Abstract

In the face of climate change, the world is looking to new fuel sources to meet the surging global energy demand. Hydrogen has been proposed as a promising energy vector being both a net-zero carbon emitter and having one of the highest gravimetric energy densities of known fuels. Production of hydrogen, however, is difficult with many of the technologies which exist today failing to be economically feasible or environmentally sustainable. Smouldering has recently been developed as a cost effective and energy efficient technology for destruction of organic wastes. The unique reaction zones created within a smouldering system have the potential to generate hydrogen if properly amended. For the first time, organic wastes were treated by an amended smouldering reaction to generate hydrogen. Calcium Oxide (CaO) and steam were added to the smouldering system which completely treated woody biomass and coal tar while generating hydrogen. The maximum hydrogen concentration achieved in the smouldering system was 33.7% resulting in a net energy positive syngas. Evidence suggests that both heterogenous gasification and the water gas shift are the mechanisms of hydrogen formation. Results indicate that a smouldering reaction can be used simultaneously as both a waste management technology and a new method for producing hydrogen-rich syngas.

Keywords

Hydrogen, Remediation, Waste Management, Smouldering, STAR, Biomass, Syngas, Gasification

Summary for Lay Audience

Fossil fuels such as coal, oil and gas have been the predominant source of energy used for the past 150 years. Exploiting this resource has brought about many major advances in human civilization, industrializing our world as well as connecting it with transportation fuels and providing electricity from power plants. The primary means of extracting energy from fossil fuels involves burning them which releases CO_2 and other greenhouse gases. Unfortunately, a legacy of burning fossil fuels has resulted in greenhouse gases slowly accumulating in the atmosphere. As their name suggests, these gases act much like a greenhouse reflecting heat energy back towards the surface of the earth causing warmer temperatures. Numerous studies have documented a warming climate causing extensive environmental damage both on land and at sea. As the main contributor to greenhouse gas emissions, the use of fossil fuels needs to be dramatically reduced and new sources of energy need to be used.

The modern world requires a tremendous amount of energy to sustain it making it extremely important to identify new sources of energy which can be green replacements for fossil fuels. Hydrogen is a gas which can also be used like a fossil fuel to generate energy except that it doesn’t produce any greenhouse gases. Hydrogen is difficult to manufacture effectively, though. STAR is a method of destroying many waste products which often cannot be treated by other technologies. Interestingly, the STAR process contains a reaction zone which could be conducive to generating hydrogen under the right conditions. This research explored, for the first time, amending the STAR process to not only destroy wastes, but also generate hydrogen. A low carbon intensity, waste-to-energy system was created as a new means to produce hydrogen.

Co-Authorship

This Thesis was written in accordance with regulations and guidelines set by the Faculty of Graduate and Postdoctoral Studies at the University of Western Ontario. All experiments and data were designed, conducted, collected, analyzed, and interpreted by the candidate under the supervision and guidance of Dr. Jason I. Gerhard. The candidate wrote the thesis and was the lead author on the manuscript chapter, which is expected to be submitted for publication:

Chapter 3: Hydrogen-Rich Syngas Derived from Smouldering Biomass and Hydrocarbon Wastes

By Joshua K. Brown and Jason I. Gerhard

Joshua K. Brown: developed the experimental program, designed equipment to be manufactured for the experiments, performed all laboratory experiments, analyzed and interpreted all results, and wrote the draft chapter.

Jason I. Gerhard: initiated the research topic, supervised experiments, assisted in data interpretation, and reviewed/revised the draft chapter.

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Chapter 1

1 Introduction

1.1 Problem Overview

The world is currently at a crossroads of environmental stewardship and energy supply. Based on the current demand, it is projected that the world will require 50% more energy by 2050 than it is using presently (U.S. EIA et al., 2021). Fossil fuels have satiated the majority of energy demand since industrialization occurred in the late 1800s. As such, fossil fuels have been exploited at an increasing rate year over year. As recently as the last decade (2009-2019), 80% of the global energy consumption was met by fossil fuels (REN21, 2021).

A legacy of poor environmental practices from the fossil fuel industry has led to a plethora of heavily contaminated sites around the world (Bhuiyan et al., 2010; Y. Han et al., 2018; Reisen et al., 2017; Soares et al., 2020a, 2020b; Williams et al., 2011; Wright et al., 2017). Rampant, burning fossil fuels over the past 150 years, however, has released greenhouse gases into the atmosphere which began warming the planet and leading to an anthropogenic climate change (IPCC et al., 2021). The concentration of CO_2, one of the major greenhouse gases emitted from burning fossil fuels, has increased 148% from pre-industrial levels (WMO, 2020). Greenhouse gases reflect infrared radiation back to earth's surface resulting in warmer temperatures (WMO, 2019). As their concentration increases in the atmosphere, so does the amount of heat which is reflected and retained. Since industrialization, the average global temperature has increased almost 1.1°C (IPCC et al., 2021). Though seemingly small, a temperature increase of this magnitude over such a brief time period has not been observed in the past 2000 years (IPCC et al., 2021).

The environmental effects of a warming climate are widespread and damaging. Weather extremes have become more prevalent with increased hurricane intensity (Holland & Bruyère, 2014), increased heavy precipitation and flooding events (Dore, 2005; Rosenzweig et al., 2002). Severe droughts have also become more common (Dore, 2005;

IPCC et al., 2021; O'Gorman, 2012; Trenberth, 2011) contributing to an increase in forest fires (Flannigan et al., 2000; Pitman et al., 2007). Aquatic environments have been particularly affected by the increased global temperature which has resulted in ocean warming and acidification (IPBES et al., 2019; IPCC, 2019; IPCC et al., 2021; Purkey & Johnson, 2010; WMO, 2020), as well as destruction of wetlands and coastal communities (Dinan, 2017; Weston, 2014; Yu et al., 2019).

Climate change is not only a looming environmental disaster, but also a serious economic issue. In the past 40 years, the effects of climate change have likely cost Canada $31 billion dollars (Warren et al., 2021). Climate change disproportionately affects poorer nations and could cost up to $23 trillion globally by 2050 (Guo et al., 2021) if efforts are not made to reduce greenhouse gas emissions. With energy demand surging and fossil fuel use needing to be reduced, new energy sources are needed.

H_2 is recognized as a potential green fuel of the future which could replace fossil fuels (Clark & Rifkin, 2006; Muradov & Veziroğlu, 2005, 2008; Pudukudy et al., 2014). H_2 has one of the highest gravimetric energy densities and is a net-zero greenhouse gas emitter when utilized. H_2 is difficult to produce economically and in an environmentally friendly way (Shiva Kumar & Himabindu, 2019). Three major technologies are currently used to produce hydrogen which are Steam Methane Reforming (SMR), Gasification, and Electrolysis. All three technologies struggle to be either green (SMR) or economically viable (Gasification and Electrolysis).

Smouldering is a unique form of combustion where the oxidant, typically air, heterogeneously reacts with a condensed phase fuel (Ohlemiller, 1985; Rein et al., 2009; Switzer et al., 2009). Charcoal burning in a conventional barbeque is a familiar example of a smouldering reaction. The nature of the smouldering reaction results in thermal zones preceding the oxidation reaction which include, inert heat, boiling, and pyrolysis (Rein, 2009; Torero et al., 2020). These thermal zones share many similarities with gasification, a hydrogen-producing technology. Smouldering distinguishes itself from many other thermal technologies because it can be self-sustaining after a brief ignition event. The smouldering reaction is resistant to quenching because heat released from smouldering is efficiently captured by the matrix allowing it to store energy and propagate the reaction (Zanoni et al., 2019). Perturbations to the system can therefore be better tolerated (Yerman et al., 2015) and feedstocks which are generally incompatible with other thermal technologies (Incineration, Gasification, etc.) can often be directly utilized by smouldering.

Smouldering has been developed as a technology to treat recalcitrant, contaminated soils (Grant et al., 2016; Pironi et al., 2011; Scholes et al., 2015; Switzer et al., 2009) as well as a waste management technology (Duchesne et al., 2020; Rashwan et al., 2016a; Sabadell et al., 2019; Solinger et al., 2020). The technology is maturing with significant research into defining its limitations and improving the process (Duchesne et al., 2020; Pironi et al., 2011; Rashwan et al., 2016a; J. Wang et al., 2021; Zanoni et al., 2019). Despite the advances in smouldering as a waste treatment technology and its similarity to gasification, little effort has been made to extend the technology as a means of H_2 production. Adapting methods traditionally utilized in gasification to smouldering is hypothesized here, for the first time, as a new means of generating H_2.

1.2 Research Objective

The objective of this work is to determine how an engineered smouldering reaction used to treat organic wastes could be manipulated to generate meaningful quantities of H_2. To achieve this, a suite of laboratory scale experiments were conducted to evaluate the effects different amendments had separately and together on H_2 production from smouldering. Coal tar and woody biomass were the primary feedstocks. Calcium oxide (CaO) and steam were the primary reaction amendments explored. The feedstock, amendments, and process parameters were adjusted until the production of H_2 gas was maximized. Detailed analysis of the emission products was conducted to determine the reaction efficiencies and mechanisms involved in the process.

1.3 Thesis Outline

This thesis is written in an integrated article format in accordance with the guidelines and regulations stipulated by the Faculty of Graduate Studies at the University of Western Ontario. Each chapter in the thesis is described below.

Chapter 2 is a review of the relevant literature and presents an overview of the current issues facing the climate and global energy supply. Hydrogen as an energy vector is presented and the predominant means of H_2 production are reviewed in the context of their process and feasibility. An introduction to smouldering combustion is included with an emphasis on the chemistry of the process. Further review of smouldering as an applied technology and the ability to modify the reaction is also presented.

Chapter 3 presents the results from laboratory scale experiments exploring the ability to amend a smouldering reaction to generate H_2 from the destruction of organic wastes. This chapter is written in a manuscript format for future submission to a peer-reviewed journal.

Chapter 4 summarizes the research conducted and the conclusions drawn from this work. Recommendations for further work are included.

Appendix A presents additional methodology details.

Appendix B presents the full experimental conditions for the entire suite of experiments.

Appendix C presents the full results for the entire suite of experiments.

Appendix D presents the temperature, emissions, and energy profiles for the focused experimental suite analyzed in Chapter 3.

Appendix E presents additional discussion on H_2 formation from a water-saturated system.

Appendix F presents additional discussion on H_2 formation from a N_2/Air cycled experiment.

Appendix G presents a picture of the experimental apparatus used in this study.

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Chapter 2

2 Literature Review

2.1 Introduction

The world we live in today has been built off of the energy we have been able to harvest from fossil fuels. Exploitation of coal, oil and natural gas over the past 150 years has brought about the industrial revolution and globalized our society. Our dependence on fossil fuels, however, has come at the expense of our environment. Mining coal and extracting oil and gas has caused both acute environmental emergencies as well as a legacy of contaminated industrial sites and lagoons of sludge with few remedial options (Bhuiyan et al., 2010; Y. Han et al., 2018; Reisen et al., 2017; Soares et al., 2020a, 2020b; Williams et al., 2011; Wright et al., 2017). Though the damage imparted to the land and sea through extracting fossil fuels is extensive, burning them for energy has been slowly bringing on a new environmental peril by gradually increasing the carbon dioxide (CO_2) in the atmosphere (IPCC et al., 2021). CO_2 acts as a greenhouse gas which reflects heat in the form of infrared radiation reaching the atmosphere back to the surface of earth, thus increasing temperatures and promoting climate change (WMO, 2019).

The effects of climate change are being actively documented and studied. All indications are that climate change is causing irrevocable damage to both aquatic and terrestrial environments (IPBES et al., 2019; WMO, 2020). Moreover, it poses a substantial risk to many countries and communities as extreme weather, drought, and forest fires become more frequent and more severe (IPCC et al., 2021). It is estimated the cost of climate change could be as high as $23 trillion globally by 2050 (Guo et al., 2021) with much of the damage occurring in the poorest nations (Guo et al., 2021; IPBES et al., 2019; IPCC, 2019). In Canada, alone, it is estimated climate change has cost $31 billion over the past 40 years (Warren et al., 2021).

Global energy demand is expected to increase by 50% by 2050 (U.S. EIA et al., 2021) and fossil fuels have accounted for approximately 80% of the global energy supply over the past decade (REN21, 2021). New energy mediums are being actively explored to curtail the use of fossil fuels and create a greener energy economy capable of meeting surging demand. Hydrogen (H_2) is a prime candidate as it has a high energy density and doesn't produce any carbon emissions (Scott, 2019). H_2, however, is difficult to generate. Three major technologies exist to produce hydrogen which are Steam Methane Reforming (SMR), Gasification, and Electrolysis. All three technologies struggle to be either green (SMR) or economically viable (Gasification and Electrolysis).

Smouldering has been applied recently as a technology (STAR) to remediate contaminated soil (Grant et al., 2016; Scholes et al., 2015) and eliminate recalcitrant wastes (Duchesne et al., 2020; Pironi et al., 2011; Sabadell et al., 2019; Solinger et al., 2020; Switzer et al., 2009). Strides have been made which control the technology and prove its ability to handle a variety of feedstocks which are otherwise problematic for competing technologies (Duchesne et al., 2020; Rashwan et al., 2016b). The smouldering reaction offers unique reaction zones which could be conducive to producing H_2 in an energy positive manner. This chapter presents the relevant background literature to frame the scope of the problem and provide evidence that STAR-based smouldering could be adapted to a H_2 production technology.

2.2 Climate and Energy

2.2.1 Energy Demand and Climate Change

The world is currently facing crisis as the global demand for energy surges, but further exploitation of traditional fossil fuel sources must be reduced. From 2009 to 2019, fossil fuels have accounted for 80.2-80.3% of the global energy consumption (REN21, 2021) and projections indicate nearly a 50% increase in global energy usage by 2050 (U.S. EIA et al., 2021). Fossil fuels can no longer be relied on for the world's swelling energy needs as burning them over the past 150 years has led to a hitherto unseen increase in global temperatures (IPCC et al., 2021). Fossil fuel emissions, the most notable being CO_2, are greenhouse gases which reflect heat in the form of infrared radiation reaching the atmosphere back to the surface of earth, thus increasing temperatures and promoting climate change (WMO, 2019). As of 2019, the concentration of atmospheric CO_2 has increased by 148% from pre-industrial levels (WMO, 2020). Currently, the global temperature is approximately 1.07°C warmer than it was in the 1800s (IPCC et al., 2021).

The effects of a warming climate have already manifested in numerous ways and the intensity and breadth of these effects will only increase if temperatures continue to rise. The world's oceans act as the main heat storage for the world accounting for 90% of the heat accumulation (WMO, 2020). The first 700-2000m (IPCC, 2019; IPCC et al., 2021; WMO, 2020) of ocean water has warmed with rates of 0.2 W/m2 across the entire planet (Purkey & Johnson, 2010) which has accelerated the melting of ice sheets and ocean-fronting glaciers which are already experiencing increased melt from the warmer ambient air temperatures (IPCC, 2019). The tremendous amount of ice which is stored in ice sheets and glaciers slowly melting has increased the global mean sea level by 20cm from 1901-2018 (Cazenave et al., 2018; IPCC et al., 2021). Rising ocean levels have the potential to destroy ecologically sensitive wetlands (Weston, 2014; Yu et al., 2019) and threatens coastal communities. Approximately 28% of the global population are situated on the coasts (IPCC, 2019) and could be impacted directly by rising ocean levels.

As well as absorbing heat from the earth's climate, oceans also absorb approximately 23% of anthropogenic CO_2 from the atmosphere (WMO, 2019). The absorbed CO_2 causes the water to become acidified which has contributed to the destruction of half the live coral since 1870 (IPBES et al., 2019) as well as damaging skeletal and shell formation of marine species (IPCC, 2019; Kuroyanagi et al., 2021; Sheppard Brennand et al., 2010; X. Wang et al., 2017).

Terrestrial effects of climate change have been as mounting in severity. Weather patterns have been shifting resulting in poleward migration of precipitation coupled with increased storm and drought intensity (Dore, 2005; IPCC et al., 2021; O'Gorman, 2015; Trenberth, 2011). For every 1°C that air warms, its water holding capacity increases by 7% (Trenberth, 2011). Drought and increased temperatures increase the risk of forest fires. Models have predicted that North America could see seasonal severity of forest fires increase by 10%-

50% by 2060 (Flannigan et al., 2000) and extreme grassland fire risks increasing in Australia by 25% by 2050 (Pitman et al., 2007).

When the atmospheric moisture is released, though, it will be in more intense precipitation events which increases the risk of flooding (Dore, 2005; Trenberth, 2011). The latter half of the 20th century has had a 2%-4% increase in the frequency of heavy precipitation events (Dore, 2005). Up to $3 billion per year in cop loss could occur in the US by 2030 due to increased soil moisture and flooding as a result of climate change (Rosenzweig et al., 2002).

Hurricanes and cyclones have been increasing with intensity as the global temperature increases. (Holland & Bruyère, 2014) found that the hurricane intensity increased as a function of anthropogenic warming. Since 1975, for every degree Celsius of global warming, the proportion of Category 4-5 hurricanes has increased by 25%-30%. The increased storm intensity poses a serious threat to coastal communities and island nations. With the anticipated increase in coastal development, (Dinan, 2017) predict that the increased intensity of hurricanes will cause damage costs in the US to increase faster than the US economy and impact 8 times as many people by 2075.

The effects of a warming climate are only anticipated to get worse if temperatures are allowed to rise. (IPCC et al., 2021) modeled 5 different scenarios the world could take in response to greenhouse gas emissions and found that continued, unmitigated exploitation of fossil fuels would lead to temperatures increasing by 2.8°C-5.7°C by the end of the century. By 2050, the cost of climate change could be as high as $23 trillion globally if temperatures increase by more than 3.2°C (Guo et al., 2021) with poorest nations facing the most damaging effects (Guo et al., 2021; IPBES et al., 2019; IPCC, 2019).

The UN has estimated that the world would need to halve its annual greenhouse gas emissions by 2030 to keep global temperatures from increasing more than 1.5°C (UNEP, 2021). To keep pace with the rising global energy demand and prevent further greenhouse gas emissions, new energy sources need to be identified and developed to replace fossil fuels.

2.2.2 Hydrogen as a Fuel Resource

One of the most promising fuel sources being explored to transition away from fossil fuels is hydrogen (Clark & Rifkin, 2006; Muradov & Veziroğlu, 2005, 2008; Pudukudy et al., 2014). Hydrogen has the highest gravimetric energy density of all existing fuels (142kJ/mol), which is nearly 3-times greater than that of gasoline (45.8kJ/mol) and natural gas (47.2kJ/mol) (Jimenez-Calvo, 2019). The concept of a "Hydrogen Economy" where hydrogen is the main global energy vector has been around since the oil shortage of the 1970s. Hydrogen is an attractive answer at the crossroads of environmental stewardship and energy production because it does not produce any greenhouse gases. When burned like traditional fossil fuels, hydrogen will oxidize with oxygen in the air and produces water (Eq. 1). Hydrogen is also easily exploited in fuel cells to generate electricity with the by-product, again, only being pure water.

$$H_2 + {}^1\!/_2\, O_2 \rightarrow H_2O, \qquad \Delta H = -285\, {}^{kJ}\!/_{mol} \qquad \boxed{\text{Eq. 1}}$$

Hydrogen is also a critical resource outside of the energy sector. As of 2018, the International Energy Agency reported that ~43% of hydrogen produced globally goes to the chemical industry with the majority being used to create ammonia for fertilizers (IEA. 2019). The UN predicts the global population is expected to rise to 9.8 billion people by 2050 and 11.2 billion by the end of the century. Farming and food production will need to be able to support this growth and fertilizers will be a critical element to ensuring the global food supply. Ammonia production will need to increase in line with population and, therefore, so will hydrogen production.

Though hydrogen is recognized as a green alternative to fossil fuels with many well-established technological applications, it is difficult to produce economically in an environmentally friendly manner (Shiva Kumar & Himabindu, 2019). There are virtually no hydrogen gas reserves on earth meaning that it must be generated from other materials.

Broadly, there are three main technologies used to generate hydrogen gas: Electrolysis, Steam Methane Reforming (SMR), and Gasification.

2.3 Hydrogen Production Methods

2.3.1 Electrolysis

Electrolysis decomposes water to produce H_2 and O_2. An electric current is applied across water resulting in hydrogen generation at the cathode and oxygen at the anode. Using an electric current to split water into O_2 and H_2 has been performed since the 1890s (Revankar, 2018) and was one of the pioneering works conducted in the field of electrochemistry. Of the technologies available for hydrogen production, it is the cleanest. No greenhouse gases are emitted from the electrolysis process and the hydrogen produced is ultra-pure (Scott, 2019). Despite the many upsides to electrolysis and its well understood mechanism, it is still a prototype technology because it struggles to be economical compared to other hydrogen production technologies. Costs are typically in excess of $10 per kg of H_2 (Shiva Kumar & Himabindu, 2019) which is 5 times greater than the cost to produce hydrogen through SMR or gasification. The electrolyser system requires a great deal of electricity at scale and struggles to be economically competitive with other technologies. Furthermore, if the electricity required for electrolysis is produced from a traditional fossil fuel source, it loses the edge in being environmentally favorable. Great effort is presently being made to couple electrolysis with renewable energy to keep the process entirely green. With current technologies, electrolysis achieves efficiencies around 80% for hydrogen production (Revankar, 2018; Shiva Kumar & Himabindu, 2019) making it one the most efficient processes.

2.3.2 Steam Reforming

Steam reforming and, in particular, steam methane reforming (SMR) is the greatest hydrogen producing technology in the world today (García, 2015). It is a mature technology which has been used to produce approximately 50% of the global hydrogen supply (Basile et al., 2015). Hydrogen is produced by SMR by reacting methane with super-heated steam homogenously (ie. both reactants are gas phase), typically under pressures between 2.5-3 MPa and in the presence of a nickel catalyst following Eq. 2 below.

$$CH_4 + H_2O \rightarrow 3H_2 + CO, \qquad \Delta H = 206\, {}^{kJ}/_{mol} \qquad \boxed{\text{Eq. 2}}$$

The reaction is highly endothermic requiring 206 kJ/mol. To achieve this, the process is typically operated between 700-900°C (Speight, 2020; Velazquez Abad & Dodds, 2017). The water gas shift reaction (Eq. 3) is used as a second step in the process to produce extra hydrogen by reacting steam with the carbon monoxide produced from the initial reforming step.

$$CO + H_2O \rightarrow CO_2 + H_2, \qquad \Delta H = -41\, {}^{kJ}/_{mol} \qquad \boxed{\text{Eq. 3}}$$

In practice, the hydrogen production efficiency of SMR is between 65%-85% (Shiva Kumar & Himabindu, 2019; Velazquez Abad & Dodds, 2017) requiring a 2.5-3 (Speight, 2020) molar ratio of steam to carbon and produces 4 moles of H_2 and 1 mole of CO_2 for every mole of methane feedstock. Costs are expected to be around \$1.80-\$2.27 per kg of H_2 (Shiva Kumar & Himabindu, 2019; Velazquez Abad & Dodds, 2017). Other hydrocarbons have been explored as alternative feedstocks because, as a compound's chain length grows, so does the amount of hydrogen it can yield. Steam reforming has been performed on bituminous heavy hydrocarbons but required temperatures between 700-1000°C (Kapadia et al., 2011). Unfortunately, this is coupled with increased CO_2 production often in higher ratios than that of methane steam reforming (Eq. 4).

$$C_xH_y + zH_2O \rightarrow \left(x + \frac{y}{2}\right) H_2 + zCO \qquad \boxed{\text{Eq. 4}}$$

As the methane for SMR is typically derived from fossil fuels, the process is not as green as it may initially seem. CO_2 is a main product in the generation of hydrogen from SMR and, in most industrial settings, methane is burned to achieve the reaction temperatures required thus producing even more CO_2. Though the end result is hydrogen, a green fuel, the carbon dioxide generated by the process is no better than if the fossil fuel was burned.

Fortunately, by containing the process, efforts can be made to introduce forms of carbon capture to prevent the greenhouse gases from being emitted to the atmosphere.

Calcium Oxide (CaO) has been proposed as an inexpensive way to reduce the carbon footprint of SMR by scrubbing CO_2 from the reaction in situ following Eq. 5.

$$CaO + CO_2 \rightarrow CaCO_3, \qquad \Delta H = -178\ {}^{kJ}/_{mol} \tag{Eq. 5}$$

Removing CO_2 from the reaction has two benefits. The first being the reduction of carbon emitted and the second being improved hydrogen production. By sorbing CO_2, a product is removed from the reaction which shifts the thermodynamic equilibrium to favour the production of more products, which includes H_2 (Speight, 2020). Overall, this can also result in a lower reaction temperature being required as well since the carbonation reaction of CaO generates heat while also shifting the thermodynamic equilibrium (Speight, 2020).

2.3.3 Gasification

Gasification was first developed in the late 1700s (Siwal et al., 2020), however, with respect to controlled hydrogen production, it is a developing technology with many prototype scale facilities operating or under commission (Jafri et al., 2020). Gasification is a thermochemical process in which a solid or liquid organic fuel is partially oxidized by a gasification agent heterogeneously (ie., reactants are different phases). The gasification agent provides the oxidant for the reaction and varies depending on the exact process being used. Common gasification agents include air, oxygen, carbon dioxide, and steam (Ahmad et al., 2016; Zhang, Cui, et al., 2019). Air is most commonly used because it is inexpensive and readily available at all scales (Zhang, Cui, et al., 2019). Many different types of organic fuels can be used as the feedstock for gasification and remains an active area of research. Coal and biomass are the most widely studied feedstocks with interest shifting away from coal and towards biomass in recent years. Converting biomass, in particular waste biomass, to syngas is considered carbon-neutral energy production (Lu et al., 2019). One of the major limitations to gasification is the cost required to pre-process the feedstock. First, the gasification agent needs to be able to flow through the fuel which means it needs to be processed into a relatively uniform, permeable matrix. This could involve chipping, pulverizing and screening. Excess moisture in the fuel will also affect gasification so a feedstock needs to be dried to a moisture content no higher than 35% (Ahmad et al., 2016). Costs are anticipated to be \$1.77-\$2.05 per kg of H_2 (Shiva Kumar & Himabindu, 2019).

Fundamentally, gasification is a multi-step process as seen in Figure 2.1.

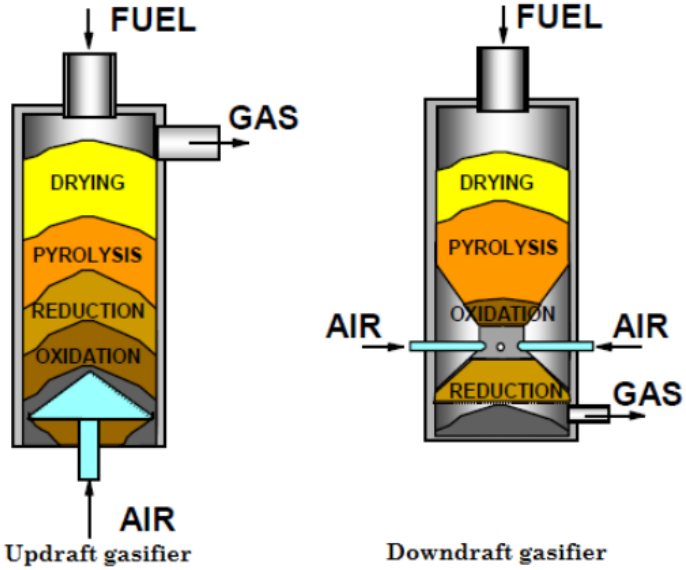

Figure 2.1: Updraft and Downdraft Gasifier Highlighting the Different Zones in the Gasification Process with Air as the Gasification Agent (Budhathoki, 2013)

First and farthest from the gasification agent inlet, the feedstock material is dried from applied heat or heat carried forward from the oxidation zone. As the dried feedstock progresses close to the gasification agent inlet, it experiences increasing temperatures in the absence of oxygen and begins to pyrolyze. The pyrolysis zone thermally decomposes the fuel producing gases, tars, and reduces the fuel to a carbon rich char. Tars created in this zone can also undergo further pyrolysis producing their own gases and char. The char and residual tars proceed to react with the gasification agent. A portion of the fuel undergoes partial combustion generating heat while the remainder of the fuel is reduced to syngas with an efficiency of 30-40% (Shiva Kumar & Himabindu, 2019) leaving behind only residual ash. Depending on the gasifier operation, some char may be a product of the process as well. Generally, gasification reactions are endothermic and require external energy, however, if a significant portion of the feedstock is allowed to combust, the net energy for the system may become exothermic (Zhang, Cui, et al., 2019). The more fuel allowed to combust, however, will reduce the amount of hydrogen produced. Ultimately, the goal of gasification is not to create heat but rather to transfer the energy of the process into chemically energetic syngas.

The product of gasification is a blend of reduced gases called syngas. Syngas primarily consists of H_2, CO, CO_2 and, if air is the gasification agent, N_2. The syngas will also contain small amounts of short-chain hydrocarbons and trace amounts of other inorganic, reduced gas species such as H_2S and NH_3 depending on the fuel (Zhang, Cui, et al., 2019). The composition and concentration of the syngas can be affected by operational inputs as well such as the temperature, residence time, pressure, catalyst, etc. (Ahmad et al., 2016; Siwal et al., 2020). Of the operation variables, temperature has been shown to have the greatest effect on the gas yield and composition (Sansaniwal et al., 2017). Temperature can be regulated externally by heating the gasifier or by increasing and decreasing the extent of oxidation occurring within the reactor (Zhang et al., 2011). Temperature control through oxidation can only occur when the gasification agent is air or oxygen.

Steam as a gasification agent has been shown to generate greater hydrogen yield than other conventional gasification agents with yields between 45%-60% and higher temperatures favouring higher yields (Franco et al., 2003). Maximum hydrogen production from steam gasification typically requires temperatures in excess of 1000K (Ahmed & Gupta, 2009; Franco et al., 2003; Weerachanchai et al., 2009). Pure steam gasification requires external energy input because it does not have the partial oxidation reaction. When O_2 was combined with steam in biomass gasification, (Gil et al., 1992) found that the maximum H_2 concentrations in syngas decreased from 55% to 30%. When steam is the gasification agent, the increased hydrogen production has been attributed to either the water-gas shift reaction (Franco et al., 2003; Umeki et al., 2010) or char gasification (Ahmed & Gupta, 2009). Interestingly, (Zhang, Xu, et al., 2019) found there was correlation between the volatility of the fuel and higher H_2 yields.

CaO has been included in gasification to improve hydrogen production. Similar to SMR, CaO has been demonstrated to scrub CO_2 from the produced gas which results in the reaction shifting to produce more products following LeChatalier's principle (Acharya et al., 2009a; L. Han et al., 2011; Pfeifer et al., 2009). The amount of H_2 produced when using CaO was 2 times (Pfeifer et al., 2009) and 2.8 times (Acharya et al., 2009b) greater than without. Likewise, the heat generated by the carbonation reaction provides energy to the system. (Guoxin & Hao, 2009) found that CaO also had a catalytic effect on the process favouring H_2 formation. Generally, increased temperature, and higher steam/carbon and CaO/carbon all favour hydrogen generation (L. Han et al., 2011).

Gasification of biomass is a promising technology in the hydrogen space because of its potential for large yields and its carbon neutrality. It can also be used and adapted for a variety of different feedstocks without fundamentally changing the process thus making it one of the most effective technologies to produce hydrogen (Ahmad et al., 2016; Heidenreich & Foscolo, 2015).

2.4 Smouldering Combustion

2.4.1 The Smouldering Reaction

Smouldering is a unique form of combustion which differs from the more conventional flaming combustion. Where flaming combustion is a homogenous, gas-phase reaction, the fundamental characteristic of smouldering is that an oxidant, typically oxygen in air, reacts heterogeneously with the surface of a solid or condensed phase, organic fuel (Ohlemiller, 1985; Rein et al., 2009; Switzer et al., 2009). The process has historically been considered a 4-step process consisting of pre-heating, evaporation, pyrolysis, and oxidation/combustion (Figure 2.2b) (Rein et al., 2009). Pre-heating consists of raising the temperature of the fuel, often through the boiling point, without fundamentally changing the fuel's structure (Rein et al., 2009; Torero et al., 2020).

Pyrolysis describes the zone in between, and therefore adjacent to, both pre-heating and oxidation. This region is heated in a relatively oxygen-free atmosphere to the point that fuel undergoes chemical and structural changes (Sinha et al., 2000). This zone exists over a temperature gradient with the hottest temperatures occurring immediately adjacent to the oxidation front and then declining with distance from oxidation. The organic material reduces to form a carbon-rich char while also producing gases and tars from the thermal degradation (Ohlemiller, 2002; Rein et al., 2009). In this zone, gasification reactions may also be taking place on either the fuel or its residual char. The semi-volatile tars may also undergo further pyrolysis producing new tars, gases and chars (Torero et al., 2020). Detailing the sequential degradation of a fuel has been an area of extensive study to better model smouldering reactions which is extensively summarized by (Torero et al., 2020). The pyrolysis zone is the area with the greatest number of chemical reactions and is responsible for the more abundant and complex emissions associated with smouldering compared to flaming combustion (Torero et al., 2020).

Oxidation or combustion occurs on the carbonaceous char which remains after pyrolysis (Ohlemiller, 2002; Rein et al., 2009). In this region, the char is at ignition temperature so it readily reacts with oxygen which contacts its surface (Rein, 2009; Rein, 2013; Tillman, 2012). Depending on the amount of oxidant, the reaction can either be fuel limited (excess oxygen) or oxygen limited (excess fuel).

The smouldering reaction zones are similar to the steps involved in gasification and, many of the zones preceding oxidation are fundamentally the same. The major difference between smouldering and gasification, though, is that smouldering is a combustion reaction which exothermically transfers the chemical energy contained in the fuel to heat through a strong oxidation reaction. This creates a high temperature, thin smouldering front with a steep temperature gradient (Figure 2.2b). Gasification, on the other hand, transfers the chemical and thermal energy of the system endothermically into high energy content gases. This results in a lower oxidation temperature relative to smouldering and a smoother, more gradual temperate gradient preceding oxidization (Figure 2.2a). Though a variety of gases will be generated in smouldering's pyrolysis zone, the products of smouldering will be primarily CO_2 and CO from combustion (Bar-Ilan et al., 2004; Ohlemiller, 2002; Torero et al., 2020). Conversely, gasification's primary products will be H_2, CO and short chain hydrocarbons (Zhang, Cui, et al., 2019), which are present only in small quantities, if at all, in smouldering (Torero et al., 2020).

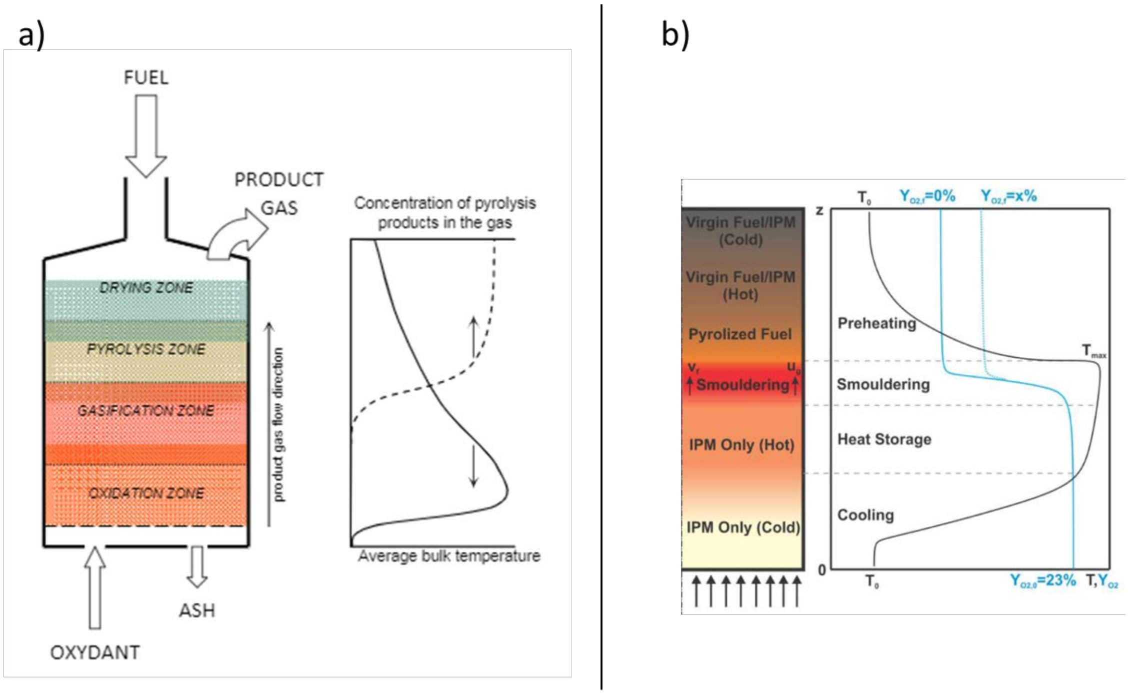

Figure 2.2: a) Gasification Reaction Zones with Temperature Profile (Siedlecki et al., 2011) and b) Smouldering Reaction Zones with Temperature Profile (Torero et al., 2020)

2.4.2 Applied Smouldering

Traditionally, smouldering has often been studied under the context of fire safety with emphasis being placed on understanding its transition to flaming (Bar-Ilan et al., 2004; Rein, 2009; Rein et al., 2008; Torero & Fernandez-Pello, 1995). As such, many studies have been conducted on peat, biomass, and coal as they relate to forest fires and coal seam fires respectively. Additionally, polyurethane foam has been an area of extensive smouldering research due to it being a potential fire hazard in residential and aerospace fields.

More recently, however, there has been an emphasis on engineered smouldering reactions to utilize the unique characteristic of the process (Torero et al., 2020). Smouldering is more persistent than flaming and can sustain itself in conditions which would extinguish a flame (Ohlemiller, 1985; Switzer et al., 2009, 2014). This is possible since smouldering occurs in a solid, porous medium which has the capacity to efficiently capture and store the energy released by the reaction (Rein, 2009; Zanoni et al., 2019). Perturbations to the system can therefore be dampened. Air delivery can also be controlled to a smouldering reactor (Pironi et al., 2011; Yerman et al., 2015) where in classical fire studies, the reaction is often fed by natural convection. Engineered smouldering typically utilizes forced air delivery through the reaction which radically alters the propagation and peak temperatures of the smouldering reaction. Additionally, the reaction can occur in spaces which do not permit flaming and on non-volatile fuels (Mahinpey et al., 2007; Scholes et al., 2015).

The useful application of smouldering has been inconsistent throughout history with periods of increased interest typically surrounding a single application. Likely, the earliest application of smouldering was to create charcoal or biochar. Evidence of this dates back to 30,000 BC (Schwarcz, 2017) and can still be performed today relatively easily. The next major applications of engineered smouldering focused on improving fossil fuel extraction. Coal seam gasification (UCG) became a novel approach to obtain syngas from coal seams by initiating a smouldering reaction which would subsequently gasify adjacent parts of the seam. Work in this field was first proposed in the late 1800s but interest had waned by the 1950s (Klimenko, 2009). There has been a resurgence in UCG as a way to utilize coal deposits as the world shifts away from direct mining and burning of coal (Bhutto et al., 2013; Shafirovich & Varma, 2009). Similarly, In Situ Combustion (ISC) for enhanced oil recovery utilizes smouldering to burn a relatively small portion of a high-viscosity oil reservoir to heat, and therefore lower the viscosity of the rest of the reservoir to improve extraction (Mahinpey et al., 2007).

Recently, smouldering has been explored as a remediation and waste management technology. Self-Sustaining Treatment for Active Remediation (STAR) was initially developed as a novel remediation technology for soil impacted by recalcitrant, non-aqueous phase liquids (NAPL) (Pironi et al., 2011; Switzer et al., 2009). The NAPL is typically an organic material which exists as a contaminant in the pore space of a soil. The soil provides a relatively inert, porous matrix which permits airflow as well as serving as a thermal insulator (Switzer et al., 2009). The NAPL is carbonaceous and can act as fuel. Smouldering of the NAPL can therefore be initiated after a short-duration heating event by forcing air through the soil matrix (Pironi et al., 2011; Switzer et al., 2009). The smouldering reaction will become self-sustaining and continue to propagate so long as an oxidant can reach the smouldering front (Yerman et al., 2015). NAPL destruction rates in excess of 99% are typical for the process (Pironi et al., 2011). When applied in-situ, smouldering is initiated by injection of hot air through a well and then sustained by continuing to blow air through the well until the reaction reaches its maximum radiance of influence where the air becomes too diffuse to sustain the reaction (Scholes et al., 2015). Even if the NAPL exists below the water table, the energy generated by the smouldering reaction is capable of creating a boiling front which precedes the smouldering front and prevents quenching (Grant et al., 2016). Ex-situ applications for STAR provide greater control of the reaction and allow the contaminated soil to be amended to improve smouldering characteristics by improving permeability (Rashwan et al., 2016b; Solinger et al., 2020) or adding fuel amendments (Duchesne et al., 2020; Salman et al., 2015). As an ex-situ technology, STAR has expanded to also be used as a waste reduction technology (Duchesne et al., 2020; Rashwan et al., 2016a; Yerman et al., 2015; Yermán et al., 2017).

Organic wastes which have been traditionally challenging to destroy have been successfully treated by STAR (Duchesne et al., 2020; Pironi et al., 2011; Sabadell et al., 2019). Biosolids are a pathogenic waste product from wastewater treatment plants. Their high moisture content and sludge-like structure do not allow them to be incinerated without extensive preprocessing. (Rashwan et al., 2016a) demonstrated that when mixed with sand, biosolids could be completely remediated through smouldering. Critically, it was found that moisture contents as high as 80% could be treated which is far in excess of what could be tolerated by other thermal technologies. Similarly, refinery sludges and coal tar, which lack the volatility for treatment in an incinerator have been completely destroyed in smouldering reactors (Pironi et al., 2011; Switzer et al., 2014). (Duchesne et al., 2020) demonstrated that there is a linear relationship between the concentration of a fuel and the smouldering temperature while using STAR to treat PFAS-impacted soils and granular activated carbon (GAC). This work also identified GAC as an ideal surrogate fuel for smouldering as it is already fully reduced to an extremely high carbon content char thus producing highly controllable smouldering temperatures capable of exceeding 1000°C.

Despite smouldering being a highly energetic reaction with active oxidation and reduction zones, little effort has been made to utilize the process for resource production. Its similarity to gasification makes it a prime candidate to produce valuable syngas such as hydrogen. Syngas production from STAR-based smouldering would have a low carbon intensity as well since it would only be utilizing waste products as the feedstock. Moreover, the many feedstocks available to STAR cannot be exploited by other technologies.

2.5 Conclusions

Nearly a century and a half of rampant fossil fuel exploitation has brought the world to a perilous situation. The climate is changing faster than it ever has before resulting in extremely damaging environmental effects which may be irrecoverable if burning fossil fuels isn't dramatically curtailed (IPCC et al., 2021). Simultaneously, energy demand has never been higher and is projected to increase steeply (U.S. EIA et al., 2021). Alternative energy sources are required to replace fossil fuels. H_2 is an ideal alternative because it is highly energetic and does not produce any greenhouse gases. Unfortunately, H_2 is difficult to produce economically however several technologies are developing more efficient ways to generate H_2.

The science of applied smouldering is expanding finding novel applications and improved control. Despite the many similarities smouldering has to other alternative fuel technologies, such as pyrolysis and gasification, it has been deemed unsuitable for H_2 production or sustainable development (Ni et al., 2006). Efforts to amend a smouldering reaction either through the addition of catalysts or gasifying agents to shift the products to syngas has never been attempted. Moreover, the high-temperature smouldering front being immediately adjacent to a chemically active reduction zone presents an opportunity to utilize the energy from smouldering to sustain H_2 forming reactions without additional energy input.

Smouldering applied through STAR is a technology transitioning from the lab to commercial application for its ability to remediate and destroy wastes which could not otherwise be treated (Grant et al., 2016). Coupling this technology with H_2 generation has the potential to create an environmentally friendly, waste-to-energy methodology which is completely novel. This work includes an experimental suite which explores generating H_2 from STAR-based smouldering. Process amendments, including CaO and steam, are investigated to determine the effects they have on the hydrogen production. Ultimately, the aim of the experimental suite was to identify and optimize the process variables to maximize hydrogen yield. Further analysis was also carried out to identify the mechanisms of H_2 formation.

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Chapter 3

3 Hydrogen-Rich Syngas Derived from Smouldering Biomass and Hydrocarbon Wastes

3.1 Introduction

The world is currently experiencing higher energy demand than ever before with projections indicating a 50% increase in global energy usage by 2050 (U.S. EIA et al., 2021). This is occurring while the world is in the midst of a climate crisis brought on by the exploitation of fossil fuels. The burning of fossil fuels over the past 150 years has increased the CO_2 concentration in the atmosphere by 148% from pre-industrial levels (WMO, 2020). The increase in greenhouse gases has resulted in the average global temperature increasing by 1.07°C over that time; a rate of temperature increase unprecedented in the past 2000 years (IPCC et al., 2021). Anthropogenic climate change brought on as a result of global warming has been devastating causing increased hurricane intensity (Holland & Bruyère, 2014), severe droughts (Dore, 2005; IPCC et al., 2021; O'Gorman, 2012; Trenberth, 2011) with increased forest fires (Flannigan et al., 2000; Pitman et al., 2007), ocean warming and acidification (IPBES et al., 2019; IPCC, 2019; IPCC et al., 2021; Purkey & Johnson, 2010; WMO, 2020), as well as destruction of wetlands and coastal communities (Dinan, 2017; Weston, 2014; Yu et al., 2019). The estimated cost of climate change could be up to $23 trillion globally by 2050 with the poorest nations being most effected (Guo et al., 2021). Despite this, fossil fuels have accounted for approximately 80% of the global energy consumption from 2009-2019 (REN21, 2021). New energy sources are needed to meet the surging demand while curtailing the use of fossil fuels.

H_2 is recognized as a potential green fuel of the future which could replace fossil fuels (Clark & Rifkin, 2006; Muradov & Veziroğlu, 2005, 2008; Pudukudy et al., 2014). Either through direct burning or use in a fuel cell, the only by-product from using H_2 is water, making it a net-zero greenhouse gas emitter. H_2 also has one of the highest gravimetric energy densities which is approximately three times greater than gasoline and natural gas.

Beyond the energy sector, H_2 is already a valuable resource with ~43% of global production currently being used to create ammonia in fertilizers (IEA, 2019). Despite its promise, H_2 is difficult to produce economically and in an environmentally friendly way (Shiva Kumar & Himabindu, 2019). Steam Methane Reforming (SMR) is the most mature H_2 production technology (Basile et al., 2015), but it produces a significant amount of CO_2 during the process and the methane is typically derived from fossil fuels. Electrolysis, though able to create high purity H_2 with great efficiency (Revankar, 2018; Scott, 2019; Shiva Kumar & Himabindu, 2019), struggles to be economically viable at large scales (Shiva Kumar & Himabindu, 2019). Gasification, in particular gasification of waste biomass, is a promising technology which can be adapted to a variety of fuels and is generally considered to have a low carbon intensity (Ahmad et al., 2016; Heidenreich & Foscolo, 2015; Lu et al., 2019). Gasification generates H_2 as well as a blend of other reduced gases collectively referred to as syngas. Pre-processing of the feedstock has been an economic limitation of the technology and it can require significant energy input to promote the endothermic H_2-forming reactions (Ahmad et al., 2016).

Smouldering shares many similarities with gasification in the thermal decomposition of fuel preceding a reaction zone. The fundamental difference being that smouldering is a combustion reaction which exothermically oxidizes the reduced, carbonaceous feedstock into primarily CO_2, CO, and H_2O generating substantial heat (Ohlemiller, 1985; Torero & Fernandez-Pello, 1996). Recently, smouldering has been applied as a cost-effective remediation technology for contaminated soils (Grant et al., 2016; Pironi et al., 2011; Scholes et al., 2015; Switzer et al., 2009) as well as a waste management technology (Duchesne et al., 2020; Rashwan et al., 2016a; Sabadell et al., 2019; Solinger et al., 2020). Smouldering occurs as a heterogeneous reaction with oxygen attacking the surface of a condensed phase fuel (Ohlemiller, 1985; Switzer et al., 2009). Charcoal briquettes in a barbeque are a familiar example of smouldering combustion. A benefit of smouldering is that it can be self-sustaining after a brief ignition event. Heat released from smouldering is efficiently captured by the matrix allowing it to store energy and propagate the reaction (Zanoni et al., 2019). This makes smouldering more resistant to quenching than flaming combustion with a greater ability to tolerate perturbations to the system (Yerman et al., 2015). Wastes which generally cannot be treated by other thermal technologies (Incineration, Gasification, etc.) without preprocessing, can often be directly and completely destroyed by smouldering.

When smouldering is employed as a remediation or waste management technique, the contaminant/waste is often embedded within or blended with an inert, porous matrix. The matrix serves to increase air permeability as well as store energy released by the combustion reaction (Ohlemiller & Lucca, 1983; Pironi et al., 2011; Rashwan et al., 2016a; Salman et al., 2015). Once started, the smouldering front will progress through the matrix in the direction of the air flux completely consuming the waste as fuel. Steps have been made to improve control over the smouldering system by optimizing permeability (Pironi et al., 2011; J. Wang et al., 2021), and porous media material, defining moisture content limitations (Pironi et al., 2011; Rashwan et al., 2016a), and controlling the temperature of the reaction (Duchesne et al., 2020). Despite the advances in smouldering as a waste treatment technology, little effort has been made to exploit the process for resource production. It’s similarity to gasification coupled with a controllable, energetic reaction adjacent to active reducing zones suggests to these authors that it is possible to modify for H_2 production.

Alumina has been widely studied as a support of catalysts used in conventional steam reforming (Adhikari et al., 2007; Artetxe et al., 2016; Hu & Lu, 2010) and gasification (Campoy et al., 2010; de Andrés et al., 2011; Erkiaga et al., 2013) and could potentially provide a more active inert media for hydrogen forming reactions in the smouldering process. Due to its thermal properties, alumina has also been shown to promote hotter and faster smouldering reactions when used as the inert matrix relative to sand (Baud et al., 2015). CaO has been shown to improve both SMR and Gasification by scrubbing produced CO_2 (Acharya et al., 2009a; L. Han et al., 2011; Pfeifer et al., 2009; Speight, 2020). As CO_2 is removed from the reaction, the thermodynamic equilibrium shifts to favour the production of more products, including H_2. This is also environmentally favourable as it reduces to total CO_2 generated by the process. CaO has also been shown to have catalytic properties which promote H_2 (Guoxin & Hao, 2009).

Steam as a gasification agent improved H_2 production efficiency with higher temperatures favouring higher yields (Franco et al., 2003). Steam can contribute to H_2 formation through the water-gas shift, heterogeneous char gasification (steam-char) and even reforming reactions (steam-HC vapour) (Ahmed & Gupta, 2009; Franco et al., 2003; Umeki et al., 2010). Higher volatility fuels were shown to correlate with higher H_2 yields (Zhang, Xu, et al., 2019) which would indicate homogenous reforming reactions are likely occurring. Steam can be added to the injected air required for smouldering allowing H_2-forming reactions to occur. Moreover, smouldering can produce temperatures greater than 800°C which are favourable for H_2 generation with steam.

This study explores, for the first time, using smouldering to produce H_2. An experimental suite was conducted to evaluate the effect the fuel/feedstock, porous media, CaO, and steam had on the production of H_2. The system was then optimized for maximum H_2 yield. Further analysis was conducted to elucidate the mechanisms of H_2 formation from the smouldering system. This work demonstrates for the first time that smouldering can be implemented as a waste management and remediation technology to generate H_2 with fuels which are difficult to utilize in other technologies.

3.2 Materials and Methods

3.2.1 Smouldering Mixture Preparation

Granular activated carbon (GAC) (McMaster Carr, 3190K523, 40-60 mesh), coal tar (CT) (Alfa Aesar, Catalog# 42488), and wood chips (WC) (BRQ Fibre et Broyure Inc., Trois Rivieres, QC) were the primary fuels used in this study and their elemental analysis is shown in Table 3.1. Canola oil (Saporito Foods) and crumb rubber (Emterra, 10-20 mesh) were also explored briefly as alternate fuels but were not analyzed in depth.

Table 3.1: Elemental Analysis of Primary Fuels

Fuel	Carbon (%)	Hydrogen (%)	Nitrogen (%)	Sulfur (%)	Oxygen (%)	Ash (%)
Coal Tar	80.75	5.72	1.19	0.85	10.78	0.71
Wood Chips	47.76	5.28	0.10	0.45	41.59	4.82
GAC	87.54	0.65	0.08	0.38	9.86	1.48

Fuels were mixed with sand (K & E Sand and Gravel, WP2-50A60, 8-16 mesh) in a stand mixer (KitchenAid, Professional 600TM). To ensure smouldering temperatures above 800°C were achieved, 30g/kg of GAC was added to all mixtures (Duchesne et al., 2020). CaO was first mixed into the coal tar to minimize the formation of calcium hydroxide ($Ca(OH)_2$) . Being in the coal tar solution helped prevent the steam from coming in contact with the CaO until the coal tar began undergoing pyrolysis/combustion and temperatures were above the dehydration temperature of calcium hydroxide (>400°C) (Criado et al., 2014; Irabien et al., 1990). Sand was the primary bulking matrix used in this study for Tests 1-8. Tests 9-11 used alumina (InTerra, aSORB Activated Alumina, 1.5-2mm) in place of sand as the bulking matrix to explore the effect it has on the reaction. Test 12 used woodchips in place of sand as the bulking agent to create a fully smoulderable matrix. In this instance, the other fuels were added to the woodchips such that their total fuel mass loading was the same as it was when sand was used as the bulking agent. Details of the fuel and CaO loading, matrix, air flux, and steam rate used in each test of the experimental suite can be seen in Table 3.2.

Table 3.2: Experimental Conditions for Smouldering Experimental Suite

Test	Bulking Matrix	Organic Fuel	Fuel Conc (g/kg)	GAC Conc (g/kg)	GAC Mass (g)	Coal Tar Mass (g)	Wood Chips Mass (g)	Total Fuel Carbon (g)	CaO Ratio (mass)	Air Flux (cm/s)	Steam Rate (g/min)	Steam/C Ratio (mol/mol)
1	Sand	GAC	0	30	189.2	-	-	165.6	-	2.5	9.95	5.3
2	Sand	Coal Tar	30	30	173.9	174.3	-	293.0	-	2.5	9.95	3.8
3	Sand	Coal Tar	30	30	164.3	164.0	-	276.3	-	2.5	18.46	6.9
4	Sand	Coal Tar	30	30	162.9	163.0	-	274.2	1:1 CT:CaO	2.5	18.5	7.3

5	Sand	Coal Tar	60	30	151.3	302.4	-	376.6	2:1 CT:CaO	2.5	21.3	6.1
6	Sand	Coal Tar	120	30	156.4	625.3	-	641.8	2:1 CT:CaO	2.5	18.8	6.6
7	Sand	Coal Tar	120	30	156.9	626.8	-	643.5	2:1 CT:CaO	5.0	23.0	3.4
8	Sand	Wood Chips	125	75	213.3	-	355.2	356.4	2:1 WC:CaO	5.0	20.5	3.1
9	Alumina	Coal Tar	200	50	151.1	603.4	-	619.5	2:1 CT:CaO	5.0	13.0	2.0
10	Alumina	Coal Tar	200	50	148.4	593.9	-	609.5	2:1 CT:CaO	5.0	21.6	3.0
11	Alumina	Wood Chips	220	132	214.6	-	357.2	358.5	2:1 WC:CaO	5.0	19.6	2.4
12	Wood Chips	Wood Chips & Coal Tar	-	30	155.5	626.8	518.3	889.8	2:1 CT:CaO	5.0	21.1	2.1

3.2.2 Experimental Apparatus

All experiments were conducted in a purpose-built smouldering reactor similar to (Monhol & Martins, 2015). A cross-section of the reactor can be seen in Figure 3.1.

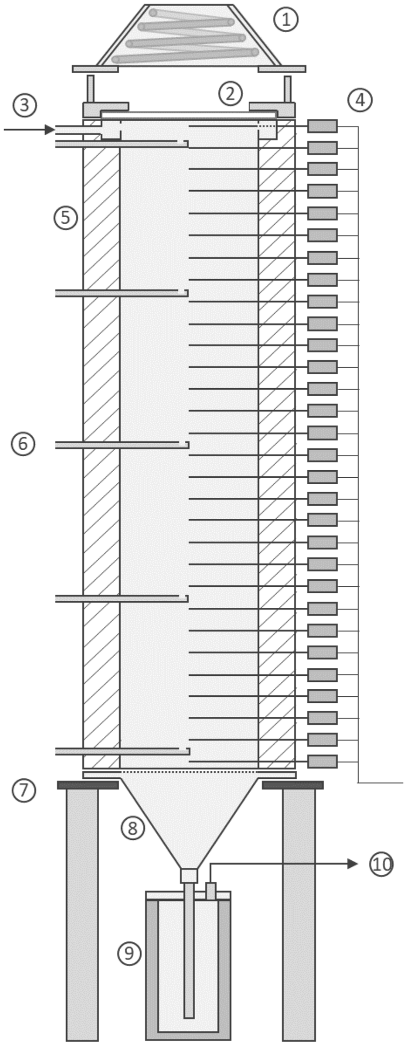

Figure 3.1: Radiative Smouldering Reactor – 1. Cone heater, 2. Quartz window, 3. Air inlet to circumferential air plenum, 4. Thermocouples (30 TCs with 3cm spacing), 5. Insulation, 6. Sampling probes (5 SPs with 21cm spacing), 7. Reactor stand, 8. Reducing cone with perforated flange face, 9. Knock-out with chilled water jacket, 10. Emissions outlet

The 11cm diameter, 94cm tall stainless steel reactor is wrapped in two layers of insulation (Firwin Plus, 160kg/m3, 0.22W/mK at 1000°C) with the first being ¼” thick and the second being 2” thick; all contained in a stainless steel shell. This diameter ensures the reaction will not be strongly influenced by edge effects while the height allows for a smouldering reaction to reach steady-state. In this study, a steady-state smouldering reaction is characterized by the peak temperatures, emission concentrations and smouldering velocity being uniform and having little variation over space and time. The reactor is sealed on the bottom end by a reducing funnel flange topped with a perforated plate covered in a 100mesh screen to support the smouldering bed. The top of the reactor is sealed with a 127mm x 6.35mm optical quartz window (Esco Optics, P650250) held by a custom flange. Graphite gaskets are used between all flange connections. A radiative cone heater (FTT, 240V/5kW, Part# U135) offset 5cm from the quartz window supplies a relatively even heat flux across the top of the smouldering bed material. Radiative heating allows the smouldering material to be completely isolated from the heating source and is similar to commercial applications.

Smouldering experiments were conducted in a top-down orientation for this experimental suite. Clean filter sand was first placed in the bottom of the column a top the perforated plate up to TC17 (43cm). The smouldering mixture was then packed on top of the filter sand in small lifts until flush with the top flange and then sealed under the quartz window (TC1-TC16, 51cm). The cone heater would be set to 1000°C and pre-heat the mixture to ignition temperature. Once 450°C was measured at the first TC after a short duration of pre-heating (20-30 minutes), air was introduced to the column to initiate the smouldering reaction.

Air is supplied at a set rate by a mass flow controller (Omega, FMA5400/5500 Series) to the reactor through four radial wall ports located immediately below the quartz window flange. Experiments were conducted at a Darcy flux of either 2.5cm/s or 5cm/s. Steam was added to the system by having the air line pass through the headspace of a custom-built, 4L steam generator before going into the column. The rate of steam generation was controlled by adjusting the power delivered by two resistance heaters (Watlow Ltd., 120V/450W) with a 120V AC, single phase power supply (STACO Energy products) up to a maximum rate of 23g/min. The steam generator was seated on a mass balance (Accu-

Weigh, PPC-200W) and the weight loss recorded so that the exact steam rate for each experiment could be determined.

Once the smouldering front became self-sustaining (ie. the smouldering front is generating enough energy to propagate), the heater was turned off and the smouldering reaction would proceed downwards, fed only by the air supply and embedded fuel.

3.2.3 Temperature Measurement and Sampling

The reactor is instrumented to provide high-resolution temperature data. Centerline temperatures are measured by K-type thermocouples (TC#) (Omega, KQIN-18U-6) at 3cm intervals along the length of the column. All thermocouple data was recorded in approximately 2-second intervals on a data logger (Agilent, 34980A).

3.2.4 Gas Sampling and Analysis

In-situ gas samples were taken from the bottom two of the five multi-purpose sampling probe (SP4 and SP5) locations. Emissions were continuously drawn by a chilling conditioning drawer (Universal Analyzers Inc., SCD) from SP5 (86.5cm) for real-time measurement of CO_2, CO, and O_2 (MGA3000 Multi-Gas Analyzer). The emission gas was conditioned prior to measurement by the analyzer by first passing through a knock-out canister and desiccant tower (Drierite, 26800) to dry the gas stream. Concentrations from the gas analyzer were recorded on the same time interval and data logger (Agilent, 34980A) as the temperature measurements.

Emissions were also collected from SP4 (65.5cm) at an early (TC2 peak temperature), mid (TC8 peak temperature), and late time (TC14 peak temperature) for Gas Chromatography – Thermal Conductivity Detector (GC-TCD) analysis. The sampling probe was connected to a 5L Tedlar bag (Restek, Catalog# 22052) which was opened during the sampling period and allowed to fill from the natural pressure within the column. A custom-built vacuum chamber was used to transfer the contents of the Tedlar bag grab samples to GC vials for GC-TCD analysis. GC-TCD was used to quantitatively analyze the grab samples from each experiment for hydrogen and methane (Table 3.3, Appendix A). The mid-time results are most indicative of the steady-state reaction process and steady-state H_2 concentrations unaffected by the ignition and extinction boundary conditions and are therefore shown alone for simplicity in this manuscript. The early- and late-time results can be seen in in Appendix C. The syngas energy was calculated from the enthalpy of combustion for the emission mass flows of H_2 and CO as well as CH_4 if it was detected.

3.3 Results and Discussion

Results from the twelve tests are summarized in Table 3.3. The results show that the methods employed in this work improved the steady state H_2 concentration from 0.7% up to 26.2%. The effect of each amendment and the relevant mechanisms and reactions occurring are discussed in detail in Section 3.3.4.

Table 3.3: Gaseous Production Results from Smouldering System with Velocity, Temperature, and Energy

Test	Average Front Velocity (cm/min)	Average Peak Temp (°C)	Steady-State CO_2 Conc (%)	Steady-State CO Conc (%)	Steady-State H_2 Conc (%)	Steady-State CH_4 Conc (%)	Total CO_2 Mass (g)	Total CO Mass (g)	Total CH_4 Mass (g)	Total H_2 Mass (g)	Total Syngas E (kJ)
1	0.45	823.5	13.6	5.5	0.7	-	368.0	95.0	-	1.2	1131
2	0.41	1055.9	14.5	9.8	2.5	-	477.0	207.3	-	3.4	2570
3	0.50	1011.5	13.9	9.8	6.2	-	425.2	159.8	-	5.7	2427
4	0.55	1059.7	19.1	9.8	10.2	-	489.8	171.2	-	13.4	3626
5	0.53	1017.2	18.9	8.6	12.0	-	667.5	178.4	-	16.8	4184
6	0.45	1010.9	18.1	5.6	14.3	-	671.8	124.7	-	21.3	4267
7	0.94	1213.5	17.7	9.1	13.8	-	712.6	189.0	-	21.2	4906
8	0.99	931.3	21.2	5.2	10.3	0.60	702.0	101.9	4.8	12.3	3043
9	1.47	1235.5	15.2	9.8	12.7	0.07	507.1	164.6	0.7	15.7	3919
10	1.27	1144.8	15.6	9.1	17.4	0.10	538.7	168.1	1.0	22.3	4915
11	2.38	932.7	20.7	8.7	12.6	0.59	563.1	94.2	6.4	19.3	4038
12	-	999.1	22.4	6.2	26.2	0.32	2026.6	271.1	7.4	58.2	11392

3.3.1 Hydrogen Generation Zone

A smouldering reaction creates a unique set of chemical and thermal conditions which can be manipulated to generate hydrogen gas. Figure 3.2 shows a conceptual diagram illustrating the temperature and emission profiles for the key smouldering zones as described by (Torero et al., 2020) coupled with the H_2 formation zone hypothesized for the first time here.

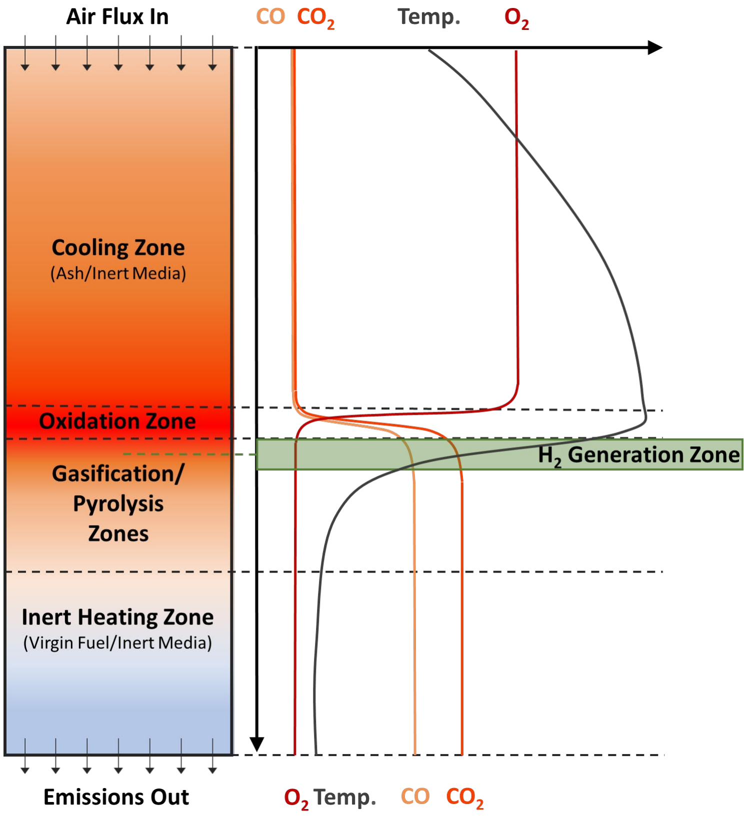

Figure 3.2: Smouldering reaction zones with corresponding temperature and emission profiles and H_2 Generation Zone

The oxidation zone provided by the thin smouldering front consumes oxygen entering the reactor and produces thermal energy. The heat released from oxidation is efficiently captured by the adjacent media providing the energy to pyrolyze and gasify the fuel ahead. Pyrolysis and gasification do not have well defined boundaries and would likely overlap.

Gasification, however, will likely occur very near the smouldering front where the temperature is the hottest while pyrolysis will dominate further away.

Within a narrow band preceding the smouldering front, there exists super-heated carbon char, light hydrocarbon gases, and carbon oxides in an anoxic environment perfectly suited to heterogeneous and homogeneous hydrogen forming reactions. To further enhance the process, the CaO catalyst blended with the fuel is also exposed in this space. Finally, by supplying steam with the air stream, it is carried through the smouldering front to provide the final major reactant into the newly created hydrogen generation zone.

3.3.2 Process Amendment Results

The effect of fuel type/loading, bulking matrix, CaO, and steam rate were all explored to find the impact on hydrogen production. The steady-state H_2 concentrations and H_2 production rates can be seen for all tests in Figure 3.3a and Figure 3.3b, respectively.

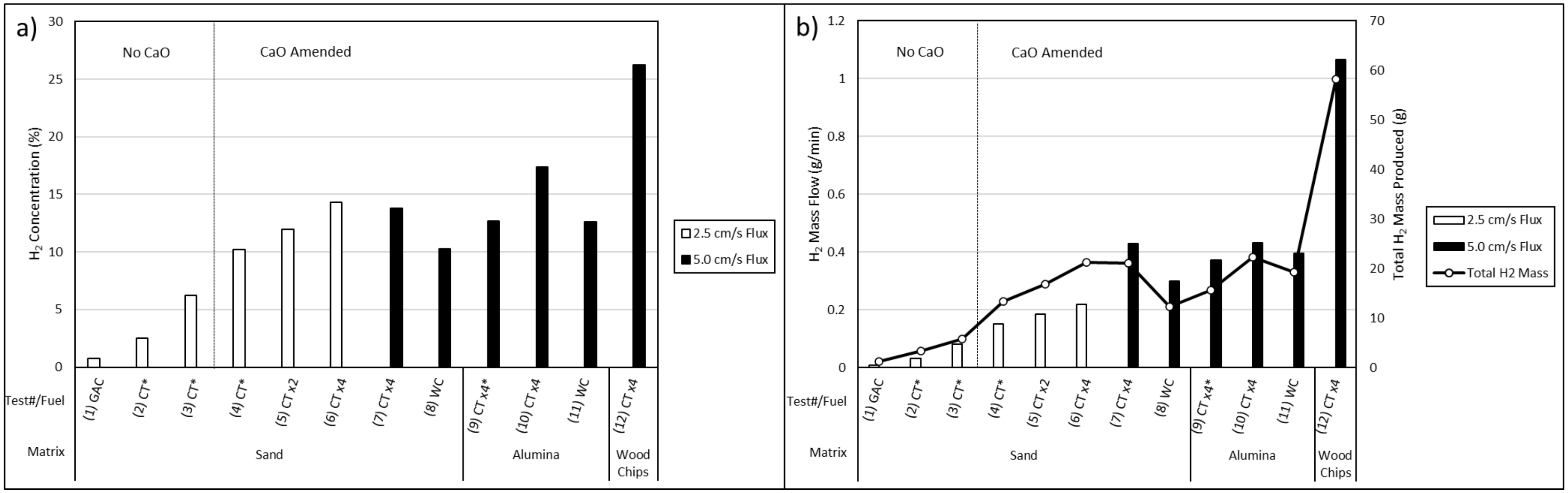

Figure 3.3: a) Steady-state H_2 concentration emitted from smouldering reactor. b) Steady-state H_2 mass flow and total H_2 mass. GAC: Granular Activated Carbon, CT: Coal Tar, WC: Wood Chips. Experiments with asterisks indicate CO measurement was above the detectable range of the instrument (10%)

A GAC/Steam system is shown as the base case for the first experiment (Test 1). Since GAC does not produce H_2 when it is smouldered without steam, it was a conservative fuel amendment which could be added to increase combustion temperatures without convoluting the H_2 values from the other fuels used in this study. The quantity of GAC used (30g/kg) is equal to what is added to every subsequent experiment to ensure a smouldering temperature exceeding 800°C and the steam rate (9.95g/min) is at the minimum explored in this work. These operational conditions yielded a steady-state hydrogen concentration of 0.7% with a peak concentration of 0.9% and a total yield of 1.22g (Figure 3.3, Table 3.3).

A 1:1 mass ratio of CaO to coal tar was added to Test 4 resulting in a 64% increase in hydrogen concentration from Test 3 without CaO. Increasing the fuel to CaO ratio to 2:1 was found to improve H_2 production (Appendix C) and the 2:1 ratio was used for the remainder of the experimental suite.

Unlike the sand tests (1-8) which required some development of the smouldering front to reach steady state hydrogen emissions, the alumina tests (9-10) typically had higher hydrogen concentrations throughout the entire test length and measured the peak hydrogen concentrations at the early-time sampling period (Appendix C). The thermal properties of alumina resulted in the smouldering reaction reaching steady state rapidly and progressing faster resulting in a more energetic, and therefore efficient, syngas production.

3.3.3 Process Efficiency

3.3.3.1 Air Flux

An important difference between the H_2 concentration and the H_2 mass production rate occurs during Test 7, when the air flux is doubled. It can be seen in Figure 3.3 that the change in air flux has virtually no effect on the hydrogen concentration but it doubles the mass production rate. This can be understood since the smouldering velocity and, therefore, the global process reaction rate is linearly related to the air flux. Twice as much H_2 is therefore produced over the same time period when the air flux is doubled so long as the increased air flux does not supply excess oxygen to the system. This is important as it makes the reaction more efficient and the syngas will have a higher energy content. The emitted gas species' concentration and the syngas energy for Test 6 and Test 7 are shown in Figure 3.4 which illustrates the positive effect increasing the air flux has on energy efficiency.

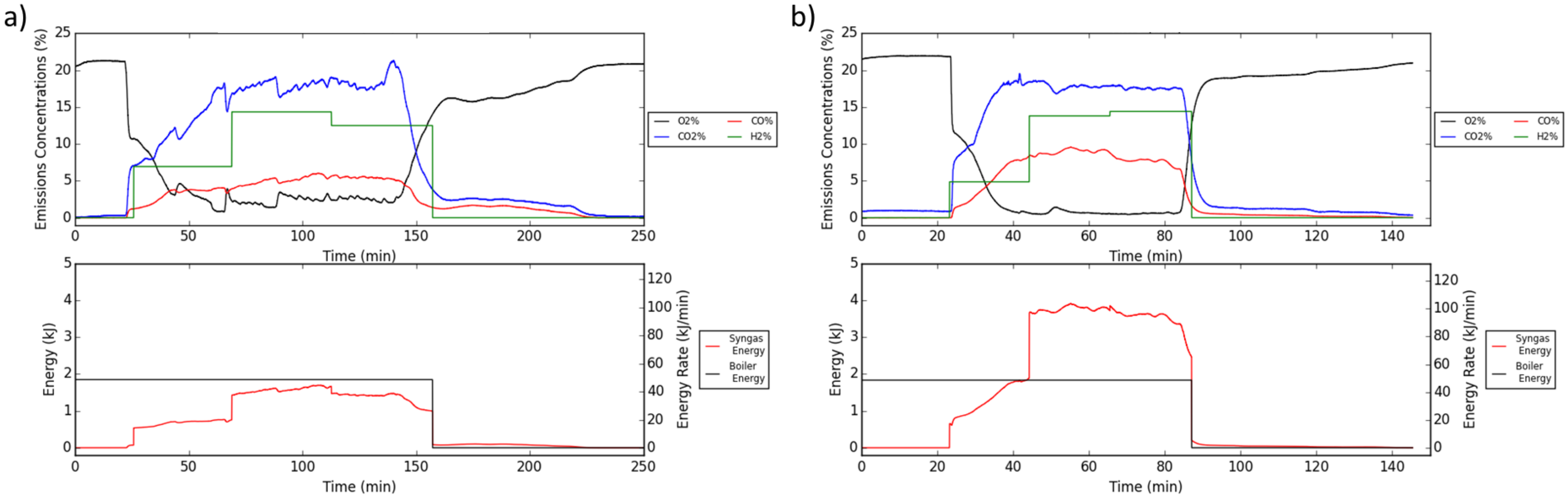

Figure 3.4: a) Test 6 (2.5cm/s air flux) gas emissions concentrations during smouldering reaction and syngas energy compared to boiler input energy. b) Test 7 (5.0cm/s air flux) gas emissions concentrations during smouldering reaction and syngas energy compared to boiler input energy

The increase in energy seen in Test 7 (Figure 3.4b) was substantial enough that the syngas becomes net energy positive with respect to the steam generator during steady state operation. Since the steam needs to be created in order to produce meaningful yields of hydrogen, it is ideal that energy produced from the product syngas was able to offset the steam generator during steady state operation. The heater energy for ignition is only a short-duration event over the course of smouldering and would eventually be balanced out by the syngas energy if the reaction was allowed to run long enough. The effect of the heater energy would continue to diminish relative to the energy generated by the process as scales increased (Sabadell et al., 2019; Scholes et al., 2015; Switzer et al., 2014) or if a continuously fed smouldering reactor was used (Fabris et al., 2017).

3.3.3.2 Feedstock, Carbon and Steam

The primary mechanisms which produce H_2 involve the reaction of steam with carbon. The efficiency of converting carbon and steam in the system to H_2 is explored in Figure 3.5. The carbon consumed is derived from the CO_2, CO, and CH_4 emissions instead of the loaded fuel mass. Upon excavating the reactors, it was evident some of the liquid fuel mobilized out of the reaction zone, especially as the loading concentration reached the saturation point for the media. As such, the carbonaceous gases more accurately reflected the amount of carbon participating in the smouldering and hydrogen forming process. It is important to note that this includes both carbonaceous gases generated from hydrogen-forming reactions as well as smouldering combustion.

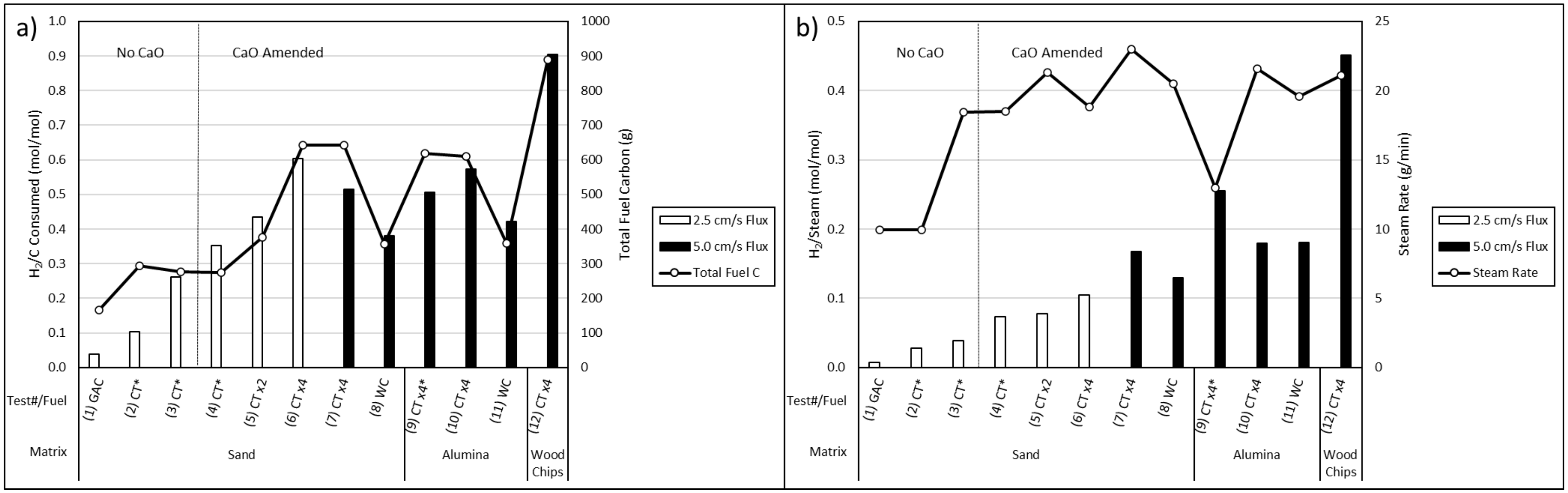

Figure 3.5: a) H_2 production efficiency with respect to carbon consumed and b) H_2 production efficiency with respect to steam. Experiments with asterisks indicate CO measurement was above the detectable range of the instrument (10%)

The hydrogen generation with respect to carbon (Figure 3.5a) improved with each amendment until the matrix became fully saturated with coal tar (Test 6). Adding coal tar to the system (Test 2) provided an additional carbon fuel reactant capable of volatilizing which could also participate in homogeneous reactions compared to GAC alone and thus improved the process yield and efficiency. A similar increase was observed when the steam rate was doubled (Test 3), again providing more reactant for the hydrogen-forming reactions. An increase in efficiency was again achieved when the CaO catalyst was added to the system. Doubling (Test 5) and then quadrupling (Test 6) the fuel provided more carbon to the reaction and produced a more efficient process. Test 6 (120 g/kg) marked the point of fuel saturation of the porous medium.

The hydrogen generation efficiency with respect to steam followed a similar trend to carbon for the early amendments. When the air flux was doubled in Test 7, there was small drop in efficiency with respect to carbon but an increase with respect to steam. The reduced carbon efficiency may be due to increased oxygen in the system which is competing with the steam as a reactant with carbon. The combustion reactions are thermodynamically favourable and are therefore producing more CO_2 and CO with no associated H_2. Indeed, when the air flux was increased, the average smouldering temperature also increased. This indicates more energy is being generated and, therefore, more carbon is undergoing combustion. In essence, the higher air flux is reducing the amount of fixed carbon available for the gasification reaction. Since the global reaction is progressing faster due to the increased air flux, the same quantity of steam was able to interact with more hot carbon char and carbonaceous pyrolysis/combustion gases thus making the process more efficient with respect to steam. This effect is seen strongly in Test 9 when the steam rate was 60% of the previous experiments. The steam efficiency is high, however, the cost of this efficiency is evident in Figure 3.3, as the hydrogen production rate and the total mass of hydrogen are both reduced compared to Tests 7 and 10 which had all other fuel, air flux, CaO, and steam variables the same. Despite the efficiency with respect to steam, the process is becoming steam-limited, reducing its overall hydrogen yields. With the fuel carbon held constant, it is expected that increasing the steam supplied to the system would increase the hydrogen production with decreasing efficiency until it asymptotically reaches a maximum hydrogen production rate.

Carbon and steam are the two major reactants in the production of hydrogen and both must be present in adequate quantities lest the process become limited by one of the reactants. Figure 3.6 compares the molar ratio of steam to carbon consumed by the process as well as comparing the ratio of oxygen to steam supplied.

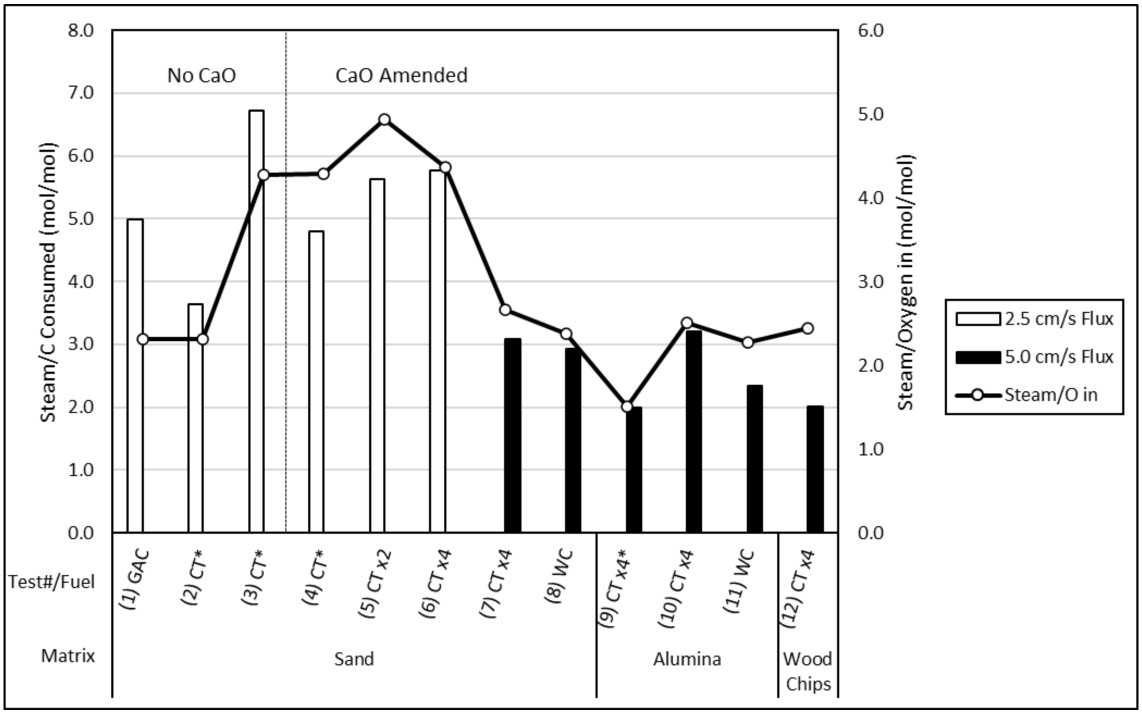

Figure 3.6: Ratio of steam to carbon as well as the ratio of steam to oxygen. Experiments with asterisks indicate CO measurement was above the detectable range of the instrument (10%)

The results from early amendments do not follow a similar trend to Figure 3.3 which indicates that the steady improvement observed in hydrogen production was not due to the steam/carbon balance over this period. There was more than an adequate amount of steam injected in the system for the process to proceed. When the air flux is increased in Test 7, the steam/carbon ratio decreases from 5.8 to 3.1. Above, it was shown that this test with increased air flux marked a divergence in carbon efficiency and steam efficiency but had no effect on the total hydrogen production. Evidently, a steam to carbon ratio of 3 will not negatively impact the reaction and a higher quantity of steam will not yield greater results. Likewise, decreasing the steam/oxygen supplied ratio from ~4.4 to 2.7 did not negatively affect the process.

Subsequently, Test 9 reduced the amount of steam injected to a steam/carbon ratio just below 2.0 which lowered the supplied steam/oxygen ratio to 1.5. This resulted in an overall reduction in hydrogen production. Though Test 9 has an alumina matrix, it is apparent that the difference in hydrogen production is due to the steam/carbon, steam/oxygen ratios and not a matrix effect. This is made evident in Test 10 when the same alumina system was adjusted back to similar steam/carbon (3.2) and steam/oxygen (2.5) ratios as coal tar Test 7. The hydrogen production also rebounded to similar H_2 concentrations and total mass yields as seen in Figure 3.3. Generally, then, the smouldering hydrogen production process should maintain the steam/carbon ratio between 2-3. A lower ratio will result in a steam-limited system which would negatively impact H_2 generation and any higher will cease to have a meaningful effect.

The produced hydrogen decreased when wood chips were used as the fuel source with the same mass concentration as coal tar. The wood chips have a significantly lower carbon content than the coal tar used in this study. Elemental analysis found the wood chips had a carbon content of 47.76% while coal tar’s carbon content was 80.75% (Table 3.1) meaning less carbon fuel was available to participate in hydrogen forming reactions. To adequately compare the results from the wood chips experiments to the coal tar, they must be compared to a test with a similar carbon loading. The most similar coal tar test was Test 5 which had 376g of fuel carbon compared wood chip Tests 8 and 11 which had 356g and 358g of fuel carbon respectively. One other critical difference between these tests is that the wood chips experiments were operated at twice the air flux as Test 5. Figure 3.3 shows that wood chip Test 8 had similar H_2 concentrations and total mass production with Test 5 being higher in both regards as it has a greater amount of carbon in the system. The carbon efficiencies, as seen in Figure 3.5a, are similar as would be expected since a difference in air flux doesn't strongly affect the metric. The hydrogen mass production rate (Figure 3.3) and steam efficiency (Figure 3.5b) are both higher for the wood chips tests, however this is a result of the higher air flux used during those tests rather than the fuel type. Ultimately, wood chips and coal tar appear to behave similarly as a fuel for hydrogen production in a smouldering system when compared on a total carbon basis. As with coal tar, when alumina is used as the bulking matrix for the wood chips fuel, the hydrogen production increases compared to the sand matrix. The average methane for both wood chip tests was 0.60% compared to 0.07% when using coal tar as the fuel. Methane is a common gas in the pyrolysis of wood (Mohan et al., 2006) so its increased concentration is most likely a product of its pyrolysis chemistry and not a result of the process generating hydrogen.

Hydrogen production was maximized when woodchips were used as the bulk media and mixed with the coal tar fuel mixture (Test 12). The steady-state H_2 concentration was 26.2% with a peak concentration of 33.7% and a total yield of 58.2g. This improved the steady-state concentration by 50.9% and the total yield by 161% compared to the next best producing system (Test 10). The organic, smoulderable matrix in Test 12 permitted a significantly higher fuel loading improving the fuel carbon content in the reactor by 41% from Test 10 while also ensuring all the steam would contact organic material rather than inert media. Indeed, as seen in Figure 3.5, when wood chips are used as the bulk matrix, the hydrogen production is the most efficient with respect to both carbon and steam compared to any test using inert media. Interestingly, the increased fuel in the system reduces the steam/carbon ratio down to 2.0 which is where there was evidence of being steam limited in Test 9. The steam/oxygen ratio was still higher in this test than Test 9, but it is possible that despite the high hydrogen production, the process was steam-limited and could have produced even greater yields of H_2 if more steam had been supplied. In steam gasification, studies have found that the optimal steam/biomass mass ratio for H_2 production was between 1-1.5, with decreasing yields at higher ratios (Chang et al., 2011;

Li et al., 2009). The steam/biomass ratio for Test 12 was 0.93 which would suggest it was below the optimum ratio.

Additional experiments (Appendix C) were conducted to explore hydrogen production from smouldering unamended, virgin fuels including GAC, coal tar, crumb rubber, and wood chips. The H_2 concentrations emitted during smouldering are all very small since H_2 is not a thermodynamically favourable product of combustion. The little H_2 produced during conventional smouldering would be a product of pyrolysis ahead of the smouldering reaction, where the majority of emission products are generated (Torero et al., 2020). GAC, containing virtually no molecular hydrogen, did not produce any H_2. Wood chips produced the greatest quantity of H_2 followed by coal tar and then crumb rubber. This indicates that there is a negative correlation between fuel processing and H_2 production.

3.3.4 Driving Mechanisms of the Process

3.3.4.1 Heterogeneous Gasification

Heterogeneous gasification can occur just preceding the smouldering front where fuels have been reduced to carbon-rich char and have been heated to several hundred degrees Celsius as shown in Figure 3.2. Steam can heterogeneously react with the char in the presence of CaO and an absence of oxygen which has all been consumed by the smouldering reaction. Solid, non-volatile GAC was used as the lone fuel source in Test 1 and was capable of producing H_2. Heterogeneous gasification is the only mechanism available to produce H_2 in this system which demonstrated that gasification is one of the reaction mechanisms of the process. The gasification reaction produces equal molar parts H_2 and CO.

$$C + H_2O \rightarrow H_2 + CO\ (+131\frac{kJ}{mol})$$

It is therefore possible to compare the molar ratio of H_2 to CO to determine if gasification alone is responsible for the hydrogen production or if further mechanisms need to be considered. Figure 3.7 plots the molar ratio of H_2 to CO.

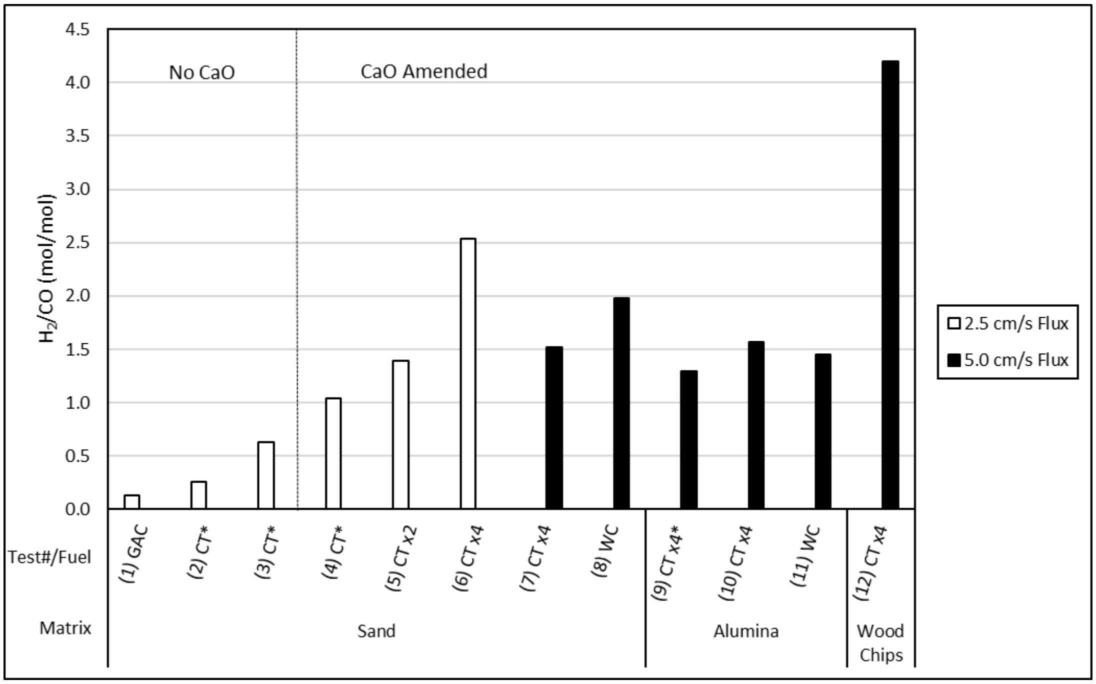

Figure 3.7: Ratio of H_2 to CO generated from the reaction. Experiments with asterisks indicate CO measurement was above the detectable range of the instrument (10%)

The molar ratio of H_2 to CO is greater than 1 for the majority of tests which indicates that gasification alone is not the sole mechanism. This is even further reinforced since the CO values are inflated because smouldering also produces CO as a product of combustion and cannot be separated from the CO from gasification.

In Test 2, when coal tar was used in addition to GAC as the fuel, the H_2 concentration increased by more than the additional carbon mass solely gasifying. The influencing difference between the coal tar and GAC is that coal tar releases volatile species during the pyrolysis process which are able to react homogeneously with steam, producing greater yields of H_2 than from gasification alone. This is in agreement with previous work which found that more volatile fuels increased H_2 yield in steam gasification (Zhang, Xu, et al., 2019). Early, unoptimized, tests which used coal tar and steam (Test 1-3) are overly influenced by the smouldering contribution of CO to their limited H_2 production which causes them to fall below a H_2 to CO ratio of 1. This is not indicative that only gasification is occurring. It is expected that in all systems where a volatile hydrocarbon is released, homogeneous hydrogen-forming reactions are participating as well. The exact proportion of H_2 which comes from heterogenous gasification cannot be determined here, but these results suggest there are additional reactions.

3.3.4.2 Homogeneous Reactions

In the smouldering system, the heat transfer ahead of the oxidation front is contained to a very small region in space (Torero et al., 2020) which results in the gasification zone and pyrolysis zone overlapping as shown in Figure 3.2. Gaseous species exist very near the reaction front allowing them to react homogenously with steam that is present in an anoxic environment resulting in steam reforming. CO is also present in the hot, anoxic zone both from combustion and gasification reactions. The CO could undergo a water-gas shift when interacting with steam in this zone.

Steam reforming occurs when gaseous hydrocarbons react with steam following:

$$C_xH_y + zH_2O \rightarrow \left(x + \frac{y}{2}\right) H_2 + zCO$$

Importantly, steam reforming can potentially produce H_2 at a ratio greater than 1 with respect to CO and could therefore also be contributing the extra H_2 which needs to be accounted for from Figure 3.7.

The water-gas shift reaction consumes CO to produce H_2 and CO_2.

$$CO + H_2O \rightarrow CO_2 + H_2 \, (-41 \frac{kJ}{mol})$$

This reaction increases the ratio of H_2 to CO and could account for the excess H_2 from Figure 3.7 as well. The participation of this reaction is confirmed by comparing the molar quantities of oxygen supplied to the amount emitted as CO_2; only the combustion reaction and the water-gas shift create CO_2. Supplied air feeds the combustion reaction and, in the event of complete combustion, the ratio of CO_2 emitted to O_2 supplied could never exceed

1. Steam supplies more molecular oxygen and, when it undergoes the water-gas shift reaction, produces CO_2. Figure 3.8 shows the ratio of oxygen emitted to oxygen supplied.

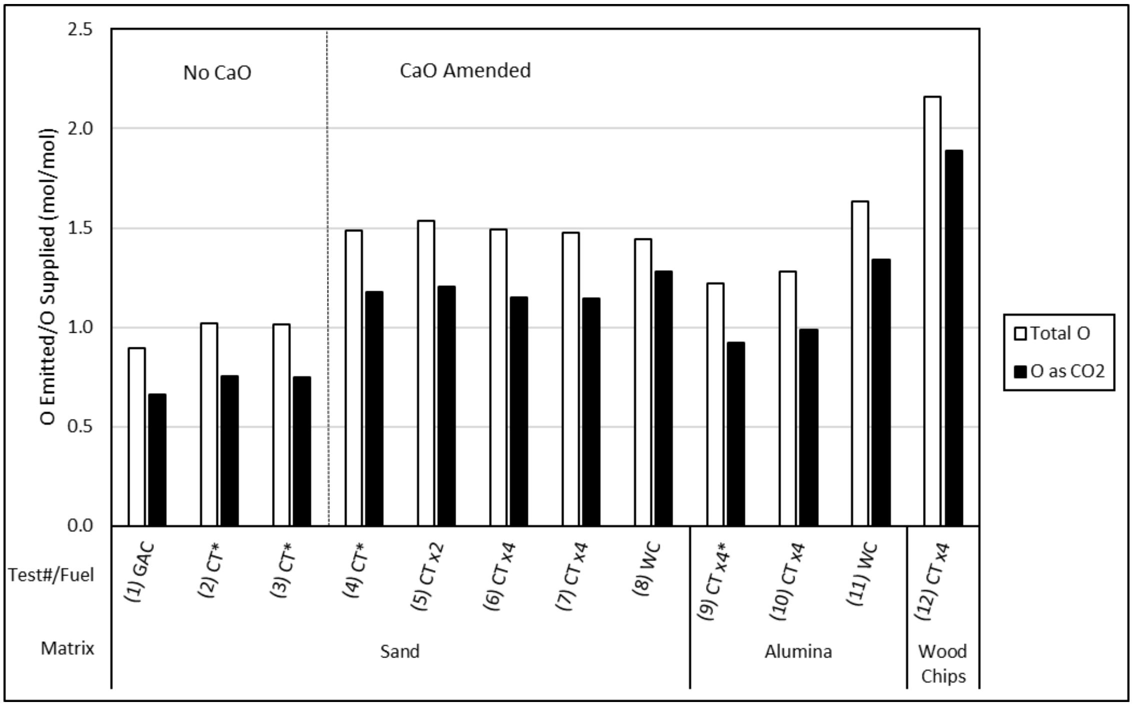

Figure 3.8: Ratio of the molar quantity of the total oxygen emitted from the reaction as well as oxygen emitted as CO_2 compared to the molar quantity of oxygen supplied as air to fuel to smouldering process. Experiments with asterisks indicate CO measurement was above the detectable range of the instrument (10%)

The white bars show the total oxygen emitted (as CO, CO_2, and O_2) vs the oxygen supplied while the black bars show specifically the ratio of CO_2 emitted to O_2 supplied. For the majority of tests, the ratio of CO_2 emitted to O_2 supplied is greater than 1 indicating the water-gas shift reaction has occurred.

There is likely a small inflation of CO_2 from the pyrolysis of coal tar and/or wood chips. The elemental analysis found that coal tar and wood chips had oxygen contents of 10.78% and 41.59% respectively (Table 3.1) and a small portion of this molecular oxygen does emit as CO_2 during pyrolysis (Torero et al., 2020). The oxygen balance was compared to the H_2 to steam ratio, Figure 3.5b. For steam to form H_2, the molecule must split producing equal molar amounts of H_2 and O. Therefore, the excess O (oxygen in emissions as CO, CO_2, and O_2 beyond what was supplied by air) to steam ratio should match the H_2 to steam ratio. Figure 3.9 adds the oxygen ratio to Figure 3.5b (excluding uncatalyzed tests) for comparison.

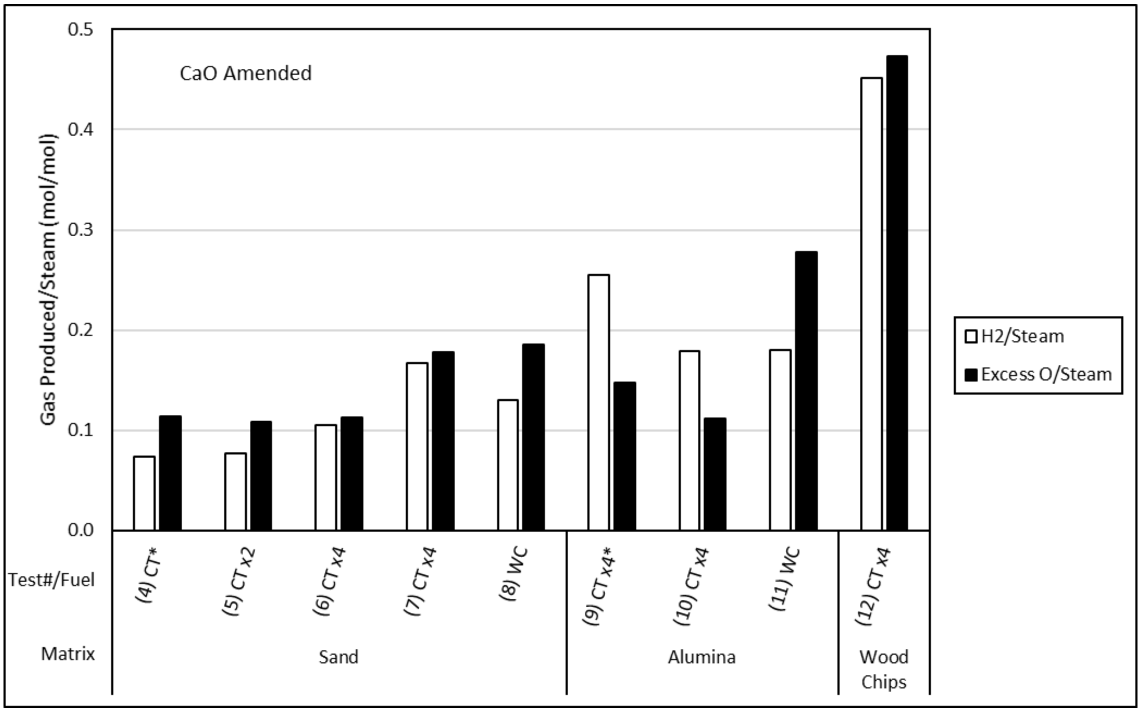

Figure 3.9: Molar comparison of the excess oxygen and H_2 emitted from the reaction to the steam supplied. Experiments with asterisks indicate CO measurement was above the detectable range of the instrument (10%)

There is good agreement between the H_2 and O ratios giving confidence to the mass balance. The oxygen ratio is higher than H_2 in most tests likely due to the extra CO and CO_2 released from the pyrolysis of coal tar and/or wood chips. Interestingly, when alumina is used as the matrix with the coal tar fuel mixture, the H_2 ratio is dominant, possibly indicating a favourable matrix effect.

3.4 Conclusions

A method of generating syngas with a significant hydrogen concentration from the smouldering of waste was demonstrated for the first time. Critical to the process was the unique reaction zone created by the smouldering front being amended with a mineral catalyst (here: CaO) and steam injection. Results showed that the reaction could be optimized to generate H_2 concentrations as high as 33.7% while completely destroying waste tars and biomass. Moreover, the theoretical syngas energy generated from this process was net-energy positive indicating this is a viable technology for resource recovery or low carbon intensity energy production.

Increasing the fuel loading (carbon content) and steam supplied both had a positive correlation on the quantity of H_2 generated but with decreasing efficiency. The optimum molar steam/carbon ratio for this system was determined to be between 2-3. Evidence from this study also identified that heterogeneous gasification, the water-gas shift, and likely steam reforming are all contributing to the smouldering-driven global hydrogen generation process. The specific contribution of each mechanism will be examined in future work, as will the capture and treatment of emitted products.

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Chapter 4

4 Conclusions and Recommendations

4.1 Conclusions

This thesis explored the utilizing STAR-based smouldering as a new technology for generating H_2. The possibility to create a newly hypothesized H_2 generating region within a smouldering system was presented for the first time. A suite of laboratory scale experiments was conducted to determine the effect various process parameters and amendments had on the ability to produce H_2. The primary feedstocks investigated were granular activated carbon (GAC), coal tar, and woody biomass. Airflux, steam injection, alumina, and calcium oxide (CaO) were all added and/or adjusted as the primary amendments to the reaction to maximize the concentration of H_2. Experimental results were primarily quantified based on the concentrations of the produced gases, in particular H_2, and the theoretical energy of the syngas. A detailed mass balance was carried out which provided insights into the efficiency of the different amendments. Further analysis of the mass balance provided evidence of the different mechanisms of H_2 formation.

Results suggest that:

- CaO and steam injection both improve H_2 generation from a smouldering reaction but work synergistically when used together in a smouldering system to maximize H_2 production.
- An optimal ratio of fuel to CaO was determined to be 2:1.
- Concentrations of H_2 increased with increasing steam injection, however with decreasing efficiency. It was found that the optimal molar steam to carbon ratio was between 2-3. Above this ratio the reaction became inefficient and below, the total H_2 production was decreased.
- Theoretical energy from the syngas was achieved which was greater than the energy required by the boiler to generate steam for the system.

- Increasing the airflux caused the reaction to progress proportionately faster and therefore more efficiently with higher syngas energy content.
- Alumina provided a favourable matrix which accelerated the reaction resulting in H_2 production reaching steady-state faster than in a sand system. Alumina also appeared to favour the production of higher quantities of H_2 when coal tar was used as the feedstock.
- The maximum H_2 production occurred when the woody biomass was used as an organic, smoulderable matrix blended with coal tar. A maximum H_2 concentration of 33.7% was achieved in this configuration with a steady-state H_2 concentration of 26.2%. This amounted to a 50.9% improvement in the steady state concentration from the next best result of coal tar in an alumina matrix. Hydrogen concentrations achieved here make the technology competitive with other thermal technologies in the market.
- There is evidence that both a heterogeneous gasification reaction and a homogeneous water-gas shift reaction are contributing to the production of H_2. The proportion each mechanism is contributing to the total H_2 yield requires further investigation.

In summary, smouldering presents a new, efficient, waste-to-energy technology to produce hydrogen with the potential to be a process with a relatively low carbon intensity. CaO and steam are critical amendments to the reaction and evidence of both heterogeneous and homogenous hydrogen formation mechanisms were identified. H_2 concentrations as high as 33.7% were achieved in this system however there still remains the potential to further optimize the process variables. The results obtained here make the technology competitive with existing methods of H_2 production from waste feedstocks.

4.2 Recommendations

This study was the first laboratory scale investigation on producing H_2 from a smouldering reaction. As such, many different variables were tested sequentially while the best methodology for producing H_2 was determined. With much of the preliminary investigation completed and an understanding of the mechanisms at play established, there are many areas of research which can be explored to further understand and improve the system.

The following is recommended:

- Further work should be carried out to evaluate different catalyst. Several mineral catalysts similar to CaO exist and have been implemented in similar work carried out in gasification. Moreover, a mineral catalyst was selected in this study because it was hypothesized it would be able to endure the high temperatures of smouldering and resist being poisoned by the fuels. It is possible metallic catalysts could be utilised as well.
- Additional feedstocks should be explored to determine the effect they would have on H_2 formation. Numerous biomass wastes exist around the globe from various industries and a targeted study would determine if any types of feedstock would improve or detract from the H_2 production found here.
- Utilizing a continuous emissions monitoring system for H_2 would greatly improve the data set compared to grab samples. Integration over the entire test length would be far more accurate and determining transient effects of H_2 production would be possible.
- A greater investigation into the mechanisms of H_2 formation would be beneficial for understanding how to control production. This would also be beneficial to any modeling work on the reaction.
- Performing a lifecycle analysis would provide more credibility to the claim of the technology having a low carbon intensity.
- Further analytical analysis of the produced syngas should be undertaken to measure its true energy content.
- Ultimately, the effect scale needs to be explored. The efficiency of smouldering and its behaviour have been shown to change at scale.

Undoubtedly the generation of H_2 would also be impacted. Likewise, mechanical efficiencies for materials such and the heaters or the steam generator would change, and the total system energy efficiency would need to be re-evaluated.

Appendices

Appendix A: Additional Methodology

GC-TCD Method

Gas Chromatography – Thermal Conductivity Detector (GC-TCD) was used to quantitatively analyze the grab samples from each experiment for hydrogen and methane. A CombiPAL (Agilent G6500-CTC) autosampler injected 500µL samples into the GC-TCD unit (Agilent 7890A) with 5.0 Nitrogen (Praxair) as the carrier gas. The split inlet temperature was 250°C and the oven was held at 40°C for the duration. A two-column system with backflush was used to prevent large, high boiling compounds from contaminating the column required for permanent gas separation. The first column was an HP PlotQ (Agilent, 30m x 0.53mm x 40µm) connecting to a backflush valve operating under 1.5mL/min constant flow for 7.25 minutes, then -1.5mL/min (backflush) for 9 minutes. The second column coming from the backflush valve to the detector was a Molesieve 5A (Agilent, 30m x 0.53mm x 25µm) operating under constant flow for the duration. The TCD operated under negative polarity being held at 270°C with a reference flow of 12mL/min and a combined makeup flow of 4.4mL/min.

Smouldering Front Velocity

The smouldering front velocity was calculated following (Pironi et al., 2011; Torero & Fernandez-Pello, 1996). This methodology identifies the smouldering front from the thermocouple data as the time when the temperature rises steeply. Two temperatures along this rise are chosen as reference. The time it takes for the reference temperatures to be recorded at the following thermocouples are recorded. The distance between the thermocouples is divided by the recorded time for both reference temperatures and the resulting velocities are averaged. The front velocity calculated at each thermocouple interval for the entire smouldering pack is averaged to give the average smouldering front velocity for the test.

Gaseous Product Yields and Syngas Energy

All gas measurements were volumetric concentrations. In order to determine the mass of each species produced, the volumetric gas concentrations needed to be converted based on the volume of gas emitted by the reaction. The volumetric flowrate of air to the reactor (Q_{in}) was kept constant throughout the experiments, however, the volume of gas emitted (V_{emit}) changes as more gaseous species are generated from the combustion, gasification, reforming, and water gas shift reactions. The volume of gas emitted from the smouldering reactor couldn't be measured directly, however, it could be calculated. The volume of gas emitted at any time was determined by assuming nitrogen doesn't participate in any reaction such that the change in nitrogen concentration is proportional to the change in volume. The proportionality of volume to concentration of an inert gas follows the ideal gas law since the samples are all taken at very nearly the same temperature and pressure. The emitted volume could then be calculated for any discrete time interval (t) following:

$$V_{emit} = \frac{x_{N_{2\_in}}}{x_{N_{2\_emit}}} Q_{in} t$$

The mass of any emitted gas species (m_i) could then be determined over the discrete measurement interval by converting the volumetric concentrations (σ_i) to mass concentrations and multiplying by the volume of gas emitted over the same period (V_{emit}).

$$m_i = \left(\frac{M_i \sigma_i}{24.45}\right) V_{emit}$$

With species mass known, the syngas energy (E_{Syn}) could be calculated at each discrete measurement interval by summing the energies from the enthalpies of combustion ($\Delta H^{\circ}_{C_i}$) for H_2, CO, and CH_4.

$$E_{Syn} = m_{H_2} \Delta H^{\circ}_{C_{H_2}} + m_{CO} \Delta H^{\circ}_{C_{CO}} + m_{CH_4} \Delta H^{\circ}_{C_{CH_4}}$$

Likewise, the moles of any species (mol_i) could be determined from the mass at each discrete measurement interval by:

$$mol_i = \left(\frac{m_i}{M_i}\right)$$

The total carbon emitted was found by summing mol_{CO_2}, mol_{CO}, and mol_{CH_4} while the total oxygen emitted was calculated by summing $2mol_{CO_2}$, mol_{CO}, and $2mol_{O_2}$.

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Appendix B: Full Experimental Suite

Table B.1: Experimental Conditions for all Tests

Test	**Objective**	**Bulking Matrix**	**Organic Fuel**	**Organic Conc (g/kg)**	**GAC Conc (g/kg)**	**GAC Mass (g)**	**Coal Tar Mass (g)**	**Wood Chips Mass (g)**	**Total Fuel Carbon (g)**	**CaO Ratio (mass)**	**Air Flux (cm/s)**	**Steam Rate (g/min)**	**Steam/Carbon Ratio (mol/mol)**
A	GAC Baseline	Sand	GAC	-	30		-	-		-	2.5	0	
B	Coal Tar Baseline	Sand	Coal Tar	22.2	22.2			-		-	2.5	0	
C	Tire Shred Baseline	Sand	Crumb Rubber	30	30		-	-		-	2.5	0	
D	Wood Chips Baseline	Sand	Wood Chips	30	30		-			-	2.5	0	
E	Coal Tar - CaO	Sand	Coal Tar	30	30			-		2:1 Sand:CaO	2.5	0	
F	Coal Tar - x2 Mass - CaO	Sand	Coal Tar	60	30			-		2:1 Sand:CaO	2.5	0	
G	Coal Tar - x2 Flux - CaO	Sand	Coal Tar	30	30			-		2:1 Sand:CaO	5	0	
1	GAC - Steam	Sand	GAC	0	30	189.2	-	-	165.6	-	2.5	13.3	5.3

H	GAC - x1.5 Mass - Steam	Sand	GAC	0	45		-	-		-	2.5	14.4	
I	GAC - x1.5 Mass - x2 Flux - Steam	Sand	GAC	0	45		-	-		-	5	14.8	
2	Coal Tar - Steam	Sand	Coal Tar	30	30	173.9	174.3	-	293	-	2.5	13.3	3.8
3	Coal Tar - x2 Steam	Sand	Coal Tar	30	30	164.3	164	-	276.3	-	2.5	18.46 Before Shut-off	6.9
J	Coal Tar - Water Saturated	Sand	Coal Tar	30	30			-		-	5	240.2	
4	CaO+Steam - 1:1 CT:CaO	Sand	Coal Tar	30	30	162.9	163	-	274.2	1:1 CT:CaO	2.5	18.5	7.3
K	CaO+Steam - 1:1.5 CT:CaO	Sand	Coal Tar	30	45			-		1:1.5 CT:CaO	2.5	19.9	
5	CaO+Steam - 2:1 CT:CaO	Sand	Coal Tar	60	30	151.3	302.4	-	376.6	2:1 CT:CaO	2.5	21.3	6.1
6	CaO+Steam - x4 Mass - 2:1 CT:CaO	Sand	Coal Tar	120	30	156.4	625.3	-	641.8	2:1 CT:CaO	2.5	18.8	6.6

7	CaO+Steam - x4 Mass - x2 Flux - 2:1 CT:CaO	Sand	Coal Tar	120	30	156.9	626.8	-	643.5	2:1 CT:CaO	5	23.0	3.4
L	N2 Cycling	Sand	Coal Tar	120	30	152.6	617.7	-	632.4	2:1 CT:CaO	5 (Intermittent)	22.1	3.3
9	Alumina Matrix - Reduced Steam	Alumina	Coal Tar	200	50	151.1	603.4	-	619.5	2:1 CT:CaO	5	13.0	2
10	Alumina Matrix	Alumina	Coal Tar	200	50	148.4	593.9	-	609.5	2:1 CT:CaO	5	21.6	3
8	Woodchips - Sand Matrix	Sand	Wood Chips	125	75	213.3	-	355.2	356.4	2:1 WC:CaO	5	20.5	3.1
11	Woodchips - Alumina Matrix	Alumina	Wood Chips	220	132	214.6	-	357.2	358.5	2:1 WC:CaO	5	19.6	2.4
12	Woodchips Matrix + Coal Tar	Wood Chips	Wood Chips & Coal Tar	-	300	155.5	626.8	518.3	889.8	2:1 CT:CaO	5	21.1	2.1

Appendix C: Full Experimental Results

Table C.2: Gaseous Production Results from Smouldering System with Velocity, Temperature, and Energy for Full Experimental Suite

Test	**Objective**	**Front Vel. (cm/min)**	**Avg. Peak Temp (°C)**	**CO2 Conc (%)**		**CO Conc (%)**		**H2 Conc (%)**		**CH4 Conc (%)**		**Total CO2 Mass (g)**	**Total CO Mass (g)**	**Total CH4 Mass (g)**	**Total H2 Mass (g)**	**Total Theor. Syngas E (kJ)**
A	GAC Baseline			Early		Early		Early	0	Early	-			-		
				Mid		Mid		Mid	0	Mid	-					
				Late		Late		Late	0	Late	-					
B	Coal Tar Baseline	0.34	909.1	Early		Early		Early	0.1	Early	-			-		
				Mid		Mid		Mid	0.14	Mid	-					
				Late		Late		Late	0.14	Late	-					
C	Tire Shred Baseline	TBD	878.8	Early		Early		Early	0.12	Early	-			-		
				Mid		Mid		Mid	0.13	Mid	-					
				Late		Late		Late	0.12	Late	-					
D	Wood Chips Baseline	0.42	975.9	Early		Early		Early	0.12	Early	-			-		
				Mid		Mid		Mid	0.22	Mid	-					

				Late		Late		Late	0.23	Late	-					
E	Coal Tar - CaO	0.31	954.3	Early		Early		Early	0.05	Early	-			-		
				Mid		Mid		Mid	0.28	Mid	-					
				Late		Late		Late	-	Late	-					
F	Coal Tar - x2 Mass - CaO	0.35	1133.5	Early		Early		Early	0.37	Early	-			-		
				Mid		Mid		Mid	0.49	Mid	-					
				Late		Late		Late	0.4	Late	-					
G	Coal Tar - x2 Flux - CaO	0.93	1024.2	Early		Early		Early	0.14	Early	-			-		
				Mid		Mid		Mid	0.22	Mid	-					
				Late		Late		Late	0	Late	-					
1	GAC - Steam	0.45	823.5	Early	12.15	Early	4.44	Early	0.89	Early	-	368	95	-	1.22	1131.6
				Mid	13.56	Mid	5.48	Mid	0.72	Mid	-					
				Late	13.39	Late	4.94	Late	0.67	Late	-					
H	GAC - x1.5 Mass - Steam	0.46	875.7	Early		Early		Early	0.66	Early	-			-		
				Mid		Mid		Mid	0.67	Mid	-					
				Late		Late		Late	0.61	Late	-					
I	GAC - x1.5 Mass - x2 Flux - Steam	0.88	903.4	Early		Early		Early	0.37	Early	-			-		
				Mid		Mid		Mid	0.84	Mid	-					

				Late		Late		Late	0.51	Late	-					
2	Coal Tar - Steam	0.41	1055.9	Early	12.44	Early	9.57	Early	1.24	Early	-	477	207.3	-	3.37	2570.75
				Mid	14.47	Mid	9.83	Mid	2.51	Mid	-					
				Late	14.07	Late	9.83	Late	2.59	Late	-					
3	Coal Tar - x2 Steam	0.5	1011.5	Early	12.9	Early	9.83	Early	3.5	Early	-	425.2	159.8	-	5.74	2427.3
				Mid	13.9	Mid	9.83	Mid	6.21	Mid	-					
				Late	17.4	Late	5.67	Late	1.88	Late	-					
J	Coal Tar - Water Saturated	0.61	1152.4	Early		Early		Early	0.7	Early	0.028					
				Mid		Mid		Mid	1.07	Mid	0.042					
				Late		Late		Late	0.91	Late	0.053					
4	CaO+Steam - 1:1 CT:CaO	0.55	1059.7	Early	5.22	Early	8.60	Early	8.58	Early	-	489.8	171.2	-	13.4	3626
				Mid	19.1	Mid	9.83	Mid	10.18	Mid	-					
				Late	19.7	Late	9.83	Late	9.96	Late	-					
K	CaO+Steam - 1:1.5 CT:CaO	0.52	1022.3	Early		Early		Early	8.3	Early	-			-		
				Mid		Mid		Mid	7.45	Mid	-					
				Late		Late		Late	6.02	Late	-					
5		0.53	1017.2	Early	16.7	Early	7.24	Early	7.22	Early	-	667.5	178.4	-	16.83	4184.1

	CaO+Steam - 2:1 CT:CaO			Mid	18.9	Mid	8.61	Mid	11.96	Mid	-					
				Late	20.6	Late	8.93	Late	11.21	Late	-					
6	CaO+Steam - x4 Mass - 2:1 CT:CaO	0.45	1010.9	Early	14.9	Early	3.67	Early	6.93	Early	-	671.8	124.7	-	21.25	4267.58
				Mid	18.1	Mid	5.65	Mid	14.34	Mid	-					
				Late	20.9	Late	5.27	Late	12.49	Late	-					
7	CaO+Steam - x4 Mass - x2 Flux - 2:1 CT:CaO	0.94	1213.5	Early	18.3	Early	8.21	Early	4.86	Early	-	712.6	189	-	21.17	4906.3
				Mid	17.7	Mid	9.08	Mid	13.81	Mid	-					
				Late	17.5	Late	7.07	Late	14.35	Late	-					
L	N2 Cycling	0.72 *Inludes N2	1200.3	Early	15.6	Early	5.46	Early	9.13	Early	0.04	721.86	180	0.65	25.93	5526
				N2 A	2.8	N2 A	1.1	N2 A	3.6	N2 A	0.02					
				Mid	19.6	Mid	7.51	Mid	12.72	Mid	0.03					
				N2 B	2.9	N2 B	1.6	N2 B	6.54	N2 B	0.02					
				Late	21.4	Late	8.42	Late	14.28	Late	0.04					

9	Alumina Matrix - Reduced Steam	1.47	1235.5	Early	16	Early	9.83	Early	13.97	Early	0.08	507.1	164.6	0.72	15.66	3919.8
				Mid	15.2	Mid	9.83	Mid	12.69	Mid	0.07					
				Late	14.3	Late	9.83	Late	13.38	Late	0.08					
10	Alumina Matrix	1.27 *Two Fronts	1144.8	Early	16.8	Early	9.83	Early	21.63	Early	0.08	538.7	168.1	1.05	22.31	4915
				Mid	15.6	Mid	9.10	Mid	17.37	Mid	0.1					
				Late	15.6	Late	9.43	Late	14.25	Late	0.14					
8	Woodchips - Sand Matrix	0.99	931.3	Early	19.2	Early	5.32	Early	7.51	Early	0.5	701.96	101.9	4.82	12.34	3043.1
				Mid	21.2	Mid	5.19	Mid	10.26	Mid	0.6					
				Late	21.1	Late	5.37	Late	8.52	Late	0.19					
11	Woodchips - Alumina Matrix	2.38	932.7	Early	-	Early	-	Early	14.26	Early	0.63	563.1	94.2	6.44	19.29	4038.7
				Mid	20.66	Mid	8.70	Mid	12.62	Mid	0.59					
				Late	21.5	Late	6.97	Late	14.19	Late	0.5					
12		-	999.1	Early	17.6	Early	9.83	Early	33.72	Early	0.74	2026.6	271.1	7.36	58.24	11392.4

	Woodchips Matrix + Coal Tar			Mid	22.4	Mid	6.24	Mid	26.21	Mid	0.32					
				Late	21.3	Late	5.08	Late	23.66	Late	0.21					

The experimental study was conducted in phases to determine the individual effect each amendment had on hydrogen production. The emitted hydrogen concentrations across all tests can be seen in Figure C.1. Three hydrogen concentration measurements were taken at an early time, mid time, and late time as described previously.

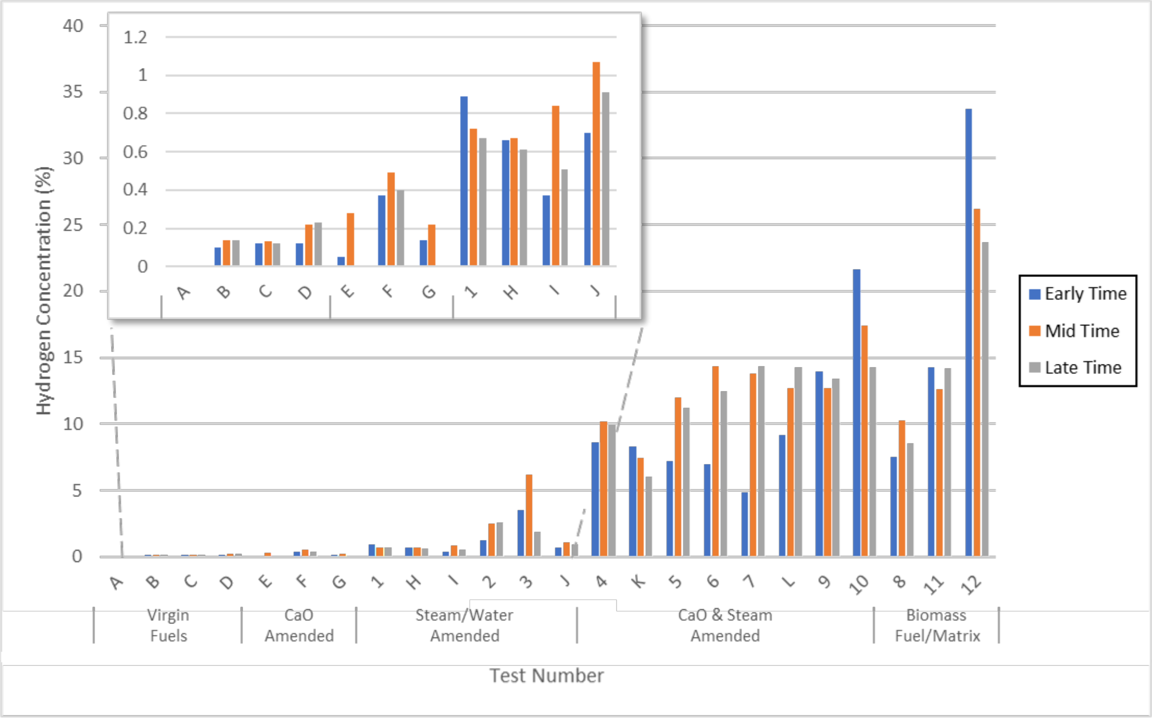

Figure C.1: Hydrogen concentrations from the smouldering system at early- mid- and late-times

Calcium Oxide (CaO) was used as a catalyst in two phases of the experimental program. All are discussed in the manuscript other than the experiments In Phase II. Granular CaO (Carmeuse, HiCal QL Water Grade 11560, ¼” x 10 mesh) was used in place of sand doubling as both a bulking agent and catalyst.

Appendix D: Focused Experimental Suite Plots

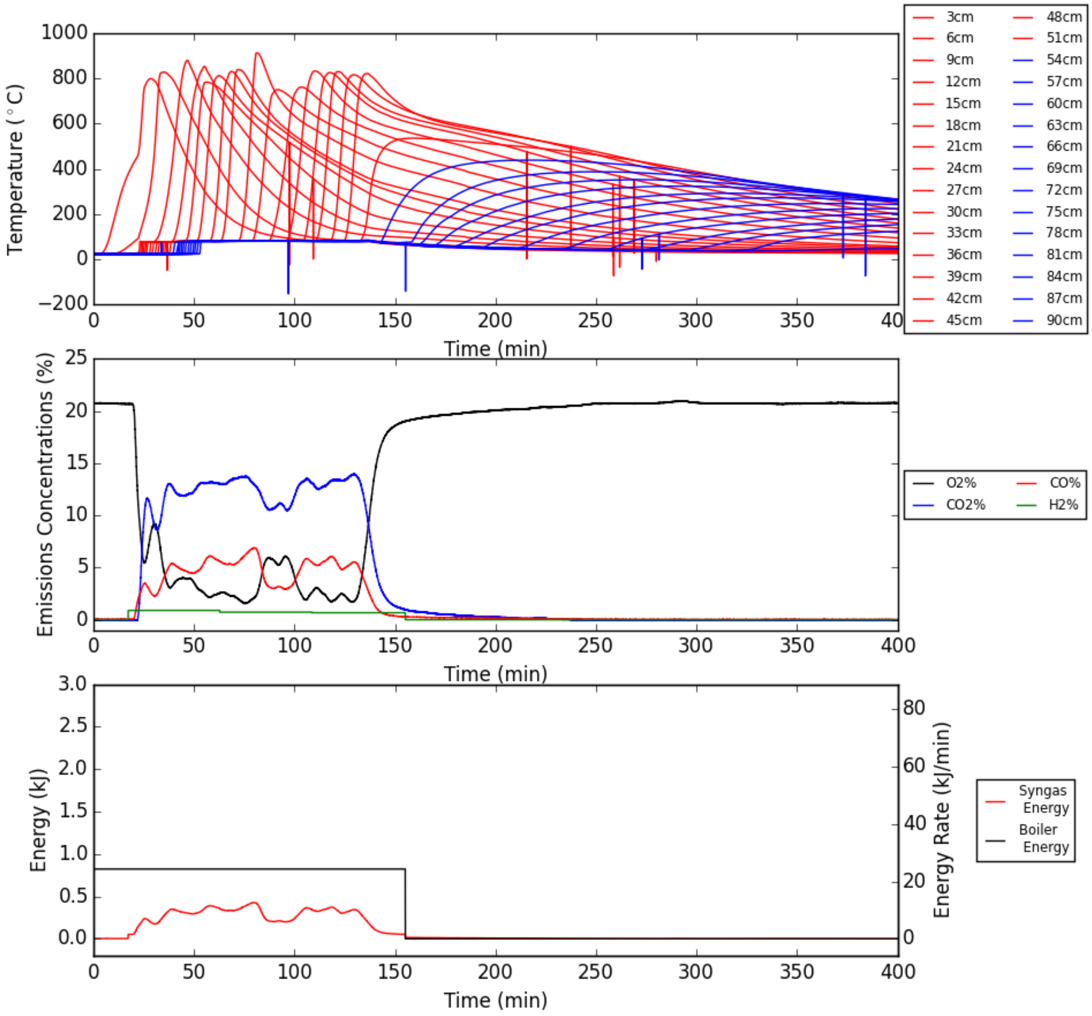

Figure D.2: Test 1 - GAC + Steam - temperature, emissions, and energy profiles

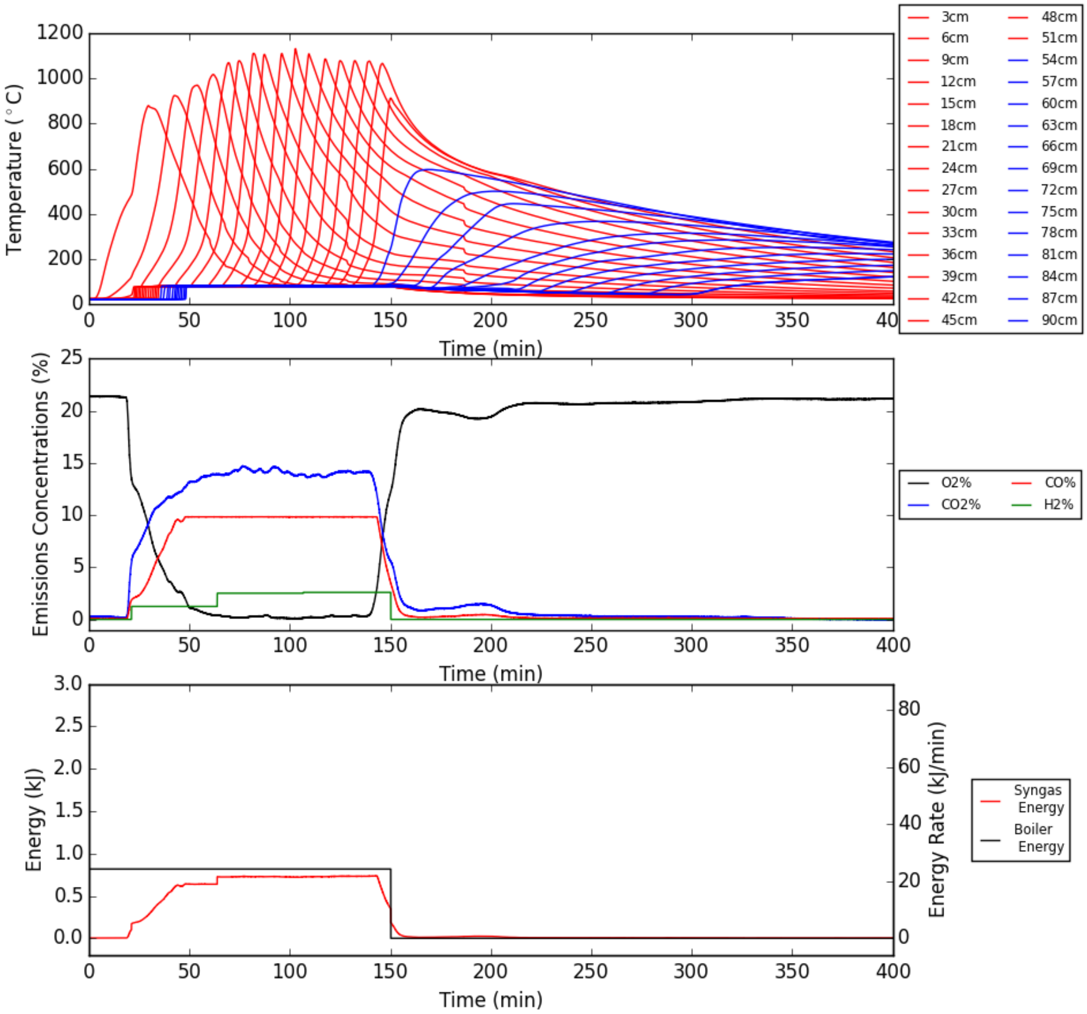

Figure D.3: Test 2 - Coal Tar + Steam - temperature, emissions, and energy profiles

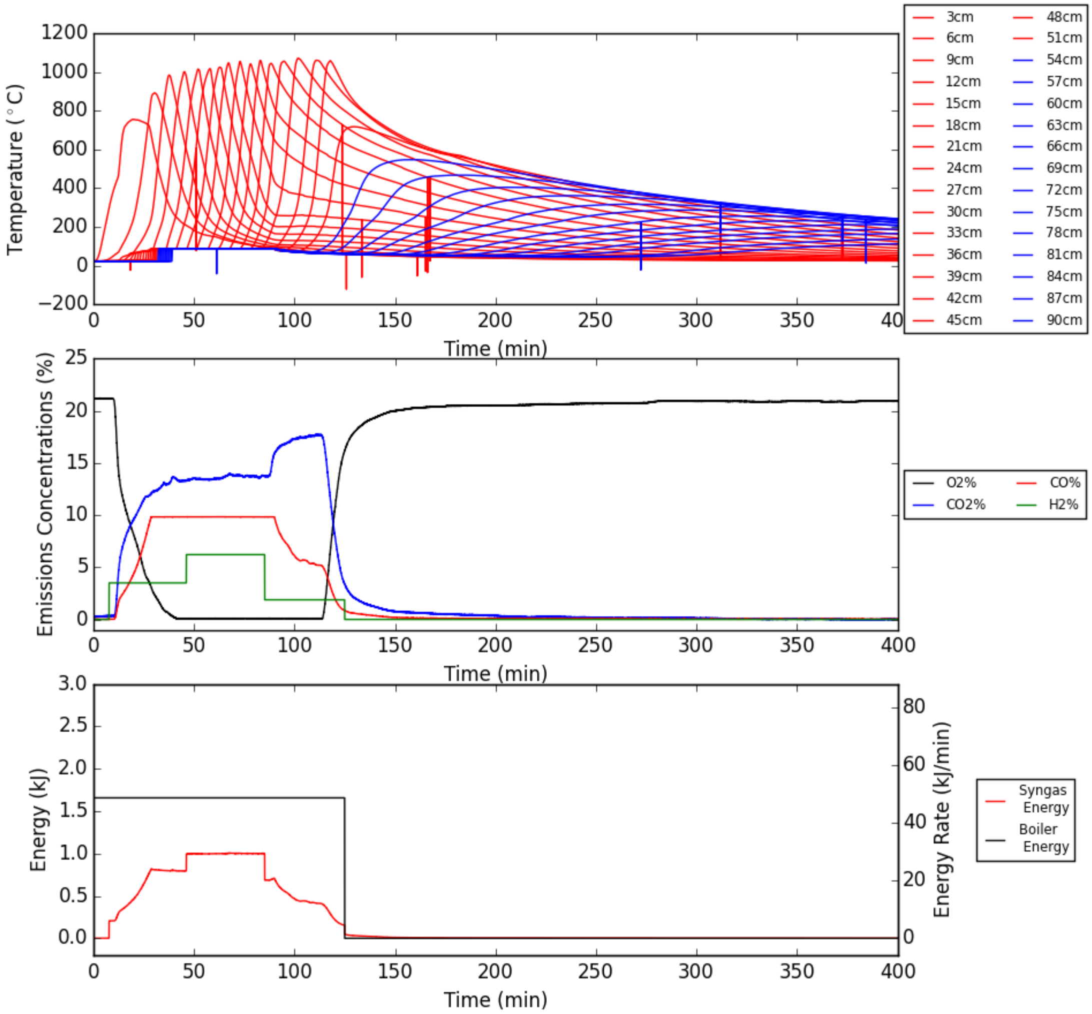

Figure D.4: Test 3 - Coal Tar + x2 Steam - temperature, emissions, and energy profiles

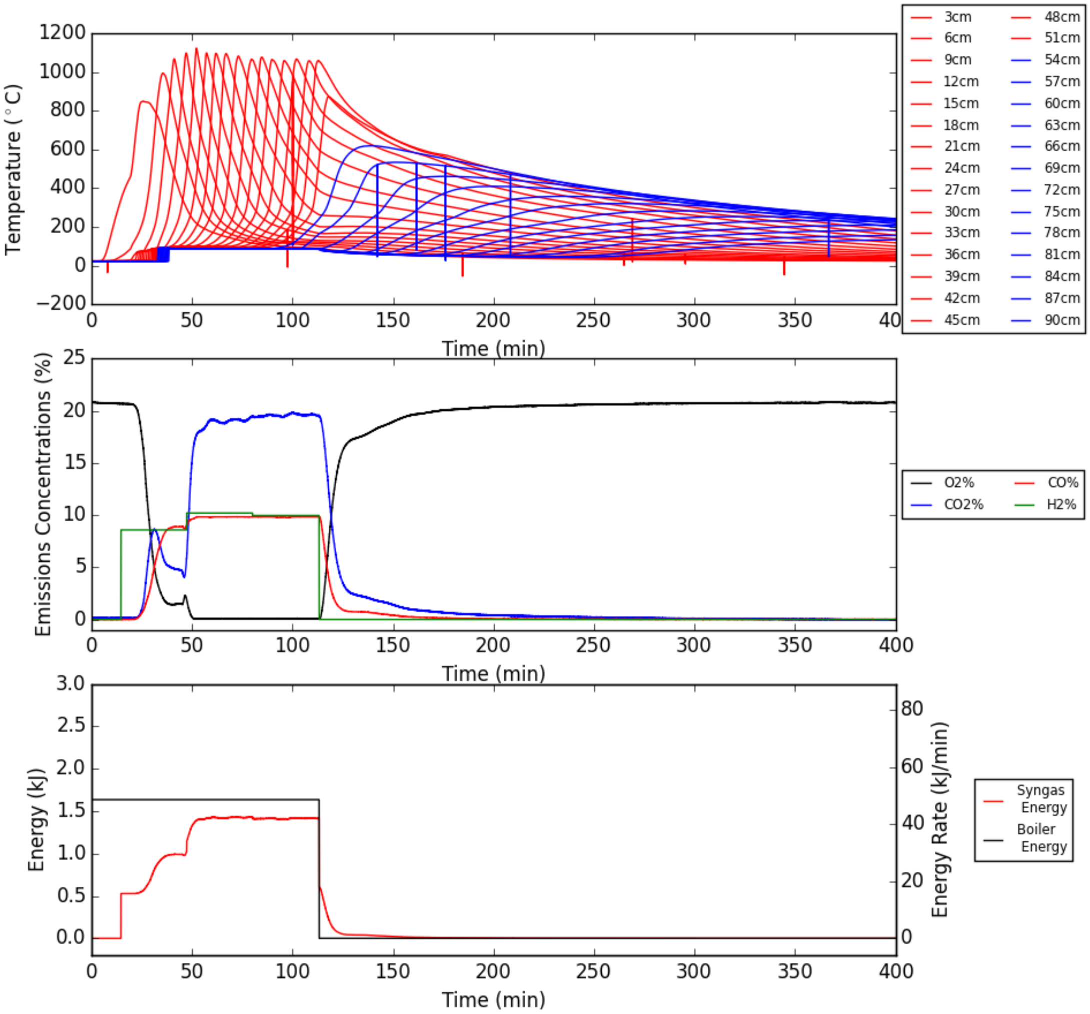

Figure D.5: Test 4 - CaO+Steam - 1:1 CT:CaO - temperature, emissions, and energy profiles

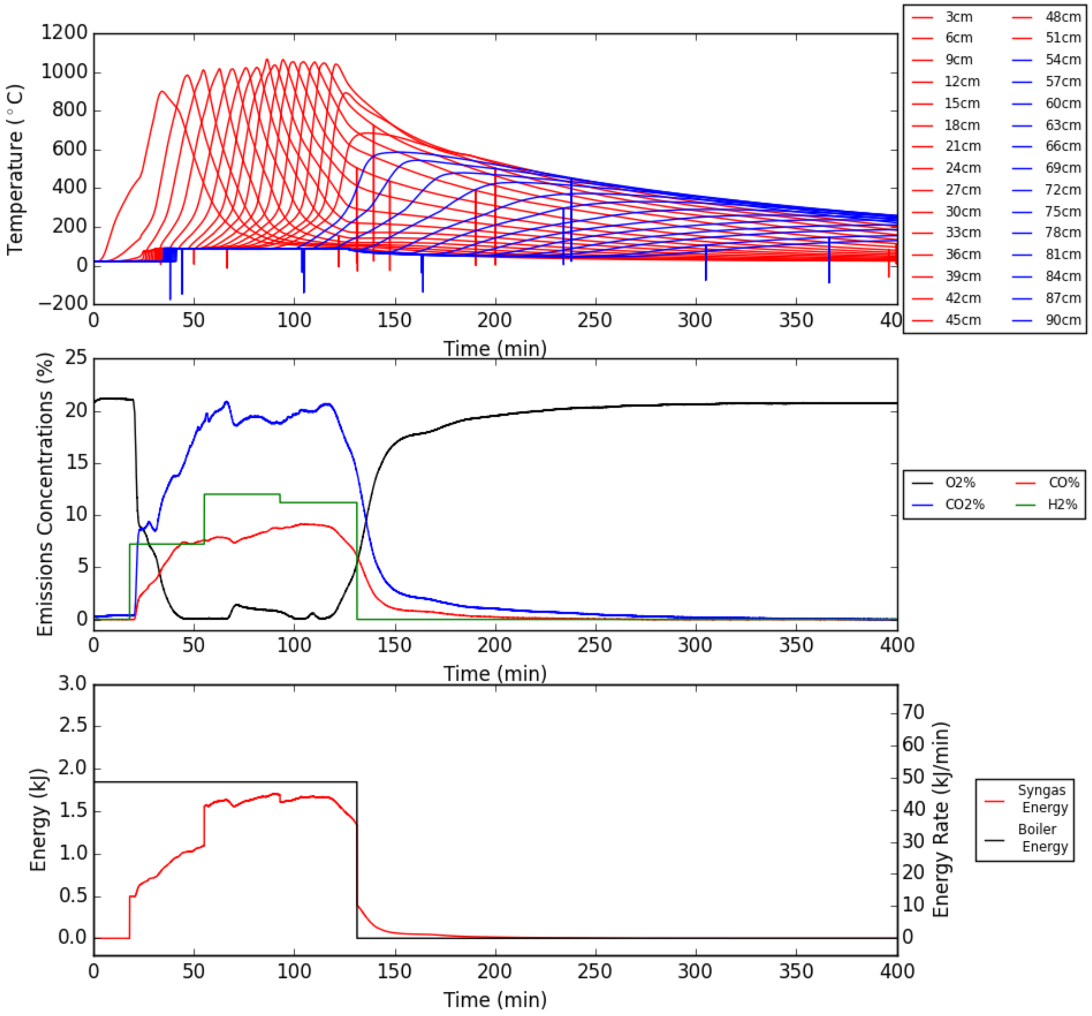

Figure D.6: Test 5 - CaO+Steam - 2:1 CT:CaO - temperature, emissions, and energy profiles

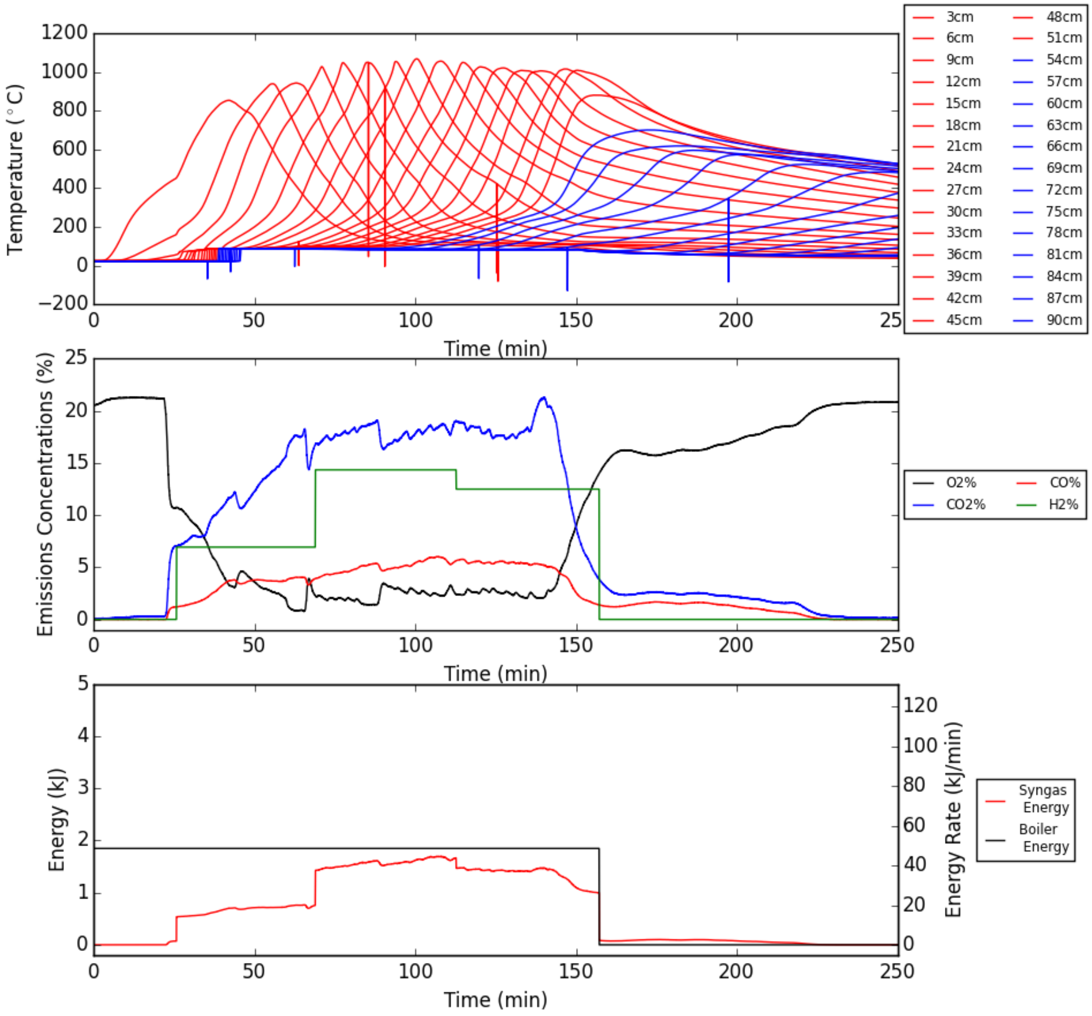

Figure D.7: Test 6 - CaO+Steam - x4 Mass - 2:1 CT:CaO - temperature, emissions, and energy profiles

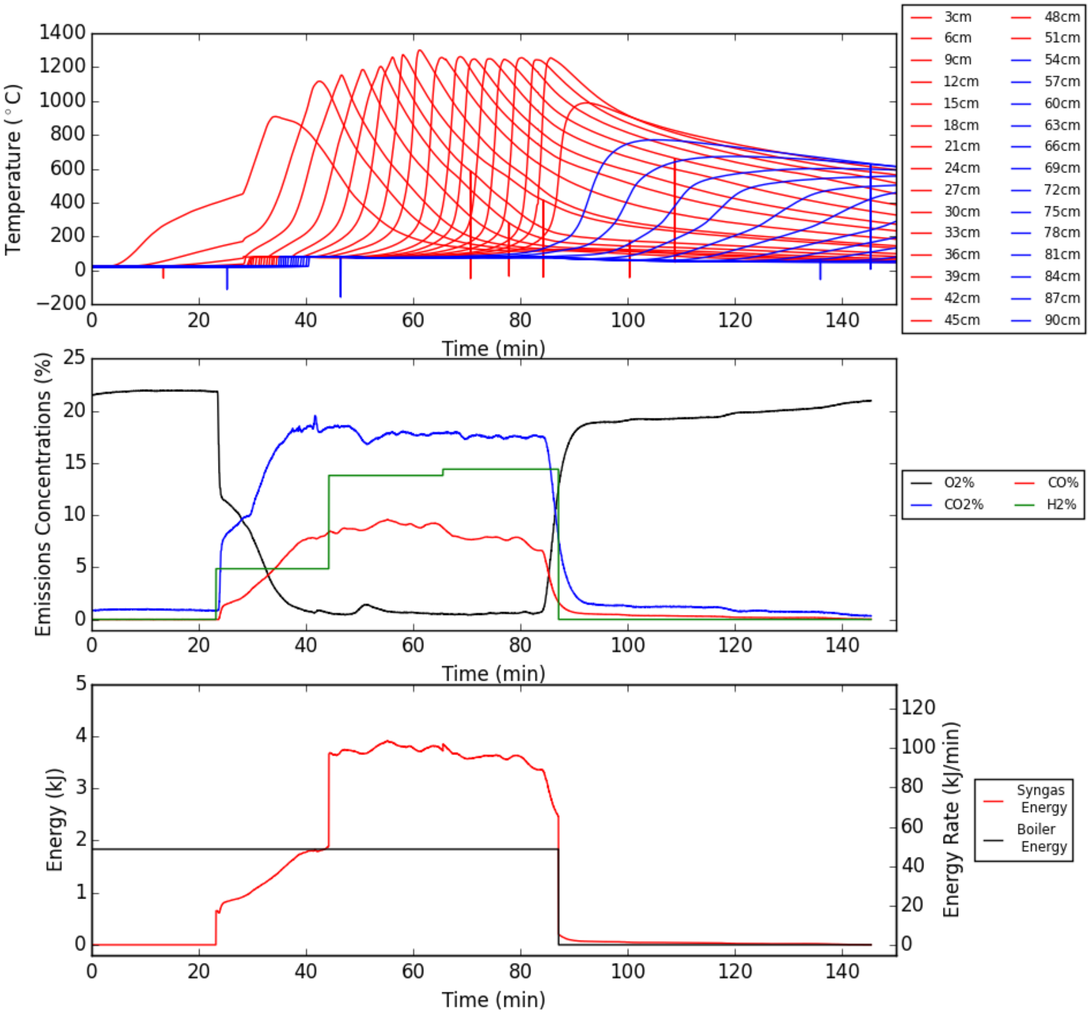

Figure D.8: Test 7 - CaO+Steam - x4 Mass - x2 Flux - 2:1 CT:CaO - temperature, emissions, and energy profiles

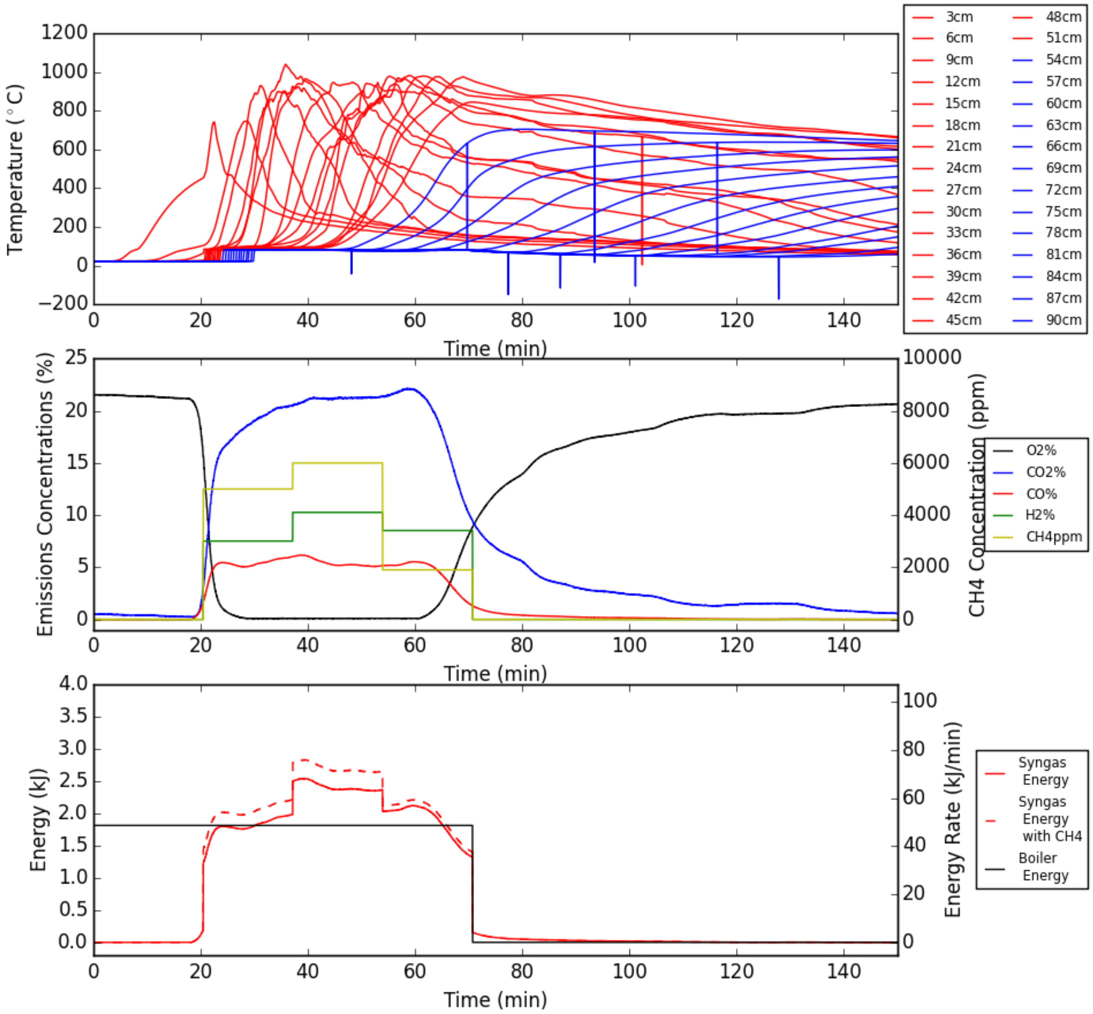

Figure D.9: Test 8 - Woodchips - Sand Matrix - temperature, emissions, and energy profiles

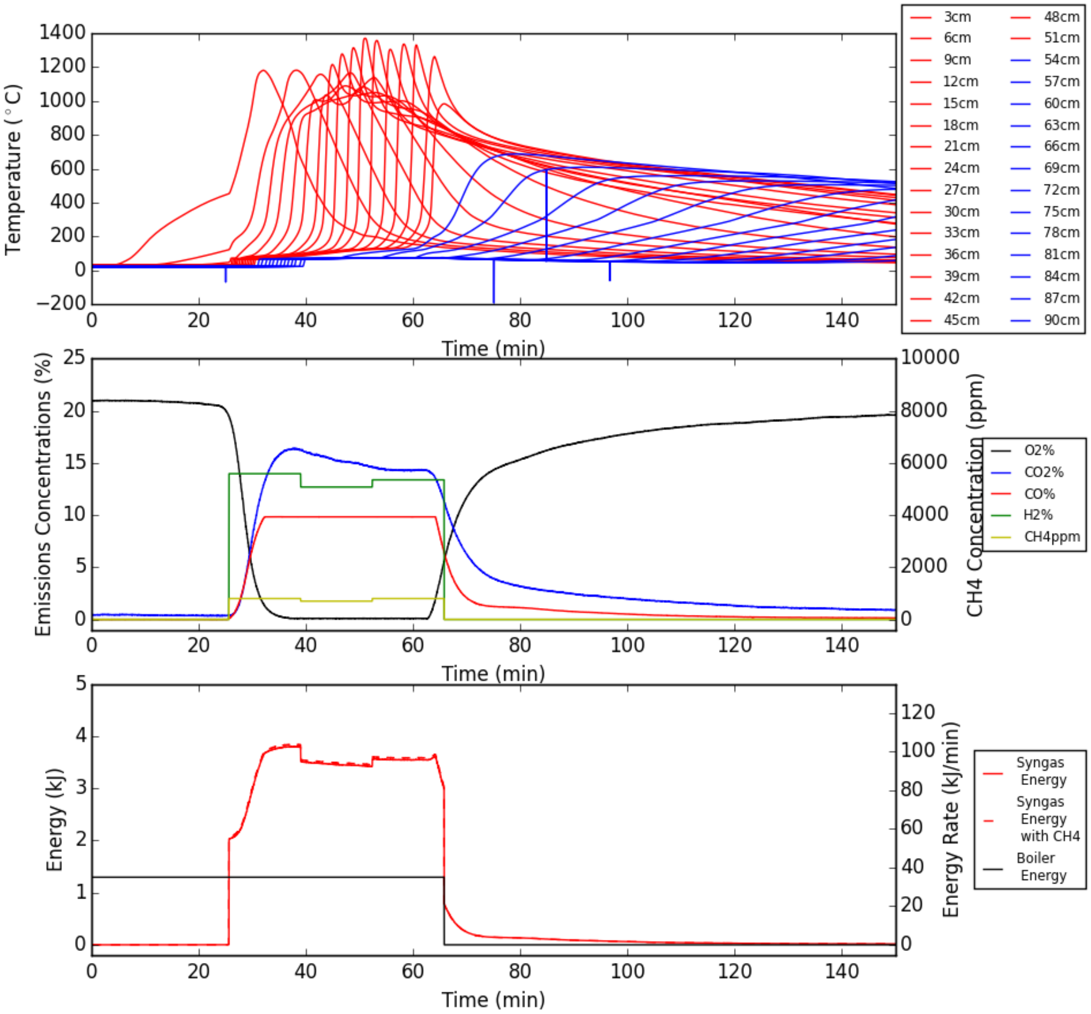

Figure D.10: Test 9 - Alumina Matrix - Reduced Steam - temperature, emissions, and energy profiles

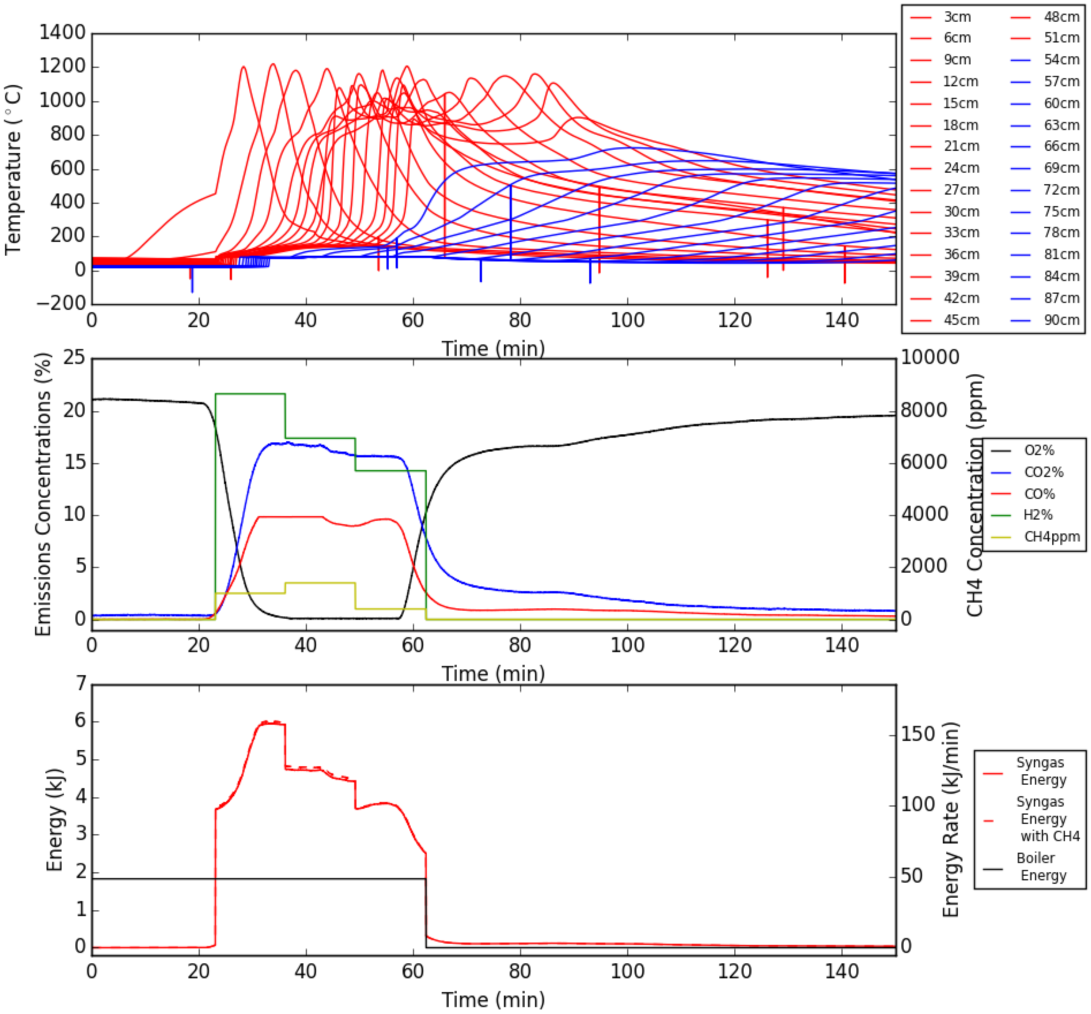

Figure D.11: Test 10 - Alumina Matrix - temperature, emissions, and energy profiles

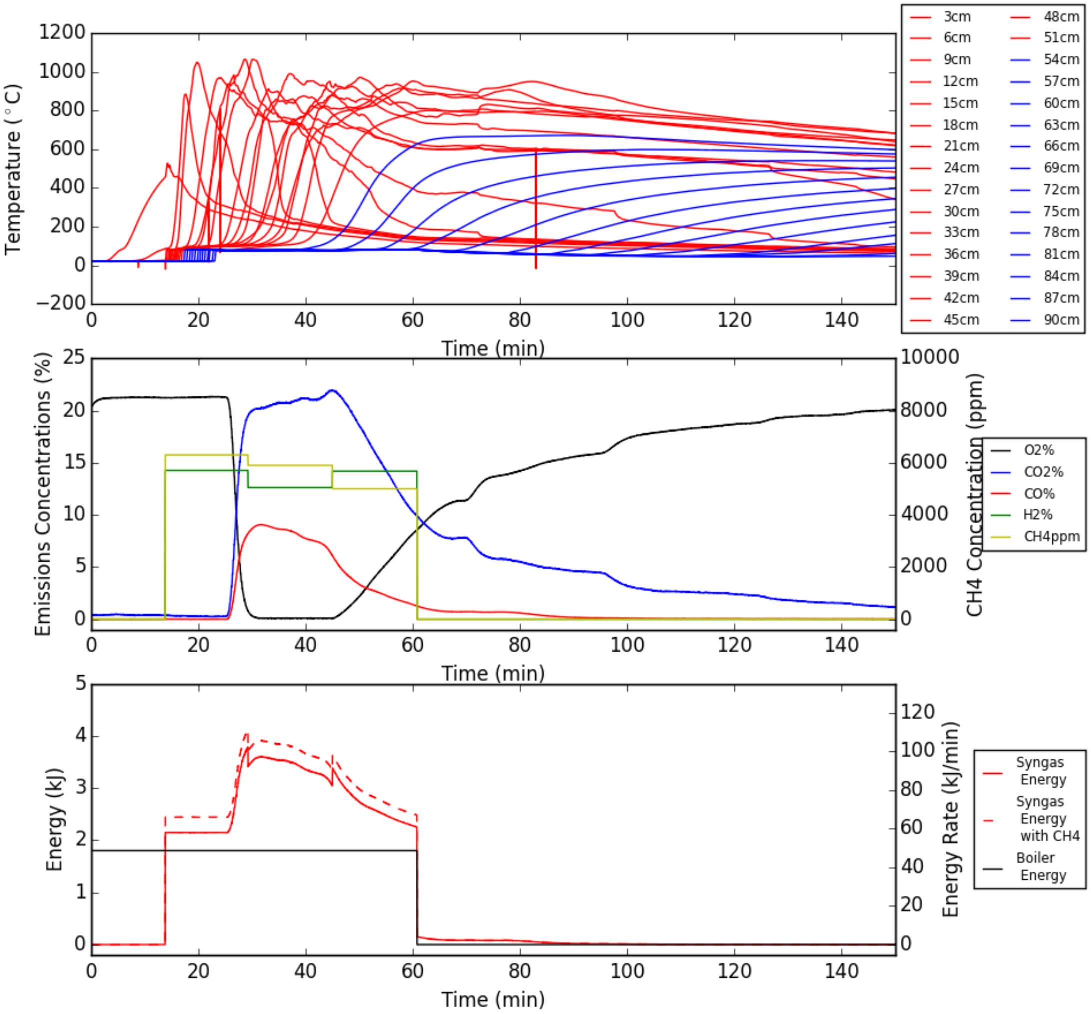

Figure D.12: Test 11 - Woodchips - Alumina Matrix - temperature, emissions, and energy profiles

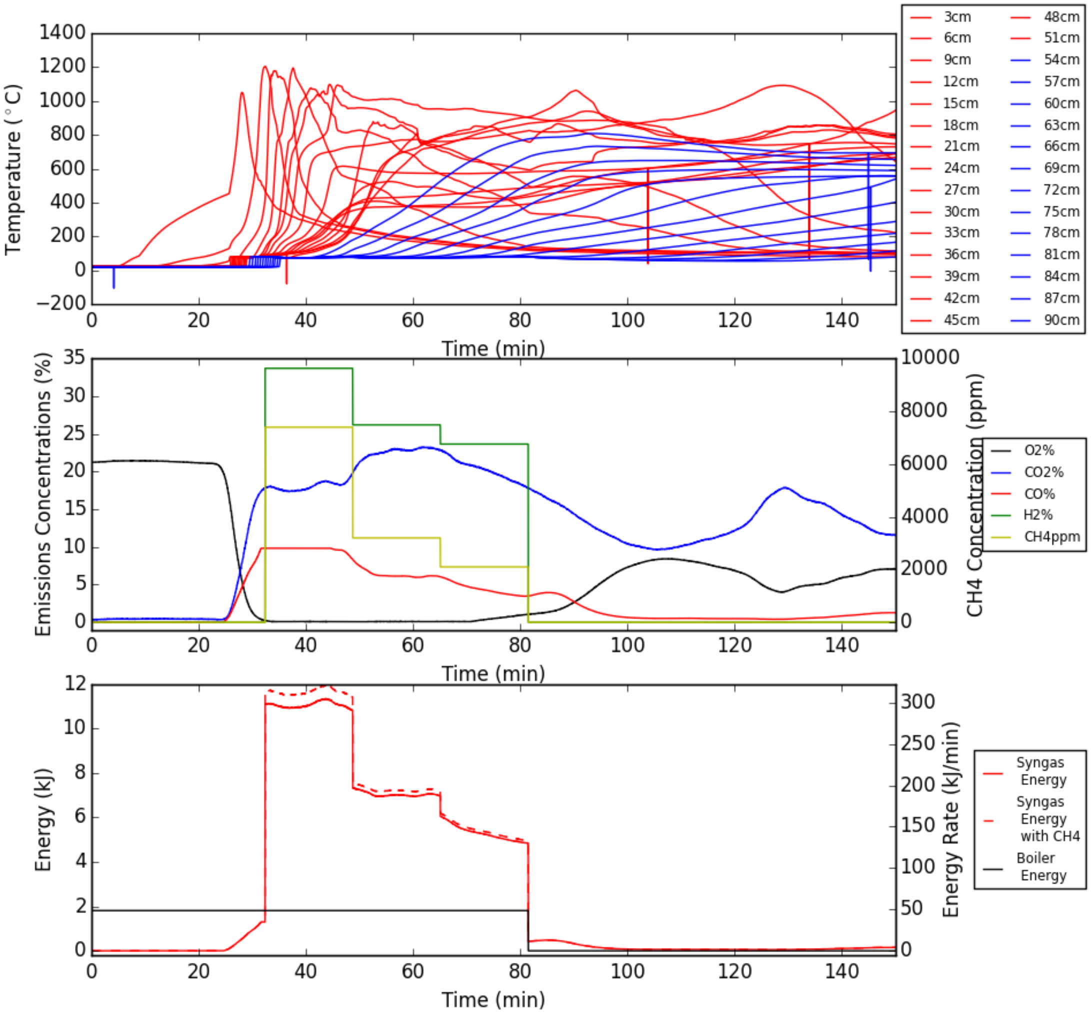

Figure D.13: Test 12 - Woodchips Matrix + Coal Tar - temperature, emissions, and energy profiles

Appendix E: Hydrogen Production from Water Saturated Systems

Water was added to the coal tar fuel mixture to the point of saturation prior to being loaded into the reactor. A boiling front is conceptually pictured preceding both the pyrolysis front and the smouldering front (Rein, 2009; Scholes et al., 2015). Strictly following this conceptual model would mean that all the water would vaporize and leave the system prior to the being able to participate in hydrogen forming reactions. Since smouldering reactions differ in time and space, though, the boiling front conceptual model can be an inaccurate oversimplification. It is possible for localized parts of the system to still hold water while the surrounding area has completely vaporized all water and proceed to reach temperatures exceeding the boiling point. With a fast-moving smouldering front, it is possible for these localized pockets of moisture to come in contact with both pyrolysis products as well as high temperatures from being near the smouldering front. Heat, carbon chars, pyrolysis gases, combustion gases, and water all in contact provide reaction conditions conducive to both steam reforming and gasification. Organic fuels may contain bound water which can remain bound in the fuel at temperatures exceeding the traditional boiling point of water. This would also provide a method for water to remain in the system at elevated temperatures to participate in hydrogen forming reactions.

When the base-case coal tar fuel mixture was used and water was added to the matrix until the system was fully saturated (240.2g water). This system produced H_2 at a concentration of 1.0% at steady state. Interestingly, producing hydrogen at a concentration well exceeding the virgin fuel experiment indicates that the water must be participating in the reaction. This is evidence that the conventional conceptual model of the smouldering front being completely dry from the boiling front that preceded it is an oversimplification. In terms of hydrogen production, it is evident that a water saturated system is not nearly as efficient as injecting steam. With respect to in-situ smouldering, this is a meaningful finding. If smouldering is being performed below the water table as it has been done for remediation (Grant et al., 2016; Scholes et al., 2015), it is possible that the produced gases will contain H_2 near the lower flammability limit (LFL). This is especially possible in calcareous soils where minerals such as dolomite or calcite may be present and able to further catalyze the reaction. Since H_2 gas is not an anticipated product from smouldering, its generation could prove dangerous if unaccounted for in the emissions.

References

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Appendix F: Effect of Reductive Cycling

(Kapadia et al., 2013) has shown that hydrogen yields can be increased during in situ gasification by cycling between oxidation and reduction cycles. This is accomplished by injecting air into the reaction zone to sustain high-temperature oxidation reactions and then injecting steam. Over numerous cycles this improved the hydrogen production during the steam cycles as seen in Figure F.1.

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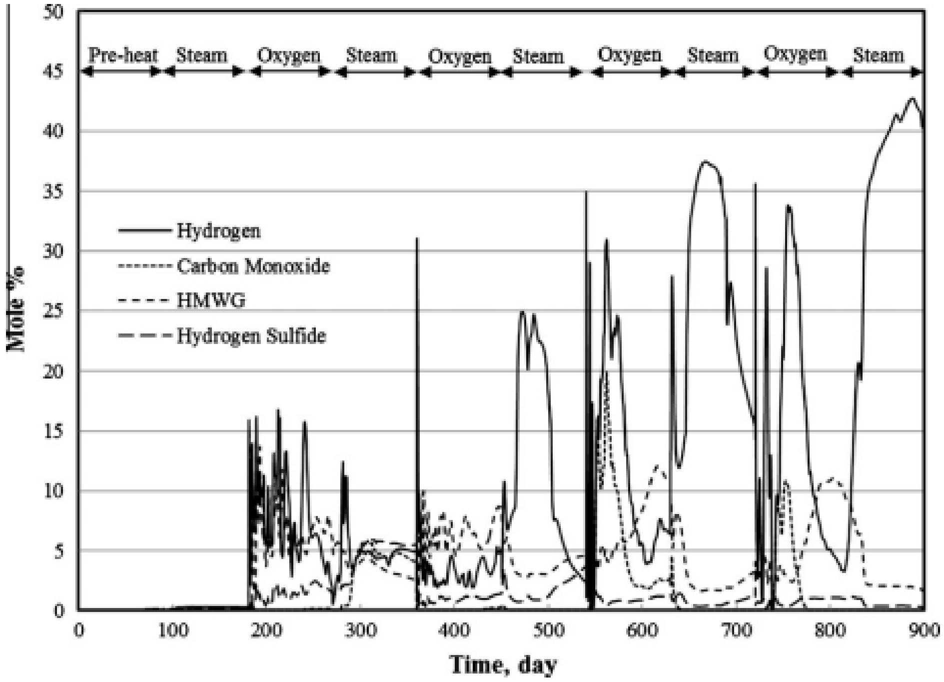

Figure F.14: Cycling of oxygen and steam in subsurface oil recovery resulting in increased hydrogen production (Kapadia et al., 2013)

Test L was conducted to determine if continuous reductive cycles could improve the hydrogen generation in the current smouldering system. The experiment was conducted identically to Test 7 except that air supplied to the reactor was cycled with pure N_2 at two regular intervals. Steam was supplied during both air and N_2 cycles. The temperature, emission and energy profiles can be seen in Figure F.2.

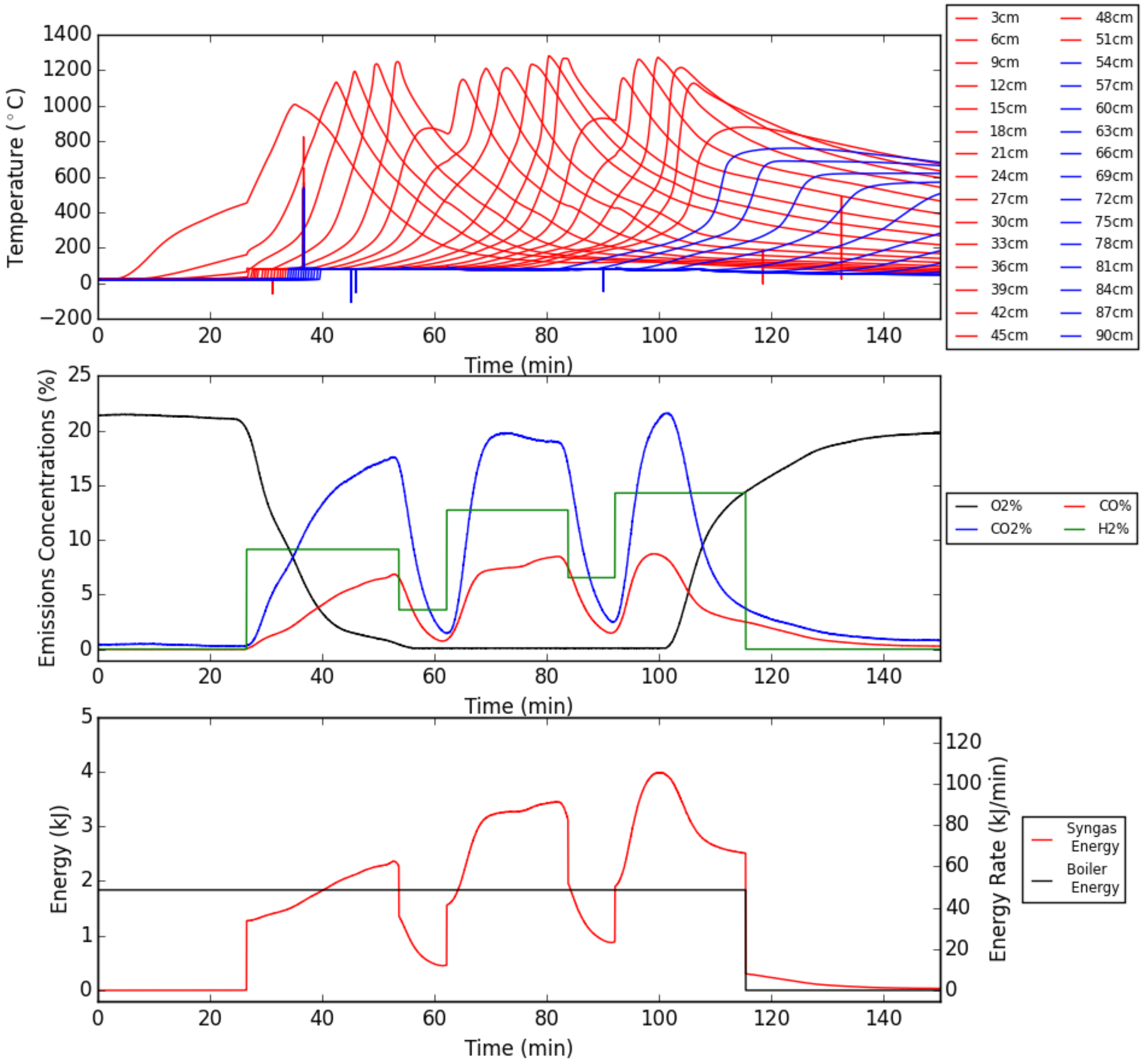

Figure F.15: Temperature histories, emission concentrations, and syngas energy from reductive cycling with N_2 (Test L)

The N_2 cycles are clearly identified by the temperature profiles exhibiting rounded heat transfer curves as opposed to the sharp peaks of combustion. This is coupled with a corresponding drop in CO and CO_2 concentrations in the emissions since combustion ceases during these cycles. During smouldering, H_2 concentrations were extremely similar to Test 7 having the same peak concentration and varying the average steady state concentration by 0.1%. Like the combustion gases, though, H_2 concentrations were reduced during the N_2 cycles to 3.6% and 6.5% respectively.

Decreasing H_2 concentrations during the N_2 cycling process can be explained predominantly by the substantial decrease in temperature during these periods. The hydrogen-forming reactions are highly endothermic and require a large supply of energy to proceed. With the smouldering stopped, there is no longer any energy being generated to supply to the hydrogen formation zone just ahead of the smouldering front. Only the thermal energy stored in the wake of the smouldering front can convectively supply energy to the reaction zone. This is an inadequate amount of energy and hydrogen-forming reactions cannot proceed efficiently. Interestingly, the second cycling period maintains slightly higher hydrogen concentrations than the first cycle because there is a greater bank of thermal energy stored by the time of the second N_2 cycle. This dampens the effect of losing energy generated from the smouldering reaction.

References

Kapadia, P. R., Wang, J. J., Kallos, M. S., & Gates, I. D. (2013). Practical process design for in situ gasification of bitumen. *Applied Energy*, *107*, 281–296. https://doi.org/10.1016/j.apenergy.2013.02.035

Appendix G: Experimental Apparatus

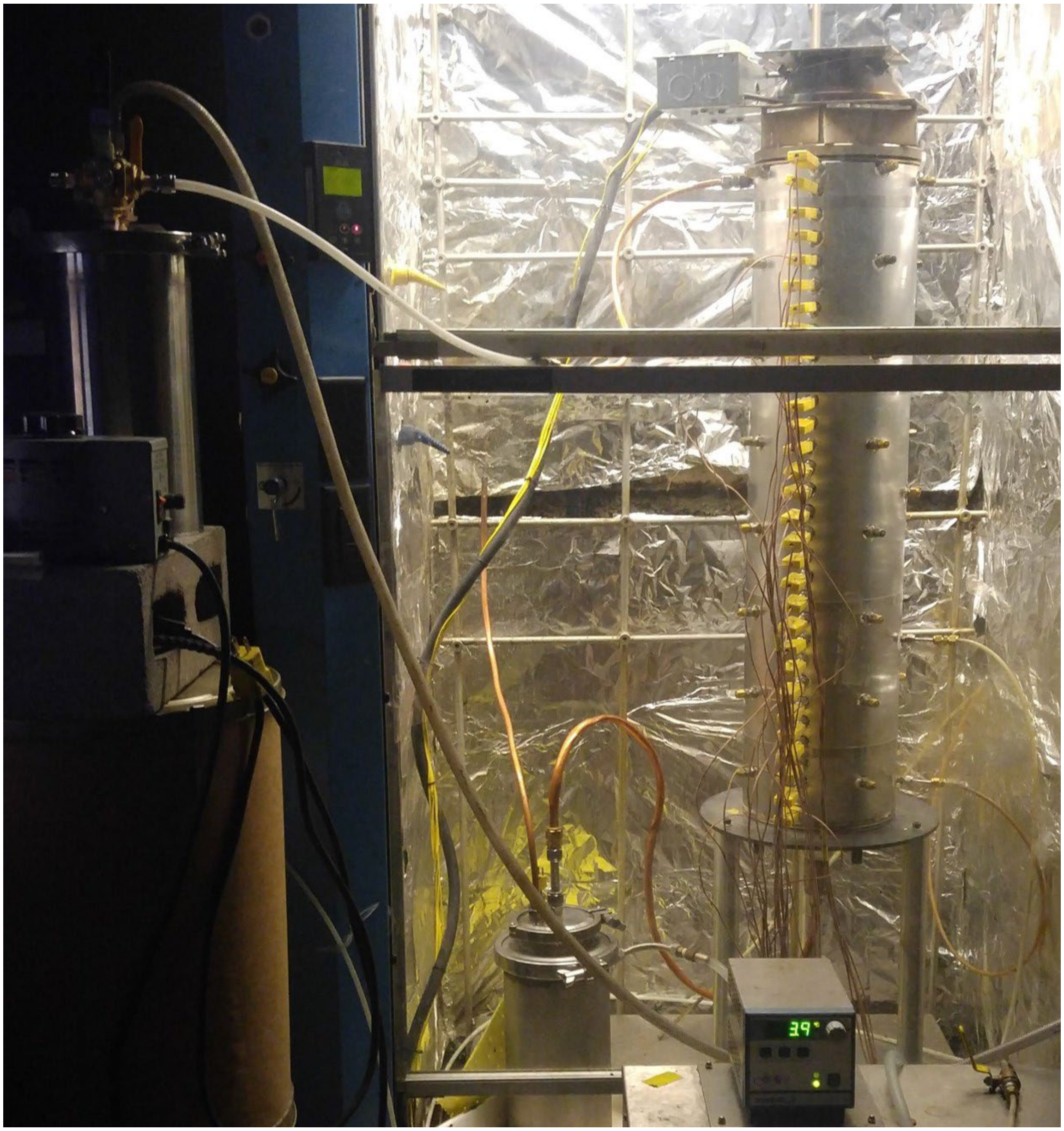

Figure G.16: Experimental Apparatus

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A. L. Duchesne, J. K. Brown, D. J. Patch, D. Major, K. P. Weber, and J. I. Gerhard, "Remediation of PFAS-Contaminated Soil and Granular Activated Carbon by Smoldering Combustion," *Environmental Science and Technology*, vol. 54, no. 19, pp. 12631–12640, Oct. 2020, doi: 10.1021/acs.est.0c03058