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Peer reviewed|Thesis/dissertation

Fuel flexibility analysis of conventional and low-NO_x gas water heater burners on
renewable fuel introduction

THESIS

Submitted in partial satisfaction of the requirements for the degree of

MASTER OF SCIENCE

In Mechanical and Aerospace Engineering

By

Shiny Choudhury

Thesis Committee:

Professor G. Scott Samuelsen

Professor Vince McDonell

Professor Manuel Gamero-Castaño

2019

DEDICATION

I dedicate all I am and this work to Kalpana Chawla, Maryam Mirzakhani, Marie Curie, Tessy Thomas, Reni Choudhury, Lalita Patel, Dushila Choudhury and numerous other strong exemplary women on whose shoulders I stand.

*'Climate change is real and severe. I promise to dedicate my life and research to making
a dent towards a greener future'*

TABLE OF CONTENTS

1.	INTRODUCTION.....	1
1.1	Overview	1
1.2	Goals.....	3
1.3	Objectives.....	3
2.	BACKGROUND.....	4
2.1	Biogas.....	6
2.2	Hydrogen enriched natural gas.....	8
2.3	Water heating technologies	11
2.3.1	Burner Configuration	12
2.3.2	Emission Regulations.....	16
2.4	Numerical Methods	17
2.5	Summary	18
3.	APPROACH	21
3.1	Task 1	22
3.2	Task 2	23
3.3	Task 3	24
3.4	Task 4	24
4.	METHODOLOGY	25
4.1	Instrumentation and data acquisition.....	25
4.2	Testing Procedure.....	27
4.3	Numerical Simulation	29
4.3.1	Low NO _x Storage water heater	29
4.3.1	Conventional storage heater.....	36
5.	RESULTS.....	39
5.1	Fuel Composition	39
5.2	Biogas Testing.....	40
5.2.1	Impact of CO ₂ Admixing.....	40
5.2.2	Ignition, flame characteristic and safe limit of operation	43

5.2.3	Energy Efficiency	45
5.2.4	Emissions	47
5.2.5	Methane Leakage	54
5.2.6	Biogas Simulation Results	55
5.3	Hydrogen Testing	62
5.3.1	Impact of H ₂ admixing	62
5.3.2	Ignition, flame characteristic and safe limit of operation	63
5.3.3	Emissions	68
5.3.4	Hydrogen Simulation Results	74
6.	SUMMARY, INSIGHTS, CONCLUSIONS, AND RECOMMENDATIONS..	79
6.1	Summary	79
6.2	Biogas-addition insights	79
6.2.1	Conclusion	82
6.3	Hydrogen-addition insights	83
6.3.1	Conclusion	85
6.4	Recommendations	86
7.	REFERENCES	87

LIST OF FIGURES

Figure 1. Schematic of a Rheem PROG40-38N RH62 Water Heater burner assembly [62]	13
Figure 2. Schematic of a Rheem 6G40-38FN4 Water Heater burner [64]	14
Figure 3. Schematic of a typical conventional water heater (Left) and low-NO _x burner (Right).	15
Figure 4. Experimental setup schematic	29
Figure 5. Radiant screen burner	30
Figure 6. Schematic of a typical low-NO _x water heater burner (Left) and area of interest for simulation (Right)	31
Figure 7. Manual CRN visualization to burner flame.....	33
Figure 8. CRN for low-NO _x water heater burner.....	34
Figure 9. Pancake burner assembly (left), burner schematic (right).....	36
Figure 10. Schematic of a typical conventional water heater burner (Left) and area of interest for simulation (Right)	37
Figure 11. Heating value and Wobbe Index variation with NG+CO ₂ mixtures.	42
Figure 12. Flame shape for conventional water heater with increasing CO ₂ content.....	44
Figure 13. Recovery efficiency and heating time as a function of CO ₂ addition for low NO _x water heater.....	47
Figure 14. Emissions for low NO _x storage water heater with increasing CO ₂ concentration	51
Figure 15. Emissions for conventional storage water heater with increasing CO ₂ concentration	53
Figure 16. Methane emissions for both the water heaters.....	55
Figure 17. Adiabatic flame temperature at CRN exhaust with increasing CO ₂ %	56
Figure 18. CO emission from low-NO _x water heater on CO ₂ addition (simulation vs experiments).....	57
Figure 19. NO emissions from low-NO _x water heater on CO ₂ addition (simulation vs experiments).....	58
Figure 20. N ₂ O levels simulated	59

Figure 21. NO emissions for conventional water heater.....	61
Figure 22. NO _x and CO emission spike during relight for low-NO _x burner at 10% H ₂ in natural gas	66
Figure 23. Flame shape for conventional water heater with increasing H ₂ content.....	67
Figure 24. Gas storage water heater and pipeline connection.....	69
Figure 25. Emissions for low-NO _x storage water heater with increasing H ₂ concentration..	71
Figure 26. Emissions for conventional storage water heater in both safe and unsafe limits of operation with increasing H ₂ concentration.....	73
Figure 27. Adiabatic Flame Temperature (AFT) at CRN exhaust with increasing H ₂ %	75
Figure 28. CO emission from low-NO _x water heater on H ₂ addition (simulation vs experiments).....	76
Figure 29. NO emission from low-NO _x water heater on H ₂ addition (simulation vs experiments).....	77

LIST OF TABLES

Table 1.	Maximum H ₂ limits pertaining to residential appliance reported by various studies	11
Table 2.	Regulation chronology on water heater NO _x emissions.....	16
Table 3.	Analyte range and calibration levels for experiments on low-NO _x and Conventional Water Heater	26
Table 4.	Burner operation procedure for CO ₂ /H ₂ admission testing	28
Table 5.	Boundary condition	32
Table 6.	Details for parameters of reactors in CRN for low-NO _x water heater.....	34
Table 7.	Change in Equivalence ratio and air-fuel flow rate at low-NO _x burner head.....	35
Table 8.	Change in Equivalence ratio and air-fuel flow rate at conventional burner head	38
Table 9.	Natural gas composition as supplied to UCI Combustion Lab (UCICL).....	39
Table 10.	Characteristics for CH ₄ , H ₂ , and, CO ₂	39
Table 11.	Equivalence Ratio (Φ) shift for low-NO _x water heater on CO ₂ addition	43
Table 12.	Safe limit of operation	45
Table 13.	Change in Wobbe Index with increasing CO ₂ in natural gas	56
Table 14.	Equivalence Ratio (Φ) shift for low-NO _x water heater on H ₂ addition	63
Table 15.	The safe limit of operation.....	68
Table 16.	Stoichiometric water content in hydrogen rich fuel.....	69
Table 17.	Wobbe Index variation with H ₂ addition	74

ACKNOWLEDGMENTS

I would like to thank my supervisor, Professor G. Scott Samuelsen for giving me the opportunity to work and conduct research in UCI Combustion Laboratory. Also, for guiding me with his plethora of experiences in tailoring the right path of research and life for myself. I would like to thank my co-supervisor, Professor Vince McDonell for helping me with all my research queries, replying to my emails at odd hours, and editing and reediting my papers patiently and providing me guidance in career. Also, Professor Manuel Gamero-Castaño for graciously agreeing to be on my thesis committee and teaching me through his course on how to think about science.

I would also like to thank all the students and staff in Advanced Power and Energy Program for making lab a fun and enriching experience. Max R. Venaas, who patiently helped me in my experiments and Yan Zhao who was a valuable mentor. Alejandra, Alice, Scott, Daniel, Nick, Devashish and, Candy you guys made lab home.

My family who forever stands by my side, and my little sister Annie (not so little anymore) who has started advising me and amazing me with her wisdom. Lastly, I would like to thank Namit Anand who cooked for me, made sure my gadgets were on point, confiscated my phone, and made me believe in myself and pushed me to do the unimaginable. I could not have done this without the love, kindness and understanding I received from everyone.

ABSTRACT OF THE THESIS

Fuel flexibility analysis of conventional and low-NO_x gas water heater burners on
renewable fuel introduction

By

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Master of Science in Mechanical and Aerospace Engineering

University of California, Irvine, 2019

Professor G. Scott Samuelsen, Chair

Residential water heating is the single most significant end-use for natural gas in California-- more than half of the net energy consumption for a typical Californian household goes into fulfilling hot water demands. Aided by cost-effective natural gas available in the state, about 90% of water heaters are natural gas-fueled storage tank systems, with 40-50-gallon capacity. In order to decarbonize residential spaces, a strong focus on water heating is essential.

This research focuses on the impact of renewable fuel (biogas and renewable hydrogen) injection into pipelines for gas-fired storage water heaters. Two representative models of storage water heaters were chosen for experiments. First, a conventional storage unit; meeting 40 ng/J NO_x emission requirement, second, a low-NO_x storage water heater

meeting 10 ng/J NO_x emission requirement. This research answers how much CO₂/H₂ content in natural gas can be tolerated without loss of critical performance parameters with reliable operation.

Characteristics like ignition delay, flashback, blow-off, ignition, flame structure, and emissions (NO₂, N₂O, NO, CO, CO₂, UHC, and NH₃) at different concentrations of CO₂/H₂ mixed with natural gas is investigated. The study found less than 10% H₂ tolerance for both the water heaters, less than 15% CO₂ tolerance for low-NO_x water heater and no CO₂ tolerance for the conventional storage model. NO_x/NO emission reduction is achieved for both the water heaters with increased CO₂/H₂ and a simultaneous CO/UHC increase is observed. Further, both the water heater emission and stability performance were simulated using a chemical reactor network (CRN).

1. INTRODUCTION

1.1 Overview

Baltimore, Maryland, in 1816 became the first city in the United States, to use manufactured natural gas to light its streets with natural gas. In the 19th century world, natural gas was used almost exclusively as a source of light, but with Robert Bunsen's invention in 1855 of the Bunsen burner vast new opportunities to use natural gas opened. In 20th century, elaborate pipelines began to be laid and this led to the advent of natural gas use for heating and cooking. United States saw a rapid expansion in use of natural gas for appliance such as water heaters, cooking ranges, processing and manufacturing plants, and boilers for electricity generation [1].

Today, natural gas is a vital component of the world's supply of energy. In 2017, 31.8% of the primary energy production in U.S was using natural gas, followed closely by petroleum at 28%, then coal at 17.8%. All the above energy sources constitute 'fossil fuels', which emit greenhouse gases (GHG) that trap heat in the atmosphere. This additional trapped heat has been shown to increase the average global temperature of the earth's surface, a phenomenon termed 'Global Warming'. 2016 was the warmest year on record, and every one of the past 40 years has been warmer than the 20th century average [2]. Certain consequences of global warming are inevitable today, including growing wildfire risks, severe heat waves and increasing sea levels, but we can retard the rate of future more horrifying consequences. We must significantly reduce the heat trapping emissions into the atmosphere, and even though natural gas is one of the cleanest, safest, and least

polluting of most energy sources; the whole picture is presented without inclusion of drilling and extraction of natural gas from wells, and its transportation in pipelines which results in methane leakage [3]. Methane which forms the primary component of natural gas, is 34 times stronger than CO₂ at trapping heat over a 100-year period and 86 times stronger over 20 years [4].

Ninety-nine percent of the natural gas used in the United States comes from North America. Because natural gas is the cleanest burning fossil fuel, it is playing an increasing role in helping to attain national goals of a cleaner environment, energy security and a more competitive economy. The two million-mile underground natural gas delivery system has an outstanding safety record.

Residential water heating is the single most significant end use for natural gas in California. Natural gas is used to heat water in nearly 90 percent of homes and represents 49 percent of the average 354 therms of annual household consumption per the 2009 Residential Appliance Saturation Survey. Nearly 90% of California's 12.3 million households use natural gas water heaters, with 2,111 million therms consumed yearly overall. According to the Energy Information Administration (EIA), an average California household could see its annual natural gas water heating consumption drop 35 percent using an advanced water heater combined with an improved distribution piping system.

Current focus from climate change mitigation policies incentivizes gas-fired appliances, by not accounting for their emissions into the net count. The hope is--most emission reduction will result from adopting increasingly energy efficient electric appliances, run by cleaner grids.

1.2 Goals

The goals of this research are (1) to establish the operational limit of water heating appliances (conventional and low-NO_x storage water heater) operated on mixtures of renewable fuels and natural gas (biogas and hydrogen enriched natural gas), (2) to provide direction regarding equipment modifications to allow higher levels of renewable fuels to be used, and (3) to assess the impact of renewable fuel injection into natural gas on the emission of NO₂, N₂O, NO, CO, CO₂, UHC, and NH₃.

1.3 Objectives

To meet the goals of the research, the following four objectives were established:

- Establish fuel composition of interest, design and fabricate fuel mixture delivery mechanism, and choose appropriate analyzers for emission measurement
- Conduct experiments to test performance and emission characteristics of each water heater on various blends of simulated biogas (NG+CO₂) and hydrogen enriched natural gas (NG+H₂)
- Establish numerical models and evaluate impact of fuel composition on emission and stability
- Analyze data and provide physical insights

2. BACKGROUND

2016 was the warmest year on record, and every one of the past 40 years has been warmer than the 20th century average [1]. Anthropogenic activities are likely to increase global temperature by 1.5°C between 2030 to 2052 under “business as usual” scenarios [6]. Subsequently, arctic warming, coastal and fluvial flooding, warm-water corals at risk of extinction, effect on the terrestrial ecosystem, tourism decline, and increasing heat-related morbidity and mortality, are in sight and inevitable [6]. *Get active, get connected, get real, and don't get down*; are the timeless and timely recommendations from Peter M. Vitousek in his 1994 work on global warming. He compellingly put, *'We're the first generation with the tools to see how the Earth system is changed by human activity; at the same time, we're the last with the opportunity to affect the course of many of those changes'* [7].

Greenhouse Gas or GHG emissions are the single most important factor in global warming, they result in the proverbial ‘thickening’ of our atmospheric blanket and that results in trapping of additional heat [8] . In U.S the recent trends in GHG emissions show a decrease in the gross values. Yet a 1.3% increase occurred in 2017 emissions compared to the baseline 1990’s level (which is widely used as the reference year from emission abatement policies [9]). California stands as a world leader in its aggressive climate change goals and actions. Since 2007, California has seen a consistent decrease in GHG emissions. The state’s 2020 target [10], of bringing down the emissions to the 1990’s level was achieved in 2016 [11]. Increasing the share of renewables through extensive deployment of wind, solar and geothermal energy has a direct impact in lowering of gross emissions. California also has the highest venture capital investment in renewable energy and was

titled ‘Epicenter of the US CleanTech Market’ in 2013 [12]. About 10.4 million people worldwide were employed in the renewable energy industry globally in 2017, primarily in solar and bioenergy industry [13]. California similarly has successfully deployed investment in renewables, all the while increasing its GDP.

Furthering California’s climate change commitment, in 2005, Executive Order (EO) S-3-05 set an ambitious goal of reducing GHG emissions in 2050 to 80% of 1990’s levels [14]. More recently, in 2016, a 40% decrease from 1990’s emissions level by 2030 was mandated by the passage of Senate Bill 32 (SB 32) [10]. In 2016, the majority of GHG emissions was led by transportation sector (41%), but building heating resulted in 7% of the emissions directly from residential spaces [15]. Decarbonizing Californian homes, in both space heating and water heating, can directly target emission reduction.

Very few works have looked at combustion performance or emissions on biogas or increased hydrogen on water heating appliances in an urban setting. However, use of biogas in farms, to the end of creating a self-reliant setting has been investigated [16] [17]. These studies do not look at emissions per se and focus mainly on global efficiency gains and becoming self-reliant by utilizing farm manure. Biogas is deemed a lucrative source of energy in developing nations, primarily because of the readily available organic waste. Utilization of biogas in all aspects of rural energy fulfillment was investigated in Nigeria [18]. India provides subsidies for setting biogas plants [19]. The use of biogas specifically in water heating and its impact on emissions has been sparsely investigated. Similarly, for increased hydrogen impacts in water heating application very few studies exist. With hydrogen economy gaining momentum, the impact on end use should be thoroughly

investigated. A proof of concept storage water heater functioning on catalytic combustion of hydrogen was an interesting find [20], also one of the very few studies available on gas water heater functioning on hydrogen. Since countries like United Kingdom are going full force on hydrogen admission to its pipelines, the 2019 study by the Institute of Engineering and Technology (IET) summaries '*In the domestic sector the conversion of existing natural gas appliances to operate on 100% hydrogen is not viable and so their replacement would be required*' [21], necessitating thorough research.

The following sections are background on the fuel considered in current research, water heating technologies and regulations around the water heaters in California.

2.1 Biogas

Biogas is a gaseous fuel produced from biomass via anaerobic digestion of organic matter and is primarily composed of methane and carbon dioxide, with some trace compounds. Biogas from landfill is composed of 45-55% methane, 30-40% carbon dioxide, and about 5-15% nitrogen. Biogas sourced from sewage digesters has 55-65% methane, 45-35% carbon dioxide and less than 1% nitrogen. Similarly, biogas from digesters has 60-70% methane, 30-40% carbon dioxide, and less than 1% nitrogen [22] [23]. Depending on the source of biogas, we can also find trace compounds like sulfides, siloxanes, halogenated compounds, and aromatics. For instance, certain varieties of aromatics, heterocyclic compounds, ketones, halogenated aliphatic, terpenes, etc. are found in landfill sourced biogas as compared to other sources [24].

A 2015 study by E3 showed the role of decarbonizing pipelines with ‘decarbonized gas’, which includes biogas, hydrogen and renewable synthetic gases produced in a manner of low GHG emission approach. The E3 study concludes that- ‘decarbonizing sectors which are otherwise difficult to electrify, including but not limited to certain residential and commercial end uses, like cooking, space, and water heating will be a step closer to achieving the ambitious 2050 emission reduction mandate’ [25]. Renewable natural gas (RNG) or biomethane is a direct product of anaerobic digestion and can be upgraded from biogas by removal of CO₂, hydrogen sulfides, oxygen and siloxanes [26]. Biomethane can then be used as vehicle fuel in natural gas engines or can be directly injected into the existing pipelines, with little or no variation in end-use. Some of the biomethane upgrade technologies like, membrane separation, pressure swing adsorption (PSA), amine scrubbing, and water wash are technologically mature and currently in use. These are usually deployed individually but can sometimes be installed in a series with one another [26].

For using biomethane in residential spaces, the quality and composition must be upgraded. Different countries and even regions within countries have different requirements for upgrading biogas to biomethane, which can then be injected directly into the gas grids. The regulations are made keeping in mind, less compromise is made on heating value delivered and various health and system-level damage possible due to the gas composition. The regulations vary widely. European Union standards, for instance, allows <2% CO₂, with no strict regulation on the heating value requirement, however, Italian regulations allow less than 0.5% CO₂, within a Wobbe Index of 47.32 - 52.33 MJm⁻³ [27]. Switzerland and Germany allow <6% CO₂ in biomethane for gas grids [28]. More

recently the Bioenergy Association of California (BAC) and other similar organizations have been pushing for lowering the minimum heating value requirements for pipeline gas in the state, reducing testing and purification requirements before injecting renewables, and allowing injection of variable BTU biogas wherever appropriate [29]. If favored, all the recommended steps by BAC for biogas injection will increase investment in biogas production and infrastructure.

The US has high renewable methane potential. Biogas can be sourced from many organic sources like landfill, wastewater, and animal manure, industrial, institutional and commercial organic waste. Biogas can be produced from lignocellulosic biomass [30], also, there is attention in biofuel and biogas production from various kinds of algae [31]. In the US, 5% of the natural gas utilized in the electric power sector and 56% of the natural gas is transportation can be directly replaced with biogas [32]. California has the highest methane potential in the US, amounting to >10,000 tones/yr. Aided by high amounts of animal manure and landfills, California can benefit hugely by investing in biogas use. The recent passing of two bills the Assembly Bill 3187 (AB 3187) [33] and the Senate Bill 1440 (SB 1440) [34] favor investing in biomethane infrastructure and investing more in Renewable Natural Gas (RNG). Bioenergy is the 2nd largest job creator among renewables with more than 3.07 million people working in the sector [13].

2.2 Hydrogen enriched natural gas

In 1783 Antoine Lavoisier names hydrogen as a standalone element. In 1834 Faraday's law of electrolysis published. In 1874 Jules Verne in *The Mysterious Land* envisages '*water will one day be employed as fuel, that hydrogen and oxygen of which it*

is constituted will be used.' In 1970, John Bockris and Lawrence W. Jones hypothesize a 'hydrogen economy' [35] [36]. Moving ahead to 2013, a 2 MW power-to-gas installation in Falkenhagen pumping 360 cc/hr. hydrogen into natural gas grid [37], and in 2017, the 'Hydrogen Council' formed for an expedited hydrogen economy [38]. Today, hydrogen is envisioned to provide a clean, secure and reliable energy future [39]. When produced using renewable energy, hydrogen facilitates a reduction in carbon dioxide emissions [40] and hence can be considered a 'greener' alternative to fossil fuel. Current greenhouse gas (GHG) trajectory exceeds the global warming limits posed by the Paris agreement [41] [42], and thus a greener future needs expedited global deployment of all the clean technology solutions we have.

Renewable energy like solar and wind by nature are fluctuating and intermittent for useful power generation. Prior this intermittent nature of power generation was localized to smaller power grids with high renewable power generation, but with a growing percentage of renewables in regional and national grids, these fluctuations become prominent. Batteries, compressed air, flywheels, capacitors, etc., are suited for short term storage of intermittent power, but fail to provide reliability in long term storage [43]. Hydrogen in this scenario can play a unique role. Using power-to-gas, intermittent electricity is utilized to produce hydrogen via electrolysis and then stored in pressure vessels for future use.

The stored hydrogen, in turn, can be utilized to generate electricity via fuel cells or combustion during intermittent operation. Apart from stabilizing grids, the hydrogen produced can be directly injected into the existing natural gas grids to decarbonize the

pipelines [44]. Hydrogen mixed with natural gas is not a new concept, it has roots at the beginning of natural gas grid establishment. ‘Town gas’ or ‘water gas’ had 30-50% hydrogen by volume [45]. Even though hydrogen content eventually phased out in the US, some areas like Hawaii, Southeast Asia, and China still continue the use of gas with significant blends of hydrogen (going up to 80% in some cases) [46] [47] [48]. A 2015 study by E3 showed the role of ‘decarbonized pipeline gas’, which includes biogas, hydrogen and renewable synthetic gases produced using a low GHG emission approach. The E3 study concludes that- *‘decarbonizing sectors which are otherwise difficult to electrify, including but not limited to certain residential and commercial end uses, like cooking, space, and water heating will be a step closer to achieving the ambitious 2050 emission reduction mandate’* [25].

Preliminary studies have shown that transport of hydrogen admixed mixtures in natural gas pipelines is possible in the current infrastructure [49] [50], though detailed analysis and experimentation is required for actual implementation [51]. Hydrogen and natural gas differ widely in chemical and physical properties and this has an effect on safe transition with regards to transportation, utilization, and maintenance of gas network integrity [52]. The NATURAHLY project by European Commission (6th framework), was aimed at investigating scenarios under which hydrogen can be injected into natural gas pipelines within acceptable ramifications on safety, durability and end-use appliance performance [53]. Blending hydrogen into natural gas pipelines at low concentrations can be viable without significantly impacting the durability of pipelines and end-use application [44]. Table 1 shows the hydrogen limits reported by various studies pertaining to end-use/domestic appliance performance. As shown, significant variation in the

estimated maximum concentration of hydrogen that can be injected into the pipeline is evident.

Table 1. Maximum H₂ limits pertaining to residential appliance reported by various studies

Study	Year	Country	H ₂ %	Consideration
Haeseldonckx et al.[54]	2006	EU	17%	General end use
De Vries et al. [53]	2006	EU	~50%	Lean appliance operation
			<10%	Rich appliance operation
Melaina et al.[44]	2013	US	5-15%	Spanning all domestic appliances
Jones et al.[55]	2018	UK	30%	Spanning all domestic appliances
Zhao et al.[47]	2019	US	15%	Cooktop burner
The Future of Hydrogen (IEA) [56]	2019	~Global	5%	General end use

2.3 Water heating technologies

In California, a vast number of water heaters are atmospheric and natural gas fed models, even though they are inefficient due to high standby losses (20-35% of annual water heater energy) [57]. These models are popular in meeting higher water flow rate requirement for limited periods of time. Aided by cost effective natural gas available in the state, about 90% of water heaters are natural gas-fueled storage tank systems, with 40-50-gallon capacity. Roughly 6% of units are electricity based and 4% are propane gas (liquefied petroleum gas or LPG) water heaters [58]. Due to the wide usage of storage

water heaters, two representative models were chosen for experiments in this research. First, a conventional storage unit; meeting 40 ng/J NO_x emission requirement is considered. Second, a low-NO_x storage water heater meeting 10 ng/J NO_x emission requirement is studied. Both water heaters are rated 38,000 BTU/hr. with 40-gallon capacity. These two models span the state's water heater distribution with non-retired (conventional) and future (low-NO_x) models.

2.3.1 Burner Configuration

Oxides of nitrogen or NO_x play an important role in the formation of smog, the degradation of atmospheric visibility and the acidification of rain [59]. In combustion devices, the main source of nitrogen for NO_x formation is air, both primary and secondary, required for the combustion of gaseous fuel. NO_x being a notorious pollutant, many states have regulated NO_x emissions from combustion devices [60]. It is widely accepted that reducing peak combustion temperatures, below 1810K substantially precludes NO_x formation, by reducing thermal NO_x. However, reducing peak temperature might result in products of incomplete combustion (PIC), for example, CO, UHC, etc. and reduced thermal efficiency of the process. Another method for reducing NO_x is premixing the air-fuel mixture before combustion. It's a challenging optimization problem, and many technologies have been developed to reduce NO_x emissions for water heater burners.

NO_x emission for water heating was initially regulated to ≤ 40 ng/J and for this, a widely used peripheral flame burner was adopted [61]. This burner discharges the fuel/air mixture to the periphery of the burner. The flame formed, as a result, interacts with a

secondary plate which provided secondary air and acts as a heat sink which eventually reduced peak flame temperature of the flame.

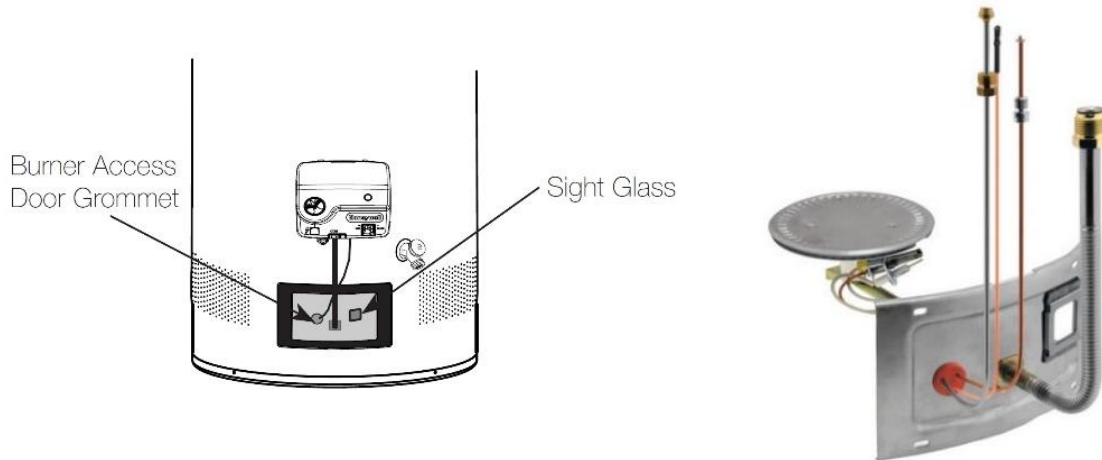


Figure 1. Schematic of a Rheem PROG40-38N RH62 Water Heater burner assembly [62]

The secondary plate, crucial to this design, optimized the need for sufficient secondary air for CO emission reduction, while maintaining low flame temperatures which reduced NO_x emissions. Figure 1 shows the burner assembly of a conventional water heater. While this design is ubiquitous in water heater burners, NO_x regulations resulted in new concepts to reduce emissions. Rule 1121, '*Control of Nitrogen Oxides from residential type, natural gas-fired water heaters*', adopted in 1999 by South Coast Air Quality Management District (SCAQMD) regulates NO_x for present water heater technologies ≤ 10 ng/J. A class of Low- NO_x burners was developed to meet these requirements.

In 1991, Alzeta with sponsorship from SCAQMD, and A.O Smith developed the first low-NO_x burner that met the 10ng/J requirement [63]. This was composed of layers of fiber screen on the combustion surface, and a large portion of the energy was given off as radiant energy from the fiber screen. Burner surface temperature subsequently dropped and stayed within 1100K- 1650K which is less than the open flame burner temperature and hence reduces thermal NO_x formation. One important consideration for radiant screen burners is that the flame stays on the burner surface, or else the flame will be lifted, and the surface becomes non-radiant. A narrow range of 0.8 - 1.2 equivalence ratio (Φ) for natural gas needs to be maintained for the avoidance of non-radiant conditions. Generally, storage water heaters are natural draft and do not have a blower attached for exhaust venting. Power venting is common in recent models of water heaters like the tankless water heaters.

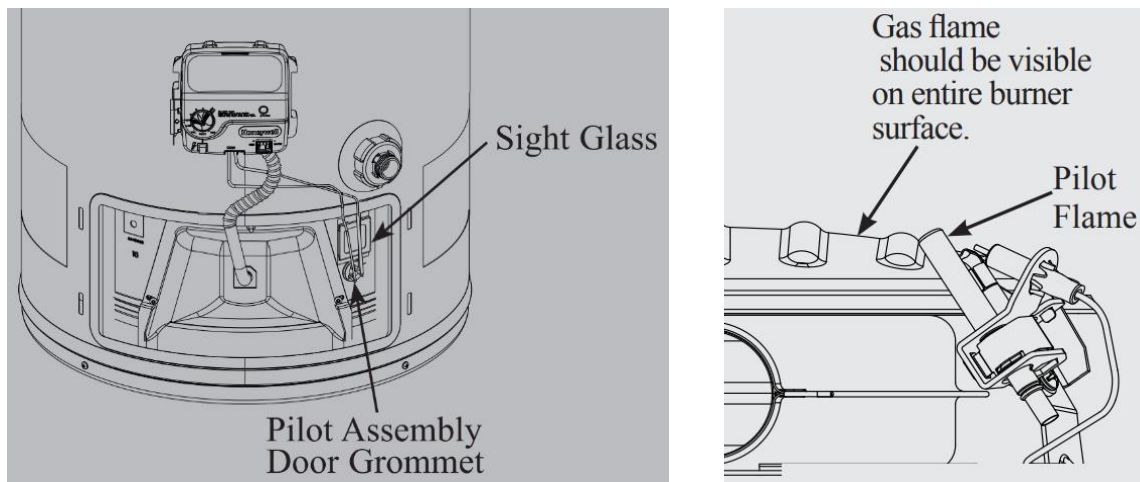


Figure 2. Schematic of a Rheem 6G40-38FN4 Water Heater burner [64]

Figure 2 shows a schematic of a low-NO_x burner assembly. Many models of low-NO_x emission water heater burners were invented in the 1990s. Polidoro developed a hyper-stoichiometric, stainless-steel burner that limited excess air by premixing air-fuel

mixture outside the burner [65]. A lot of current low-NO_x water heater technologies are atmospheric burners and are sold as ‘radiant head’ and ‘ultra-low-NO_x’.

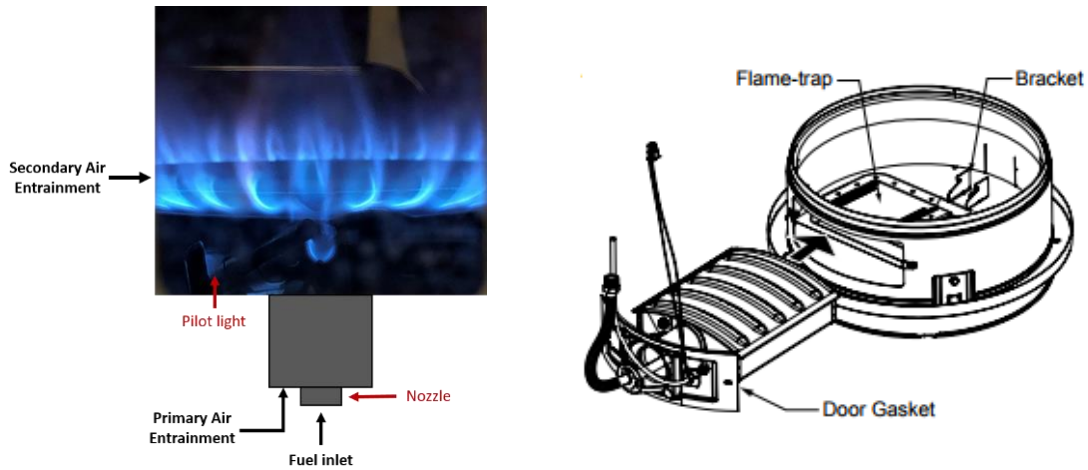


Figure 3. Schematic of a typical conventional water heater (Left) and low-NO_x burner (Right).

Figure 3 (Left) shows a schematic for a typical storage-tank water heater burner, also known as “pancake burner”. Primary air entrainment occurs with the nozzle fuel stream into the burner enclosure. Secondary air entrainment occurs when the flame is established in the air rich enclosure. Generally, high levels of premixing is assumed for the primary air-fuel mixture, though it is a partially premixed operation with high mixing due to the geometry of the burner. The primary air-fuel mixture is rich in composition ($\Phi > 1$), but overall equivalence ratio, including secondary air is lean in operation ($\Phi < 1$) [66]. Radiant screen burner/ Low-NO_x burner has an overall equivalence ratio on the leaner side ($\Phi < 1$) and expends around 32.5% of the fuel energy in the form of radiation [67]. Both primary excess air and radiation aids in decreasing the flame temperature which subsequently reduces the NO_x emissions.

2.3.2 Emission Regulations

As mentioned above, Rule 1121 is one widely accepted regulation for water heater emission compliance for Californian homes. It applies to manufacturers, retailers, and installers of natural gas-fired water heaters, with heat input rates $\leq 75,000$ BTU/hr. [68]. Rule 6 (Last Amended: November 7, 2007) from Bay Area Air Quality Management District adopted on April 1, 1992, has a clause essentially similar to Rule 1121 with a distinction of mobile and non-mobile homes [69]. The salient points of current gas water heater regulations, as relevant to this research work are summarized below in Table 2:

Table 2. Regulation chronology on water heater NO_x emissions

Date	NO _x * (ng/J)	NO _x * (lb/bBTU)	NO _x (ppmv @ 3% O ₂)
Until July 1, 2002	40	71	55
On and after July 1, 2002	20	35	30
On and after January 1, 2006	10	17.5	15

*Calculated as NO₂ equivalent

Various auxiliary regulations apply for emissions from residential appliances and hence by default to water heaters. Rule 409 (Amended August 7, 1981) [70] by Air Resource Board (ARB) says, ‘A person shall not discharge into the atmosphere from the burning of fuel, combustion contaminants exceeding 0.23 gram per cubic meter (0.1 grain per cubic foot) of gas calculated to 12 percent of carbon dioxide (CO₂) at standard conditions averaged over a minimum of 15 consecutive minutes.’ Rule 74.11 (November 11, 2009) from Ventura County Air Pollution Control District, essentially adopted clauses

in Rule 1121 and made a revision to remove the word ‘residential’ from its provision and applied the 10ng/J NO_x emission regulation for both commercial and residential spaces alike [71]. Rule 69.5.1 (Effective July 1, 2016) again by ARB [72] applies to natural gas-fired water heaters with a rated input capacity of $\leq 75,000$ BTU/hr. in San Diego County. This regulation has similar NO_x emission limits as Rule 1121 of 10 ng/J for non-mobile homes but allows 40 ng/J emissions for water heating units in mobile homes. The most recent standard, published by American National Standard Institute (ANSI) in 2017 [73], regulates residential storage water heaters.

Most regulations for water heaters pertain to NO_x emissions. Carbon monoxide (CO) is not strictly regulated, however, it is generally agreed that carbon monoxide emissions be below 800ppm (@ 3% O₂) [74]. Carbon monoxide is proven to have serious health effect and can even lead to death at higher concentrations and long exposures [75], NO_x is tagged as a health concern likewise; though levels of indoor NO_x concentrations are not strictly regulated [76]. Generally, storage water heaters are installed in basements of typical households or at least away from inhabitants for proper ventilation and aeration. Additionally, from July 1st 2003 all residential water heaters with storage capacity 50 gallons or less have to be flammable vapor ignition resistant (FVIR) certified, this makes sure that the water heaters do not accidentally end up igniting unattended combustible vapor in its vicinity [73].

2.4 Numerical Methods

Stability and a detailed emission analysis by exploring chemical kinetic mechanisms is explored in this study. Equivalent chemical reactor network for combustion

is a computationally attractive and precise method to that end. S.L. Bragg introduced the concept of using chemical reactor networks for modelling combustion reactors as a series of idealized perfectly stirred reactors (PSR) and plug flow reactors (PFR) [77]. Reactor network development varies from utilization of a few reactors for simulation [78] [79] to filling up of volumetric space with hundreds of idealized reactors [80] [81].

In this research we focus on emission simulation by utilizing a few idealized reactors. This study builds on a previous research work by Colorado et al. [82] and circumvents the need to perform a CFD simulation. On a fundamental level, if boundary conditions are met, we should be able to precisely model pollutant emission from reactor networks. Manual reactor network for chemistry simulation lower computational time drastically, where CFD or automatic CRN based on it can take days. The reactor networks in this study were built by observing the reactor networks of similar burners in previous work and detailed geometry and mechanism of present burners. GRI 3.0 reaction mechanism was used for all reactor networks in this research [83]. In order to develop the CRN, the first step is dividing the combustor volume into the distinct regions or zones. Each of the zones is characterized by the particular physical properties of the flow and the flame behavior. The two basic models used to build the network of reactors are the perfectly stirred reactor (PSR) and the plug flow reactor (PFR).

2.5 Summary

Regulations drive the market. Concerning climate change, a 2018 study ‘World Energy Outlook’ by the International Energy Association (IEA) concluded that *‘the*

world's energy destiny lies with decisions and policies made by governments'. Appliances in areas where relatively hydrogen rich fuel is supplied are designed and catered to satisfy safety concerns with reliable performance [47]. There is no reason why we cannot build new appliances or retrofit old ones to perform reliably on high hydrogen content. As a first step, we should look for inspiration from functioning devices in areas like Hawaii, China or Southeast Asia. Eventually, regulations will determine the course of market evolution, and hope is that the right policies will lead us to a hydrogen economy. It is evident from Table 1. that answering for a maximum limit of hydrogen admission into pipelines within acceptable safety and performance in end-use (specifically residential appliances), is a work in progress.

Similarly, for biogas, the E3 study of 2015 showed the role of decarbonizing pipelines with 'decarbonized gas', which includes biogas, hydrogen and renewable synthetic gases produced in a manner of low GHG emission approach. The E3 study concludes that- 'decarbonizing sectors which are otherwise difficult to electrify, including but not limited to certain residential and commercial end uses, like cooking, space, and water heating will be a step closer to achieving the ambitious 2050 emission reduction mandate' [25].

As reasoned, renewable fuel introduction in pipelines for end use application is promising. However, the impacts on end use is only beginning to be understood. **Since the highest limit of CO₂/H₂ admission will be driven by the least tolerant end-use operation, more work is required to establish a practical limit.** This research investigates water heating performance and operation of two representative models, the

low-NO_x storage and the conventional storage, on higher renewable fuel introduction to natural gas pipelines.

3. APPROACH

The goals of this thesis work are to investigate the mechanisms that give rise to various emissions (NO_2 , N_2O , NO , CO , CO_2 , UHC, and NH_3) from two representative gas water heater models (conventional storage and low- NO_x storage) in north America operating on mixtures of natural gas and renewable gas (biogas and hydrogen enrichment). To that end, both the conventional storage water heater and low- NO_x storage water heater models are experimentally and numerically evaluated.

The following sequential tasks were carried out to answer the questions posed previously:

- Task 1 – Establish fuel composition of interest, design and fabricate fuel mixture delivery mechanism, choose appropriate analyzers for emission measurement
- Task 2- Conduct experiments to test performance and emission characteristics of each water heater on various blends of simulated biogas ($\text{NG}+\text{CO}_2$) and hydrogen enriched natural gas ($\text{NG}+\text{H}_2$)
- Task 3- Establish numerical models and evaluate impact of fuel composition on emission and stability
- Task 4- Analyze data and provide physical insights

A description of various tasks is explained in detail below:

3.1 Task 1

Establish fuel composition of interest, design and fabricate fuel mixture delivery mechanism, choose appropriate analyzers for emission measurement:

To investigate the impact of higher renewable fuel introduction in natural gas on emissions and stability of water heater burner, binary mixtures of renewable fuel and natural gas were tested under this task.

Since the fuel of interest is established in the prior sections as increased biogas and increased hydrogen in natural gas, a binary mixture of natural gas and carbon dioxide (to simulate biogas) and natural gas and hydrogen were considered in the present study. A mixing panel with appropriate selection of sonic orifice was designed for creating precise binary blends of fuel mixture on site.

Hydrogen addition to natural gas pipelines has been proposed to decarbonize pipelines and decrease the C/H ratio of fuel mixture in general. This will have implications like decrease in the net CO₂ emissions and increased efficiency of grids due to higher H₂ creation due to intermittent power generation in renewable grids vis power-to-gas scenario. However, blending hydrogen into pipelines may have grave implications on end use applications owing to the characteristic differences in hydrogen and natural gas. This prompts a closer look on end use applications, and for this study on water heating in California on higher hydrogen fuel. Similarly, biogas which is primarily a renewable fuel can help in decarbonizing pipelines. Since the primary composition of biogas is CH₄ and CO₂, a reference operational state for water heaters operating on natural gas was first established, and then experiments with mixtures of natural gas and CO₂ were conducted to

simulate biogas addition to pipelines. Further an array of analyzers were chosen for emission measurement.

3.2 Task 2

Conduct experiments to test performance and emission characteristics of each water heater on various blends of simulated biogas (NG+CO₂) and hydrogen enriched natural gas (NG+H₂):

Conventional storage water heater and low-NO_x storage water heaters are experimentally tested on natural gas to establish base combustion and operation performance, then both the water heaters are tested on blends of natural gas and CO₂ and natural gas and hydrogen. All the experiments are conducted to simulate fuel blend delivery in status quo pipeline; hence delivery point pressures are kept invariant per fuel blend. The burner flames were optically accessible via small quartz window at the base of both water heaters but were hard to monitor. Emissions were taken via various analyzers, details of which are summarized in later sections. Operational limits and emissions within and beyond the safe limit are investigated for both the low-NO_x and conventional storage water heaters. For the conventional water heater, we were able to monitor emissions beyond the safe limit of operation.

3.3 Task 3

Establish numerical models and evaluate impact of fuel composition on emission and stability:

Numerical model suitable for establishing accurate chemistry of conventional and low-NO_x storage water heater burner need to be determined. The mechanism of flame formation, geometry of burner, levels of mixing and governing physics of both the burners differ and hence for an accurate determination the following queries are addressed:

1. Explore literature for combustion mechanism of both burners.
2. Identify reaction mechanism ideal for chemistry simulation of individual burners
3. Identify area of interest for simulation and create a virtual geometry.
4. Simulate and reason accurate mechanism (chemical reactor network) for individual burners.

3.4 Task 4

Analyze data and provide physical insights:

Data on emission and stability limits from both experiments and simulations will be analyzed and reasoned. Insight based on physical and chemistry effects will be discussed and various observations and recommendations will be made. This task will be conducted in parallel with experimental work.

4. METHODOLOGY

California pipelines provide gas service pressure to the service delivery point (typical residential spaces) at 8" water column or approximately 2 kPa, unless special residential spaces or higher BTU/hr. [84] requirements demand higher delivery point pressures. Typically, residential appliances are designed to feed fuel at the delivery point pressure, hence extending, typical water heaters are designed for fuel supply under 10.5" w.c. (2.62 kPa) In a future where the composition of gas supplied will have increases concentrations of renewables, a fixed gas supply pressure is expected. Simulating the explained scenario, experiments were conducted with fuel mixtures supplied to the water heaters at 8" w.c. (2kPa).

4.1 Instrumentation and data acquisition

For measurement of emissions, a Horiba PG-350 analyzer was used for NO_x, NO, CO, CO₂, and O₂, a Horiba MEXA-QCL 1400 was used for NO₂, N₂O, NO, and NH₃, and finally, a Horiba FMA 220 for unburnt hydrocarbon (UHC) was used. The data from all analyzers were logged simultaneously with a National Instrument CompactRIO data acquisition system interfaced with the DAQ device using LabView. A thermocouple was used to monitor water temperature. Due to tight insulation of the combustion chamber, no access to the flame was available for temperature measurements. A small quartz window allowed for visualization of the flame. However, the inner window surface for the low-NO_x water heater was fouled which precluded clear images.

Emission samples were collected 3” below the top of the central flue, consistent with the methodology of Singer et al.[85]. A stainless-steel probe was used with Teflon tube and Swagelok fittings. Since the water heaters are the ‘non-condensing’ type, the emissions are wet initially. Emission measurements were made on a dry basis; hence, a water dropout/condenser system was used just before the sample was admitted into the analyzers. Information on the uncertainty of emissions and range of measurement can be found briefly in Table 3 and also in a detailed manner in Zhao et al. [43] work on cooktop burner.

Table 3. Analyte range and calibration levels for experiments on low-NO_x and Conventional Water Heater

Analyte	Sample Location	Equipment	Range	Accuracy
Carbon Dioxide (CO₂)	3” below the top of the central flue	Horiba PG-350	0-10 Vol%	±1% of the full range
Oxygen (O₂)	3” below the top of the central flue	Horiba PG-350	0-25 Vol%	±1% of the full range
Carbon Monoxide (CO)	3” below the top of the central flue	Horiba PG-350	0-500 ppm	±1% of the full range
Nitric Oxide (NO)	3” below the top of the central flue	Horiba QCL	0-250 ppm	±1% of the full range

Nitrogen Oxide (NO_x)	3" below the top of the central flue	Horiba PG-350	0-250 ppm	±1% of the full range
Unburnt Hydrocarbon (UHC)	3" below the top of the central flue	Horiba FMA 220	0-100 ppm	±1% of the full range
Ammonia (NH₃)	3" below the top of the central flue	Horiba QCL	0-50 ppm	±1% of the full range

4.2 Testing Procedure

A gas storage water heater provides hot water on demand by combusting gaseous fuel (natural gas, propane, etc.) at a thermostatically controlled temperature. The hot exhaust encounters the storage tank base and the central flume (aided with baffles) to heat water via heat transfer. The burner unit is equipped with a standing pilot light, a thermocouple, a spark igniter, and various other accessories to facilitate safe operation. A separate fuel line feeds directly to the pilot light. When a tap is turned on, hot water flows from the top of the water heater to fulfill demands, and simultaneously cold water replaces the deficit at the bottom of the tank all the while enhancing mixing between the two (hot and cold-water stream). This prompts the thermostat to open the main burner gas valve on and relight the main burner aided by the standing pilot.

Table 4. Summarizes the burner operation procedure for both the water heaters. The procedure for testing is consistent with Singer et al. [85] work on fuel interchangeability for appliances. Figure 4. Is a schematic of the experimental setup. A set point temperature

of 150°F (65.6 °C) was fixed for experiments. Operational limits and emissions within and beyond the safe limit were investigated for both the low-NO_x and conventional storage water heaters. For the conventional water heater, we were able to monitor emissions beyond the safe limit of operation. The procedure for the same is summarized in the table below.

Table 4. Burner operation procedure for CO₂/H₂ admission testing

Operation Procedure	
Within safe limit	<ol style="list-style-type: none"> 1. Test for cold start operation for each fuel mixture (NG+CO₂/H₂) to observe initial ignition behavior 2. Observe for a stable pilot operation for 5 mins (300s) following ignition, then allow the tank to achieve set point temperature of 150°F (65.6 °C) 3. When the main burner goes off, leave water heater on stand-by for 15 mins (900s) and observe pilot behavior 4. Draw 10 gallons (37.8 L) of water (25% of total volume of a 40-gallon tank) to create temperature deficit in tank. This will prompt the main burner to turn on. Observe pilot and main burner behavior during relight (with hydrogen, instability is highly probable during this stage). 5. Allow the tank to achieve set point temperature and repeat procedure per fuel blend 6. Collect emissions during all stages (1-5)
Beyond safe limit	<ol style="list-style-type: none"> 1. Cold start with 100% Natural Gas 2. When the main burner turns on, slowly control the fuel blend by increasing hydrogen or carbon dioxide and decreasing NG to the desired blend via the gas control panel. 3. Observe for a stable flame formation for 5 mins (300s), then take emissions for the 15 mins (900s) 4. Before the main burner goes off when set-point is about to reach draw 10 gallons of water to create temperature deficit and keep the main burner on. 5. Repeat Step 2. For a higher CO₂/H₂ emission testing.

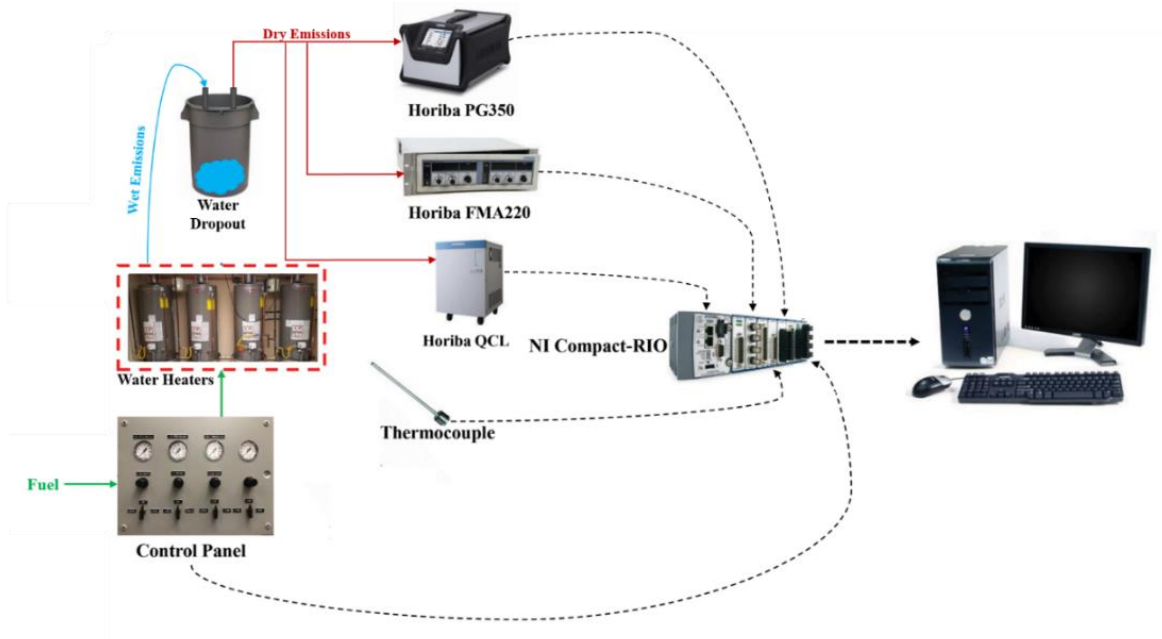


Figure 4. Experimental setup schematic

4.3 Numerical Simulation

4.3.1 Low NO_x Storage water heater

The low-NO_x storage water heater was designed to meet the strict NO_x regulations of ≤ 10 ng/J for residential units with heat input rates $\leq 75,000$ BTU/hr. [68]. For achieving low levels of NO_x three methods were adopted, (1) premixing fuel and air before combustion, (2) lean operation at burner head, and (3) utilizing a radiant screen to decrease peak flame temperature.

4.3.1.1 Virtual Combustion Chamber

A typical radiant burner is shown in Figure 5. For this research a low- NO_x storage water heater rated 38,000 BTU/hr. and a 40-gallon capacity was chosen for experiments. The geometry is composed of a burner structure with radial fuel ports and a flame spreader which evenly distributes the flame on its surface [86]. A brief description of the history of low- NO_x burner development and configuration is given in Section 2.3.1.

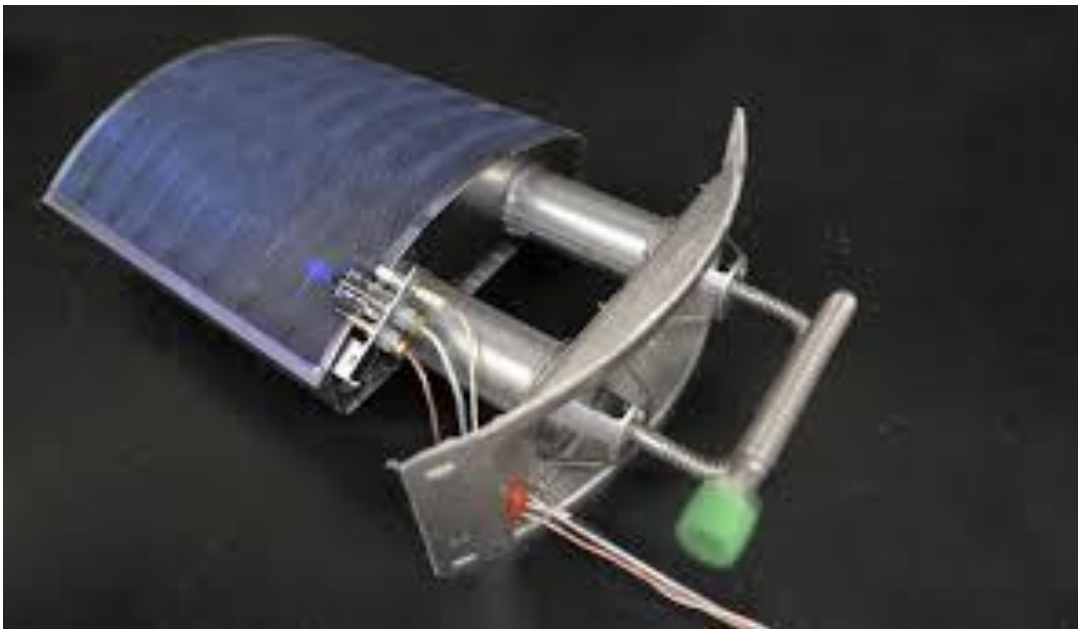


Figure 5. Radiant screen burner

For accurate blow-off prediction and chemistry modelling, the area of interest for combustion was identified. Figure 6 represents a schematic for the low- NO_x water heater under consideration in this research, on the right is our area of interest. Since the low- NO_x water heater relies on high levels of premixing and radiant energy emission from the burner screen, it was easy to create a network of idealized reactors to simulate accurate emissions and stability for the burner.

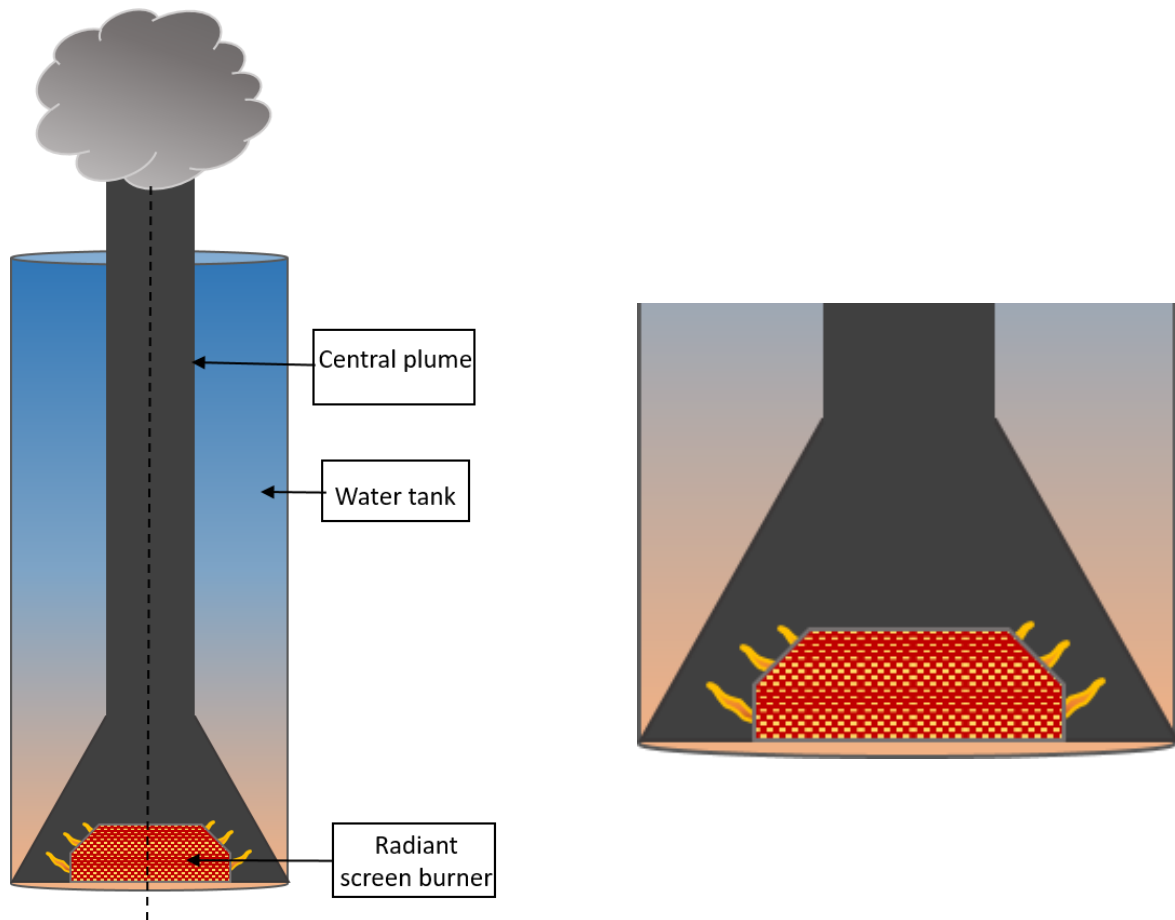


Figure 6. Schematic of a typical low-NO_x water heater burner (Left) and area of interest for simulation (Right)

4.3.1.2 . Boundary Condition

For emission simulation, focus on the fuel air premixing, equivalence ratio, burner surface radiation losses and post flame region are simulated. We get excellent agreement with this region of interest. Table 5 gives a detailed summary of the boundary condition for the area of interest upon which the reactor network is modeled and optimized.

Table 5. Boundary condition

Boundary Name (type)	Details
Premixed injector (mass flow inlet)	Premixed air-fuel mixture Mass flow rate injector Constant pressure delivery (2kPa) Equivalence ratio (ϕ) Initial temperature---300K
Burner surface	Radiant energy---32.5% Temperature range---1200-1650 K

4.3.1.3 CRN model

Radiant screen burner/low- NO_x water heater burner has an overall equivalence ratio on the leaner side ($\Phi < 1$) and expends around 32.5% of the fuel energy in the form of radiation [67]. Both primary excess air and radiation aids in decreasing the flame temperature which subsequently reduces the NO_x emissions. Using experimental trend and burner behavior a reactor network made of two PSRs, one PFR, a fuel-air inlet and a secondary air inlet is created to match the trends. The CRN represents a mixing zone (PSR1), a premixed reaction (PSR2) with secondary air supplied at flame front and the zone downstream of PSR2, which is considered the immediate post flame; a PFR describes this region better than a PSR. The temperatures in the post flame are uniform and the flow velocity vectors is unidirectional (perpendicular to the surface) therefore it is ideally represented with a PFR (PFR1).

The post flame region is important regarding the time the species spend in that zone. At that point the combustion products are mainly carbon dioxide (CO_2), water (H_2O), remaining of oxygen (O_2) and nitrogen (N_2); also a lower proportion of pollutant species

like NO_x and products of incomplete combustion like carbon monoxide (CO) and unburned hydrocarbon (UHC) appear in that region. The reactions at that point are slow compared to the active flame region (PSR1). The long residence time in that region will help to oxidize the remaining CO into CO_2 , but also will help to increase the NO_x emissions if the temperature conditions are favorable for the nitrogen chemistry. Since we are focusing on the fuel delivery and near flame region, a manual CRN saves computational time and yields precise pollutant trends.

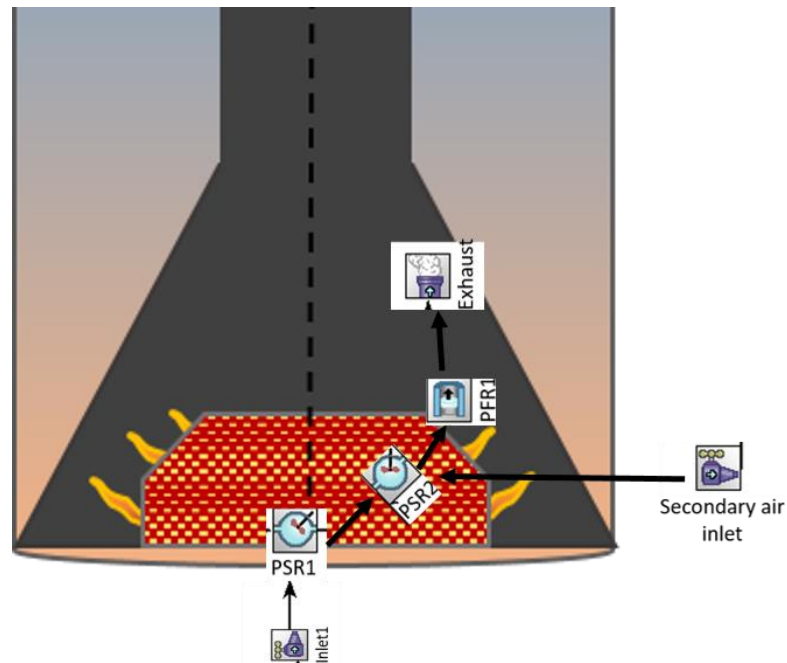


Figure 7. Manual CRN visualization to burner flame

The CRN Results for NO_x and CO are compared to the experimental trends obtained. The reaction mechanism used to model the reactions was the GRI 3.0 [87]. With the aim of studying the sensitivity of the results to the reaction mechanism the mechanism

developed by UC San Diego was also tested. UC San Diego mechanism under predicts NO_x for our reactor network. Hence the rest of the results will be estimated using GRI 3.0. Figure 7 and Figure 8 illustrate the manual CRN used for this study on low- NO_x water heater.

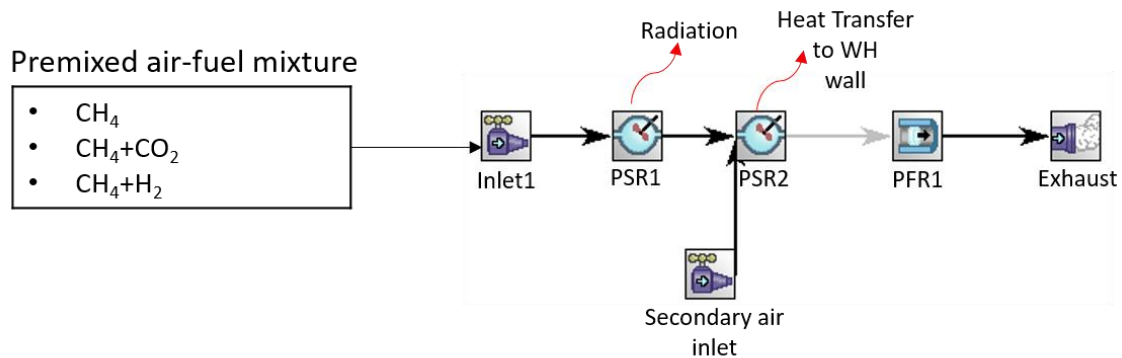


Figure 8. CRN for low- NO_x water heater burner

Specifics of the various inputs for the CRN are summarized in the table below. The table includes, residence time, volume of combustion zone, pressure and heat loss values by reactor name.

Table 6. Details for parameters of reactors in CRN for low- NO_x water heater

PSRs	units	PSR1	PSR2	PFR	units	PFR1
Res. Time	s	0.005	5	End point	cm	4
Temperature	K	600	1400	Area	cm^2	314
Pressure	atm	1	1	Pressure	atm	1
Heat Loss	%	2	32	Heat loss	%	0
Volume	cm^3	1400	10000			

Since the density of CO₂ and H₂ are very different from the density of natural gas, the mass flow rate of air-fuel mixture will vary with varying mixture composition. Simultaneously, the equivalence ratio at burner head varies. Table 7. summarized the equivalence ratios and mass flow rates of various mixtures with CO₂ and H₂ addition to natural gas.

Table 7. Change in Equivalence ratio and air-fuel flow rate at low-NO_x burner head

% of CO ₂ /H ₂	NG+CO ₂		NG+H ₂	
	M ^o fuel(g/s)	Φ	M ^o fuel(g/s)	Φ
0%	0.234	0.847	0.234	0.847
5%	0.240	0.668	0.226	0.674
10%	0.246	0.602	0.219	0.656
15%	0.252	0.548	NA	NA

All emissions are on a dry basis and indicates that the water from the combustion products is removed before the combustion products are analyzed with the gas analyzer. This presentation (ppmdv) is representative of the measures in the field and is also typical of units found in regulatory or permit limits.

The CRN results for emissions and lean blow off limits were obtained using ANSYS Chemkin 19.2 and the GRI 3.0 reaction mechanism [87]. While it is recognized that the specific chemistry mechanism used can influence the absolute values of the emissions predicted [88], the trends are generally insensitive to the mechanism used.

4.3.1 Conventional storage heater

Conventional storage water heaters were the first to incorporate NO_x reduction mechanisms. When regulations maintained ≤ 40 ng/J from residential water heaters with heat input rates $\leq 75,000$ BTU/hr., various mechanisms were adopted for reducing NO_x. A few were, (1) rich primary air-fuel premixing, (2) lean operation at burner head, (3) secondary air entrainment to established flame, and (4) a secondary plate to act as heat sink and decrease peak flame temperature.

4.3.1.1 Virtual Combustion Chamber

A typical pancake burner conventional storage water heater is shown in Figure 9 (left). For this research a conventional storage water heater rated 38,000 BTU/hr. and a 40-gallon capacity was chosen for experiments. The burner flame receives both primary and secondary air. The air-fuel mixture is rich at the burner head, with $\Phi \sim 3.5$ for natural gas.

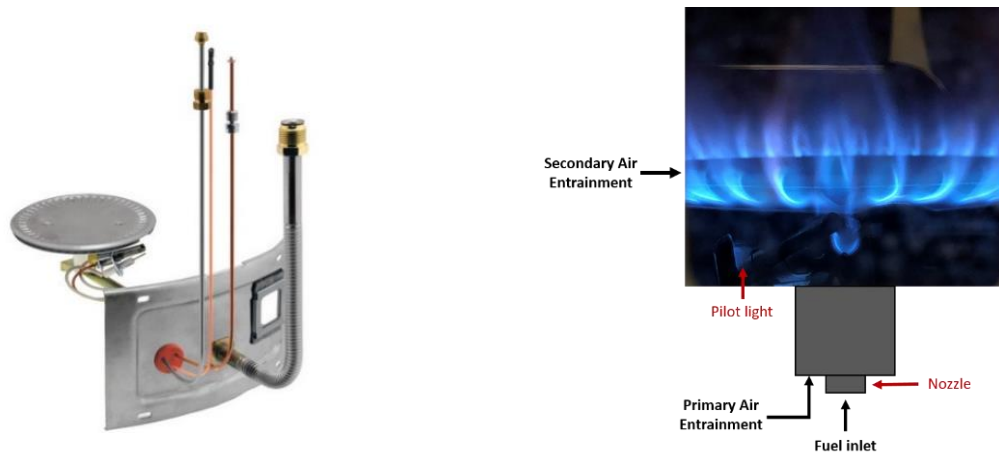


Figure 9. Pancake burner assembly (left), burner schematic (right)

For accurate blow-off prediction and chemistry modelling, the area of interest for combustion was identified. Figure 10 represents a schematic for the conventional water heater under consideration in this research, on the right is our area of interest.

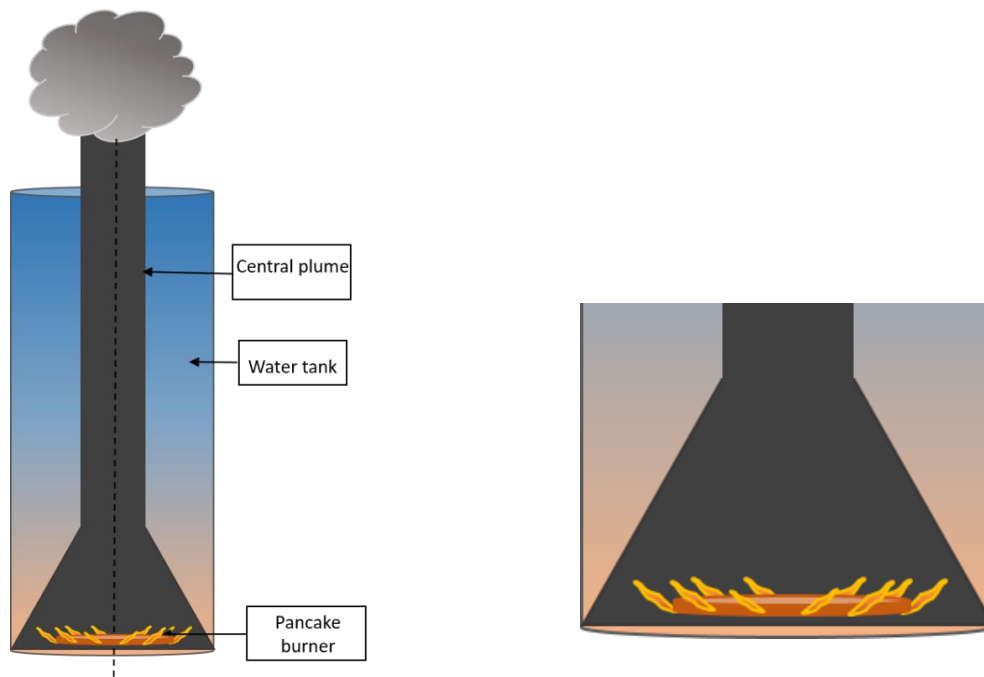


Figure 10. Schematic of a typical conventional water heater burner (Left) and area of interest for simulation (Right)

Since the conventional water heater relies on high levels of premixing and rich operation at inlet and lean operation overall, a network of idealized reactors (Figure 8) similar to the low-NO_x water heater was utilized to simulate accurate emissions and stability for the burner. Since the density of CO₂ and H₂ are very different from the density of natural gas, the mass flow rate of air-fuel mixture will vary with varying mixture composition. Simultaneously, the equivalence ratio at burner head varies. Table 8 summarized the equivalence ratios and mass flow rates of various mixtures with CO₂ and H₂ addition to natural gas.

Table 8. Change in Equivalence ratio and air-fuel flow rate at conventional burner head

% of CO ₂ /H ₂	NG+CO ₂		NG+H ₂	
	M°fuel(g/s)	Φ	M°fuel(g/s)	Φ
0%	0.234	0.685	0.234	0.685
5%	0.240	0.555	0.226	0.549
10%	0.246	0.475	0.219	0.539
15%	0.252	0.448	NA	NA

5. RESULTS

5.1 Fuel Composition

Pipeline Natural Gas delivered across residential spaces allow for some deviation in composition and already has in it some percentage of carbon dioxide along with higher hydrocarbons [47], air and other components in micro amounts (Table 9).

Table 9. Natural gas composition as supplied to UCI Combustion Lab (UCICL)

Natural gas content		
Content	Molecular Formula	Molecular Fraction
Methane	CH ₄	95.8%
Ethane	C ₂ H ₆	1.4%
Propane	C ₃ H ₈	0.4%
Iso-butane	C ₄ H ₁₀	0.05%
n-butane	C ₄ H ₁₀	0.05%
Iso-pentane	C ₅ H ₁₂	0.025%
n-pentane	C ₅ H ₁₂	0.025%
C6	C ₆ H ₁₄	0.017%
C7	C ₇ H ₁₆	0.017%
C8	C ₈ H ₁₈	0.016%
Carbon dioxide	CO ₂	1.9%
Oxygen	O ₂	0%
Nitrogen	N ₂	0.3%

Table 10. Characteristics for CH₄, H₂, and, CO₂

Property	Unit	CH ₄	H ₂	CO ₂
Density	kg/m ³	0.648	0.0813	1.784
Viscosity	10 ⁻⁵ Pa·s	1.11	0.89	1.50
Laminar Flame Speed	m/s	0.4	2.1	NA
Low Flammability[89]	ϕ	0.53	0.14	NA
	Vol %	5	4	NA
High Flammability[89]	ϕ	1.6	2.54	NA
	Vol %	15	75	NA
Ignition Energy	10 ⁻⁵ J	33	2	NA
Lower Heating Value[90]	MJ/m ³	34.0	10.2	0
	MJ/kg	49.9	120.1	0
Higher Heating Value[90]	MJ/m ³	37.8	12.5	0
	MJ/kg	55.5	142.1	0
Adiabatic Flame Temperature	K	2226	2318	NA
Wobbe Index	MJ/m ³	51.9	48.5	0

For our study, we use natural gas sourced from SoCal Gas to UCI Combustion Laboratory, it has a methane content of 95.8% and can be assumed to have properties similar to pure methane. Energy content and other characteristics of methane, carbon dioxide and hydrogen has been summarized in Table 10. Water heater operation and emissions were monitored with 100% methane and pipeline natural gas operation in a prior work [91]. Little to no variation was concurred and hence pipeline natural gas was utilized to understand the impacts of hydrogen admixing with natural gas for storage water heaters. A control panel was designed with suitable sonic orifices [91] to blend fuels (NG+H₂/CO₂) on a volumetric basis. The ‘fuel-mixture’ or percentages used in the study should be assumed as on a volumetric basis.

5.2 Biogas Testing

5.2.1 Impact of CO₂ Admixing

Biogas composition lies on a wide spectrum, depending on where is sourced from, hence it can be quiet challenging to find the right upgrading technology for a given source. Due to various incentives, both environmental and economic, biogas is seen as a widely used viable technology for the future energy market. Under current regulations of upgrading biogas to Renewable Natural Gas (RNG), which can then be directly injected into pipeline allows for small deviation from pipeline-quality natural gas. This adds the cost of upgrading on top of sourcing and infrastructure to support RNG production.

We perform a calculation similar to one in one by Zhao et al [47], to determine under the current regulation how much CO₂ in natural gas will be tolerated in pipelines based on Wobbe Index and heating requirements. Equations (1-3) are used for the determination of Wobbe Index, the heating value of fuel mixture and Wobbe Index of the fuel mixture.

$$\text{Wobbe Index} = \frac{\text{Higher Heating Value}}{\sqrt{\text{Fuel Specific Gravity}}} \quad (1)$$

$$\text{HHV}_{\text{Mix}} = (1 - x\%) \text{HHV}_{\text{NG}} + x\% \text{HHV}_{\text{CO}_2} \quad (2)$$

$$\text{WI}_{\text{Mix}} = \frac{\text{HHV}_{\text{Mix}}}{\sqrt{\frac{(1 - x\%) \rho_{\text{NG}} + x\% \rho_{\text{CO}_2}}{\rho_{\text{Air}}}}} \quad (3)$$

As shown in Figure 11., according to Wobbe Index regulations <5% CO₂ can be injected directly into pipelines. According to heating value, it is even lower than that (<3% CO₂).

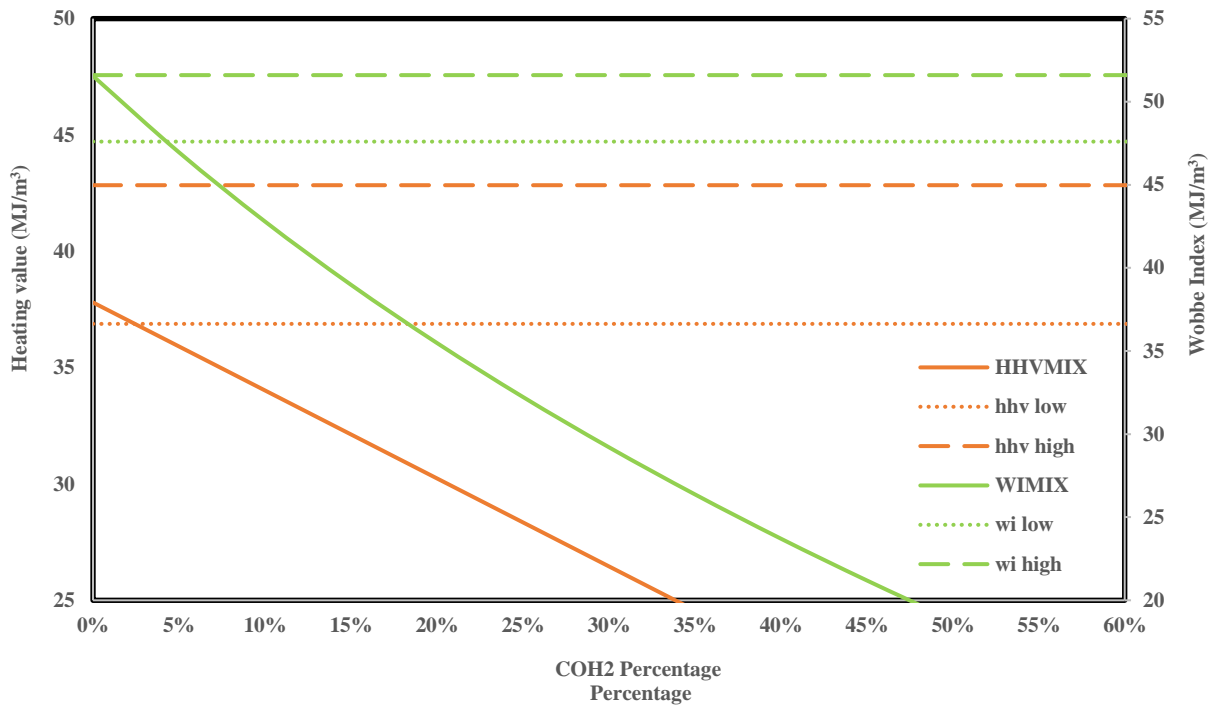


Figure 11. Heating value and Wobbe Index variation with NG+CO₂ mixtures.

For this research natural gas and carbon dioxide (CO₂) were mixed at various concentrations to simulate biogas. A mixing panel was designed with appropriate sonic orifice distribution for critical control of required gas mixture flow rates [91]. All residential appliances fall within a range of FAR (fuel to air) ratio for required operation. As mentioned above in the burner configuration, the low-NO_x water heater burns lean at the burner head. **At constant pressure delivery, changing the fuel composition changes the air/fuel ratio at the burner head and hence the equivalence ratio [53].** In this study, increasing CO₂ content in natural gas increases the overall mass flow rate of the fuel and hence the FAR_{act}, simultaneously FAR_{stoic} increases faster according to Eq (4) and hence decreasing the overall equivalence ratio.

$$\Phi = \frac{FAR_{act}}{FAR_{stoic}} \quad (4)$$

Assuming complete combustion of the fuel, we can calculate the equivalence ratio by measuring the CO₂ concentration in the exhaust. As can be seen in Table 11, the equivalence ratio decreases with increasing CO₂ concentration. The CO₂ % in exhaust was measured experimentally using Horiba PG-350 analyzer.

Table 11. Equivalence Ratio (Φ) shift for low-NO_x water heater on CO₂ addition

Fuel Composition	CO ₂ [Vol%]	Φ
100% NG	8.44%	0.847
95% NG+5% CO ₂	7.95%	0.668
90% NG+10% CO ₂	7.53%	0.602
85% NG+15% CO ₂	7.19%	0.548

5.2.2 Ignition, flame characteristic and safe limit of operation

For the low-NO_x water heater beyond 10% CO₂ addition, the pilot operation becomes unstable and the probability of blow off increases. At both 5% and 10% CO₂ addition a stable though increasingly flat flame is observed, and pilot operation is stable both during idling and relight of the main burner. At 15% CO₂, a stable but almost flat flame was observed at the burner head. The pilot was sustained during idling but blows off as soon as gas flows through the fuel port when relight is attempted. This experiment was

repeated thrice and each time a similar observation was recorded. Hence a reliable limit of operation as 10% CO₂ for the low NO_x water heater is reported.

For the conventional gas storage water heater, a stable flame is established up to 25% CO₂ addition, with the flame becoming increasingly shorter beyond 30% CO₂ addition Figure 12. A stable pilot operation, on the other hand, could not be established even at 5% CO₂ addition. One reason for the low tolerance could be the pressure difference (hence higher flow rates) requirement of both CO₂ and natural gas to create a mixture of fixed composition. We speculate the high flow rate of fuel mixtures might be blowing off the pilot. On visual examination, we confirmed our speculation as the pilot blows off just before relighting of the main burner. Higher limits for CO₂ addition with premixed blends of gas cylinders might be possible.



Figure 12. Flame shape for conventional water heater with increasing CO₂ content

Limit for safe and reliable operation is determined (Table 12). The determination is assuming no change in status quo water heaters in residential spaces. Hence, with 10% CO₂ concentration low-NO_x models will operate reliably and for the conventional models, further research is required, though a modification of pilot light is speculated to increase the limit of CO₂ introduction.

Table 12. Safe limit of operation

Water Heater	CO ₂ limit
Low NO _x gas storage water heater	10%
Conventional gas storage water heater	0%

5.2.3 Energy Efficiency

Energy Efficiency of water heater units is calculated according to ASHRAE 118.2 [92]. An energy factor (EF) is the typically used metric for energy efficiency determination for appliances [93]. It combines the thermal efficiency and standby efficiency for residential appliance units. For every dollar spent on a water heater, EF dollars will be translated to heating water and (1-EF) dollar will be wasted. For a gas storage water heater the EF is calculated over a 24 hour period, with 6 equal volume water draws, input-output water temperature measurements and fuel energy input. The

determination also takes into account, standby losses and recovery efficiency. Recovery Efficiency (RE) is the energy absorbed by water to reach a set point temperature to the energy produced during combustion per hour [94].

For this research, a setpoint temperature of 150 °F (65.6 °C) is used and kept invariant for all the tests (Eq. (5)). During water heater operation, when the setpoint temperature has reached the main burner goes off and a pilot flame is sustained for relight purposes. For recovery efficiency calculations 10 gallons (37.8 L) of water is drawn after idle operation of 15 mins (900 s) after setpoint temperature was reached. Assuming negligible losses during ignition and idling, the time in minutes taken by the water heater for reaching the setpoint temperature is compared.

$$\text{Recovery Efficiency} = \frac{\Delta m \cdot \Delta T \cdot C_p}{t \cdot m \cdot \Delta H_{\text{rxn}}} \quad (5)$$

$$\Delta H_{\text{rxn}} = \sum_{\text{all}} \Delta H_f^{\circ}(\text{products}) - \sum_{\text{all}} \Delta H_f^{\circ}(\text{reactants}) \quad (6)$$

The plot below shows the change in recovery efficiency of the storage water heater with an increasing CO₂ percentage. Till 10% CO₂ addition there is little compromise on recovery efficiency (~76%), though there is a decreasing trend with increasing CO₂. This makes sense since the additional CO₂ in fuel mixture absorbs a part of the combustion energy. The heating time required to reach a setpoint temperature increases gradually from 13.5 mins with 100% NG to 19 mins with 10% CO₂ addition.

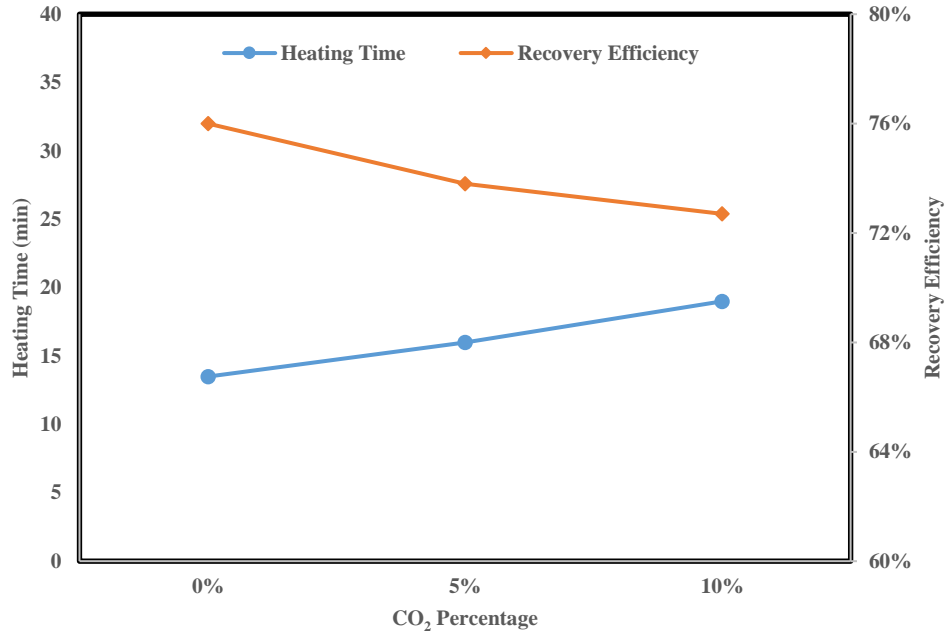


Figure 13. Recovery efficiency and heating time as a function of CO₂ addition for low NO_x water heater

5.2.4 Emissions

The Clean Air Act of 1970 [95] steered the Environmental Protection Agency (EPA) to establish national emission standards for stationary combustion sources and hazardous air pollutants. Due to the ambiguity in emission reporting methods, in 1978 the EPA came up with a comprehensive, standardized review for emission correction and reporting [96]. Correction methods are based on what concentrations or experiment parameters are known, such as, pollutant concentration, fuel type, fuel energy content, O₂ concentration, CO₂ concentration, effluent volumetric rate, fuel input rate, etc. To avoid the effect of dilution, the engine and gas turbine industry has adopted correcting emissions to 15% O₂ in exhaust [97]. Pollutant concentrations for boilers, heaters, and ovens are generally corrected to 3% O₂ in the exhaust.

In the present work, emissions are reported using three correction methodologies, (1) corrected to 3% O₂ in the exhaust as Eq. (7) (primarily used for stationary combustion systems, automobiles, etc. [96]), (2) corrected to 12% CO₂ in the exhaust (used for correction of pollutants in the oxygen-rich environment) as Eq. (8) [98], and (3) calorific correction, which is the mass of pollutant per unit energy of fuel as Eq. (9) (generally used for low heating load burners). 12% CO₂ correction is also popularly known as “air-free” correction since it is stoichiometric quantitatively [47]. Calorific correction of pollutants to nanograms of the analyte to per unit Joule of fuel energy is widely accepted for emission reporting in residential appliances [85]. Calorific/energy corrections eliminate the effect of emission fluctuations based on stoichiometric water content, which has been shown to work against the favor of hydrogen-rich fuel. It is also deemed useful for fuel interchangeability studies since it relates emission levels to the energy of fuel and removes the dependence of CO₂ or O₂ concentration. Both HHV (higher heating value) and LHV (lower heating value) can be used for calorific correction, but the water heaters in the present work are non-condensing and therefore the actual heating load consumed was observed to be the LHV. However, since HHV is used in formulation of regulations for water heating appliances we use HHV for calorific corrections in our research.

$$C_i(@ \text{ ppmv } 3\% \text{ O}_2) = (C_{i,\text{ppm}}) * \frac{20.95 - 3}{20.95 - O_{2,\text{msd}}(\text{Vol}\%)}$$
 (7)

$$C_i(@ \text{ ppmv } 12\% \text{ CO}_2) = (C_{i,\text{ppm}}) * \frac{12}{\text{CO}_{2,\text{msd}}(\text{Vol}\%) - \text{CO}_{2,\text{amb}}(\text{Vol}\%)} \quad (8)$$

$$C_i \left(\frac{\text{ng}}{\text{J}} \right) = \frac{0.1 * C_{i,\text{ppm}}}{\text{CO}_{2,\text{msd}}(\%) - \text{CO}_{2,\text{amb}}(\%)} \frac{\text{mol CO}_2}{\text{MJ Fuel}} * M_i \frac{\text{g}}{\text{mol}} \quad (9)$$

The emissions from Low-NO_x water heater are as shown in Figure 14, and for conventional storage are shown in Figure 15. Emission collection procedure has been explained in ‘Experimental Methodology’. The emission reported correspond to averaged concentrations over each burn cycle within standard variance. The three plots represent the three correction methods. Each plot informs on the concentration of NO_x, NO, CO and UHC as a function of CO₂ content in NG+CO₂ mixture. Since increasing CO₂ content decreases the overall energy delivered to the combustion device, each plot shows a trendline informing the ‘Energy Content’ of the fuel mixture in BTU/hr. as well.

For the low-NO_x water heater burner, we observe a decrease in NO_x and NO with increasing CO₂ content. Simultaneously, CO and UHC increases. True to the design of the model, NO_x emissions stay below 10ng/J. The safe limit of operation was determined to be 10% CO₂ in natural gas for the low-NO_x burner. With respect to emissions for pure natural gas with calorific correction, NO_x and NO decrease from 7.78 ng/J to 4.21 ng/J and 3.46 ng/J to 0.6 ng/J respectively. Simultaneously, CO and UHC increase from 11.85 ng/J to

52.2 ng/J and 12.13 ng/J to 27.17 ng/J respectively. Since the water heater units are closed and insulated, it was difficult to conduct a cold flow analysis to deduce equivalence ratio.

However, by measuring the exhaust O₂/CO₂ concentrations from the central plume showed that the combustion was lean, with an overall equivalence ratio ~0.71. A similar level of mixing was shown in a previous study of a low-NO_x burner as ~0.725 [67]. Since low-NO_x water heater burners primarily rely on the radiative surface, lean combustion and flame spreading to lower the NO_x emissions, the addition of CO₂ further aids this mechanism. Since CO₂ is inert in nature, its addition displaces per unit volume energy content of the fuel mixture. It also functions as a heat sink and lowers the flame temperature by increasing the heat capacity of the mixture. Around 32.5% of the fuel energy goes into radiation of the burner screen, which is shown to lower the flame temperature by ~400 K [67]. Higher temperatures are conducive to NO_x formation, via the Zeldovich mechanism. CO emissions, on the other hand, goes up. This inverse relationship between NO_x and CO is a common observation in combustion devices running on biogas.

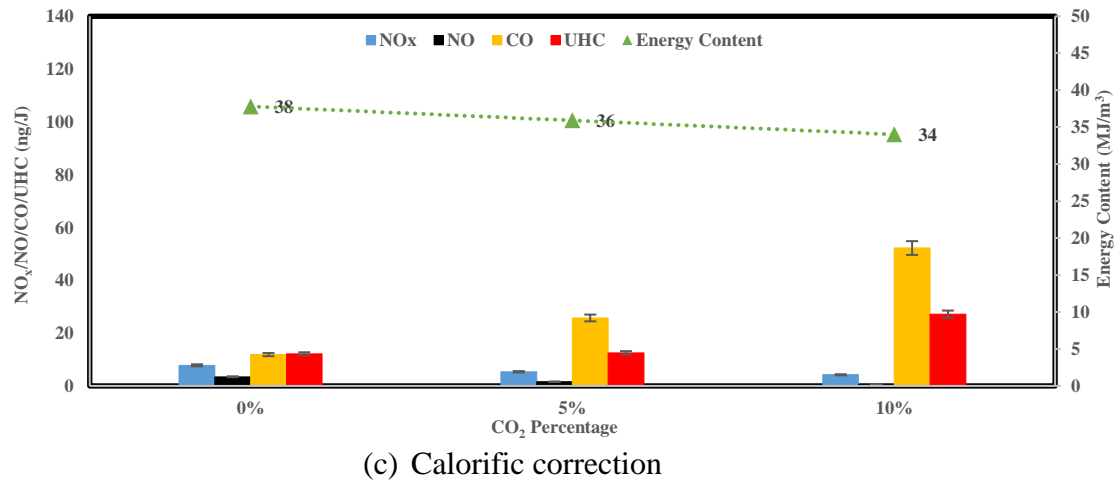
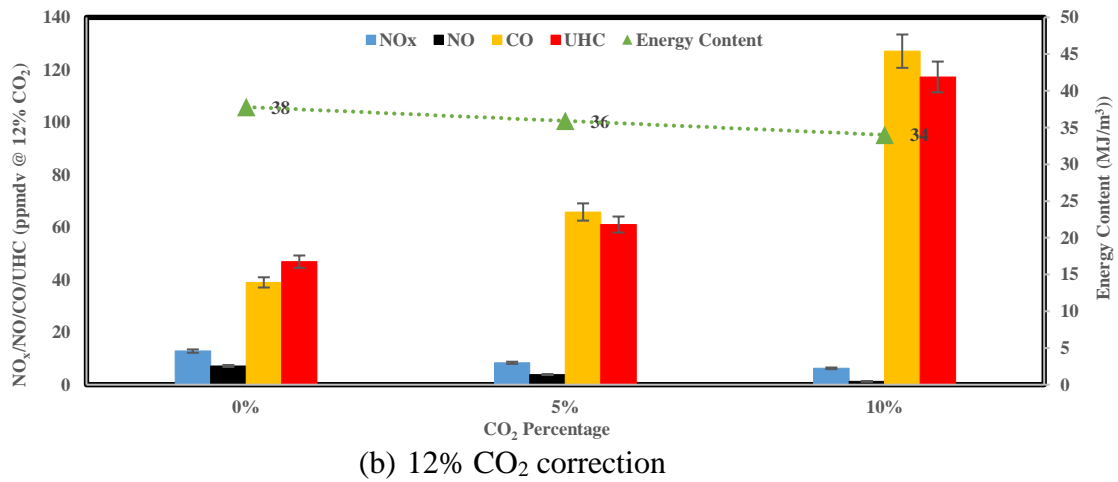
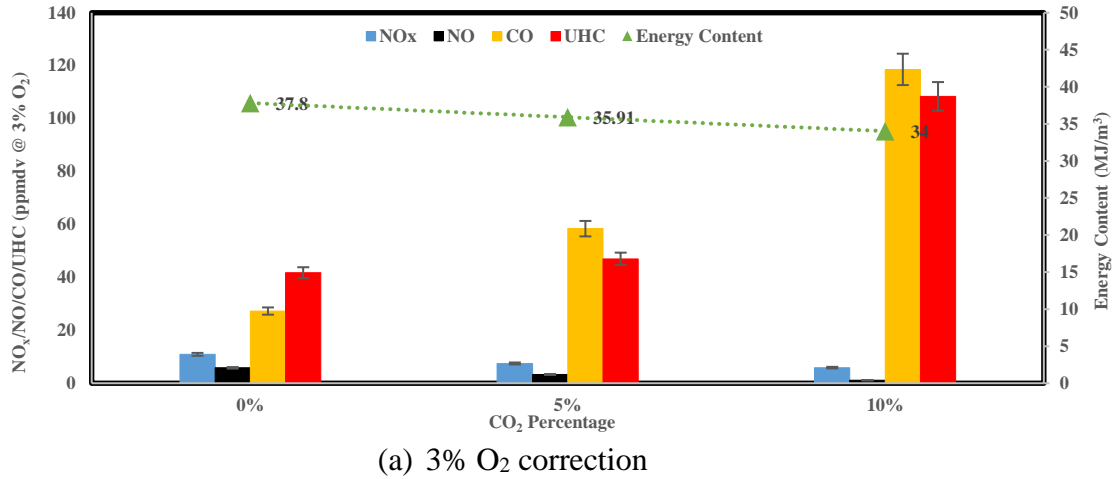
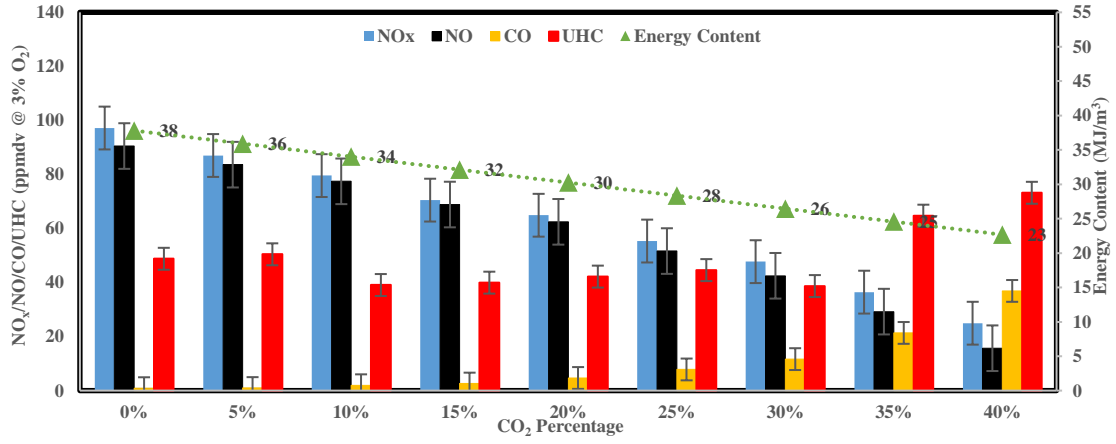


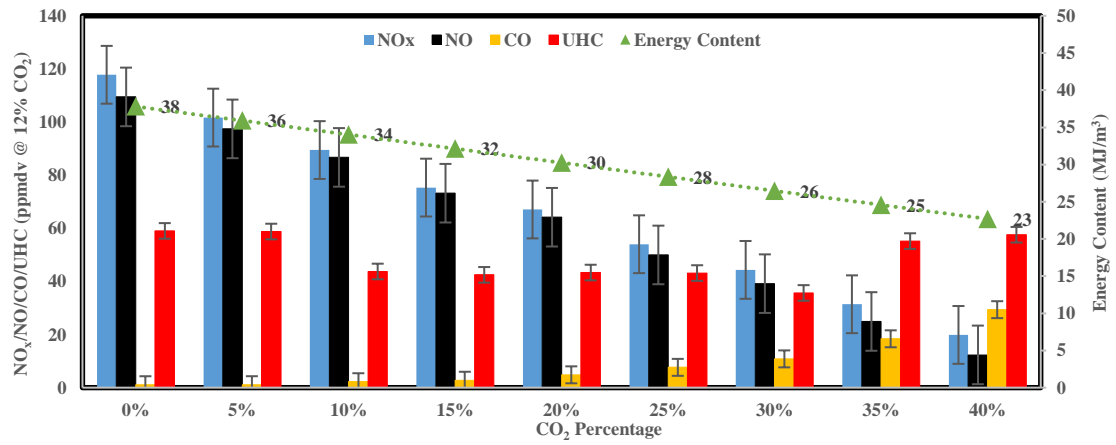
Figure 14. Emissions for low NO_x storage water heater with increasing CO₂ concentration

The conventional water heater the burner could not establish a flame even at 5% CO₂ mixing. A main burner flame was sustained even at 40% CO₂ addition (Figure 15), but the pilot blows off during relight. As mentioned earlier, partly the reason could be the huge difference in flow rates of the CO₂ and NG which was required to make the mixture of fixed composition. To determine CO₂ tolerance, further study with premixed CO₂+NG mixture should be attempted. Emission data with 15 min burn cycles per fuel blend was collected for this model. Emissions with the three correction methods mentioned earlier are shown in Figure 15. Inspection of the exhaust O₂/CO₂ concentration showed the overall equivalence ratio of ~0.63. A previous study of ‘pancake burners’ showed the equivalence ratio of air-fuel mixture in the burner head is rich [66], whereas the overall equivalence ratio is towards the leaner side.

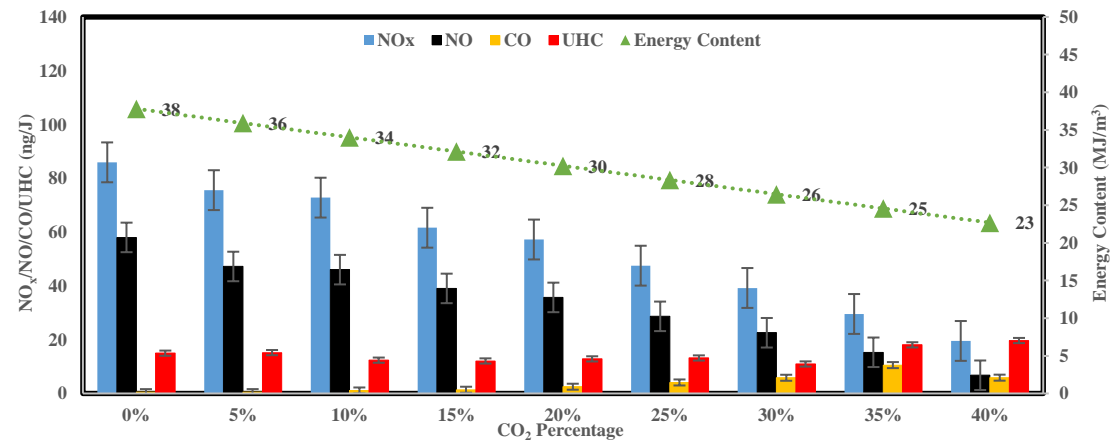
A similar trend to the low-NO_x water heater of decreasing NO_x and NO and simultaneous increase in CO and UHC was observed for the conventional model. Fuel variability impact on residential appliances was conducted by LBNL [85] and for natural gas, the emissions reported are around 20 ng/J higher than what the LBNL study observed. We suspect this to be a unique behavior of our particular model. Nonetheless, the trend of emissions is expected to be similar. With respect to emissions for pure natural gas with calorific correction, NO_x and NO decrease from 85.9 ng/J to 72.8 ng/J and 58 ng/J to 47.2 ng/J respectively. Similarly, CO and UHC increases slightly but remain constant in magnitude. No N₂O or NH₃ was observed within the detectable ranges for both the water heater.



(a) 3% O₂ correction



(b) 12% CO₂ correction



(c) Calorific correction

Figure 15. Emissions for conventional storage water heater with increasing CO₂ concentration

5.2.5 Methane Leakage

Methane emissions from residential spaces were largely ignored in greenhouse gas inventory estimation; since they assumed complete combustion and hence minimal leakage [99]. An extensive study by Fisher et al. [100] in their 2018 study showed methane emission, both active (at steady state) and inactive (idle operation), from residential spaces being substantial and hence cannot be ignored in overall GHG quantification. Key findings include pilot operation as significant contributors of methane emissions both during active and inactive operation. Around 56-63% of Californian homes have water heating units with pilot lighting in them [101]. The two models of water heaters used in this study have pilot light for reignition, hence a methane leakage quantification was performed.

Methane emissions were monitored for a period of operation which included ignition, steady state operation, flame quenching and idle operation. For the natural gas operation, the fuel was supplied to both the water heaters directly through the pipeline and testing was conducted with no other tests requiring the use of natural gas in the testing environment. This allowed us to assume negligible methane emissions from fittings and pipelines in test zone and hence negligible background methane which had to be accounted for. The emissions are averaged over 2 cycles of testing and represent continuous operation. As can be seen from Figure 16, both Low-NO_x and the conventional water heaters emit fuel at steady state and idle operation. More methane is emitted at idle operation which correlates to pilot emissions, since the main burner fuel is turned off.

Overall more methane is emitted by the low-NO_x water heater both at steady and idle operation. The results clearly suggest that the methane emissions during idle operation can

be eliminated by electric ignition, all the while saving natural gas needed for pilot operation.

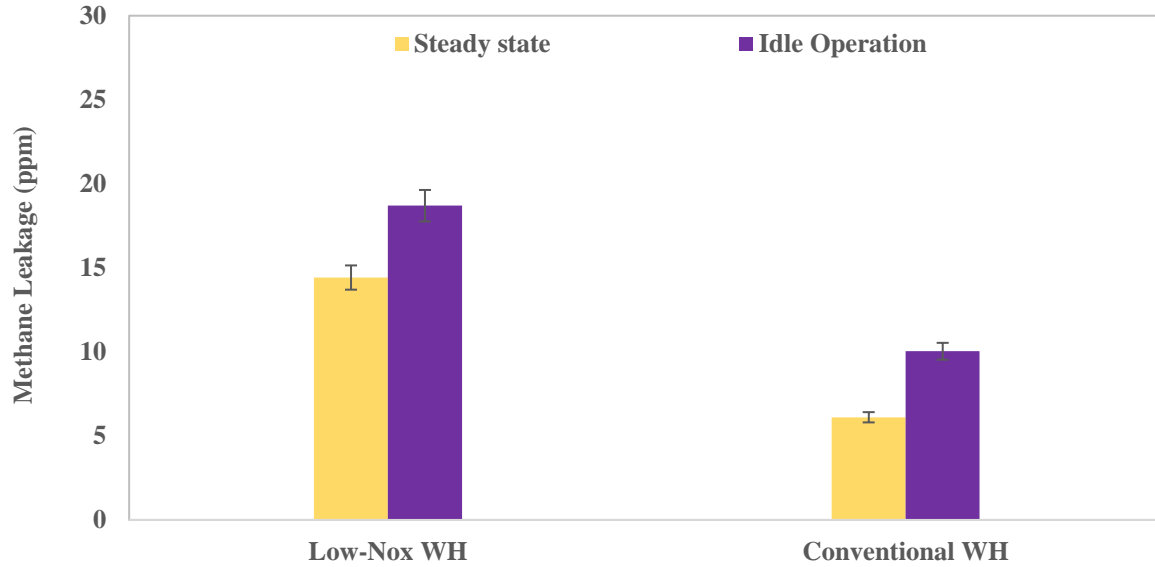


Figure 16. Methane emissions for both the water heaters

5.2.6 Biogas Simulation Results

5.2.6.1 Low-NOx storage water heater

During the experiment, the fuel mixture is kept at 2,000 Pa (8 inches of water) to simulate the residential pipeline pressure. The test fuels are shown in Table 13 with respective Wobbe Index. These fuels represent those that would be found in landfills or anaerobic digestion processes.

Table 13. Change in Wobbe Index with increasing CO₂ in natural gas

Biogas (NG+CO ₂)	Wobbe index (BTU/scf)
100% CH ₄	1361.7
95% CH ₄ – 5% CO ₂	1250.38
90% CH ₄ –10% CO ₂	1147.45

CO₂ in natural gas acts mostly like a diluent in the fuel and adds no additional heat generation. Figure 17 shows the effect of increased CO₂ percentage on the adiabatic flame temperature (AFT) at the burner exhausted in simulation.

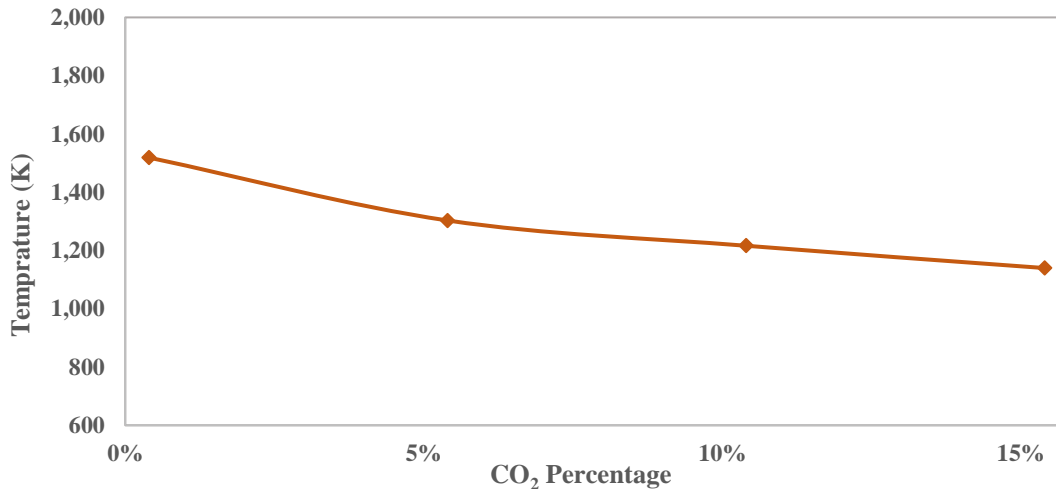
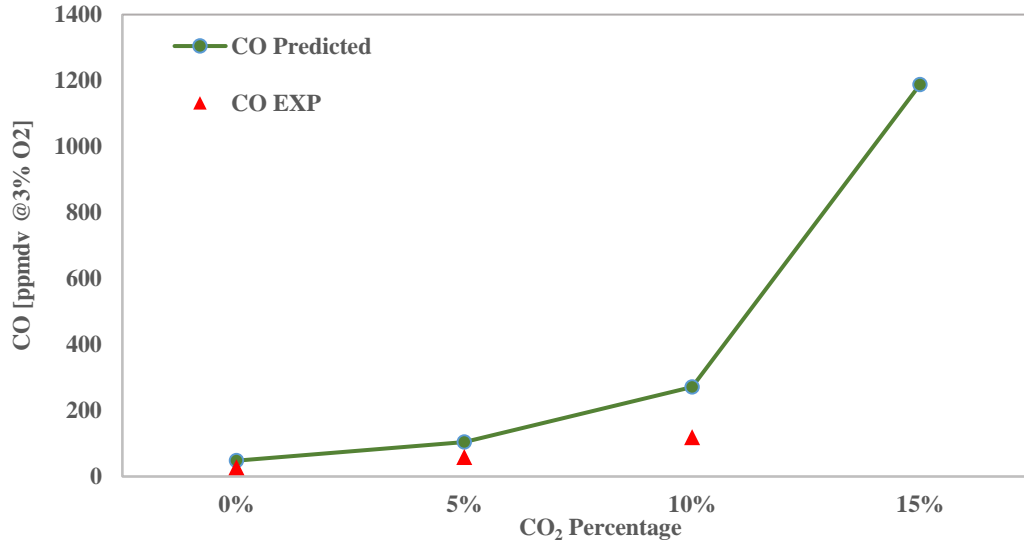


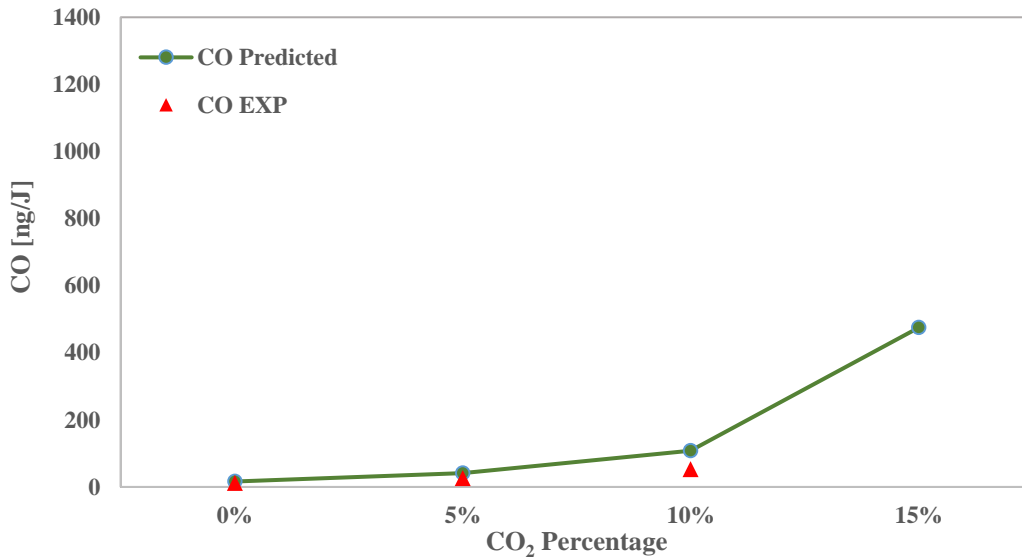
Figure 17. Adiabatic flame temperature at CRN exhaust with increasing CO₂ %

As shown, CO₂ injection into the fuel brings down the flame temperature, therefore, thermal NO_x decreases, and CO increases due to the flame quenching effect from CO₂. Figure 18 shows the emission of CO for the low-NO_x water heater burner. We see a good agreement in emissions for experiments and simulation for both the trend and magnitude of values. CO emission increases with increasing CO₂ %. **It's worth mentioning that combustion failure appears at 15% CO₂ injection in the simulation model, which is**

around the same blow off limit for the experiment. The shoot up of CO emission is a good indicator of blow-off. The CRN is able to accurately predict blow-off for our model.



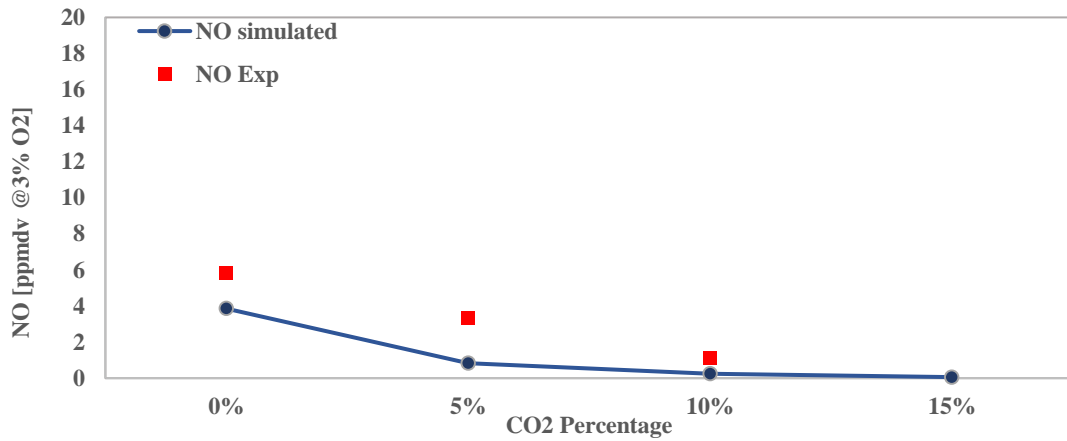
(a) 3% O₂ in exhaust



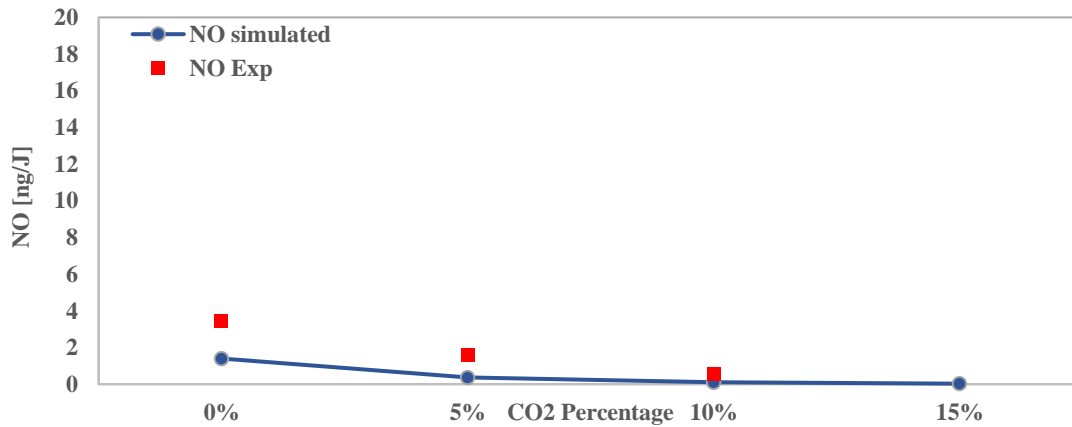
(b) Calorific correction

Figure 18. CO emission from low-NO_x water heater on CO₂ addition (simulation vs experiments)

Figure 19 show the NO emissions with increasing CO₂ %. Again, the model is able to accurately capture the magnitude and trend of NO emission. The simulation levels of NO₂ were of the order 10e-8 and hence the NO_x emissions are proportional to the NO results. UCSD mechanism predicts lower NO and NO₂ and hence NO_x compared to GRI 3.0.



(a) 3% O₂ in exhaust



(b) Calorific correction

Figure 19. NO emissions from low-NO_x water heater on CO₂ addition (simulation vs experiments)

N₂O levels were hard to measure, probably because they were below the least of the analyzer (Horiba QCL). However, Figure 20 shows the N₂O trend with increasing CO₂ percentage.

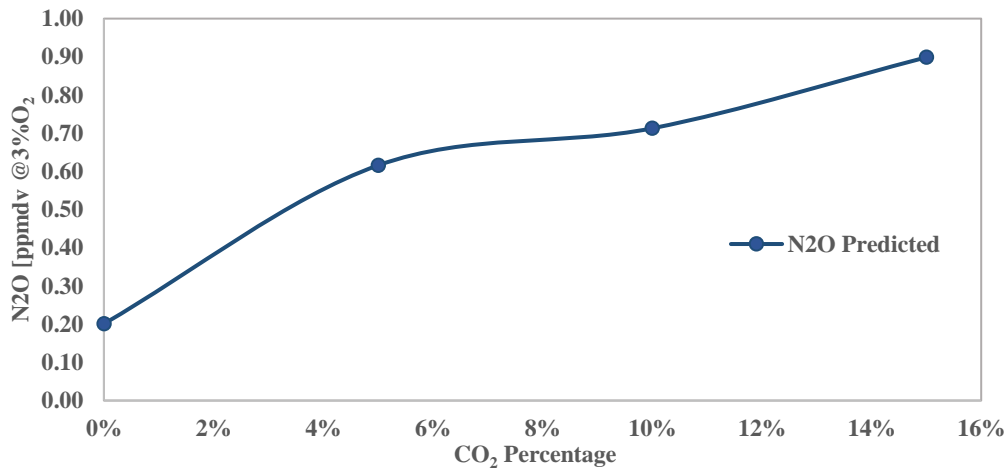


Figure 20. N₂O levels simulated

Takeaways for **further research on emission trends and burner modification to low-NO_x water heater burner** on biogas addition (NG+CO₂):

1. By measuring the CO₂ and O₂ concentration in exhaust stream with increasing CO₂ in natural gas we see a decrease in equivalence ratio of the fuel-air mixture (Table 11), the combustion is increasingly lean.
2. At constant delivery point pressure, the equivalence ratio falls quickly for 5% CO₂ addition and falls slower for higher CO₂ %. Experimentally verifying the air-fuel ratio can provide additional insight.
3. By design the low-NO_x water heater burner is premixed in operation, there is air-fuel mixing before the fuel reaches the burner, though there is secondary air

entrainment via the mesh window at the base of water heater. For modification of burner further, measurement of primary and secondary air entrainment will aid further.

4. The adiabatic flame temperature (AFT) decreases with increasing CO₂ in natural gas, this was verified via simulation (Figure 17). Measurement of flame temperature in experiments might provide some insight.
5. The simulation can precisely predict CO emissions both in magnitude and trend, the model also predicts blow-off at 15% CO₂ addition which was similar to the experimental observation.
6. Simulation predicts low levels of NO₂; hence NO_x emissions and trends are proportional to the NO emissions and trend. Exploring various mechanism and reactions and reaction rates can provide insight.
7. Experiments were conducted with fuel blends which were created using a mixing panel with different sonic orifices and due to difference in gravimetric properties different fuel have different pressure storage and that might be worth exploring further in terms of equivalence ratio change with premixed fuel blends.

5.2.6.2 Conventional Storage

For the conventional storage water heater, we see emissions changing rapidly for simulations as compared to experiments. Emissions for 100% natural gas was established in this research, however, with biogas addition or hydrogen addition the model captured trend but not the values (Figure 21).

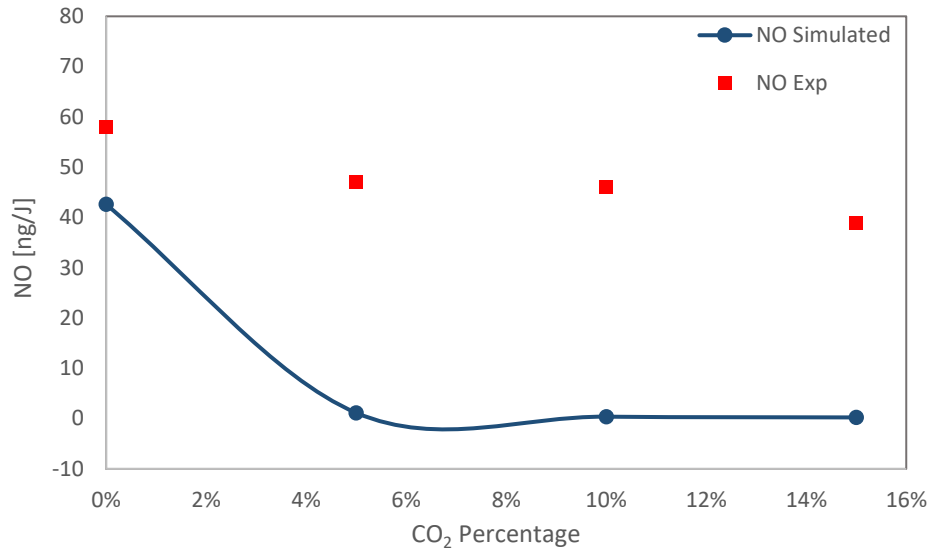


Figure 21. NO emissions for conventional water heater

A few observations made and directions for further research:

1. The NO_x emissions for the particular water heater model tested was about ~20 ng/J higher than regulation. The influence of renewable fuel introduction hence shoes the trend to be expected with the change. It is possible that due to the uniqueness of the model studied, the model is not able to capture the appropriate boundary conditions.
2. Since we could measure the emissions at the exhaust, we could reverse calculate the overall equivalence ratio. However, since the mixture at the burner head is rich, the study will benefit by experimentally investigating the air-fuel mixing at the burner inlet.

5.3 Hydrogen Testing

Part of this thesis, specifically the hydrogen addition experiment results is accepted for publication in *Elsevier- International Journal of Hydrogen Energy* as a journal article named ‘**Combustion performance of low-NO_x and conventional storage water heaters operated on hydrogen enriched natural gas**’ (Authors in order: Shiny Choudhury, Vince McDonell, and Scott Samuelsen)

5.3.1 Impact of H₂ admixing

As can be seen from Table 10. the properties of methane and hydrogen vary widely. Due to this difference in physical and chemical properties, we simply cannot replace hydrogen into the existing natural gas pipelines. Before hydrogen plays the role of a major energy carrier in our world, we need to transition by utilizing the existing natural gas pipelines for end-use requirements [44]. Wobbe Index plays a vital role in fuel interchangeability discussions; this is because it gives us an insight into energy delivered at constant pressure gas supply. Wobbe Index is primarily beneficial in understanding the effects of fuel composition variation. For hydrogen admixing into natural gas pipelines, the Wobbe Index goes down owing to the low volumetric energy content of hydrogen [53]. This poses as a limiting factor for hydrogen injection since pipelines need to obey distribution requirements. Residential appliances operate within a range of air/fuel ratios and premixing levels.

As mentioned above, the low-NO_x water heater relies on high levels of premixing and operates lean ($\Phi < 1$). With hydrogen addition at constant pressure, the equivalence ratio at the burner head will vary. Assuming complete combustion Table 14. Equivalence Ratio

(Φ) shift for low-NO_x water heater on H₂ addition. shows the change in equivalence ratio with increasing hydrogen content in natural gas for the low-NO_x water heater (CO₂ content in the exhaust was measured experimentally). As evident, with increasing hydrogen content the burner head air-fuel mixture is increasingly leaner. The air-fuel mixture for the conventional water heater is rich at the burner head as mentioned in the earlier section. With the addition of hydrogen it approaches near stoichiometric and then towards lean operation [102].

Table 14. Equivalence Ratio (Φ) shift for low-NO_x water heater on H₂ addition

Fuel Composition	CO ₂ [Vol%]	Φ
100% NG	8.44%	0.847
95% NG+5% H ₂	7.92%	0.674
90% NG+10% H ₂	7.83%	0.656

5.3.2 Ignition, flame characteristic and safe limit of operation

For the Low-NO_x water heater with increased H₂ percentage in natural gas, the flame appears more dynamic, lengthened with yellow tips. One straightforward reasoning for the observation is higher reactivity of the fuel mixture due to hydrogen. Another reason for flame lengthening could be the increased volumetric flow rate of the resultant mixture due to the lower density of hydrogen at fixed delivery point pressures. The colored tips observed can be explained due to the presence of excited water molecules and, trace metal or metal oxide particles in the hydrogen cylinders due to embrittlement [103]. For the conventional storage water heater, a similar observation of flame being more dynamic on

hydrogen addition was seen (Figure 12). Each flame from individual fuel port for the pancake burner showed increased interaction downstream.

For both for the low-NO_x and the conventional storage water heater at 10% H₂ addition, the probability of failure due to instability increases. ‘Instability’ being used loosely to mean either flashback, blow-off, delayed ignition, etc. To determine a ‘safe limit’ of operation, testing methodology outlined in Table 4. was followed. Storage water heater burners have two modes of operation during steady-state: ‘*main burner on and pilot on*’ while heating the tank water to set-point temperature, and ‘*main burner off and pilot on*’, when set-point temperature has reached. In order to determine operational limit for safe operation on hydrogen addition we need to observe cold start ignition, main burner and pilot flame stability, relight, and, water heating time.

In this experiment, below 10% H₂ addition there were no issues with ignition for cold start for both the models. Thereafter, both the water heater burner function without any instability till the tank has reached set point temperature, following which the fuel supply shuts off and the burner flame goes off. After the first 15 mins (900s) of idle operation, 10 gallons (37.8L) of hot water was drawn to create a temperature deficit, during which relight of main burner is attempted by the standing pilot flame. With increasing hydrogen in natural gas, the relight time increases (ignition delay). At 10% H₂, during relight a deflagration like event was observed for both the water heaters. For the same sequence of operation on 100% natural gas, relight occurs as soon as the cold water starts mixing into the tank signifying no issues with faulty fuel valve or in the purging of fuel gas from combustion chamber. Within the safe limit of hydrogen addition, the pilot operation

remains stable for both the water heaters, though it gets visibly shorter and duller in appearance.

The low-NO_x water heater has a primarily lean premixed operation at the burner head, and adding hydrogen to natural gas at constant pressure causes fluctuation in equivalence ratio (Table 14). In general, $\Phi_{\text{NG/H}_2} - \Phi_{\text{NG}} < 0$ [53]. For the low-NO_x water heater, during onset of instability there was a simultaneous spike in emissions of CO and NO_x as can be seen in Figure 22. Simultaneously, the flame appeared turbulent and vigorous with numerous yellow tips. It's well established that increasing hydrogen content in hydrocarbon fuel for premixed operation increases the burning speed, with high methane fuel being more sensitive to hydrogen than others [104]. Increase in burning speed will anchor the flame nearer to the burner surface which could overheat the burner and lead to failure [102]. Anchoring closer to the burner might also lead to exceeding the acceptable radiative mode. Flashback is generally characterized as '*an uncontrolled upstream propagation of the flame, due to a local imbalance in the flow velocity and flame speed*' [105], and since we did see a flame, appearing more vigorous with delayed ignition, it is hard to conclude the event as flashback, though a loud popping sound was unmistakable. Increased primary air, fuel accumulation in chamber, acoustic instability or a weaker pilot could have led to the ignition delay as a combination of factors or individually.

For the conventional storage water heater however, a main burner flame seized to establish after the deflagration like event. The air-fuel mixture for the conventional model is rich at the burner head, and on increasing hydrogen the mixture approaches near stoichiometric composition. Like the low-NO_x model, increasing hydrogen in fuel will

anchor the flame nearer to the fuel port which can possibly overheat the burner surface and lead to failure. To reason the observed instability using burning speeds, a precise measurement of equivalence ratio at the burner head is required. Since both the water heaters were tightly insulated with a small quartz window, we could not visually record the instability. **Further research is required for conclusively deciding the cause of instability (flashback/delayed ignition), though the onset of it at 10% H₂ addition is established in the current work.**

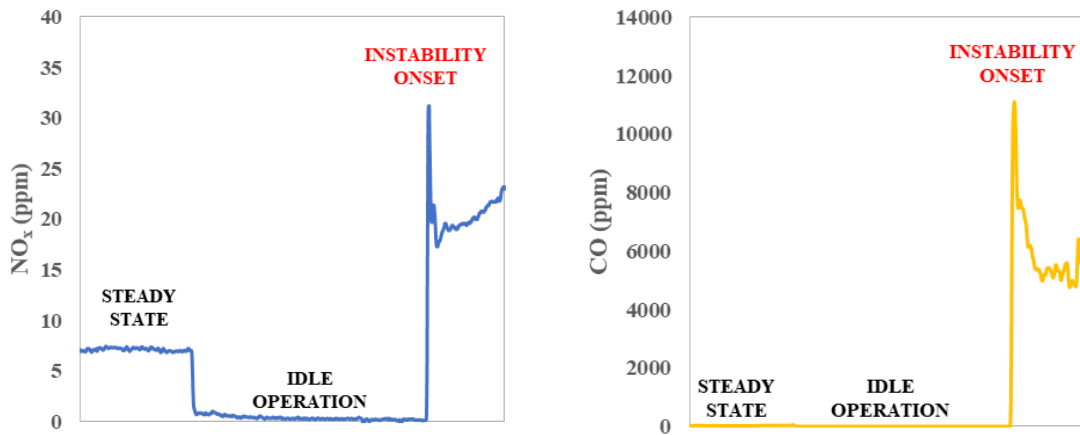


Figure 22. NO_x and CO emission spike during relight for low-NO_x burner at 10% H₂ in natural gas

Depending on the model type, age, and maintenance level of residential appliances the failure propensity and maximum H₂ tolerance will differ [44]. The maximum allowable H₂ in gas-fired appliances varies widely based on the mode of operation, equivalence ratio, etc. Hence, an instability cannot be reasoned simply by comparing laminar flame speeds

and flow rate of fuel. For rich operation, H₂ tolerance of <10% H₂ was reported by NATURAHLY work [53]. For lean premixed operation, however, a higher tolerance between 30-40% H₂ was reasoned in the same study. But the present work found an upper limit <10% H₂ for both models of water heaters. Possibly premixed operation without a cyclic operation like the water heaters and without radiant fiber screen burners has higher H₂ tolerance.



Figure 23. Flame shape for conventional water heater with increasing H₂ content

The limit for safe and reliable operation is summarized in Table 15. The determination is assuming no change in status quo water heaters in residential spaces.

Hence, with <10% H₂ addition for both the low-NO_x and conventional storage water heater is expected to deliver reliable operation without instability.

Table 15. The safe limit of operation

Water Heater	H₂ limit
Low NO_x gas storage water heater	<10%
Conventional gas storage water heater	<10%

5.3.3 Emissions

All the emissions reported are on a dry basis, which means the water produced in the exhaust was condensed out before emission measurements (Figure 4). For hydrogen rich fuel, the amount of moisture produced relative to hydrocarbon fuel is higher. Table 16 informs on the stoichiometric water content in hydrogen rich fuel assuming complete combustion. Since other pollutants or products of incomplete combustion are in parts per million levels, we can assume the water content of exhaust increases with increasing H₂ levels. Due to the increased moisture content, the relative emissions (NO_x, NO, CO, UHC, etc.) on a dry basis appears higher for hydrogen rich fuel. If not considered, this bias can work against hydrogen fuel in terms of emissions regulation. Calorific/energy corrections eliminate the effect of water content and relate emission to the energy content of the fuel. Hence, the correct correction methodology is crucial while comparing combustion performance with different kinds of fuels.

Table 16. Stoichiometric water content in hydrogen rich fuel

Fuel Composition	Water Content [Vol%] _{stoic}
100% CH ₄	19.01
80% CH ₄ +20% H ₂	20.017
20% CH ₄ +80% H ₂	27.22
100% H ₂	51.54

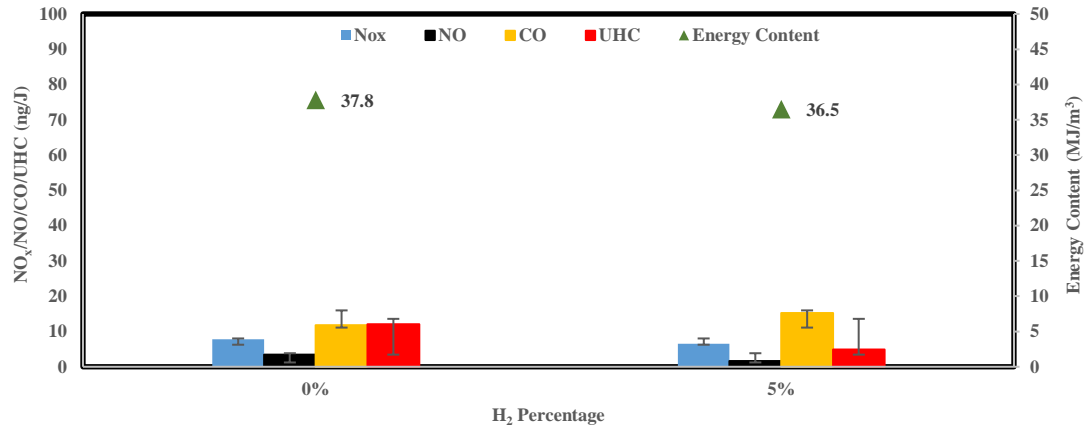
Figure 24 shows the hot and cold-water line connections and the exhaust hood. Emissions for the low-NO_x and conventional water heaters are shown in Figure 25 and Figure 26 respectively. Around 2000 data points are averaged over each burn cycle at steady-state and reported in three correction methodology as mentioned above with standard deviation. Each plot informs on NO, NO_x, CO, and UHC of the function of increasing H₂ percentage in natural gas.



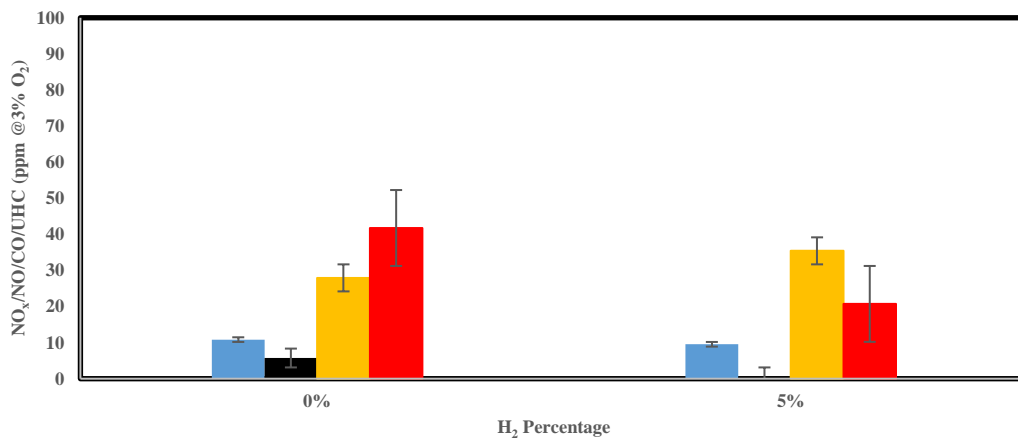
Figure 24. Gas storage water heater and pipeline connection

Due to lower emission values of low- NO_x water heater, clustered columns are used for emissions, while trendline is used for the conventional water heater model. The calorific correction plot for each water heater informs on the energy content (HHV) of the fuel mixture in MJ/m^3 . Addition of H_2 for both the water heaters has a slight impact on the emission. Though fluctuations are observed, they roughly stay within the standard deviation for all H_2 percentages. For the Low- NO_x water heater, a decrease in NO_x and NO emissions with increasing H_2 content is observed. Simultaneously, the CO increases and UHC decreases. The NO_x emissions stay below $10 \text{ ng}/\text{J}$, as required by regulation. NO_x and NO in calorific correction vary from $7.7 \text{ ng}/\text{J}$ to $6.5 \text{ ng}/\text{J}$ and $3.5 \text{ ng}/\text{J}$ to $1.6 \text{ ng}/\text{J}$ respectively. CO and UHC vary from $11.8 \text{ ng}/\text{J}$ to $15.8 \text{ ng}/\text{J}$ and $12.1 \text{ ng}/\text{J}$ to $4.1 \text{ ng}/\text{J}$ respectively, though the UHC data fluctuates a lot.

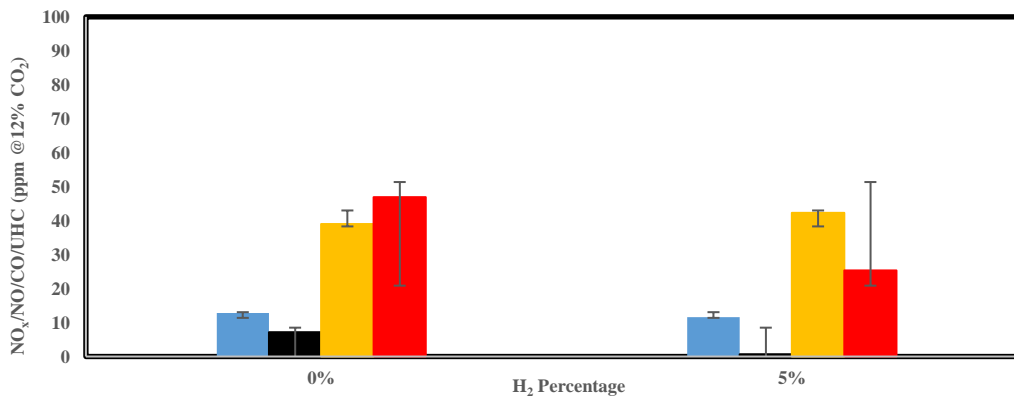
For the low- NO_x water heater, the combustion is primarily lean, with $\Phi \sim 0.847$ for natural gas. When hydrogen is added into the fuel, the equivalence ratio goes down and the fuel volumetric flow rate increases at constant pressure. This results in lesser energy delivered per unit time relative to natural gas. Addition of H_2 promotes the formation of OH and H intermediates which gives the overall mixture a higher burning velocity. This facilitates the flame anchoring closer to the surface as compared to natural gas flame, thus promoting better heat transfer and, hence cooling the flame. The lowered flame temperature reduced NO_x formation via the Zeldovich mechanism. Lower flame temperature aided with higher primary and secondary air entrainment with H_2 addition increases the CO emissions slightly. Though as can be seen from the calorific correction plot, the emissions lie within standard deviation with 5% H_2 addition.



(a) Calorific correction



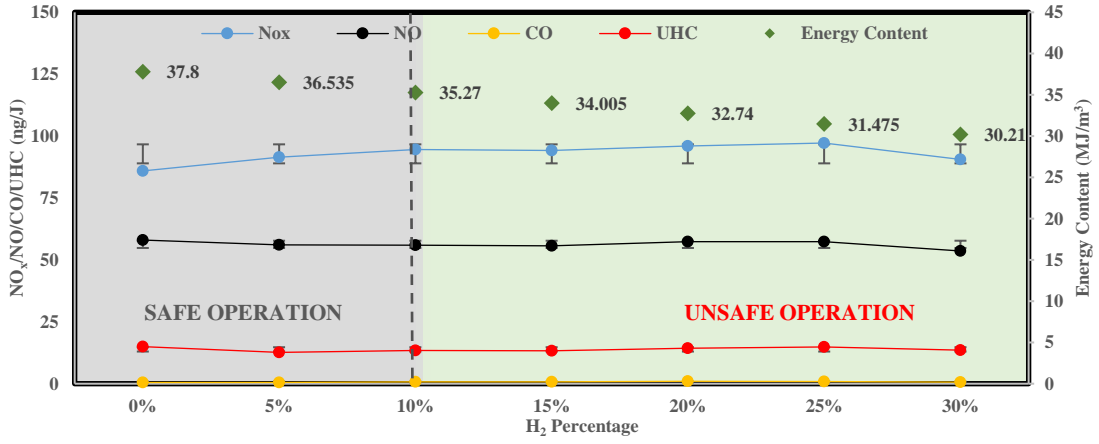
(b) 3% O₂ correction



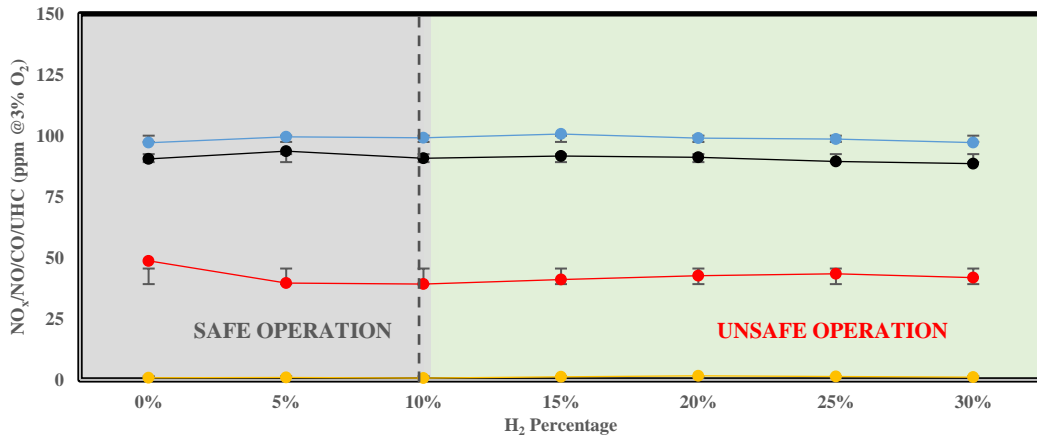
(c) 12% CO₂ correction

Figure 25. Emissions for low-NO_x storage water heater with increasing H₂ concentration

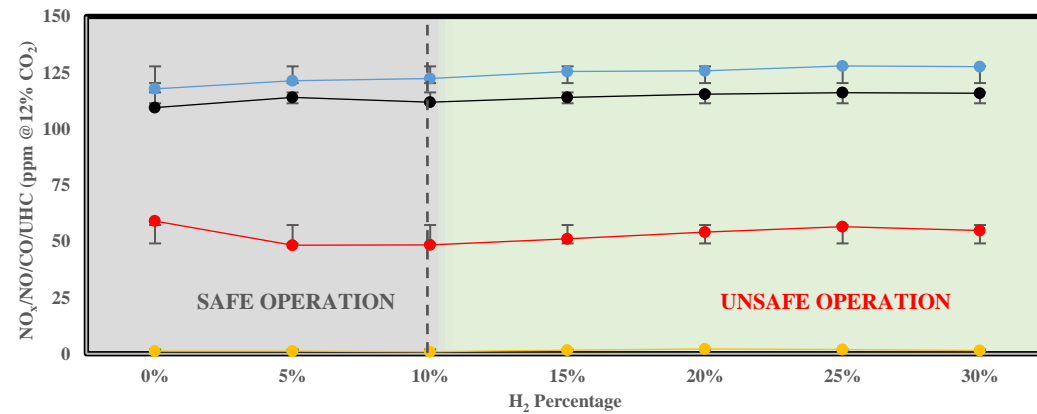
The conventional model burns fuel rich in the burner head but burns lean after secondary air entrainment which reduces emissions. The NO_x emission for the conventional model is ~ 20 ng/J higher than the 40 ng/J requirement by regulation [68]. This behavior is suspected to be unique to the water heater model tested. Therefore, the emission reported should not be taken as a representation of hydrogen addition impact on absolute values, but rather be seen for the trend to be expected with hydrogen addition. As mentioned above, we could perform emission testing for the conventional model beyond safe limit of operation (procedure mentioned in Table 4). Within safe operation a slight increase in NO_x with 5% H_2 addition is observed but remains invariant within measurement uncertainty for up to $\sim 30\%$ H_2 addition in the unsafe zone. NO follows a similar trend as NO_x , whereas CO and UHC emissions stay below 20 ng/J. With 30% H_2 addition the energy delivered is $\sim 20\%$ lesser than 100% natural gas. Within the safe limit of operation ($<10\%$) for the conventional water heater NO_x and NO vary from 85.94 ng/J to 91.75 ng/J and 58 ng/J to 56.12 ng/J respectively. CO and UHC vary from 0.48 ng/J to 0.53 ng/J and 14.97 ng/J to 12.68 ng/J. For both the water heaters, negligible amounts of N_2O or NH_3 was observed.



(a) Calorific correction



(b) 3% O₂ correction



(c) 12% CO₂ correction

Figure 26. Emissions for conventional storage water heater in both safe and unsafe limits of operation with increasing H₂ concentration

5.3.4 Hydrogen Simulation Results

5.3.4.1 Low NO_x storage water heater

The operating conditions of different natural gas/H₂ mixtures are shown in Table 17. Compared to natural gas/CO₂ mixture operating condition, the heating load doesn't vary much due to the similarity of the Wobbe Index between natural gas and hydrogen. Table 17 shows the change in flow rate and equivalence ratio with hydrogen addition to low-NO_x water heater.

Table 17. Wobbe Index variation with H₂ addition

Hydrogen enriched natural gas (NG+H ₂)	Wobbe index (BTU/scf)
100% CH ₄	1361.73
95% CH ₄ – 5% H ₂	1343.94

With hydrogen addition there are two main factors at play; (1) the fuel mixture getting increasingly reactive because of hydrogen, and (2) the equivalence ratio going down quickly due to differences in chemical and physical properties of hydrogen and natural gas.

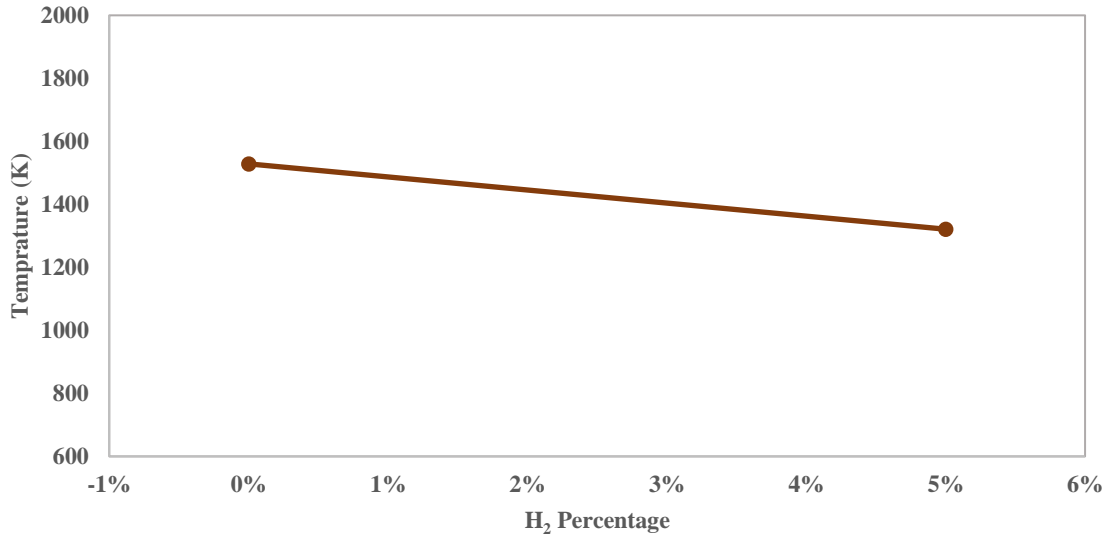
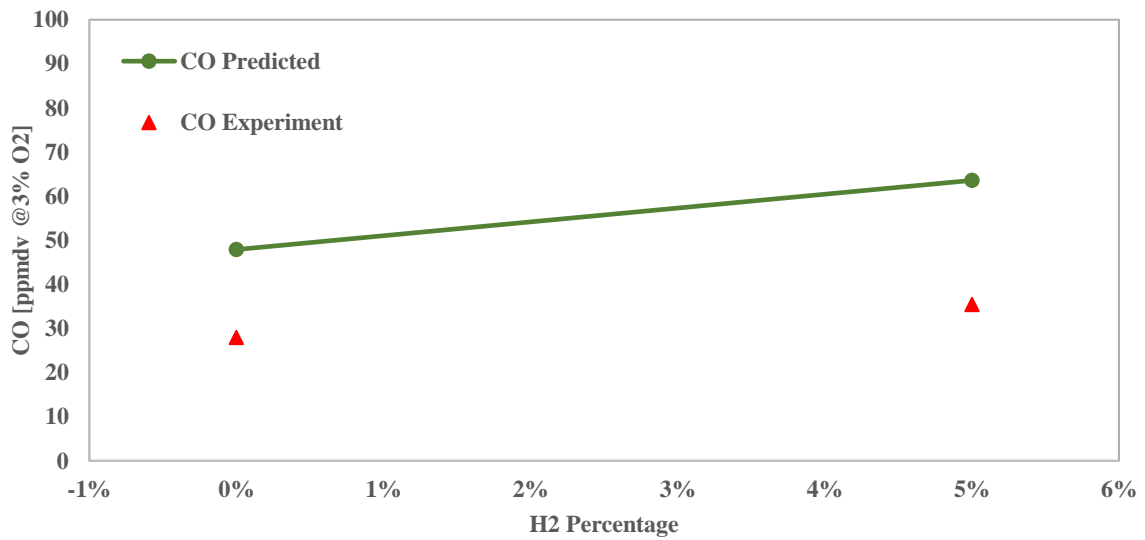
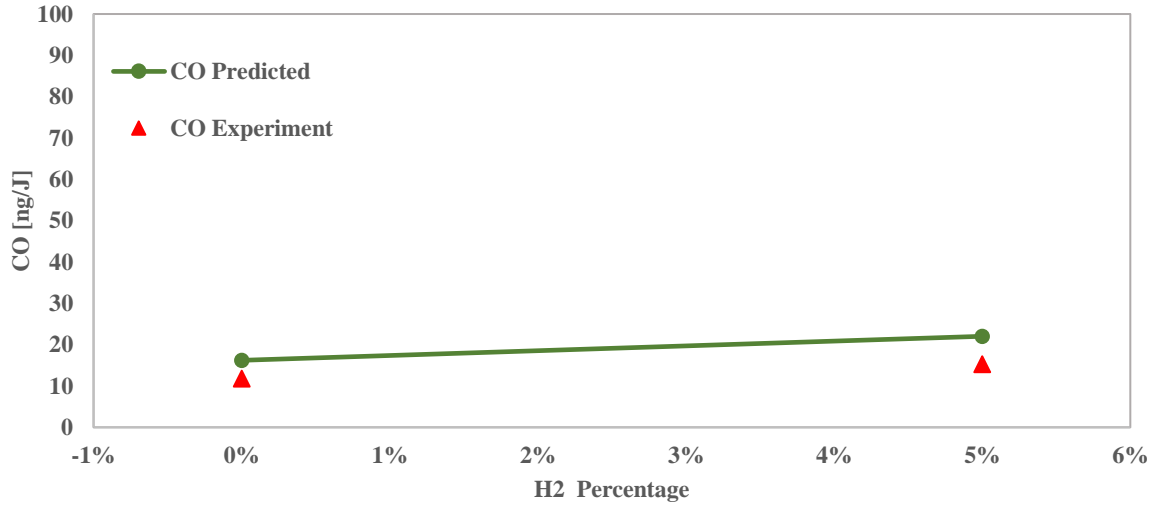


Figure 27. Adiabatic Flame Temperature (AFT) at CRN exhaust with increasing H₂ %

Figure 27. Provides insight into change in adiabatic flame temperature on hydrogen addition at the measured equivalence ratio.



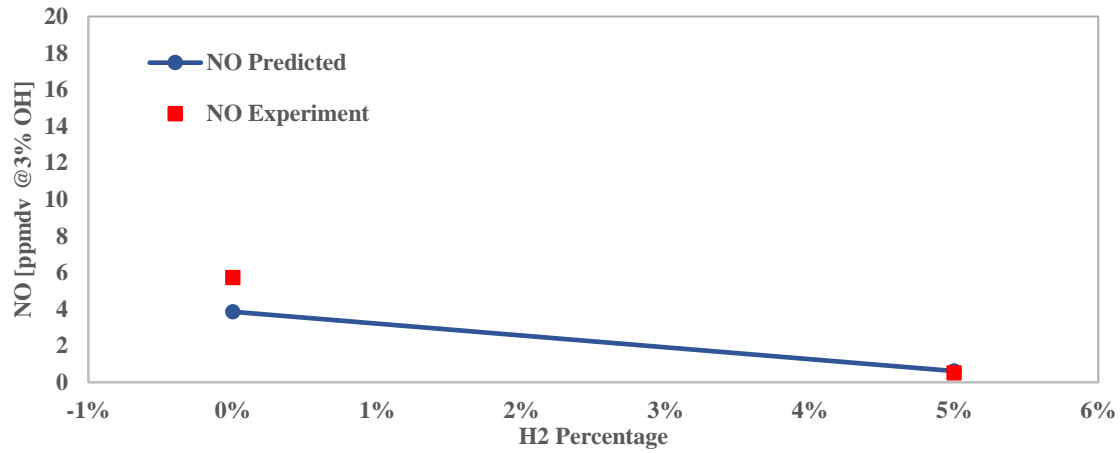
a) 3% O₂ Correction



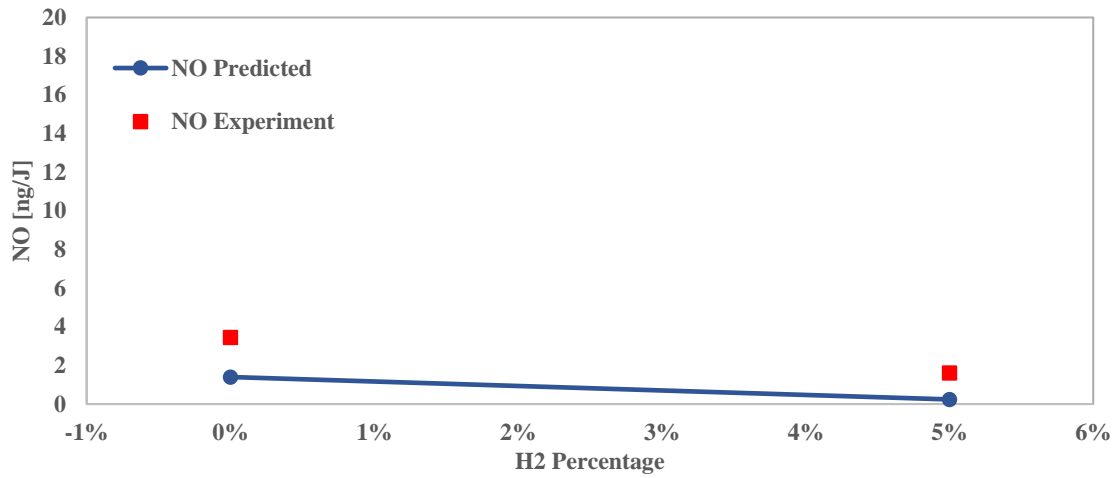
b) Calorific correction

Figure 28. CO emission from low-NO_x water heater on H₂ addition (simulation vs experiments)

The CO/NO emission results comparison are shown in Figure 28 and Figure 29. The simulation shows that hydrogen injection can help decrease NO with a simultaneous increase in CO emission. The experiment data is a good match with the simulation result. There is a slight change in emissions with H₂ addition, but the model is able to capture the trend. Again, the simulation levels of NO₂ were of the order 10e-8 and hence the NO_x emissions are proportional to the NO results. UCSD mechanism predicts lower NO and NO₂ and hence NO_x compared to GRI 3.0.



a) 3% O₂ correction



b) Calorific correction

Figure 29. NO emission from low-NO_x water heater on H₂ addition (simulation vs experiments)

Takeaways for further research on emission trends and burner modification to low-NO_x water heater burner on hydrogen addition (NG+H₂):

1. By measuring the CO₂ and O₂ concentration in exhaust stream with increasing H₂ in natural gas we see a decrease in equivalence ratio of the fuel-air mixture (Table 11), the combustion is increasingly lean.
2. At constant delivery point pressure, the equivalence ratio falls quickly for 5% H₂ addition and falls slower for higher H₂ %. Experimentally verifying the air-fuel ratio can provide additional insight.
3. The AFT goes down with increase in H₂, experimentally verifying flame temperature might provide extra insight.
4. Simulation could predict emissions well, but since the flow dynamics are highly coupled with the chemistry in CHEMKIN it is hard to predict flashback. CFD of the burner can provide insight.

6. SUMMARY, INSIGHTS, CONCLUSIONS, AND RECOMMENDATIONS

6.1 Summary

Combustion performance and operability of conventional and low-NO_x storage water heaters, as operated on mixtures of CO₂ and natural gas mimicking the composition of biogas, were studied. In practice, regulations based on Wobbe Index and Heating Value, limit the amount of CO₂ in the natural gas pipeline to 6% and 3% (by volume), respectively. In the current study, these limits were expanded to assess the tolerance of these devices to higher levels which would enable further carbon reduction of pipeline gas. Similarly, combustion performance and operability of low-NO_x and conventional storage water heaters, as operated on mixtures of H₂ and natural gas simulating hydrogen admixing into pipelines, were studied. As methane emissions are an ongoing problem for both types of combustion-based water heaters (primarily with pilot ignition); methane emissions were investigated at various modes of operation.

6.2 Biogas-addition insights

The study provides a number of insights regarding the tolerance of both devices to increased levels of CO₂:

- The more recently developed low-NO_x water heater has a higher tolerance for CO₂ content in natural gas at 10%. Effectively no tolerance for CO₂

content was observed for the conventional water heater. As a result, the Low-NO_x technology, while significantly reducing NO_x emissions can also operate on higher amounts of CO₂ compared to the conventional technology.

- Due to the inert nature of CO₂, no benefit is acquired in terms of shorter ignition time or thermal efficiency gains. Though within the safe limits of operation reported in the previous point no significant effect on ignition times or thermal efficiency, as expected.
- For the Low NO_x water heater beyond 10% CO₂ addition, the pilot operation becomes unstable and the probability of blow off increases. At both 5% and 10% CO₂ addition a stable though increasingly flat flame is observed, and pilot operation is stable both during idling and relight of the main burner. At 15% CO₂, a stable but almost flat flame was observed at the burner head. The pilot was sustained during idling but blows off as soon as gas flows through the fuel port when relight is attempted.
- For the conventional gas storage water heater, a stable flame is established up to 25% CO₂ addition, with the flame becoming increasingly more compact beyond 30% CO₂ addition. Stable pilot operation, on the other hand, could not be established even at 5% CO₂ addition which proved to be the limiting factor for operation of this device. This was unexpected and might be a consequence of the adopted experimental methodology in current research.

- A similar trend of NO_x and NO decrease and CO and UHC increase with increasing CO₂ percentage was observed for both water heaters.
 - Within the safe limit of operation for the Low-NO_x water heater NO_x and NO decreases from 7.78 ng/J to 4.21 ng/J and 3.46 ng/J to 0.6 ng/J respectively. Similarly, CO and UHC increase from 11.85 ng/J to 52.2 ng/J and 12.13 ng/J to 27.17 ng/J respectively.
 - For the conventional water heater, even though pilot flame ceased to establish even with <5% CO₂ addition, NO_x and NO decrease from 85.9 ng/J to 72.8 ng/J and 58 ng/J to 47.2 ng/J respectively till 10% CO₂ addition. Similarly, CO and UHC increases slightly but remain constant in magnitude.
- Methane emission was detected for both the water heater at steady state (main burner engaged) and ideal operation (pilot on, main burner disengaged). Emissions at ideal state for both water heaters are higher than the steady state signifying higher pilot emissions. Overall more methane is emitted by the low-NO_x water heater both at steady and idle operation.
- For the low-NO_x water heater we were able to accurately simulate emission trend and magnitude on biogas addition with a simple reactor network, however for the conventional water heater more work is required to accurately determine the boundary conditions.

6.2.1 Conclusion

- **Low-NO_x water heater can operate on higher amounts of CO₂ in biogas as compared to conventional storage water heater which has no tolerance.**

The more recently developed low-NO_x water heater has a higher tolerance for CO₂ content in natural gas at 10%. Effectively no tolerance for CO₂ content was observed for the conventional water heater. As a result, the Low-NO_x technology, while significantly reducing NO_x emissions can also operate on higher amounts of CO₂ compared to the conventional technology. Additionally, a similar trend of NO_x and NO decrease and CO and UHC increase with increasing CO₂ percentage is observed for both water heaters.

- **Fuel leakage is detected for both water heaters at various modes of operation, with highest emissions during idle operation (pilot on, main burner disengaged).**

Methane emission was detected for both the water heater at steady state (main burner engaged) and ideal operation (pilot on, main burner disengaged). Emissions at ideal state for both water heaters are higher than the steady state signifying higher pilot emissions. Overall more methane is emitted by the low-NO_x water heater both at steady and idle operation.

6.3 Hydrogen-addition insights

The current work provides several insights regarding the tolerance of both devices to increased levels of H₂:

- For both the low-NO_x and conventional storage water heater a hydrogen tolerance of <10% by volume was observed. The more recently developed low-NO_x model shows a further decrease in NO_x emissions with increasing H₂, whereas a slight increase in NO_x emission is observed for the conventional model.
- All the emissions reported in this research are on a dry basis, which means the water produced in the exhaust was condensed out before emission measurements. For hydrogen rich fuel, the amount of water produced relative to hydrocarbon fuel is higher. Due to the increased moisture content, the relative emissions (NO_x, NO, CO, UHC, etc.) on a dry basis appears inherently higher for hydrogen rich fuels, requiring careful consideration of the correction basis used in reporting emissions levels.
- For both the Low-NO_x and conventional water heater with increased H₂%, the flame appears dynamic, lengthened with yellow tips. Within the safe limit of hydrogen addition, the pilot operation remains stable though appears shortened and duller for both the water heaters. It is worth noting that at 10% H₂ addition no issues with ignition from a cold start were observed, but during relight of the main burner after water draw, instability (flashback/ignition delay) was observed.
- For the low-NO_x water heater, the combustion is primarily lean, with $\Phi \sim 0.84$ for 100% natural gas. Addition of H₂ for both the water heaters has a slight impact on

the emission. For the Low-NO_x water heater, a decrease in NO_x and NO emissions with increasing H₂ content is observed while CO increases and UHC decreases.

- Within the safe limit of operation for the Low-NO_x water heater NO_x and NO decreases from 7.7 ng/J to 6.5 ng/J and 3.5 ng/J to 1.6 ng/J respectively. Similarly, CO and UHC vary from 11.8 ng/J to 15.8 ng/J and 12.1 ng/J to 4.1 ng/J respectively, though the UHC data fluctuates a lot.
- The conventional model burns fuel rich in the burner head but burns lean after secondary air entrainment which reduces emissions. NO_x emission for the model is ~20 ng/J higher than the 40 ng/J requirement by regulation. This behavior is suspected to be unique to the water heater model tested. Therefore, the emission reported should not be taken as a representation of hydrogen addition impact on absolute values, but rather for the trend to be expected on hydrogen addition.
 - Within the safe limit of operation for the conventional water heater NO_x and NO vary from 85.94 ng/J to 91.75 ng/J and 58 ng/J to 56.12 ng/J respectively. CO and UHC vary from 0.48 ng/J to 0.53 ng/J and 14.97 ng/J to 12.68 ng/J.
- For the low-NO_x water heater we were able to accurately simulate emission trend and magnitude on hydrogen addition with a simple reactor network, however for the conventional water heater more work is required to accurately determine the boundary conditions.

6.3.1 Conclusion

- **<10% H₂ tolerance was established for both water heaters.**

For both the low-NO_x and conventional storage water heater a hydrogen tolerance of <10% by volume was observed. The more recently developed low-NO_x model shows a further decrease in NO_x emissions with increasing H₂, whereas a slight increase in NO_x emission is observed for the conventional model.

- **Instability on H₂ addition during relight of water heater is established, but not characterized.**

For both the Low-NO_x and conventional water heater with increased H₂%, the flame appears dynamic, lengthened with yellow tips. Within the safe limit of hydrogen addition, the pilot operation remains stable though appears shortened and duller for both the water heaters. It is worth noting that at 10% H₂ addition no issues with ignition from a cold start were observed, but during relight of the main burner after water draw, instability (flashback/ignition delay) was observed.

- **Reactor network accurately predicted emissions for low-NO_x water heater, and not for conventional water heater on both hydrogen and biogas addition.**

For the low-NO_x water heater we were able to accurately simulate emission trend and magnitude on biogas and hydrogen addition with a simple reactor network, however for the conventional water heater more work is required to accurately determine the boundary conditions.

6.4 Recommendations

Three broad recommendations are derived in this work:

1. For higher tolerance on biogas for conventional storage water heater, modifying/replacing the pilot flame with a more robust design or electric ignition will benefit water heater operation. Modification of pilot in general for both the water heaters will lead to increased renewable fuel tolerance.
2. For both the water heaters, low NO_x and conventional storage, replacing the pilot flame with electric ignition will reduce methane emissions both during stable operation and idle operation.
3. Manual reactor network is a computationally attractive option to simulate emissions and stability for lean premixed operations like low-NO_x water, heater without having to disassemble the device. However, for conventional model, investing the level of fuel-air mixing and level of premixing is essential for accurately modelling emissions.

7. REFERENCES

- [1] A Brief History of Natural Gas - APGA n.d.
<https://www.apga.org/apgamainsite/aboutus/facts/history-of-natural-gas> (accessed October 17, 2019).
- [2] Global Climate Report - Annual 2016 | State of the Climate | National Centers for Environmental Information (NCEI) n.d. <https://www.ncdc.noaa.gov/sotc/global/201613> (accessed October 17, 2019).
- [3] Tollefson J. Methane leaks erode green credentials of natural gas. *Nat News* 2013;493:12. <https://doi.org/10.1038/493012a>.
- [4] Myhre G, Shindell D, Bréon F-M, Collins W, Fuglestvedt J, Huang J, et al. 8 Anthropogenic and Natural Radiative Forcing n.d.:82.
- [5] Global Climate Report - Annual 2016 | State of the Climate | National Centers for Environmental Information (NCEI) n.d. <https://www.ncdc.noaa.gov/sotc/global/201613> (accessed July 1, 2019).
- [6] Summary for Policymakers — Global Warming of 1.5 °C n.d.
<https://www.ipcc.ch/sr15/chapter/summary-for-policy-makers/> (accessed April 23, 2019).
- [7] Vitousek PM. Beyond Global Warming: Ecology and Global Change. *Ecology* 1994;75:1861–76. <https://doi.org/10.2307/1941591>.
- [8] Greenhouse Gas Inventory Data Explorer | US EPA n.d.
<https://cfpub.epa.gov/ghgdata/inventoryexplorer/#allsectors/allgas/gas/all> (accessed July 1, 2019).
- [9] US GHG Emissions and Sinks 1990-2017_EPA 2019.
<https://www.epa.gov/sites/production/files/2019-04/documents/us-ghg-inventory-2019-main-text.pdf> (accessed April 23, 2019).
- [10] Bill Text - SB-32 California Global Warming Solutions Act of 2006: emissions limit. n.d. https://leginfo.legislature.ca.gov/faces/billNavClient.xhtml?bill_id=201520160SB32 (accessed April 24, 2019).
- [11] California GHG Emissions for 2000 to 2016 2018.
https://www.arb.ca.gov/cc/inventory/pubs/reports/2000_2016/ghg_inventory_trends_00-16.pdf (accessed April 23, 2019).
- [12] California: “Epicenter of the US CleanTech Market” | Energy Central n.d.
<https://www.energycentral.com/c/ec/california-epicenter-us-cleantech-market> (accessed April 24, 2019).
- [13] WBA Global Bioenergy 2018 2018.
https://worldbioenergy.org/uploads/181203%20WBA%20GBS%202018_hq.pdf (accessed July 1, 2019).
- [14] California Executive Order S-3-05 2005.
<http://static1.squarespace.com/static/549885d4e4b0ba0bff5dc695/t/54d7f1e0e4b0f0798c>

ee3010/1423438304744/California+Executive+Order+S-3-05+(June+2005).pdf
(accessed July 1, 2019).

- [15] California's Greenhouse Gas Emission Inventory n.d.
<https://www.arb.ca.gov/cc/inventory/data/data.htm> (accessed April 24, 2019).
- [16] Jiang Z, Steinsberger SC, Shih JCH. In situ utilization of biogas on a poultry farm: Heating, drying and animal brooding. *Biomass* 1987;14:269–81.
[https://doi.org/10.1016/0144-4565\(87\)90056-4](https://doi.org/10.1016/0144-4565(87)90056-4).
- [17] D. W. Williams, T. R. McCarty, G. R. Morris, W. W. Gunkel, D. R. Price. Utilization of Biogas for Farm Production Energy. *Trans ASAE* 1976;19:1034–40.
<https://doi.org/10.13031/2013.36170>.
- [18] A MS, D MS, Dadu, D W, A MA. Appraising the combustion of biogas for sustainable rural energy needs. *Afr J Environ Sci Technol* 2013;7:350–7.
<https://doi.org/10.5897/AJEST11.264>.
- [19] Biogas | Ministry of New and Renewable Energy | Government of India n.d.
<https://mnre.gov.in/biogas> (accessed November 14, 2019).
- [20] Pangborn JB. Catalytic Combustion of Hydrogen in Model Appliances. *J Energy* 1981;5:285–8. <https://doi.org/10.2514/3.62543>.
- [21] Transitioning to hydrogen: Assessing the engineering risks and uncertainties n.d.
<https://www.theiet.org/impact-society/sectors/energy/energy-news/transitioning-to-hydrogen-assessing-the-engineering-risks-and-uncertainties/> (accessed November 14, 2019).
- [22] Jönsson O, Polman E, Jensen JK, Eklund R, Schyl H, Ivarsson S, et al. SUSTAINABLE GAS ENTERS THE EUROPEAN GAS DISTRIBUTION SYSTEM n.d.:9.
- [23] Rasi S. Biogas composition and upgrading to biomethane 2009:79.
- [24] Allen MR, Braithwaite A, Hills CC. Trace Organic Compounds in Landfill Gas at Seven U.K. Waste Disposal Sites. *Environ Sci Technol* 1997;31:1054–61.
<https://doi.org/10.1021/es9605634>.
- [25] Price S. Decarbonizing Pipeline Gas to Help Meet California's 2050 Greenhouse Gas Reduction Goal 2015:173.
- [26] Pipeline Injection Of Biomethane In California. *BioCycle* 2018.
<https://www.biocycle.net/2018/03/12/pipeline-injection-biomethane-california/> (accessed July 1, 2019).
- [27] Paolini V, Petracchini F, Carnevale M, Gallucci F, Perilli M, Esposito G, et al. Characterisation and cleaning of biogas from sewage sludge for biomethane production. *J Environ Manage* 2018;217:288–96. <https://doi.org/10.1016/j.jenvman.2018.03.113>.
- [28] Persson M, Jönsson O, Wellinger A. Biogas Upgrading to Vehicle Fuel Standards and Grid Injection 2006:19.
- [29] Levin JA, Kester G. SENATE BILL 840 2013:7.

- [30] Yue D, You F, Snyder SW. Biomass-to-bioenergy and biofuel supply chain optimization: Overview, key issues and challenges. *Comput Chem Eng* 2014;66:36–56. <https://doi.org/10.1016/j.compchemeng.2013.11.016>.
- [31] Demirbas A. Use of algae as biofuel sources. *Energy Convers Manag* 2010;51:2738–49. <https://doi.org/10.1016/j.enconman.2010.06.010>.
- [32] NREL. Biogas Potential in the United States 2013. <https://www.nrel.gov/docs/fy14osti/60178.pdf> (accessed May 12, 2019).
- [33] Bill Text - AB-3187 Biomethane: gas corporations: rates: interconnection. n.d. https://leginfo.legislature.ca.gov/faces/billTextClient.xhtml?bill_id=201720180AB3187 (accessed April 23, 2019).
- [34] Bill Text - SB-1440 Energy: biomethane: biomethane procurement. n.d. https://leginfo.legislature.ca.gov/faces/billTextClient.xhtml?bill_id=201720180SB1440 (accessed April 23, 2019).
- [35] *The Mysterious Island*. Wikipedia 2019.
- [36] W. Jones L. Towards a Liquid Hydrogen Fuel Economy 1970. <https://deepblue.lib.umich.edu/bitstream/handle/2027.42/5800/bac5758.0001.001.pdf?sequence=5&isAllowed=y> (accessed August 19, 2019).
- [37] WindGas Falkenhagen | Hydrogen n.d. <https://www.hydrogeneurope.eu/project/windgas-falkenhagen> (accessed August 19, 2019).
- [38] Hydrogen Council – A global CEO-level initiative with a united vision for hydrogen n.d. <http://hydrogencouncil.com/> (accessed August 19, 2019).
- [39] The Future of Hydrogen n.d. <https://www.iea.org/publications/reports/thefutureofhydrogen/> (accessed August 17, 2019).
- [40] Gondal IA. Hydrogen integration in power-to-gas networks. *Int J Hydrog Energy* 2019;44:1803–15. <https://doi.org/10.1016/j.ijhydene.2018.11.164>.
- [41] The Paris Agreement | UNFCCC n.d. <https://unfccc.int/process-and-meetings/the-paris-agreement/the-paris-agreement> (accessed August 19, 2019).
- [42] US EPA O. Global Greenhouse Gas Emissions Data. US EPA 2016. <https://www.epa.gov/ghgemissions/global-greenhouse-gas-emissions-data> (accessed August 19, 2019).
- [43] Hydrogen from renewable electricity: An international review of power-to-gas pilot plants for stationary applications | Elsevier Enhanced Reader n.d. <https://doi.org/10.1016/j.ijhydene.2012.12.010>.
- [44] Melaina MW, Antonia O, Penev M. Blending Hydrogen into Natural Gas Pipeline Networks: A Review of Key Issues. *Renew Energy* 2013:131.
- [45] Manufactured and Natural Gas Industry n.d. <https://eh.net/encyclopedia/manufactured-and-natural-gas-industry/> (accessed August 19, 2019).

- [46] Synthetic Natural Gas (SNG) | Hawaii Gas. Hawaii Gas Clean Energy Co n.d. <http://www.hawaiigas.com/clean-energy/synthetic-natural-gas/> (accessed August 19, 2019).
- [47] Zhao Y, McDonell V, Samuelsen S. Influence of hydrogen addition to pipeline natural gas on the combustion performance of a cooktop burner. *Int J Hydrog Energy* 2019;44:12239–53. <https://doi.org/10.1016/j.ijhydene.2019.03.100>.
- [48] Marchetti C. Hydrogen and Energy 1973. <http://wilsonweb.physics.harvard.edu/HUMANRIGHTS/PHYSICS/ENERGY/MARCHETTI-008.pdf> (accessed August 20, 2019).
- [49] Union PO of the E. Techno-economic assessment of hydrogen transmission & distribution systems in Europe in the medium and long term. 2006. <https://publications.europa.eu/en/publication-detail/-/publication/08331a6f-05a4-4aed-89fe-fb92840b8cc5> (accessed August 19, 2019).
- [50] Pangborn J, Scott M, Sharer J. TECHNICAL PROSPECTS FOR COMMERCIAL AND RESIDENTIAL DISTRIBUTION AND UTILIZATION OF HYDROGEN 1977. [https://doi.org/10.1016/0360-3199\(77\)90050-7](https://doi.org/10.1016/0360-3199(77)90050-7).
- [51] Altfeld K, Pinchbeck D. Admissible hydrogen concentrations in natural gas systems 2013. http://www.gerg.eu/public/uploads/files/publications/GERGpapers/SD_gfe_03_13_Report_Altfeld-Pinchbeck.pdf (accessed August 13, 2019).
- [52] A mathematical framework for modelling and evaluating natural gas pipeline networks under hydrogen injection | Elsevier Enhanced Reader n.d. <https://doi.org/10.1016/j.ijhydene.2008.07.103>.
- [53] de Vries H, Florisson O, Tiekstra GC. SAFE OPERATION OF NATURAL GAS APPLIANCES FUELED WITH HYDROGEN/NATURAL GAS MIXTURES (PROGRESS OBTAINED IN THE NATURALHY-PROJECT) 2007:12.
- [54] Haeseldonckx D, D'haeseleer W. The use of the natural-gas pipeline infrastructure for hydrogen transport in a changing market structure 2006. <https://doi.org/10.1016/j.ijhydene.2006.10.018>.
- [55] Jones DR, Al-Masry WA, Dunnill CW. Hydrogen-enriched natural gas as a domestic fuel: an analysis based on flash-back and blow-off limits for domestic natural gas appliances within the UK. *Sustain Energy Fuels* 2018;2:710–23. <https://doi.org/10.1039/C7SE00598A>.
- [56] The Future of Hydrogen n.d. <https://www.iea.org/publications/reports/thefutureofhydrogen/> (accessed August 19, 2019).
- [57] 2016 Residential Compliance Manual_CEC 2016. <https://www.energy.ca.gov/2015publications/CEC-400-2015-032/CEC-400-2015-032-CMF.pdf> (accessed May 14, 2019).
- [58] Factsheet Residential Domestic Hot Water (DHW) Energy Code 2016.

- [59] CATC. Nitrogen Oxides (NO_x), Why and How They are Controlled 1999:57. https://doi.org/EPA_456/F-99-006R.
- [60] US EPA R 01. Nitrogen Oxides Control Regulations | Ground-level Ozone | New England | US EPA n.d. <https://www3.epa.gov/region1/airquality/nox.html> (accessed July 2, 2019).
- [61] Low NO_x burner 2001.
- [62] Residential Gas Water Heater, 40.0 gal. Tank Capacity, Natural Gas, 38,000 BtuH - Water Heaters. Grainger n.d. <https://www.grainger.com/product/RHEEM-Residential-Gas-Water-Heater-38UN59> (accessed November 18, 2019).
- [63] Kushch AS, Goldstein MK. High intensity, low NO_x matrix burner. US5711661A, 1998.
- [64] Rheem XG40T12DU36U0 n.d. <https://www.rheem.com/product/performance-platinum-ultra-low-nox-powered-damper-40-gallon-natural-gas-water-heater-with-12-year-limited-warranty-xg40t12du36u0/s> (accessed November 18, 2019).
- [65] Leclerc G, Weiland E. Perfectionnements apportés à un brûleur de chauffe-eau, chauffe-bain, chaudière à gaz. EP0769656B1, 1999.
- [66] Wang H. The Effect of Primary Air Distribution on Emissions from a Natural Gas Water Heater 2013:44.
- [67] Smith NA. Flame Temperature Imaging of a Low NO_x Burner via Laser Rayleigh Scattering n.d.:74.
- [68] Rule 1121 Control of Nitrogen Oxides from Residential Type, Natural Gas-Fired Water Heaters n.d.:7.
- [69] Regulation 9 Inorganic gaseous pollutants_Rule 3 NO_x from heat transfer operations 1982. <http://www.baaqmd.gov/~media/dotgov/files/rules/reg-9-rule-3-nitrogen-oxides-from-heat-transfer-operations/documents/rg0903.pdf?la=en> (accessed April 23, 2019).
- [70] RULE 409. COMBUSTION CONTAMINANTS n.d.:1.
- [71] Revisions to Rule 74_11 Natural Gas fired water heaters_Ventura County 2009. <http://www.vcapcd.org/pubs/Rules/7411/R7411SR5c.pdf> (accessed April 23, 2019).
- [72] Rule 69_5_1 Natural Gas Fired Water Heaters 2016. <https://www.arb.ca.gov/drdb/sd/curhtml/r69-5-1.pdf> (accessed April 23, 2019).
- [73] ANSI Z21.10.1-2017/CSA 4.1-2017 - Gas water heaters, volume I, storage water heaters with input ratings of 75,000 Btu per hour or less n.d. <https://webstore.ansi.org/Standards/CSA/ANSIZ21102017CSA?source=blog> (accessed April 23, 2019).
- [74] ANSI Z21.86-2016/CSA 2.32-2016 - ANSI Z21.86-2016/CSA 2.32-2016 - Vented gas-fired space heating appliances n.d. <https://webstore.ansi.org/Standards/CSA/ANSIZ21862016CSA32> (accessed April 23, 2019).
- [75] Health NC for E. CDC - Carbon Monoxide Poisoning - Frequently Asked Questions 2018. <https://www.cdc.gov/co/faqs.htm> (accessed April 23, 2019).

- [76] US EPA O. Nitrogen Dioxide's Impact on Indoor Air Quality. US EPA 2014. <https://www.epa.gov/indoor-air-quality-iaq/nitrogen-dioxides-impact-indoor-air-quality> (accessed April 23, 2019).
- [77] Bragg SL. Application of Reaction Rate Theory to Combustion Chamber Analysis. AERONAUTICAL RESEARCH COUNCIL LONDON (UNITED KINGDOM); 1953.
- [78] Nguyen TH. Chemical reactor network application to predict the emission of nitrogen oxides in an industrial combustion chamber. *Combust Explos Shock Waves* 2017;53:406–10. <https://doi.org/10.1134/S0010508217040049>.
- [79] Rutar T, Malte PC. NO_x Formation in High-Pressure Jet-Stirred Reactors With Significance to Lean-Premixed Combustion Turbines. *J Eng Gas Turbines Power* 2002;124:776–83. <https://doi.org/10.1115/1.1492829>.
- [80] Stagni A, Cuoci A, Frassoldati A, Faravelli T, Ranzi E. A fully coupled, parallel approach for the post-processing of CFD data through reactor network analysis. *Comput Chem Eng* 2014;60:197–212. <https://doi.org/10.1016/j.compchemeng.2013.09.002>.
- [81] Cuoci A, Frassoldati A, Stagni A, Faravelli T, Ranzi E, Buzzi-Ferraris G. Numerical Modeling of NO_x Formation in Turbulent Flames Using a Kinetic Post-processing Technique. *Energy Fuels* 2013;27:1104–22. <https://doi.org/10.1021/ef3016987>.
- [82] Colorado A. Pollutant Emissions and Lean Blowoff Limits of Fuel Flexible Burners Operating on Gaseous Renewable and Fossil Fuels 2016. <https://escholarship.org/content/qt2488h7t1/qt2488h7t1.pdf> (accessed July 28, 2019).
- [83] GRI-Mech 3.0 n.d. <http://combustion.berkeley.edu/gri-mech/version30/text30.html> (accessed October 30, 2019).
- [84] Southern California Gas Company Gas Service Guidebook 2013:73.
- [85] Singer B, Apte M, Black D, Hotchi T, Lucas D, Lunden M, et al. Natural Gas Variability in California: Environmental Impacts and Device Performance - Experimental Evaluation of Pollutant Emissions from Residential Appliances 2009.
- [86] Suchovsky - 1999 - FLAME SPREADER-TYPE FUEL BURNER WITH LOWERED NO_x E.pdf n.d.
- [87] Smith GP, Golden DM, Frenklach M, Moriarty NW, Eiteneer B, Goldenberg M, et al. GRI-MECH 3.0. [Http://WwwMeBerkeleyEdu/Gri_mech/](http://WwwMeBerkeleyEdu/Gri_mech/) n.d.
- [88] Colorado A, McDonell V. Reactor network analysis to assess fuel composition effects on NO_x emissions from a recuperated gas turbine. *Proc. ASME Turbo Expo 2014 Turbine Tech. Conf. Expo. GT2014 June 16 – 20, Düsseldorf, Germany: 2014*.
- [89] *Combustion - 5th Edition* n.d. <https://www.elsevier.com/books/combustion/glassman/978-0-12-407913-7> (accessed July 7, 2019).
- [90] *Industrial Burners Handbook*. CRC Press n.d. <https://www.crcpress.com/Industrial-Burners-Handbook/Jr/p/book/9780849313868> (accessed July 7, 2019).
- [91] Zhao Y, Choudhury S, McDonell V. Influence of Renewable Gas Addition to Natural Gas on the Combustion Performance of Cooktop Burners. *Vol. 8A Heat Transf. Therm.*

- Eng., Pittsburgh, Pennsylvania, USA: ASME; 2018, p. V08AT10A012.
<https://doi.org/10.1115/IMECE2018-87932>.
- [92] Index | ASHRAE 118.2 Method of Testing for Rating Residential Water Heaters n.d.
<http://spc1182.ashraeps.org/> (accessed July 13, 2019).
- [93] Energy factor. Wikipedia 2017.
- [94] Water Heating Basics and Facts n.d. <https://www.hot-water-heaters-reviews.com/water-heating-basics.html> (accessed July 13, 2019).
- [95] US EPA O. Overview of the Clean Air Act and Air Pollution. US EPA 2015.
<https://www.epa.gov/clean-air-act-overview> (accessed April 23, 2019).
- [96] Stack Sampling Technical Information- A collection of monographs and papers_Volume 1 1978. <https://www.epa.gov/sites/production/files/2016-06/documents/tid-020.pdf> (accessed April 23, 2019).
- [97] Lefebvre AH, Ballal DR, Ballal DR. Gas Turbine Combustion : Alternative Fuels and Emissions, Third Edition. CRC Press; 2010. <https://doi.org/10.1201/9781420086058>.
- [98] Garg S, Castaldini C. Derivation of Oxygen Correction Factors for Oxygen-Enriched Incinerators. JAPCA 1989;39:1462–5. <https://doi.org/10.1080/08940630.1989.10466641>.
- [99] Walpert TH. Measuring Residential Natural Gas Leakage and its Impact on CH₄ Emission Inventories in California 2013.
https://nature.berkeley.edu/classes/es196/projects/2013final/WalpertT_2013.pdf (accessed August 10, 2019).
- [100] Jr EGB. Natural Gas Methane Emissions from California Homes n.d.:68.
- [101] Residential Appliance Saturation Study n.d.
https://ww2.energy.ca.gov/appliances/rass/previous_rass.html (accessed August 10, 2019).
- [102] Slim BK, Levinsky HB. SHOULD WE ADD HYDROGEN TO THE NATURAL GAS GRID TO REDUCE CO₂-EMISSIONS? (CONSEQUENCES FOR GAS UTILIZATION EQUIPMENT) n.d.:15.
- [103] Zhao Y, Soto Leytan KN, McDonell V, Samuelsen S. Investigation of visible light emission from hydrogen-air research flames. Int J Hydrog Energy 2019;44:22347–54.
<https://doi.org/10.1016/j.ijhydene.2019.06.105>.
- [104] Effects of hydrogen addition on laminar flame speeds of methane, ethane and propane: Experimental and numerical analysis | Elsevier Enhanced Reader n.d.
<https://doi.org/10.1016/j.ijhydene.2017.07.190>.
- [105] Flashback - an overview | ScienceDirect Topics n.d.
<https://www.sciencedirect.com/topics/engineering/flashback> (accessed August 8, 2019).