at 200 °C.



Figure 23: CO2 Equivalent Emissions of Aluminum-Water Fuel at Different Reactor Temperatures and Type of Aluminum

In comparing Aluminum-water to our baseline fuel, natural gas, when operating at 200 °C utilizing primary aluminum, aluminum-water fuel will emit 2.037 kg<sub>CO2e</sub>/kg<sub>Al</sub>, 2.85 times the amount of carbon emission as natural gas. However, upon operation at 210 °C or above, using secondary aluminum, the total emission will equate to 0.802 kg<sub>CO2e</sub>/kg<sub>Al</sub>, only 1.12 times that of natural gas. Another major different between natural gas and aluminum-water carbon emission is the distribution of carbon emission contribution throughout its life cycle. For natural gas, 95.5%

of its total carbon emission is due to combustion during power generation. For aluminum, for both primary and secondary aluminum, the largest contribution at 90 and 91 %, respectively, is from processing.

It is worth noting that most of the carbon emissions related to aluminum production and usage is extrinsic; the emissions result from the today's high-carbon economy. On the other hand, natural gas has a lot of intrinsic carbon emissions due to the fugitive releases as well as the required flaring and venting processes. This allows room for a significant carbon emission reduction through powering the refineries with clean energy. In doing so, the carbon emission of aluminum fuel will be a fraction of natural gas.



Figure 24: Carbon Emission Distribution of Natural Gas



Figure 25: Carbon Emission Distribution of Primary Aluminum



Figure 26: Carbon Emission Distribution of Secondary Aluminum

# Conclusion

Aluminum is investigated as a potential fossil fuel replacement for its reactive properties upon reaction with water. This source of fuel is highly energetic, produces low carbon emissions, and is a safe energy carrier, meeting all three requirements of a novel alternative fuel. Previous research indicates increased reaction completeness, hydrogen yield, and hydrogen production rates at increased temperature. This translates to smaller reactor sizes, thus increased power densities of high temperature reactors. This work exhibits increased cycle efficiency of a system of high temperature operating reactors. Additionally, a potential thermodynamics cycle employing an aluminum-water reactor connected in series with a hydrogen turbine and a steam turbine is proposed. A regenerative system involving a multi-stage turbine and closed feedwater heater is suggested to improve the efficiency of the cycle. The carbon cycle analysis concludes that using primary aluminum will yield similar emissions as oil combustion while secondary aluminum usage will result in similar carbon emissions as natural gas. However, when compared to natural gas, aluminum fuel has less intrinsic carbon emissions. In utilizing electricity generated using clean energy sources such as wind, solar, etc. to power the refineries, the extrinsic carbon emissions will decrease, making the overall process more carbon efficient. Another important advantage of aluminum fuel is that it is an infinitely recyclable material; this source of fuel will never reach depletion. Overall, aluminum - water fuel exhibits great potential as an energetic, clean, and sustainable fuel.

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Table 1 – Metal powders used in the study, including their specific surface area (acquired using BET method), Sauter mean diameter (d <sub>32</sub> , acquired using Malvern) and metal density.					
Metal	Symbol	Powder name	Specific surface area [m²/g]	d <sub>32</sub> [μm]	Metal density [g/cm <sup>3</sup> ]
Boron	В	B-3135	3.793	1.1	2.37
Magnesium	Mg	MG-101	1.290	15.6	1.74
Aluminum	Al	H-10	0.468	13.3	2.70
Silicon	Si	SI-100	1.128	6.6	2.33
Titanium	Ti	TI-104	0.246	20.2	4.51
Chromium	Cr	CR-102	2.918	1.9	7.15
Manganese	Mn	MN-101	0.671	6.6	7.30
Iron	Fe	FE-102	0.254	19.6	7.87
Nickel	Ni	NI-124	0.008	56.7	8.91
Copper	Cu	CU-115	0.077	30.3	8.96
Zinc	Zn	ZN-101	0.934	6.2	7.14
Selenium	Se	R-130-2	0.607	8.4	4.81
Zirconium	Zr	ZR-105	0.105	241.0	6.52
Molybdenum	Мо	MO-102	0.206	18.7	10.20
Tin	Sn	SN-103	0.060	128.0	7.26
Tungsten	W	WP-103	0.075	15.1	19.30

Figure 27: Specimen Details for Comparative Studies Experiment [26]

Table 4: Temperature vs. Gibbs Free Energy According to Data from NASA CEA

### Temperature **Heat of Reaction** Sat. Pressure **Gibbs Free Energy of** Reaction $(^{o}C)$ (kPa) Reaction (kJ/kg) (kJ/kg) Path 25 104.2 -17100.0 -15830.7 Equation 8 202.4 -17233.9 -14755.7 Equation 8 100 200 1554.9 -17539.7 -14512.4 Equation 8 300 8587.9 -17669.0 Equation 9 -14734.1 22,064 -17895.1 -14594.6 Equation 9 373.95

### Online Software



Figure 28: Temperature vs. Vapor Pressure of Water [46]

Temperature	Specific Heat
T (°C)	c_p (kJ/(kg K))
10	4.192
20	4.182
30	4.178
40	4.179
50	4.182
60	4.185
70	4.191
80	4.198
90	4.208
100	4.219
110	4.233
120	4.248
130	4.27
140	4.29
150	4.32
160	4.35
170	4.38
180	4.42
190	4.46
200	4.51
220	4.63
225	4.65
240	4.78
250	4.87
260	4.98
275	5.2
300	5.65
325	6.86
350	10.1
360	14.6

Figure 29: Specific Heat of Water as a Function of Temperature [46]