PULSE COMBUSTION SPRAY DRYING FOR THE REMOVAL OF TOTAL DISSOLVED SOLIDS FROM FLOWBACK AND PRODUCED WATERS GENERATED DURING THE HYDRAULIC FRACTURING PROCESS

A Thesis in
Environmental Engineering
by
Thomas J. Geeza

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The thesis of Thomas J. Geeza was reviewed and approved* by the following:

Frederick S. Cannon
Professor of Environmental Engineering
Thesis Advisor

William D. Burgos
Professor of Environmental Engineering
Environmental Engineering Graduate Officer

Mark S. Klima
Associate Professor of Mineral Processing and Geo-Environmental Engineering
Associate Department Head of Energy and Mineral Engineering

*Signatures are on file in the Graduate School.
ABSTRACT

The hydraulic fracturing industry is one of the fastest growing industries in the United States, providing thousands of jobs and infusing billions of dollars into the economy each year. Despite the many benefits of this technology, the industry has been harried by environmental regulations that seek to protect surface water and groundwater from contamination as a result of drilling operations. Many of the problems facing the hydraulic fracturing industry center upon the treatment, transportation, and disposal of high volumes of highly saline brine, which is unable to be treated by conventional wastewater treatment or desalination technologies. This research studied the merits of a pulse combustion spray drying system for treatment of these high salinity brines.

Tests were performed analyzing the thermodynamic efficiency of a supercharged pulsed jet combustor. Results showed that brine solutions up to and exceeding saturation concentrations can be processed and treated by the system with salt recovery between 80 and 100% at energy usage levels acceptable to industry. This technology fills a gap in the desalination market focused on brines exceeding 150,000 mg/L, the maximum concentration of the next alternative process. A pilot scale unit is set to be implemented at a flowback and produced water treatment facility by the summer of 2015.
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# LIST OF UNITS

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>mg</td>
<td>Milligrams</td>
</tr>
<tr>
<td>g</td>
<td>Grams</td>
</tr>
<tr>
<td>kg</td>
<td>Kilograms</td>
</tr>
<tr>
<td>mol</td>
<td>Moles</td>
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</tr>
<tr>
<td>m</td>
<td>Meters</td>
</tr>
<tr>
<td>mL</td>
<td>Milliliter</td>
</tr>
<tr>
<td>L</td>
<td>Liters</td>
</tr>
<tr>
<td>°F</td>
<td>Degrees Fahrenheit</td>
</tr>
<tr>
<td>°C</td>
<td>Degrees Celsius</td>
</tr>
<tr>
<td>mg/L</td>
<td>Milligrams per liter</td>
</tr>
<tr>
<td>psi</td>
<td>Pounds per square inch</td>
</tr>
<tr>
<td>psia</td>
<td>Pounds per square inch, absolute</td>
</tr>
<tr>
<td>MJ/kg*</td>
<td>Megajoules (of propane) per kilogram (of water evaporated)</td>
</tr>
<tr>
<td>K</td>
<td>Kelvin</td>
</tr>
<tr>
<td>atm</td>
<td>Atmospheres</td>
</tr>
<tr>
<td>bar</td>
<td>100,000 Pascal</td>
</tr>
<tr>
<td>kPa</td>
<td>Kilopascals</td>
</tr>
<tr>
<td>Hz</td>
<td>Hertz</td>
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<tr>
<td>HP</td>
<td>Horsepower</td>
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<td>gal</td>
<td>Gallons</td>
</tr>
<tr>
<td>GPM</td>
<td>Gallons per Minute</td>
</tr>
<tr>
<td>-----</td>
<td>--------------------</td>
</tr>
<tr>
<td>scfm</td>
<td>Standard Cubic Feet Per Minute</td>
</tr>
</tbody>
</table>

*The unit of MJ/kg was developed as a way to standardize energy comparisons between runs. This unit represents the lower heating value (LHV) of propane times the mass flow rate of propane divided by the mass of water evaporated during that test. The lower heating value assumes that the enthalpy contained in the products of combustion is not recovered by the system, and is a conservative estimate of input energy.*
## LIST OF ACRONYMS

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>LHV</td>
<td>Lower Heating Value</td>
</tr>
<tr>
<td>NPDES</td>
<td>National Pollutant Discharge Elimination System</td>
</tr>
<tr>
<td>TDS</td>
<td>Total Dissolved Solids</td>
</tr>
<tr>
<td>PAH</td>
<td>Polycyclic Aromatic Hydrocarbons</td>
</tr>
<tr>
<td>NORM</td>
<td>Naturally Occurring Radioactive Material</td>
</tr>
<tr>
<td>VOC</td>
<td>Volatile Organic Compound</td>
</tr>
<tr>
<td>TCE</td>
<td>Trichloroethane</td>
</tr>
<tr>
<td>COD</td>
<td>Chemical Oxygen Demand</td>
</tr>
<tr>
<td>MSF</td>
<td>Multi-State Flash Evaporation</td>
</tr>
<tr>
<td>RO</td>
<td>Reverse Osmosis</td>
</tr>
</tbody>
</table>
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Chapter 1
Introduction and Background

The oil and gas industry in the United States has long faced challenges related to environmental regulations for the use and disposal of waste products from the drilling process. In 1979 the EPA first passed guidelines for water use and disposal of oil and gas waste streams. With advanced in hydrofracturing technology and the discovery of large shale gas formations across the United State, new regulations were required to protect surface and groundwater, aquatic ecosystems, and human health. In 2001 regulatory provisions were added to address synthetic based drilling fluids and other non-aqueous drilling fluids. The injection of fluids into the subsurface during the hydraulic fracturing process is not regulated under the Safe Drinking Water Act, but disposal of flowback water is regulated under the Clean Water Act as dictated by the National Pollutant Discharge Elimination System (NPDES). Since 1989 the number of natural gas and gas condensate wells in the U.S. has nearly doubled, from 262,483 wells in 1989 to over 500,000 in 2011. This number fluctuates as demand, reserves, and production vary by location. In Pennsylvania alone there are more than 7,000 active wells which use an average of 4.4 million gallons of water per well. These fluids contain a wide variety of contaminants that range from metals to organic molecules. The presence and concentration of these compounds depend on geologic formations, proprietary fluid mixes, and time and stage of sampling. All of the produced and flowback waters contain elevated total dissolved solids (TDS) with a dominant species of sodium chloride with concentrations as high as 300,000 mg/L. With a secondary standard as dictated by the EPA of 500 mg/L for TDS, extensive treatment of the fluids is necessary to facilitate reuse of this water outside of recycling within the hydrofracturing industry. [1] [2] [3] [4] [5]
1.1 The History of Hydraulic Fracturing

Hydraulic fracturing refers to the introduction of pressurized fluids into a well to stimulate and enhance recovery of oil and gas resources from otherwise difficult to harvest geologic formations. The earliest attempts at recovering difficult to access resources in tight geologic formations was documented in records dating as early as 1890, where high explosives were used to create flow paths in rock to allow resource extraction [6]. The process of hydraulically fracturing wells was performed as early as 1910. It is referenced in United States Geological Survey documents from the time period regarding mining operations in an area of granite formations [7]. In 1947 the first controlled hydrofracturing tests were performed by the Stanolind Oil Company using Napalm and river sand to observe and quantify the effects of the process. Subsequent findings determined a 75% increase in average yield for a treated well, but this practice was determined to be very dangerous and was discarded early on. Early fracturing fluid mixes were comprised mostly of petroleum fuels such as crude oil, gasoline, and diesel mixed with mature river sands acting as proppant to stabilize fractures. In 1953 water was first used as a fracturing fluid. It was combined with gels, friction reducers, acids, alcohols, and surfactants. These additives facilitated proppant transport and reduced friction in the fractures which caused faster and more complete gas extraction. Research advanced rapidly as hydraulic fracturing proved to be an effective technology for greatly increasing well production with newer estimates suggesting increases in yield as high as 90% for natural gas wells. [8] [9] [10]

During the 1980’s the improvement of existing horizontal drilling techniques combined with hydraulic fracturing made massive volumes of previous inaccessible oil and gas reserves
available for extraction in the U.S. New pump, drill casing, and bore steering designs allowed wells to be drilled horizontally, providing access to formations otherwise inaccessible. Horizontal drilling proved to be more effective than conventional vertical drilling in the majority of sedimentary formations. New U.S. Energy and Information Agency estimates assert numbers of over 750 trillion cubic feet of ‘technically recoverable’ gas and 24 billion barrels of already discovered oil in shale formations [11] [12]. Technical recoverability refers to reservoirs that can be accessed and recovered using available technology, but this term does not consider economic viability [13]. Shown in Figure 1.1, the majority of the gas reserves in the U.S. are held in 20 separate geologic formations referred to as ‘plays’, the largest of these being the Barnett, Haynesville, Fayetteville, Woodford, Bakken, Eagle Ford, and Marcellus. Research conducted in this paper focused on the Marcellus formation, which majorly underlies Pennsylvania, New York, Ohio, and West Virginia.

![U.S. shale gas reserve map by region.](image)

Figure 1.1: U.S. shale gas reserve map by region. [15]
1.2 The Hydraulic Fracturing Process

Hydraulic fracturing is one of the most materials and energy intensive industrial processes, employing a wide range of drilling equipment and techniques developed over years of research and innovation. The hydraulic fracturing process begins when a potential gas reservoir is analyzed by geologists and engineers and it is determined that the cost of fracturing the well will provide an economically favorable cost-to-profit ratio. Often the presence of low permeability and hard rock formations such as shale layers prompts the decision to hydraulically fracture a well to increase its total output and rate of output. These wells are referred to as ‘unconventional’ wells, meaning without the hydraulic fracturing process, the resources contained in them would not be economically viable to extract. [14] [6]

The operation begins by establishing a drilling site above a formation suitable for hydrofracturing. A well is drilled to depths ranging from 4000 to 10,000 feet below ground surface using a double layer steel casing. Gaps between casing segments are filled by cement. Once the shale formation is reached, all casings are set, and the cement is secure, the hydrofracturing fluid is pumped into the rock formations under extreme pressure, up to 10,000 pounds per square inch (psi). This pressure varies with formation geometry, the mechanical properties of the rock, pipe friction, depth, fluid density, fluid viscosity, in situ pressure, and closure pressure exerted by the surrounding rock. Figure 1.2 shows in cross section a horizontally drilled well. The section of the well in contact with the drinking water aquifer is several thousand feet above the well section into which hydrofracturing chemicals flow. Figure 1.3 shows the depth to reservoir in the Marcellus formation, typically between 5,000 and 9,000ft.
Figure 1.2: Subsurface diagram of typical Marcellus drilling operation showing casing design and drilling depth. [15]
Figure 1.3: Depth below ground surface of Marcellus shale formations by 1000ft contour intervals. [15]

Under adequate pressure, the rock fractures along bedding plains and weaknesses in its structure allowing gas trapped in these formations to flow out at much greater rates and in much greater volumes than can be achieved with conventional drilling. Many shale gas formations run for long distances horizontal to the ground surface. Drilling multiple wells to the appropriate depth to extract the trapped gas is not economically feasible, so the technique of horizontal drilling was developed to allow a single bore well to reach a much larger subsurface area and focus the fracturing pressure on the most valuable formations. By slowly rotating the cutting
head of the drill over several hundred feet, wells can transition from vertical to horizontal, maximizing well-formation contact. [6] [16] [17]

Once the well has been fractured, however, the newly created flow paths must be mechanically held open or the pressure of the surrounding rock would simply close the fracture, preventing continued access to any contained resources. To accomplish this task, proppant, which is in most cases sand, is typically carried along with the hydrofracturing fluid into the newly created fractures and left behind as the drilling fluids and gas return to the surface. As the fractures close, the sand remains in place. Sand’s high compressive strength and high permeability and porosity provide excellent flow paths and resists fracture closure, creating minimal resistance to gas and fluid flow. [6]

Once fracturing is complete, the pressure buildup in the shale formations causes natural gas, drilling fluids, other liquid petroleum products and naturally occurring water in the shale formation to flow to the surface. Wells may continue to produce water for many years after they have been taken out of service. The water that returns to the surface within the first 1-3 weeks is known as flowback water and contains many of the chemicals used in the drilling operation. The water that continues to flow out of the well after this time period is known as produced water and contains elevated concentrations of dissolved solids and lower concentrations of drilling chemicals as compared to flowback water. The gas is then transported to an onsite facility where it is compressed into a liquid for shipping and distribution. Fluids are stored in retention ponds, tanks, or pits in preparation for transport, treatment, or recycling. [6] [18]
1.3 Economic Implications of Hydraulic Fracturing

The discovery and subsequent utilization of natural gas has spurred what some have called an “energy revolution” in the U.S., boosting our hydrocarbon fuel production beyond that of once-dominant Saudi Arabia and Russia in both oil and natural gas. The challenges of job creation and economic growth, increased demand in the energy market, and the promise of massive profits have paired with technological advancements to rapidly raise the rate of hydraulic fracturing. For the first time in 2013 the United States became a net exporter of crude as well as the largest producer of natural gas in the world (Figure 1.4). The economic benefits of hydraulic fracturing are far-reaching and have helped move the U.S. towards energy independence and economic stability in increasingly volatile markets. [11] [19] [20] [21].

Figure 1.1: Total fossil fuel production in 2013 with projected values through 2015 [14]
While the economic benefits of natural gas extraction are obvious and undeniable, there is concern about the economic viability of development and extraction of hydraulically fractured wells. This uncertainty stems from supply uncertainty and price elasticity, production cost uncertainty, and the need for infrastructure development. The rapid increase of natural gas production has driven down prices but this price drop also increased demand for natural gas as a low cost, low emissions alternative to petroleum-based fuels. Natural gas provides a greater amount of power per unit of CO₂ produced than other fossil fuels. Due to this increased efficiency, the electric power, transportation, and industrial sectors are expected to continue to exert a large demand for natural gas as CO₂ regulations become stricter. Uncertainty in total volume and rate of production as well as rate of consumption casts doubt on the continued economic feasibility of continued well production, increased demand across nearly all sectors seems to indicate favorable economic conditions for further development (Figure 1.5). [13]
Figure 1.2: Increase in natural gas demand by sector, noting a net total increase in nearly all sectors 1990-2040 projected [13]

The overall cost of production also prompts speculation concerning the economic future of hydrofracturing. The cost of water and water treatment, infrastructure, capital cost, and complying with environmental regulations all contribute to the uncertainty in the economic viability of continued development. The implementation of pipelines would allow rapid, large-scale movement of high volumes of natural gas quickly and efficiency to areas of high demand, but policy regarding land use, environmental impacts, and cost has thus far prevented the implementation of these systems. The Natural Gas Association of America predicts infrastructure expenditures of more than $205 billion will be required to develop storage, processing, and transportation for the projected volumes being produced annually. [13]
1.4 Environmental Impacts of Hydraulic Fracturing

Despite the many benefits of the hydraulic fracturing process and shale gas extraction, there exist a variety of environmental concerns surrounding the natural gas industry. The major points of potential environmental impact are greenhouse gas emissions in the form of methane, and the contamination of groundwater, surface water, and the water used in the hydrofracturing process. In Pennsylvania, the hydraulic fracturing of a well uses between 3 and 5 million gallons of water per well with an average value of 4.4 million gallons. This number varies with each well and depends on subsurface geometry, formation geology, well size, and various other parameters. [22] [23] [24] [25]

1.4.1 Down Well Fluids

Hydrofracturing fluids consist of a wide range of compounds, with exact mixes being proprietary to whatever company is managing a given well. Many of these compounds present health risks to workers in the field, nearby wetlands, surface water, and drinking water supplies in the area, but safety precautions and preventative measures have thus far prevented any documented cases of widespread contamination. Because solution chemistry can vary widely between wells, it is difficult to determine the best treatment process for these fluids. Despite differences in formulas across industry, nearly every mixture shares certain characteristics that aid in the fracturing and extraction process that must be dealt with when the water returns to the surface. [26] [27] [28] [29]

There are several types of fluids commonly used in industry, with some fluids being a combination of more than one of the major fluid types. Fluids are chosen at the engineer’s discretion to maximize the effectiveness of the well in creating flow paths for the gas and
holding open fractures in the shale. The fluid must be viscous enough to carry proppant, but not so viscous that it cannot reach the full length of the fracture and extend the fracture further into the shale bed. It must also be able to degrade quickly to not impede the flow of gas out of the well. Table 1.1 outlines a typical composition for hydrofracturing fluid. [30]

The mains types of base fluid are gelled fluids, foamed gels, water with potassium chloride, and acids. Gelled fluids and foamed gels do an excellent job of transporting high % volumes of proppant into the formations, and a combination of gelled fluids and foamed gels can reduce required fluid volumes by as much as 75% as compared to a water-potassium chloride solution. Deisel fuel has been added as a water substitute, as its capacity to dissolve and transport guar gum, the product typically used in gelled fluids, is much higher than water. Benzene, a known carcinogen, makes up to 0.1% of diesel fuel and has been shown to cause adverse health effects in workers even at extremely low concentrations, causing concerns related to its fate and transport in the environment. [31] [32] The Maximum Contaminant Level for benzene in drinking water as reported by the EPA is 5 parts per billion (ppb). [33] [30]

Foamed gels reduce necessary fluid volumes by creating foam emulsions of carbon dioxide or nitrogen gas. These gels serve a dual purpose of carrying proppant into fractures and taking up space in the subsurface that would otherwise need to be filled with water. Various formulas call for different foaming agents so no single set of compounds can be identified as existing in every mixture. Foamed gels may contain harmful compounds such as glycol ethers, ethanol, isopropanol, and diethanolamine. The Material Safety Data Sheet for foaming agents used in hydrofracturing specifies liver and kidney damage as possible side effects but does not identify a single compound responsible for these effects. [30]
Table 1.1: Outline of a typical hydraulic fracturing fluid composition by volume, representative of the common constituents of down well fluids. [34]

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Composition (% by vol)</th>
<th>Example</th>
<th>Purpose</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water and sand</td>
<td>99.50</td>
<td>Sand suspension</td>
<td>“Proppant” sand grains hold microfractures open</td>
</tr>
<tr>
<td>Acid</td>
<td>0.123</td>
<td>Hydrochloric or muriatic acid</td>
<td>Dissolves minerals and initiates cracks in the rock</td>
</tr>
<tr>
<td>Friction reducer</td>
<td>0.088</td>
<td>Polyacrylamide or mineral oil</td>
<td>Minimizes friction between the fluid and the pipe</td>
</tr>
<tr>
<td>Surfactant</td>
<td>0.085</td>
<td>Isopropanol</td>
<td>Increases the viscosity of the fracture fluid</td>
</tr>
<tr>
<td>Salt</td>
<td>0.06</td>
<td>Potassium chloride</td>
<td>Creates a brine carrier fluid</td>
</tr>
<tr>
<td>Scale inhibitor</td>
<td>0.043</td>
<td>Ethylene glycol</td>
<td>Prevents scale deposits in pipes</td>
</tr>
<tr>
<td>pH-adjusting agent</td>
<td>0.011</td>
<td>Sodium or potassium carbonate</td>
<td>Maintains effectiveness of chemical additives</td>
</tr>
<tr>
<td>Iron control</td>
<td>0.004</td>
<td>Citric acid</td>
<td>Prevents precipitation of metal oxides</td>
</tr>
<tr>
<td>Corrosion inhibitor</td>
<td>0.002</td>
<td>n,n-dimethyl formamide</td>
<td>Prevents pipe corrosion</td>
</tr>
<tr>
<td>Biocide</td>
<td>0.001</td>
<td>Glutaraldehyde</td>
<td>Minimizes growth of bacteria that produce corrosive and toxic by-products</td>
</tr>
</tbody>
</table>

Water and potassium chloride solutions are only effective in geologic formations where proppant is not entirely necessary such as coal bed methane wells. In typical fracturing operations a water-potassium chloride solution is not an effective option. [30]

Acids are added to hydrofracturing fluids to aid limestone rock dissolution and in cleaning rough well casings that have become encrusted with cement. Because of high dilution
factors and the high level of buffering added by limestone formations, acids are not typically an environmental health concern at the concentrations relevant to hydrofracturing fluids. [30]

Base fluids alone are typically not enough to ensure high levels of extraction efficiency, so various additives are included to serve specific purposes. Some of these compounds have known levels of toxicity even at very low concentrations, but most additives are benign and similar to common household products such as detergent and gelatin. It is important to note that hydrofracturing fluid is approximately 99% water, but even small percentages of highly toxic fluids can pose a danger to human health [30] [35].

Breakers are used to break down cross-linked gels after proppant has been applied to decrease fluid viscosity and increase fracture permeability to gasses. Breakers typically consist of enzymes, acids, or oxidizers depending on the type of gel used. Breakers may contain glycol ethers, ammonium sulfate, copper, ethylene glycol, magnesium peroxide, and magnesium oxide. Glycol ethers, a volatile common solvent, may cause liver and kidney damage with short term exposure to high concentrations, but low applied concentrations and rapid volatilization make the relevant risks low. [36] [30]

Biocides are added to diminish and control bacterial growth, which may lead to clogging in pipes and fractures as well as premature degradation of gels. The addition of organic compounds may act as an electron donor, enhancing bacterial growth in otherwise low bacterial concentration regions. Biocides often contain polycyclic aromatic hydrocarbons (PAHs) which are cited in the literature as toxic, mutagenic, and carcinogenic [37] [38] [30].
Corrosion inhibitors are added to prevent acids from eating through steel casings. These compounds are typically solvents and are reported to cause liver, kidney, hear, lung, and nervous system damage. [30]

Scale inhibitors prevent precipitation and crystallization of minerals that are dissolved into the drilling fluids from the surrounding formations. Precipitation can cause clogging of fractures and pressure buildup in undesirable areas. Scale inhibitors are typically polymeric compounds with carboxylic and acrylic acids. [39]

Surfactants serve to decrease surface friction between fluids and surround rock. Various surfactants are used throughout industry, with concentrations ranging from 500 to 1000 ppm [39]. Surfactants, while themselves typically not harmful at concentrations relative to hydrofracturing, have been proposed as a mechanism to track the effects of hydrofracturing on local water quality [40].

One compound that can serve many purposes in hydrofracturing fluids is methanol. Methanol can act as a corrosion and scale inhibitor, friction reducer, and as a water displacement compound increasing water recovery. [41]

1.4.2 Flowback and Produced Waters

The water that returns to the surface following hydrofracturing can be separated into 2 categories: flowback water and produced water. Flowback water is defined loosely as the water returning to the surface from the well within the first 1-4 weeks, whereas produced water may continue to flow out of a well for up to 30 years long after production has ceased [42]. Once drilling and pumping are complete and proppant has been applied to the newly created fractures, pressure seals can be relieved, causing between 10 and 70% of the injected water to flow back to
the surface. This broad range of water recovery percentage is a function of well geology, well type, and fracturing techniques. The general composition of flowback water is outlined in Table 1.2. [43] [24] [44] [45] [46] [47]

Table 1.2: Median concentration values of flowback water at day 14 based on 7 horizontal wells drilled into Marcellus formations. [48]

<table>
<thead>
<tr>
<th></th>
<th>Concentrations in mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Injected fluid median, day 0</td>
</tr>
<tr>
<td>pH</td>
<td>7.0</td>
</tr>
<tr>
<td>Alkalinity as CaCO₃</td>
<td>126</td>
</tr>
<tr>
<td>Total dissolved solids</td>
<td>735</td>
</tr>
<tr>
<td>Total organic carbon</td>
<td>205</td>
</tr>
<tr>
<td>Chemical oxygen demand</td>
<td>734</td>
</tr>
<tr>
<td>Cl</td>
<td>82</td>
</tr>
<tr>
<td>Br</td>
<td>&lt;10 (&lt;0.2–19)</td>
</tr>
<tr>
<td>SO₄</td>
<td>59</td>
</tr>
<tr>
<td>NH₃-N</td>
<td>16</td>
</tr>
<tr>
<td>P</td>
<td>0.36</td>
</tr>
<tr>
<td>Al</td>
<td>0.3₀</td>
</tr>
<tr>
<td>Ba</td>
<td>0.6</td>
</tr>
<tr>
<td>B</td>
<td>0.5</td>
</tr>
<tr>
<td>Ca</td>
<td>32</td>
</tr>
<tr>
<td>Fe</td>
<td>0.68</td>
</tr>
<tr>
<td>K</td>
<td>&lt;50 (3–57)</td>
</tr>
<tr>
<td>Li</td>
<td>0.04</td>
</tr>
<tr>
<td>Mg</td>
<td>3.7</td>
</tr>
<tr>
<td>Mn</td>
<td>0.074</td>
</tr>
<tr>
<td>Na</td>
<td>80</td>
</tr>
<tr>
<td>Sr</td>
<td>0.82</td>
</tr>
<tr>
<td>Zn</td>
<td>0.08</td>
</tr>
</tbody>
</table>

Flowback water generally consists of many of the same chemicals used in the hydrofracturing operation as additives to the primary fluid [47]. A 2011 estimate puts the amount
of produced water generated by the Marcellus play in Pennsylvania alone at over 330 million gallons, with a projected number of 19.2 billion gallons over its entire development. [44] It is difficult to speculate about the danger to human health or potential environmental impact of a given flowback fluid due to widely varying chemicals used in the hydraulic fracturing process. The contaminants of concern that are commonly found in all Marcellus flowback waters are the same as those added during operations such as biocides, breakers, and corrosion inhibitors. While individually these compounds are reported to exhibit toxic characteristics on their own, they often undergo degrading reactions, reducing their toxicity. [49]

Produced waters include of traces of the compounds used in the hydrofracturing process, but also organics, heavy metals, dissolved salts, and naturally occurring radioactive materials (NORM) found in the fractured formations. The ratios and concentrations of these compounds varies widely between wells due to variation in geologic formations between sites. Much of the volume of produced water is simply water that was trapped in the shale and released when the shale was made more permeable by fracturing [49]. Produced waters often contain a wide range of organics, including organic acids, polycyclic aromatic hydrocarbons, a wide array of volatile organic compounds (VOCs), and phenols. Most of the organics are low molecular weight (C$_2$-C$_5$) as they are more soluble than larger organic molecules, with total organic concentrations reaching 5,000 mg/L or greater. While many of these organic compounds are not toxic at their native concentrations, their toxicity can be cumulative, resulting in a total net acute toxicity of the flowback solution at the concentrations found in recently extracted flowback water. Fortunately many of these compounds can be readily degraded by ultraviolet light or bacterial activity. Other contaminants are known to be toxic at concentrations present in solution. A study of various flowback and produced waters by Abualfaraj et al. found compounds such as barium,
benzene, pentachlorophenol, radium, vinyl chloride, and 1,2-dichloroethane at over 10 times their maximum contaminant level in samples taken from the Marcellus play [50]. Efforts are being taken to reduce the production of these compounds through a better understanding of the complex chemistry involved. [49] [51] [52]

Metals are another contaminant of concern in produced waters. Metal concentrations depend heavily on the underlying geology and conditions such as pH and temperature. Lead, barium, iron, manganese, and zinc are commonly found in appreciable concentrations and can be carried out of formations as precipitated particulate solids or sorbed to shale as well as dissolved in solution. [49]

NORMs are also a contaminant of concern in produced waters. Radium 226 and radium 228 are the most abundant observed radioactive species. The compounds exist in appreciable concentrations due to uranium and thorium decay in deep subsurface formations. Temperature changes as the fluid approaches the surface can drive radium compounds out of solution, concentrating the radium in precipitate form and creating potential risk of harmful radiation exposure. [49]

Of all of the contaminant found in flowback and produced waters, perhaps the most difficult and energy intensive contaminant to effectively deal with is TDS, majorly in the form of highly soluble chloride salts such as sodium, calcium, and magnesium chloride as well as alkalinity in the form of carbonates such as HCO₃ and CO₃²⁻. The salts associated with flowback and produced waters are due to salts being dissolved from shale formation as well as highly saline aquifers being tapped in the drilling and fracturing process [53]. Regardless of the source, chloride concentrations exceeding 150,000 mg/L are not uncommon, with Marcellus shale brines often exceeding 200,000 mg/L [25] [45]. 35,000 mg/L sodium, 10,000 mg/L calcium, 2,000
mg/L strontium, and 1,000 mg/L magnesium are typical concentrations of other compounds that contribute to TDS in solution. Industrial discharge standards were set to 500 mg/L on January 1, 2011 by the Pennsylvania Department of Environmental Protection, eliminating any legal discharge of these fluid [53]. At around 4 million gallons of water per well, and assuming a typical water recovery of 40% and a concentration of 150,000 mg/L, $2.27 \times 10^6$ kg of salt will be produced by each well. And with 57,000 active wells in Pennsylvania alone, this massive volume of salt is definitely a cause for concern. [3] [49]
Chapter 1 References


Chapter 2

Treatment Technologies and Disposal Options

The disposal and treatment of hydrofracturing waste water has been a problem facing the industry since its inception. Before discharge regulations took effect in the 1970s, some drilling companies simply discharged the highly saline fluid into surface waters or stored it in unlined ponds until seepage and evaporation removed the water. Like modern hydrofracturing flowback and produced waters, this fluid contains heavy metals and radioactive material such as radium 226 and 228. These contaminants when discharged without regulation at the surface caused surface and groundwater contamination near petroleum fields in Oklahoma [1] [2]. Once industrial discharge standards were put into place, hydrofracturing companies could no longer discharge these brines, so the brines were sent to wastewater treatment plants for physical-chemical remediation and to simply be diluted with all of the other incoming fluids. The treatment plants, however, had no mechanism for removal of salts, so TDS limits were very quickly exceeded [3] [4] [5]. Due to the ineffectiveness of conventional treatment plants at removing TDS and the unreliable effectiveness of immobilizing heavy metals and radioactive compounds, the practice of sending flowback and produced waters to municipal wastewater treatment plants ceased [6].

2.1 Current Disposal Techniques

With nowhere for this hydrofracturing fluid to go, there emerged several viable options for the management of this high volume of industrial wastewater. Initially these included dilution with incoming water for reuse in drilling processes, on-site treatment and subsequent reuse, off-site treatment, and disposal [3]. With treatment processes either being ineffective or too expensive, deep well injection has risen as the preferred disposal method in the industry [3] [7] [8]. Figure 2.1 shows a diagram of the deep well injection process. Deep well injection is cheap, effective at reducing the volume of water that needs to be transported, treated, or stored, and removes the water from the surface where it may be more likely
to contaminate surface water and drinking water aquifers. It is not, however, a method of actually physically treating the water and preparing it for reuse. Regulation by the Underground Injection Control program as dictated by the Safe Drinking Water Act also does not require pretreatment of fluids being injected into Class II injection wells [6]. While this seems like an excellent option, injection wells are not infinite reservoirs and have both physical limitation and growing political limitations [9]. A number of scientists also have voiced concern about seismic activity due to deep well injection, and increased rates of small tremors have been documented in regions with deep well injection, some predicting the induction of larger, more damaging events [5] [1] [10]. Other scientists believe injection induced earthquakes present a reasonable level of risk and should not prevent the practice of deep well injection [11].

The other major disposal option for hydrofracturing fluids is reuse in other drilling operations. Reuse can continue as long as new wells are being drilled or the number of active wells remains constant, or until the concentration of compounds (mostly salts) exceeds the concentration limits for a down well

![Figure 2.1: Treatment and disposal of flowback and produced water showing fluid treatment for recycling with deep well injection as the final destination. [25](#)](image-url)
fluid. One advantage of reuse over deep well injection is that transportation costs are much lower than for deep well injection, as recycled water typically must only travel an average of 60 miles between sites whereas deep injection wells are carefully regulated and only exist in certain locations, with Marcellus wastewaters traveling to wells in West Virginia (74 wells), Ohio (159 wells), and Maryland (number of wells not reported) [6] [3] [12]. The majority of this fluid is traveling to Ohio [3]. Recycled water may be temporarily stored on site in lined ponds awaiting further transportation to other drilling sites [6]. If a drilling operation does not have its own storage facilities, operations specializing in the storage of produced water can hold and treat this water until it is ready to be used in another well [6] [9]. Even with adequate storage volume and high levels of reuse and recycling, without some mechanism of salt removal, salinity increases. This can cause issues with scaling and disrupt drilling fluid chemistry, making the operation more difficult and more expensive [13] [1]. Fresh water must also still be added to maintain adequate fluid volumes and water quality [14].

2.2 Treatment Technologies

Neither deep well injection nor reuse completely address the problems associated with the salinity of produced water. To treat this persistent and ubiquitous contaminant, desalination technology is required. There are several types of desalination technologies available commercially, and extensive research has been done on desalination of brines such as ocean water and elevated salinity rivers as fresh water scarcity continues to mount worldwide [15]. Desalination technologies can be separated into two distinct groups; thermal processes and membrane processes. Membrane processes include reverse osmosis, nanofiltration, and electrodialysis. Thermal technologies include multi-stage flash evaporation, multi-effect distillation, and mechanical vapor recompression, which is also called vapor compression distillation [15]. Of the current desalination plants in operation, over 50% use reverse osmosis and 34% use thermal technologies, with the remaining percentage being accounted for by ion exchange, electrodialysis, and other smaller scale processes [16].
2.1.1 Membrane Technologies

Nanofiltration is ineffective for removing salts, and electrodialysis is ineffective at even the lowest salt concentrations seen in produced waters. This leaves reverse osmosis as the sole membrane technology feasible for treating hydrofracturing brines [15] [17] [18]. The defining factor for many desalination technologies is the maximum salinity brine they can effectively remediate. Reverse osmosis operates most effectively at salt concentrations ranging from 500 mg/L to 45,000 mg/L, being more effective and producing a lower volume retentate stream at lower salt concentrations. This range represents the salinity range of the majority of naturally occurring water on the earth’s surface. This gives reverse osmosis the ability to treat seawater with concentrations ranging from 15,000 to 36,000 mg/L [15] [16] [19].

One of the major advantages of reverse osmosis over competing technologies is its low energy cost. Table 2.1 compares the energy costs of reverse osmosis with other competing technologies. Reverse osmosis is able to desalinate water in its effective salinity range for less than 0.025 MJ/kg (megajoules of energy input per kg of treated water produced) producing a treated water stream of less than 500 mg/L TDS whereas competing thermal systems typically operate around 0.126 MJ/kg and produce a treated water stream at around 10 mg/L. Reverse osmosis is able to maintain these extremely low energy usage numbers by a combination of energy recovery systems peripheral to the

<table>
<thead>
<tr>
<th></th>
<th>MSF</th>
<th>RO</th>
<th>Electrodialysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal energy consumption [kWh/m³]</td>
<td>12</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Electrical energy [kWh/m³]</td>
<td>35</td>
<td>0.4–7</td>
<td>1</td>
</tr>
<tr>
<td>Typical salt content of raw water</td>
<td>30,000–100,000</td>
<td>1,000–45,000</td>
<td>100–3,000</td>
</tr>
<tr>
<td>Product water quality (ppm TDS)</td>
<td>&lt;10</td>
<td>&lt;500</td>
<td>&lt;500</td>
</tr>
</tbody>
</table>
membrane itself that can run at extremely high efficiencies, and by keeping the salinity relatively low. To overcome the osmotic pressure experienced by a reverse osmosis membrane, plants must pump their fluid to 800-1000 psi, accounting for nearly all of the energy used by a reverse osmosis plant [20] [15]. As salinity increases, the osmotic pressure increases, meaning more pressure is needed to overcome the osmotic pressure gradient and force water through the membrane. When concentrations such as those found in flowback and produced waters are reached, the osmotic pressure simply becomes too high, and the cost of pumping becomes astronomical [21].

Jiang et al. in their study of the feasibility of membrane technologies and ion exchange for treating flowback waters, found that estimated operational costs more than quadrupled when treating brines around 186,000 mg/L as opposed to remaining in the concentration levels of ocean water, below 45,000 mg/L. Reverse osmosis also relies on a variety of pre-treatment technologies such as ion exchange and microfiltration to remove organics and suspended solids that can clog and foul membranes. Membrane fouling can greatly increase the cost of pumping as the resistance offered by the membrane increases. Clogging can be a problematic at organic concentrations as low as 0.02 mg/L, as compared to flowback waters that can exceed organic concentrations of 5000 mg/L [16] [7].

The total cost of reverse osmosis is also a limiting factor in its implementation for treatment of hydrofracturing wastewaters. The cost of membrane replacement due to clogging and fouling, the cost of part replacement due to grit and suspended solids, the cost of high pressure pumping, and the cost of creating a system able to resist extremely corrosive environments all make reverse osmosis very expensive when applied to the high strength brines of flowback and produced water [15] [16].

According to Arnal et al., the absolute maximum working salinity of a reverse osmosis system is 70,000 mg/L, calling this the “Technical Limit” of the process [22]. Due to the high organics concentration and the extreme salinity, the cost of treating flowback and produced waters using reverse osmosis is 10-25 times the cost of treating sea water, and may simply be impossible at highly elevated brine concentrations. [18] [15] [17] [22]
2.1.2 Thermal Distillation Technologies

While thermal distillation systems vary considerably in design and scope, all common technologies rely on changing the state of the solvent water by manipulating temperature and pressure to produce a desalinated water vapor and an increased salinity concentrate. Thermal desalination technologies are considered not affected by the salinity of the water being treated, but practical operation factors seem to place the upper limit of thermal distillation at around brine concentrations of 100,000-150,000 mg/L [15] [16].

Thermal distillation systems mostly vary by the temperature and pressure at which vaporization is induced. Multi-stage flash evaporation works by directly heating water in one chamber to near its boiling point (90-115°C) and pumping it into an adjoining chamber with slightly lower pressure than the saturation vapor pressure of water, allowing the water to instantly ‘flash’ to steam. This is referred to as a single stage, with each stage producing around 1% of the total feed water as clean water. Modern systems may have up to 45 stages. This process is coupled with a steam turbine power plant that recovers the waste heat from the steam and uses that energy to power the heating and pressure regulation processes. A demisting system also removed gas phase water from salt-laden mists to control salt emissions. With all these peripheral systems in place, a multi-stage flash evaporation system can operate at as low as 0.027 MJ/kg. [16]

Multi-effect distillation uses a similar concept except that instead of heating the fluid directly in each stage, the feed brine is sprayed onto heat exchanger coils which generates steam that is then fed into the next stage’s heat exchanger coils, heating the water in the next stage. Each successive stage is kept at a lower pressure than the previous stage, allowing the water to
continue to boil at successively lower temperatures. For this reason, multi-effect distillation operates at lower temperatures than multi-stage flash systems.

One of the major drawbacks of these systems is that not only are the materials used expensive, the systems are quite large and prone to failure at many points, making them a large, risky capital expenditure (Table 2.2). Another major drawback of these types of systems is that the conversion percentage, or the ratio of the total volumetric flow rate of desalinated product water to the feed flow rate is very low, ranging from 8.4% to 31.2% (Table 2.3).

Table 2.4: Corrosion and material failure in multi-effect distillation units. [23]

<table>
<thead>
<tr>
<th>Plant</th>
<th>Corrosion type</th>
<th>No. of corroded tubes</th>
<th>Metal used</th>
<th>Types, location</th>
</tr>
</thead>
<tbody>
<tr>
<td>St. Thomas 3</td>
<td></td>
<td>6</td>
<td>90/10 Cu/Ni</td>
<td>Fluted, evaporator</td>
</tr>
<tr>
<td>St. Thomas 3</td>
<td></td>
<td></td>
<td>90/10 Cu/Ni</td>
<td>Roped, preheater</td>
</tr>
<tr>
<td>St. Croix 2</td>
<td>Pitting</td>
<td>70</td>
<td>90/10 Cu/Ni</td>
<td>First effect evaporator</td>
</tr>
<tr>
<td>St. Croix 2</td>
<td></td>
<td>190</td>
<td>90/10 Cu/Ni</td>
<td>Remaining effects</td>
</tr>
<tr>
<td>St. Croix 2</td>
<td></td>
<td>240</td>
<td>90/10 Cu/Ni</td>
<td>Stage 1, preheater</td>
</tr>
<tr>
<td>St. Croix 2</td>
<td></td>
<td>40</td>
<td>90/10 Cu/Ni</td>
<td>Stage 2, preheater</td>
</tr>
<tr>
<td>St. Croix 2</td>
<td></td>
<td>3</td>
<td>90/10 Cu/Ni</td>
<td>Stage 3, preheater</td>
</tr>
<tr>
<td>St. Croix 3</td>
<td></td>
<td>40</td>
<td>90/10 Cu/Ni</td>
<td>First effect evaporator</td>
</tr>
<tr>
<td>St. Croix 3</td>
<td></td>
<td>25</td>
<td>90/10 Cu/Ni</td>
<td>2 effect evaporator</td>
</tr>
<tr>
<td>Eilat</td>
<td>Erosion</td>
<td>150</td>
<td>Aluminum</td>
<td>Condenser</td>
</tr>
</tbody>
</table>
These systems also suffer from scaling and solids buildup on the heat exchange coils, greatly reducing the heat transfer rate and efficiency at each stage. Despite these drawbacks, multi-effect distillation is gaining momentum as the premier technology for high strength salt water desalination, attaining energy usage rates of as low as 0.011 MJ/kg (typical operation ranges between 0.011 and 0.075 MJ/kg). [16] [23]

While thermal systems can provide high levels of efficiency, generate high volumes of clean water, and treat relatively high strength brines, thermal desalination systems still face many challenges before it will be a viable treatment process for flowback and produced waters. Extreme salinity leading to scaling and corrosion of expensive materials such as titanium and nickel cobalt alloys, low conversion percentages (10-30% as compared to 40-60% for reverse osmosis), large size, complication of design, infrastructure requirements, and high cost are detrimental to the implementation of thermal desalination processes in the hydrofracturing industry. [24] [16] [23]
Chapter 2 References


Chapter 3

Pulse Combustor Literature Review

Mechanically valved pulse combustors have been providing thrust and heat since they were first developed in France in 1906 [1] [2]. Subsequent designs have emerged in industries as varied as missile propulsion to food processing [3] [2] [4]. While the supercharged pulsed jet combustor represents a new innovation in drying technology, many of the fundamental principles governing the behavior of the system may be characterized and understood by reviewing existing work on pulse combustors and pulse combustion spray drying systems. Pulse combustion literature has been reviewed herein to gain an understanding of the thermodynamics and general operational parameters of the supercharged pulse jet combustor and to anticipate what changes will increase system performance. The overarching purpose of this system is to separate dissolved solids from water via vaporization of the solvent water. Pulse combustion spray drying literature established both theoretical and mechanistic foundations for this system as well as providing insight into operation and process optimization.

3.1 Pulse Combustors

A pulse combustor is a type of engine consisting of an inlet, combustion chamber, and tail pipe that combusts fuel periodically [5] [6] [7]. Due to the unsteady nature of the combustion process, pressure, velocity, and temperature vary spatially and with time in the combustion chamber and tailpipe of a pulse combustor, enhancing heat and mass transfer [5] [8] [9]. Major advantages of pulse combustors over conventional combustion engines include increased combustion intensity by up to a factor of 10, lowered NOx and soot emissions by a factor of 3, increased thermal efficiency by as much as 40%, smaller overall combustor size, and most
importantly between 2 and 5 times the heat and mass transfer rates of steady state combustors [5] [10] [11].

The three basic types of pulse combustors are Quarter Wave or Schmidt combustors, Helmholtz combustors, and Rijke-Type Combustors. The classification of a pulse combustor is based on the resonant acoustic system governing their operation. Fuel and air injection are controlled by a valve system feeding into the combustion chamber. This valve may be a flapper, reed, aerodynamic, or mechanically actuated valve. Regardless of the combustor type or valve configuration, oscillating combustion processes are driven by Raleigh’s criterion for sustained oscillatory combustion as postulated by Lord Rayleigh in 1878 [4] [6] [5]. This allows conclusions to be draw about system performance based on the findings of other authors working with thermodynamically similar systems. The supercharged pulsed jet combustor most closely resembles a Helmholtz-type combustor with a mechanically actuated valve.

3.1.1 Thermodynamic Cycle

The pulse combustion cycle as pictured in Figure 3.1 consists of four phases; Ignition and Combustion, Expansion, Purge and Recharge, and Recharge and Compress. After a charge of air and fuel has been drawn into the combustion chamber, ignition and subsequent combustion are initiated by a spark, latent heat of the combustor body, or flamelets remaining from the previous cycle. Air and fuel are shut off, and the rapid increase in pressure causes the hot gas mixture to rapidly evacuate the combustion chamber. The momentum of these gasses creates a low pressure region in the combustion chamber, drawing in a new charge of fuel and air which is then compressed by reflected pressure waves due to the rapid expansion caused by combustion. The process begins again as the newly compressed fuel and air mixture is once again ignited. [5] [6] [12]
Pulse combustors typically operate between 50 and 200 Hz [5] [6]. The length of the thermodynamic cycle of a pulse combustor is typically controlled by the characteristic times required for fuel mixing, exhaust gas mixing, reaction time, and resonant time. These times are functions of body and tailpipe geometry, energy input frequency and timing, and the mass flow rate of fuel and oxidant into the system [4] [13] [14]. In a combustor with a mechanically actuated valve, the actuations of the valve’s opening and closing control combustor frequency. It is important for fuel and oxidant injections to correspond to the time of the lowest system pressure in the combustion chamber. This ensures that the addition of energy due to combustion is in phase with the natural resonant frequency of the system, maximizing the amplitude of the pressure wave thereby maximizing compression ratio, combustion efficiency, and gas velocity [15]. Figure 3.2 compares the waveform of a pulse combustor operating at non-resonant conditions to one operating at its resonant condition. To achieve this resonant condition a pulse
combustor with a mechanically actuated valve must utilize an active feedback mechanism capable of resolving the maximum amplitude of the acoustic signal, allowing air and fuel injection frequency to be matched to combustor frequency [6].

Figure 3.2: a) Non-optimum operation at a non-resonant condition vs b) Operation at the resonant frequency of the combustor, noting the higher maximum amplitude of condition 'b'. [15]
3.2 Pulse Combustion Spray Drying

One possible application of pulse combustors that looks to take advantage of many of the positive aspects of pulsed combustion is pulse combustion spray drying. Some of the key benefits that make pulse combustion an excellent technology of choice for spray drying are that pulse combustors have high combustion efficiency, increased mass and heat transfer, and reduced emissions [5]. Pulse combustion drying takes advantage of the rapidly oscillating pressure and velocity waves found in pulse combustors to aid in droplet breakup, increase the surface available for mass transfer, and stripping the boundary layer of water vapor found on the surface of droplets [5] [2]. These phenomena as seen in Figure 3.3 are accomplished by a

![Figure 3.3: Shearing of the boundary layer of a droplet in the flow of a pulse combustor [2].](image-url)
combination of gas-droplet interaction and sonic drying processes, resulting in atomization of the liquid feed. Atomization is the breakup of a liquid stream into a mist of small, relatively uniform droplets, with the goal of maximizing surface area available for heat and mass transfer [16] [5].

In a conventional atomization process, a high velocity liquid stream is introduced into a stagnant gas region such as a drying chamber. Atomization is due in part to the rapid change in fluid pressure, which is often exaggerated by the inclusion of a spray nozzle. The shear force generated at the boundary of the liquid-gas interface causes the liquid stream to break apart and form tiny droplets [17] [18].

Pulse combustion spray drying instead uses the rapidly fluctuating velocity and pressure waves in its exhaust region along with acoustic effects to atomize a relative slow moving liquid stream [5]. The effectiveness of this atomization is determined by the pressure generated in the combustion chamber, which determines velocity and pressure wave behavior as well as the intensity of the sound waves generated by the process. The Weber number is used to quantify the potential effectiveness of droplet breakup in a gas stream, and is defined as [19]

\[
W_e = \frac{\rho_1 \times u^2 \times r_0}{\sigma} \quad \text{Eq. 3.1}
\]

Here \(\rho_1\) is the liquid density, \(u\) is relative flow velocity between the liquid and gas stream, \(\sigma\) is the surface tension, and \(r_0\) is the initial droplet radius. This dimensionless ratio compares the drag or shear force at the fluid boundary to the surface tension. As the Weber number increases, droplet breakup undergoes various stages of droplet behavior and geometry as dictated by injection orientation and nozzle design. Droplets undergo bag breakup at relatively low Weber numbers, then transition into boundary layer stripping regimes as energy increase. At Weber numbers greater than 350, catastrophic breakup occurs (Figure 3.4) [20] [21].
While the weber number accurately described droplet breakup in steady-state multi-phase fluid systems, a pulse combustor does not have an easily calculable or predictable velocity in a given region due to its oscillatory nature: specifically in the turbulent exhaust regions, the direction of flow can rapidly change direction and magnitude throughout a given cycle. Droplet
breakup in a pulse combustor is a function of both mechanical velocity waves and pressure and acoustic wave interaction utilizing a phenomena known as sonic drying [5]. Sonic drying looks to remove moisture and speed up the drying process with limited increases in temperature [22]. While the exact mechanism of sonic drying is not fully understood, it is thought that in an ultrasonic field, moisture diffusion increases and viscosity decreases due to increases in turbulence, particle interaction, pressure, and boundary layer destruction [23] [24] [5]. It is also theorized that acoustic waves may induce cavitation at the droplet surface, which may release extremely high localized energy, with temperatures at the point of cavitation bubble collapse as high at 5000k and pressures of over 1000 atm in a rapid impulse. Some of these bubbles may evacuate the fluid surface where they instantly vaporize [5].

The presence and magnitude of these effects are dictated by the sound pressure level, sound intensity, and sound power. Sound pressure level is often reported on the decibel scale and is defined as [5]

\[ L_p = 10 \log \frac{P^2}{P_0^2} \]  
Eq 3.2

where \( L_p \) is the sound pressure level in decibels, \( P^2 \) is the sound pressure level in Pascals, and \( P_0^2 \) is the reference sound pressure of 20µPa. The critical sound pressure level at which increased drying rates become apparent in dispersed materials is defined as [5]

\[ P_{cr} = v \times \rho \times \left[ \frac{2.5 \times g \times d \times (C_s - C_g)}{\rho} \right]^{1/2} \]  
Eq 3.3

where \( P_{cr} \) is the critical sound pressure level, \( v \) is the speed of sound in the gas phase, \( \rho \) is the gas density, \( g \) is the gravitational constant, \( d \) is particle diameter, \( C_s \) and \( C_g \) are the water concentrations at the particle surface and in its center respectively.
Although sonic drying alone has many advantages in terms of kinetics and rate of mass transfer of water, in terms of total energy dissipation per kilogram of water removed it is theoretically equivalent to convective drying and in practice may be less efficient [5]. Sonic drying must be coupled with other technologies to take advantage of the kinetic benefits of high energy acoustics. Pulsed combustion spray drying may be considered a sound-assisted dryer as it couples the rate increases as afforded by sonic phenomena with the energetic advantages of pulse combustion spray drying such as high levels of combustion intensity and efficiency [5].

While the phenomena of sonic drying is important to pulse combustion spray drying, the mechanical effects of the pulsed velocity and pressure waves generated by the pulse combustor cannot be overlooked. Pulse combustors operating in the typical range of 20-250Hz and generating pressures of +/- 10 kPa can generate rapidly changing gas velocities of up to +/- 100 m/s, destabilizing droplets and further increasing heat and mass transfer rates [5] [25] [26] [2]. To compare the effects of a pulsating jet flow with a steady jet flow, Dec and Keller compared a pulse combustor to a steady jet of hot air and looked at the resulting Nusselt number, defined as the ratio of convective heat transfer to conductive heat transfer [8]. This dimensionless number is often correlated to the Prandtl and Reynolds numbers as [8]

\[
N_u = 0.023 \times Pr \times Re^{0.8} \times \int_0^1 [1 + B \times \cos(2\pi r)]dr \quad \text{Eq. 3.4}
\]
where $B$ is the ratio of the amplitude of the oscillating velocity to the mean axial velocity in the gas flow. This ratio predicts higher heat transfer efficiencies at higher Nusselt numbers, which was confirmed when pulse combustors outperformed steady jets at constant and similar Reynolds numbers, and produced both greater drying rates and efficiencies as well as higher Nusselt (Figure 3.5).

One unique advantage offered by pulse combustion spray drying is the mechanism of heat transfer. Most other thermal desalination systems use a metallic heating element which transfers heat from the heating element’s surface into the liquid.
being vaporized. Pulse combustion spray drying uses the hot exhaust gas from the pulse combustor to atomize and simultaneously heat the fluid being vaporized. Pulse combustion spray dryer designs may totally eliminate heating element contact with the high salinity brines, greatly decreasing the need for corrosion-resistant materials. Oscillating, turbulent, transient heat transfer found in the exhaust region of pulse combustors is also markedly more efficient as well as more rapid than turbulent non-transient processes of the same temperature and mass flow rate, with 25-30% greater heat transfer intensity (Figure 3.6) [15] [27]. When drying fluids with very high TDS, one must also consider how the buildup of precipitate will affect heat transfer from the heat source to the fluid. With a conductive heating element, salt will precipitate on the surface of the heating element. This causes lower heat transfer efficiency as the scale buildup may act as an insulating layer between the heating element surface and the fluid [28] [29]. It may also be difficult to clean these surfaces, as common remedies to slow corrosion involve expensive coatings such as nickel or zinc which come at a high price and can be damaged by abrasive cleaning [30]. These expensive materials are not entirely effective and represent continued maintenance cost for the lifetime of the drying system. Pulse combustors also operate at relatively low pressures, and the region of vaporization in the drying chamber operates as a relatively low temperature as compared to conventional thermal systems [5] [2]. This means that a drying chamber, which is often coupled to a pulsed combustor, can be constructed of corrosion resistant materials such as thermal plastics rather than much more expensive metals necessary to withstand high temperatures and hold high or low pressure [30]. By eliminating immersed heating elements, these problems are solved by a pulse combustion dryer.

Several operational characteristics of pulse combustors also make pulse combustion spray drying a competitive and appealing technology. Combustion efficiencies of 90-99% are well
documented for pulse combustors [27] [31] [8]. With high efficiencies comes clean, complete combustion, this is in part due to turbulence in the combustion chamber, and results in very low emissions of incomplete combustion products and harmful compounds such as nitrogen oxides and sulfur dioxides [15] [1]. The most important benefit of this combustion efficiency is that when compared to conventional dryers using a variety of designs, pulse combustion dryers may be as much as 40% more efficient [32]. The theoretical energy usage limit for vaporizing 1kg of water is 2.26 MJ/kg plus the energy required to raise the temperature of the water from the inlet temperature to its boiling point. Pulse combustion spray drying has been cited as capable of operating at only 30% more energy than the thermodynamic minimum, making it significantly less energy intensive than other directly comparable technologies, all while maintaining higher flowrates of water being treated [32]. Table 3.1 compares the energy usage of pulse combustion dryers with several types of conventional dryers.
Table 3.6: Comparison of energy consumption per kilogram of water vaporized for various industrial drying systems [2].

<table>
<thead>
<tr>
<th>Dryers</th>
<th>Typical evaporation capacity</th>
<th>Typical consumption (kJ/kg H₂O evaporate)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pulse combustion dryer</td>
<td>250–2000 kg H₂O/h per combustor</td>
<td>3000–3500</td>
</tr>
<tr>
<td>Conventional dryers</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tunnel dryer</td>
<td>–</td>
<td>5500–6000</td>
</tr>
<tr>
<td>Band dryer</td>
<td>–</td>
<td>4000–6000</td>
</tr>
<tr>
<td>Impingement dryer</td>
<td>50 kg H₂O/h m²</td>
<td>5000–7000</td>
</tr>
<tr>
<td>Rotary dryer</td>
<td>30–80 kg H₂O/h m³</td>
<td>4600–9200</td>
</tr>
<tr>
<td>Fluid bed dryer</td>
<td>–</td>
<td>4000–6000</td>
</tr>
<tr>
<td>Flash dryer</td>
<td>5–100 kg H₂O/h m²ᵃ</td>
<td>4500–9000</td>
</tr>
<tr>
<td>Spray dryer</td>
<td>1–30 kg H₂O/h m³</td>
<td>4500–11500</td>
</tr>
<tr>
<td>Drum dryer (pastes)</td>
<td>6–20 kg H₂O/h m²</td>
<td>3200–6500</td>
</tr>
</tbody>
</table>

ᵃ Depends on particle size.
Chapter 3 References


Chapter 4
Research Objectives

The objectives of the research outlined and discussed in this document were to develop a treatment process capable of separating dissolved solids from solution at brine concentrations up to and exceeding saturation limits and to characterize the energy efficiency and degree of salt-water separation achievable by the system. Characterization looked to predict system behavior in an effort to aid in the design and operation of a full-scale industrial unit.

Research on this topic began at Furness-Newburge Inc. of Versailles, Kentucky with the design and manufacture of the first supercharged pulsed jet combustor. It was proposed by Fred Cannon and Jim Furness that novel phenomena in the exhaust gas region of the supercharged pulsed jet combustor could separate salt molecules from solution through ultrasonic interaction and mechanical shearing rather than just the addition of thermal energy. This hypothesis, which resembles the documented phenomena of sonic drying, was the basis for initial testing which focused on dewatering of clays and drilling muds used in the foundry and hydrofracturing industry. With initial testing deemed promising, Dr. Fred S. Cannon and the author began testing at the Versailles, Kentucky facility of Furness-Newburge Inc.

Funding was provided for by the National Science Foundation under an Early-concepts Grant for Exploratory Research, Ben Franklin Northeast, Ben Franklin Central, and Hydro Recovery LP. These grants look for technology that is not only innovative, but will impact industry, create jobs, and bolster the economy. Focus on the hydrofracturing industry led to the testing of high strength brines previously not often considered in desalination technologies due to the large number of complications extreme salinity introduces. Developing a flexible, low capital
cost technology will allow small companies to respond to the constantly changing demand of the dynamic, rapidly progressing hydrofracturing industry.

Specific objectives of this research were to:

1) Test and prove the concept of salt-water separation using the supercharged pulsed jet combustor.

2) Analyze the thermodynamics of the system, including possible undocumented phenomena in the hot gas exhaust stream.

3) Develop a robust and cost effective technology for industry implementation.

4) Test an air sparging system coupled with the supercharged pulsed jet combustor for the removal of methanol from flowback and produced waters.

Chapter 5 focuses on objective 1, showing preliminary data and documenting qualitative observations about the system while operating at the facilities of our development partners in Versailles, Kentucky. This allowed us to develop testing methods and improve some aspects of the system such as fluid injection and heat exchange.

Chapters 6 and 7 discuss system setup, testing procedures, and system performance with the goal of completing objectives 2 and 3 by characterizing the thermodynamics of the system and subsequently developing a process useful to industry by predicting salt separation performance of the system.

Chapter 8 discusses the results and the direction of future research, as well as possible improvements to the system. In the immediate future a pilot-scale supercharged pulsed jet combustor will be in operation at an industrial treatment facility.
Appendix A contains data related to the development and testing of an air sparging system for the removal of high concentrations of methanol from hydrofracturing flowback and produced water using a bubbled reactor. This technology may be coupled with the supercharged pulsed jet combustor, adding an additional fuel source as well as preventing the release of methanol into the air.
Chapter 5

Proof of Concept

In August of 2013 through March 2014, initial testing of the supercharged pulsed jet combustor was conducted at the facilities of Furness Newburge Inc. of Versailles, Kentucky. Testing focused on observing and characterizing combustor behavior, fluid atomization, and salt precipitation and collection. As a proof of concept, fluids of various compositions were introduced into the exhaust region of the supercharged pulsed jet combustor and favorable vaporization and droplet breakup were observed. Successfully processed fluids included hydrofracturing muds, flowback water provided by Hydro Recovery LP, and a salt brine mixed from halite rock salt.

The initial hypothesis and driving force of this project was to discover how the fluctuating pressure and velocity regions of the supercharged pulsed jet combustor enhanced the drying process and facilitated salt-water separation. The phenomena of sonic drying proposes that a combination of surface cavitation, mechanical separation, and boundary layer disruption yields enhanced mass transfer rates due to sonic energy measured as sound pressure, sound intensity, and sound power [1]. Indeed many researchers have found enhancements of heat transfer, mass transfer, and drying rates in pulse combustors used as dryers, however exact mechanisms remain speculative, and further investigation is required to understand this phenomena. [1] [2] [3] [4]

During the first tests, the system was run with flowback hydrofracturing stimulation fluid provided by Hydro Recovery LP. Subsequent solids analysis showed a total inorganic dissolved solids concentration of 11.72% by mass. The research team was focused on observing
atomization and vaporization in the exhaust gas region of the supercharged pulsed jet combustor, so in the initial experiments no collection system was utilized. Various nozzle and fluid injection configurations were evaluated, and spray patterns were observed so as to develop a sense of spray intensity and vaporization efficiency at various system configurations and fluid flow rates. High levels of vaporization were observed, and salt precipitation on screens positioned parallel to hot gas flow in the exhaust region was documented as pictured. Fuel was supplied by 35 lb. propane cylinders and air was supplied by a diesel powered air compressor.

The next round of testing involved firing the supercharged pulsed jet combustor into a shed lined on the outside with fiberglass insulation and hooked into a high-flow fan and duct system designed to draw moisture out of the shed. A nozzle pattern known colloquially as the “duck bill” was utilized as the most promising from previous tests. The duck bill consisted of a $\frac{1}{4}$” diameter tube with a cut 45 degrees from parallel to the length of the tube, and with a 45 degree bend to introduce the fluid into the hot gas region with a large surface area relative to the diameter of the tube. The exhaust system did not function as intended due to seal malfunctions, but energetics were quite good, with 90% of the fluid either vaporizing or being entrained in the air at 1.5 gallons per minute of fluid flow. This number represents a vaporization performance of 0.49 MJ/kg, 80% lower than the theoretical minimum energy needed to raise the temperature and vaporize 1.5 gallons per minute of water. Subsequent testing found that this number was not necessarily indicative of vaporization performance, but rather showed how the droplets could be finely atomized by the pulse jet. The distinction being that during vaporization, a phase change separates salts from water whereas atomization maintains liquid droplets without phase change or salt-water separation.
A subsequent test utilized a toroidal nozzle constructed from a section of pipe that was bent into a circle. 1/16” holes were drilled at set intervals and angled in towards the exhaust. These holes acted as an array of spray nozzles. This allowed the fluid to be injected into a broad regions of the exhaust gas, maximizing fluid distribution and surface area. Excellent droplet breakup and atomization were observed with this nozzle, but it was perceived that this type of nozzle would very quickly clog under high salinity conditions or in the presence of particulate matter.

Screens were placed into the exhaust region as a site for salt crystal nucleation and growth. One screen approximately 2’ high by 4’ long was placed on each side of the supercharged pulsed jet combustor. The screen on the left side of the system as seen from the outlet of the combustor was backed by a metal plate, and grounded to an earth ground. The metal plate, as shown in Figure 5.1 was anchored to the side of the stand the supercharged pulsed jet combustor was mounted on and allowed to interact with the fluctuating conditions in the exhaust gas region, serving as a witness plate to characterize exhaust gas behavior. Salt precipitated in a

![Figure 5.1: Salt precipitation pattern along a witness plate placed parallel to the flow of the exhaust region of the supercharged pulse jet combustor](image-url)
specific pattern on its surface. Regions of salt precipitate and water droplet nucleation were actively observed during tests. Later tests were run with the intention of creating a dry spot on the witness plate to recreate and observe this same effect.

During further tests salt precipitated indiscriminately on any surface within approximately 2.5 feet (0.76 m) of the exhaust gas region regardless of surface material (Figure 5.2). Attraction due to charge does not seem to be the dominant factor in salt nucleation. When observed under a microscope, every observed salt crystal had a small particle at its center serving a nucleus of growth. Crystals quickly pulled moisture from the surrounding air and returned to a salt paste.

Figure 5.2: Salt precipitation onto the surface of a screen placed parallel to the exhaust of the supercharged pulsed jet combustor and backed by the witness plate.
Another test was performed on a solution of bentonite clay in water with a bentonite mass concentration of 12%. Bentonite was collected in a concentrated slurry as well as in a dry paste (8% water by mass) on a screen array in the exhaust region of the supercharged pulsed jet combustor. This test was in part an attempt to determine if the system was capable of processing viscous slurries. Pulse combustors have been shown to be an effective means of drying a wide variety solutions ranging from fecal matter to pharmaceuticals [6] [7].

Throughout testing performed in Kentucky, approximate mass balances were performed to gauge relative performance between various system configurations in an attempt to optimize running conditions. These tests were not equipped with careful quantitative flow tracking or a solid control volume, so researchers utilized average mass flow rates as determined by manual timing and mass collection using various tarps and buckets. These tests, while not rigorously quantitative, served to show that the supercharged pulsed jet combustor operated within the thermodynamic range of similar pulse combustion systems [8] [9]. These results are presented in Table 5.1.
Table 5.7: Comparison of system performances of the supercharged pulsed jet combustor as calculated by mass balance without the aid of flow tracking or a control volume. Data was used to compare relative performance numbers and draw simple conclusions about optimum run conditions.

<table>
<thead>
<tr>
<th>Date</th>
<th>Propane Flow Rate (lb/min)</th>
<th>Fluid Flow Rate (gpm)</th>
<th>(kg/min)</th>
<th>% fluid collected</th>
<th>System Performance (MJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9/21 - Early Testing</td>
<td>0.12</td>
<td>1.5</td>
<td>5.69</td>
<td>10%</td>
<td>0.49</td>
</tr>
<tr>
<td>11/15 - 4.1</td>
<td>0.18</td>
<td>0.16</td>
<td>0.61</td>
<td>40%</td>
<td>10.41</td>
</tr>
<tr>
<td>11/15 - 4.2</td>
<td>0.18</td>
<td>0.75</td>
<td>2.84</td>
<td>70%</td>
<td>4.44</td>
</tr>
<tr>
<td>11/15 - 4.3</td>
<td>0.12</td>
<td>0.38</td>
<td>1.44</td>
<td>43%</td>
<td>3.08</td>
</tr>
<tr>
<td>11/15 - 4.4</td>
<td>0.165</td>
<td>0.68</td>
<td>2.58</td>
<td>41%</td>
<td>2.28</td>
</tr>
<tr>
<td>11/15 - 4.5</td>
<td>0.164</td>
<td>0.97</td>
<td>3.68</td>
<td>54%</td>
<td>2.04</td>
</tr>
<tr>
<td>11/15 - 4.6</td>
<td>0.18</td>
<td>1.05</td>
<td>3.98</td>
<td>57%</td>
<td>2.21</td>
</tr>
<tr>
<td>11/15 - 4.7</td>
<td>0.155</td>
<td>0.68</td>
<td>2.58</td>
<td>68%</td>
<td>3.95</td>
</tr>
<tr>
<td>11/15 - 4.2.1</td>
<td>0.15</td>
<td>0.25</td>
<td>0.95</td>
<td>55%</td>
<td>7.40</td>
</tr>
<tr>
<td>11/15 - 4.2.3</td>
<td>0.15</td>
<td>0.25</td>
<td>0.95</td>
<td>23%</td>
<td>4.33</td>
</tr>
<tr>
<td>11/15 - 4.2.4</td>
<td>0.15</td>
<td>0.18</td>
<td>0.68</td>
<td>25%</td>
<td>6.17</td>
</tr>
<tr>
<td>11/15 - 4.2.5</td>
<td>0.15</td>
<td>0.18</td>
<td>0.68</td>
<td>8%</td>
<td>5.03</td>
</tr>
<tr>
<td>3/28 - r3</td>
<td>0.2</td>
<td>0.7</td>
<td>2.65</td>
<td>46%</td>
<td>2.91</td>
</tr>
<tr>
<td>3/28 - r4</td>
<td>0.2</td>
<td>0.7</td>
<td>2.65</td>
<td>50%</td>
<td>3.17</td>
</tr>
</tbody>
</table>
Testing at Furness-Newburge Inc. of Versailles, Kentucky showed that the supercharged pulsed jet combustor is capable of separating salts from water at high salt concentrations as well as drying viscous slurries of bentonite clay, all while remaining within reasonable thermodynamic energy consumption levels as compared to existing pulse combustion systems. Atomization of the fluid stream by high velocity exhaust gasses as well as salt precipitation onto surfaces in the fluctuation velocity and pressure region were also observed. The conceptual framework for continued testing was well established.
Chapter 5 References


Chapter 6

Materials and Methods

Testing of the supercharged pulsed jet combustor on Penn State’s campus took place at the High Pressure Combustion Lab under the supervision of Dr. Eric Boyer, Dr. Andrew Cortopassi, and Dr. Fred S. Cannon, with advice from Dr. Kenneth Kuo. Initial testing focused on troubleshooting and instrumenting the system to more accurately predict and understand its behavior. While testing performed in Kentucky served to establish the general capabilities of the system, testing at the Penn State facility looked to quantify and explain the phenomena involved in pulsed combustion drying. Initial testing attempted to replicate results found in Kentucky using metal mesh screen arrays. Further testing quantified system performance on the basis of energy and mass balances. These tests provide the basis for the thesis herein.

6.1 System Setup, Materials, and Procedure

The complete supercharged pulsed jet combustor system consisted of the pulse combustor body, a mechanically actuated rotating valve, a helical coiled heat exchanger coupled to the body of the combustor, and a peripheral control system controlling valve rotation speed. LabView software was used to control the rotational speed of the valve and to track temperatures and mass flow rates in the system. Thermocouples were added to the fluid lines and placed onto the body of the combustor to monitor surface temperatures. Air was supplied from tank pressurized by a 125 HP compressor. The compressor was run to fill the tanks to the desired pressure (typically 120psi). This pressurized air was then introduced into the intake of the mechanical valve as controlled by a ball valve located in the control room. Pressure and volumetric flow rate gauges were used to track mass flow rates of air to the system. 100lb
propane tanks were used as a fuel source and fed into the air line where mixing was facilitated by an orifice plate design. Combustion was initiated by a spark plug located at the top of the combustion chamber 3 inches from the end cap. Current was delivered to the spark plug by a rotating magneto attached to a flywheel which rotated in sync with injections of air and fuel as controlled by the mechanical valve. Operational frequencies ranged from 120 to 150 Hz as dictated by the voltage supplied to the motor by the control software. Brines were injected by 2 diaphragm pumps each with a maximum flow rate of 0.5 gallons per minute. Fluid was drawn out of 5 gallon buckets, which sat on a digital scale and provided constant feedback to the computer for mass flow rate analysis. Propane tanks were stored on a separate scale and mass changes were read at the beginning and end of each test to determine an average propane mass flow rate.

During a given test, the combustor was turned on and allowed to run until combustor body temperature readings indicated that the system was running at steady-state conditions with respect to temperature. Thermocouples located on the outside skin of the combustor at the back, combustion chamber, mid body, and at the end provided constant temperature feedback to the operator. Fluid was then pumped through the system and fluid temperatures were monitored to ensure no boiling occurred in the heat exchanger. During preheating fluid flowed out an exhaust line that bypassed the nozzle and control volume to maintain mass balance integrity. Once the fluid reached temperatures ranging from 90 to 100°C, a ball valve was turned allowing the fluid to flow out of the heat exchanger through the nozzle and into the hot gas region. Fluid was then either collected by the control volume or released into the air as vapor. Figure 6.1 shows a process diagram of the system.
6.2 Fluid Injection and Salt Collection Systems

The current supercharged pulse jet combustor system is an open air system. As an inherent limitation, this system did not allow for the installation of an enclosure that would have allowed the addition of a gas phase analysis to complete the system mass balance. While the liquid and solid streams were of major concern to the project, a fully enclosed control volume for the system has been developed and is being prepared for implementation at the pilot scale.

6.2.1 Salt and Fluid Collection

To perform a comprehensive mass balance of the system, a circular polypropylene container measuring 5 feet in diameter with a 1 foot wall height was placed at the outlet of the
eductor to capture liquid phase fluid being discharged by the supercharged pulsed jet combustor. Visual inspection confirmed that considerable fluid mass was not escaping the control volume and collected fluid represented the majority of liquid phase water output by the system. A 5 gallon bucket was placed on the combustor side of the eductor to capture any fluid that may be ejected from the back of the eductor due to turbulence. Both containers were weighed pre and post testing to account for all non-gas phase fluid mass. Early tests utilized metal mesh screens as a surface for salt crystallization, with balances focusing primarily on percent salt mass collection and energy usage.

TDS testing was used as a metric for salt concentration in brines. TDS testing was conducted by drawing a 10 ml sample of fluid into a 20mL disposable plastic pipette and drying that sample at 90°C for 12 hours, then 220°C for up to an hour to drive out any water that may have been trapped in the salt’s crystal structure. For all tests, background concentrations of TDS represented less than 0.05% of TDS and were therefore ignored in calculations.

6.2.2 Nozzles and Fluid Injection

Various fluid injection systems were explored for both performance enhancement and feasibility. Some of the early fluid injection systems were discarded due to inherent limitations of the system, such as pressure buildup in the heat exchanger or crystallization of salt in the injection lines. A ‘pigtail’ spray nozzle with an internal diameter of 0.25 inches was selected as it allowed adequate fluid to pass through the nozzle to prevent vaporization in the heat exchanger, did not clog or foul with precipitated salt, and provided a wide spray angle and primary atomization. Other injection systems used in testing served a specific function detailed in methods related to those tests. Unless otherwise specified, the pigtail nozzle was used for all tests.
Early tests experienced clogging and fouling in the heat exchanger due to steam pressure buildup. Many of the nozzles used during this time did not have openings of adequate size, creating too much head loss for the pump to overcome, which allowed salt to precipitate out of solution in the fluid lines. To overcome this issue and to aid in mass balance accuracy, a 1/2” pipe was bent into a downspout configuration. This nozzle was large enough to prevent pressure buildup and it directed liquid flows into the control volume, minimizing splashing and fluid loss. This nozzle configuration also allowed tests to be developed to analyze and quantify hot exhaust gas phenomena at the outlet of the supercharged pulsed jet combustor, by directly comparing system performance while utilizing the hot exhaust gas versus not utilizing the hot exhaust gas. Figure 6.2 illustrates the downspout configurations used during these tests.

![Figure 6.2: Downspout nozzle configuration during tests comparing system performance while A) utilizing the coiled body heat exchanger and hot gas exhaust and B) utilizing only the coiled body heat exchanger and no exhaust gas phenomena.](image)

As pictured in Figure 6.3, a front end coiled tube heat exchanger was also used in place of the downspout nozzle during energy balance testing. This nozzle utilized thermocouples at each end of the coiled heat exchanger to measure fluid temperature and was placed into the hot exhaust gas region of the supercharged pulsed jet combustor. This allowed the exhaust gas to flow through the center of the coil, heating the metal coil and transferring that heat to the fluid
inside. This established a lower boundary for available heat energy in the hot gas and allowed for the comparison of relative effectiveness of heat transfer between a) turbulent hot gas phenomena and b) a coiled tube heat exchanger with no fluid-fluid interaction. Energy values were determined by multiplying the mass flow rate of fluid through the heat exchanger by the enthalpy of that fluid at the temperature measured by the thermocouple. Temperature data was read into the data acquisition system and recorded into a universal data file, which could then be compared to time and flow data taken concurrently to determine exact temperatures and flow rates during any given test. Figure 6.4 shows the locations of thermocouple reading taken by the system and Figure 6.5 shows the front end coil heat exchanger as it was mounted on the combustor.

*Figure 6.3: Front end coil heat exchanger and mounting pipe array.*
Figure 6.4: Process diagram showing the location of thermocouples during front end coil testing

Figure 6.5: Front end coil heat exchanger as mounted to the supercharged pulsed jet combustor and prepared for testing with thermocouples installed.
6.2 Eductor

An eductor (sometimes called an ejector) is a simple type of flow routing nozzle often used in propulsion augmentation to increase thrust. Increased mass flow rates of air through the eductor are achieved when the hot exhaust gas passing through the eductor draws in surrounding air [1]. Mass flow rate of gas exiting the eductor may be as much as double the mass the flow rate of gas entering the eductor from the combustion tailpipe alone [2]. Given a constant cross section, this increases the velocity and subsequently turbulence of the gas in this region. As discussed in the literature review, turbulence is a major component of enhanced drying efficiency; and the increased mass flow rate of air provides a greater total water vapor transport capacity. The eductor also provides longer residence time of the fluid in contact with the hot gas as compared to the downspout fluid ejector. The combination of eductor and pigtail nozzle as seen in Figure 6.6 provided readily apparent increases in efficiency, with energy performance values as low as 4.6 MJ/kg as compared to 5.6 MJ/kg with only the downspout nozzle.
During tests using the maximum air and fuel flow rates (30 scfm air, 1.1 scfm propane) recirculation vortices were visible along the bottom edge of the eductor, showing both air entrainment and brine circulation. Fluid that would have exited out the back of the eductor was instead drawn back into the eductor and ejected out the end. Brine was also distributed over the surface of the eductor, increasing contact area and increasing the mass transfer rate of water to the gas phase.

Typical tests involved from 30 minutes to 3 hours of setup and preparation and between 10 and 40 minutes of combustor operation. Data were collected for between 5 and 30 minutes,
encompassing the combustor body and fluid preheating phase, the start of fluid introduction into the exhaust gas region, and the end of testing. At the completion of testing, temperature, valve frequency, mass flow rate, and total collection data were taken from LabView and read into an Excel file for evaluation. Equivalence ratio, fluid flow rate, water vapor flow rate, and salt collection were computed based on this recorded data. These data were documented and saved for each run. Process procedure and safety protocols are on file at the High Pressure Combustion Lab.

6.3 Calculations

A power and heat balance for the system was conducted by looking at energy transfer per unit time in the system (Figure 6.7). Propane energy input represents the mass flow rate of propane as measured by mass difference during a test divided by the time of that test multiplied by the lower heating value of propane (46.9 kJ/g). Typical tests used between 0.064 and 0.095 kg/min of propane. The lower heating value represents the heat generated through complete combustion of a fuel, not accounting for energy recovery by steam condensation of the resulting water molecules. This is the appropriate value for our tests as currently no steam energy recovery system is in place. The energy input due to compressed air was calculated by multiplying the power usage rate of the compressor by the time needed to operate the compressor to supply adequate air flow during a test. This value ranged between 3 and 6 kW. The theoretical value for completely efficient adiabatic compression was between 1.15 and 2.3 kW. Power input by the fluid pump and the motor controlling the rotating valve was calculated based on the horsepower ratings of each. Steam power output was calculated by assuming a temperature of 100°C and multiplying the mass flow rate of steam by the enthalpy of steam at that temperature. The liquid stream similarly used enthalpy of liquid water at 100°C multiplied by the mass flow rate of the
liquid phase. Combustion product power was calculated by taking a thermocouple reading at the outlet of the combustor at steady state during a test and multiplying by the mass flow rate of CO$_2$ and H$_2$O. Mass flow rates of CO$_2$ and H$_2$O were calculated by taking the mass flow rate of propane and oxygen to the system and assuming the limiting reactant was completely consumed. Using stoichiometric relationships mass flow rates for both CO$_2$ and H$_2$O were determined using the equation

$$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(g).$$  

Eq. 6.1

While this number will vary with equivalence ratio, and the thermocouple reading is only an average temperature and is subject to error due to spatial variation in temperature, combustion products account for only around 10% of the energy output of the system. Thermocouples placed along the body of the combustor recorded skin temperatures of the combustor, but due to extreme heat in the combustion chamber, interference from the heat exchanger and insulation, and variations in the wall thickness throughout the combustor, calculating a total heat output of the combustor was not attempted. A high temperature thermocouple and a bare combustor body would have been required to calculate this value, so it was found by difference after accounting for all other modes of energy loss through the system.

Power input from the pump and the motor were calculated directly from the horsepower ratings of each unit. Power from the motor was reduced as a function of total voltage sent to the motor as compared to the total voltage rating of the motor. This accounts for the fact that the motor was not operating at its maximum horsepower at all times. Regardless of the accuracy of this correction factor, the total possible power usage of the motor was slightly less than 1% of the total input energy.
To calculate the air mass flow rate into the system, an empirical equation as given by the manufacturer of the air volumetric flow meter was compared to the mass flow rate of propane as calculated by the fundamental thermodynamic equation

$$\frac{PV}{t} = \frac{n}{t}RT$$  \hspace{1cm} \text{Eq. 6.2}

where $P$ is the pressure of the gas, $\frac{V}{t}$ is the volumetric flow rate of the gas, $\frac{n}{t}$ is the molar flow rate of the gas, $R$ is the universal gas constant, and $T$ is the temperature of the gas. The temperature of the gas was assumed based on the ambient outdoor temperature, as the storage tanks holding the air were located outside and the gas had adequate time to equilibrate with the air. Values from the empirical equation were found to correspond very closely to the theoretical values, so the theoretical values were used to determine a molar flow rate of air to the system. Oxygen molar flow rate was then calculated by multiplying by the molar fraction of oxygen in air.
Chapter 6 References


Chapter 7

System Performance

System performance evaluation of the supercharged pulsed jet combustor centered on quantifying thermodynamic output and efficiency of the system. Tests monitored overall energy input and output of the system, the heat transfer from the body of the combustor to the fluid and from the hot exhaust gas to the fluid. This energy and mass balance was performed using strategically placed thermocouples and flow meters. Mass flow rate analysis tracked propane use within the combustor, monitored equivalence ratio, and established a mass balance that allowed the calculation of energy use per unit mass or water vaporized as well as salt collection percentages.

7.1 Performance Evaluation by Control Volume Mass Balance

In overview, under favorable conditions the supercharged pulse jet combustor was capable of processing a 12.5% by mass (135,000 mg/L) salt solution operating at 4.14 MJ of input energy in the form of propane per kg of water vaporized and a brine flow rate 0.56 GPM while collecting 94% of the salt in a simple polypropylene control volume, running at a fuel equivalence ratio of 0.883 at an ambient temperature of 35°F. No correlation between system performance and salt concentration across the entire spectrum of solubility has thus far been observed, so it is safe to conclude that similar vaporization performance can be expected at salt concentrations at and exceeding saturation. More favorable energetics have been observed (as low as 4 MJ/kg), but a tradeoff between fluid flow rate, percent vaporization, and salt collection influences optimum run conditions. Fluid collection was used as a metric to complete a mass balance showing fluid loss to vaporization.
The results of these tests are presented in Figures 7.1 through 7.4 and Table 7.1. During these tests the supercharged pulsed jet combustor was operated at brine flow rates ranging between 0.22 and 0.64 GPM, propane mass flow rates of 0.06 and 0.091 kg/min, air flow rates of between 25 and 33 scfm, ambient temperatures of between 28 and 60°C, and valve frequency of between 125 and 165 Hz. While operating at a flow rate of between 4.3 and 5.6 GPM and an equivalence ratio of 0.85 to 0.95 MJ/kg the open-air control volume collected between 75 and 97% of the salt input into the system. The most favorable results occurred when utilizing an eductor to increase total mass flow rate through the exhaust gas region and a large pigtail nozzle to improve atomization and fluid delivery.

A strong correlation between the volume of water captured and salt collection was observed (Figure 7.1). It was seen that the majority of salt precipitation occurred in the exhaust region of the supercharged pulsed jet combustor where particle velocity, temperature, and turbulence were highest. This caused temporary entrainment of fine salt particles into the air, which were observed settling on surfaces outside of the current control volume in very small quantities. The precipitate resembled a very fine dusting of powder. This initially raised concerns related to air emissions standards for particulate matter. By simply operating the supercharged pulsed jet combustor at higher flow rates, salt collection percentages were maintained at greater than 90% collection with collection percentages greater than 95% occurring regularly. This increase in salt collection may be due to the presence of excess water droplets in the eductor, which could act as a wet scrubbing system, capturing fine salt particles that would otherwise be entrained into the air. Salt collection percentages were heavily a function of peripheral systems at the outlet of the pulse jet. Current numbers are based off of an open system with no gas phase containment. Preliminary results from the newest generation pilot-scale system indicate that the
inclusion of a baghouse particle control system may further improve salt collection percentages for the system. This data was not included as it related to a peripheral system and not directly to the performance of the supercharged pulsed jet combustor itself and is therefore outside the scope of this work.

Figure 7.1: Salt Collection as a function of fluid collected in the control volume for tests utilizing the large pigtail nozzle and eductor using a 12.5% by mass brine.

Salt collection, when compared directly to brine flow rate exhibited the most obvious and strongest correlation (Figure 7.1). This metric does not take into account the performance of the system and looks only at the amount of salt collected as a fraction of the total salt processed during a test and the total mass flow rate of brine into the system. While there is no immediately obvious correlation, brine flow rates above 0.44 GPM all produced salt collection percentages equal to or greater than 94% except for one test which was the final test run on 4/15. During this test, the temperature of the fluid was allowed to rise too high in the heat exchanger, and salt precipitated out in the line, causing salt to become trapped in the heat exchanger and not accounted for in the salt mass balance.
Figure 7.2: Salt collection percentage as compared to total brine flow rate during runs using the eductor and large pigtail nozzle.

Fuel equivalence ratio was used as a metric to compare fuel and air consumption between runs and observe how the equivalence ratio effects overall system performance. Fuel equivalence ratio ($\varphi$) is a measure of the measured fuel-to-air ratio over the stoichiometric fuel to air ratio.

$$\varphi = \frac{\frac{m_{\text{fuel}}}{m_{\text{air}}}}{\frac{m_{\text{fuel}}}{m_{\text{air}}}}$$

Eq. 7.1

Initial tests simply employed an equivalence ratio that allowed for steady combustion with none of the ‘popping’ or ‘sputtering’ that occur at the limits of either fuel or air introduction. Later tests were able to utilize mass flow rates to look at how equivalence ratio changed between runs and at different operating conditions. Pulse combustors typically operate at equivalence ratios ranging from 0.95 to 1.10, with the majority operating below 1.0 [1] [2] [3]
This is preferred as the presence of excess air not only allows for complete combustion of the fuel but helps prevent the formation of hazardous products of incomplete combustion [5] [2]. Others assert that the optimum operational equivalence ratio for a pulse combustor is 1 [6]. Many of these studies were focused on developing thrust and optimum thrust/fuel ratios which does not necessarily correlate with increased heat transfer, drying, and desalination performance. Consequently a wide range of equivalence ratios were tested using the supercharged pulsed jet combustor.

Testing was conducted using various ‘splash plate’ configurations, a plain tube with a threaded rod through its center, a large pigtail spray nozzle (inner diameter 3/16”) and a small pigtail spray nozzle (inner diameter 1/16”). Splash plates were conical and hemispherical-shaped metal objects placed in such a way as to spread the flow of water being injected into the eductor over a larger surface area. The eductor was utilized in all of these tests.

The small pigtail nozzle provided excellent primary atomization and very evenly distributed the brine, maximizing surface area for heat and mass transfer in the exhaust region of the supercharged pulsed jet combustor. Pressure buildup and salt nucleation caused undesirable back pressure in the heat exchanger due to the very small inner diameter of the small pigtail nozzle prompting the switch to the large pigtail nozzle. The large pigtail nozzle provided adequate droplet breakup while also preventing vaporization and pressure buildup in the heat exchanger. The large pigtail nozzle out performed all other tested fluid injection systems and operated within vaporization performance ranges similar to the small pigtail nozzle. In the equivalence ratio range of 0.76-0.95 no appreciable difference in performance was observed between small pigtail and large pigtail nozzle configuration tests.
It can be observed in Figure 7.3 that as equivalence ratio decreased from 1.25 to 0.84, system performance generally increased. This is not entirely intuitive because an equivalence ratio of 1 represents the exact stoichiometric ratio of fuel to oxidant needed for complete combustion to occur. At equivalence ratios greater or less than 1 there is either incomplete combustion or excess oxidant. What we found, however, was that forcing more air through the system than was needed to combust the fuel, we were able to increase the mass flow rate of hot air leaving the system, enhancing the effects of turbulence and convective heat transfer in the exhaust regions. The lowest equivalence ratio at which the combustor continues to operate is dictated by the geometry reaction kinetics, and thermodynamics present in the combustor. At equivalence ratios below approximately 0.83, the combustor will simply no longer operate. The single data point at an equivalence ratio of 0.68 is most likely due to an error reading one of the flow rate tracking meters, as subsequent attempts to operate the combustor at this equivalence
ratio have failed. The range of equivalence ratios represented in these data is representative of the range of operable conditions. Pulse jet behavior outside of upper and lower equivalence ratio limits is not well understood.

The standard deviation for system performance as measured in MJ/kg for tests involving a pigtail nozzle and operating at equivalence ratios between 0.852 and 0.970 is 0.88, with a mean of 4.88 MJ/kg. These data include two points with equivalence ratios above 6 MJ/kg. During one of these tests, the center of the diameter of the eductor was not in line with the center of the pulse jet, causing flow to impact the walls of the eductor prematurely. This may explain the drop in performance between the two nearly identical tests run on 4/15. Upon further investigation, the second test that registered above 6.38 MJ/kg had a starting body temperature of around 250°C whereas all other tests had an average starting body temperature of around 300°C. Running the combustor until a consistent, high steady state temperature has been achieved is important for system performance. With these two data points removed, the standard deviation and mean become respectively 0.368 and 4.51 MJ/kg. By standardizing the type of nozzle used to introduce flow to the eductor, not only was system performance significantly improves, the standard deviation among the relevant sets was greatly reduced; from 2.06 MJ/kg to 0.368 MJ/kg.
Table 7.8: Performance, equivalence ratio, and temperature data for tests run using the eductor and various fluid injection systems. All tests with salt collection values utilized a 12.5% by mass brine.

<table>
<thead>
<tr>
<th>Fluid Flowrate (GPM)</th>
<th>Date</th>
<th>Performance (MJ/kg)</th>
<th>Equivalence ratio</th>
<th>Ambient Temperature (°F)</th>
<th>Nozzle</th>
<th>Salt Collection</th>
<th>Fluid Collection</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.576</td>
<td>11/20/15</td>
<td>4.00</td>
<td>0.83</td>
<td>28°F</td>
<td>Small pigtail</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.644</td>
<td>12/09/15</td>
<td>4.55</td>
<td>0.89</td>
<td>34°F</td>
<td>Small pigtail</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.303</td>
<td>11/11/15</td>
<td>5.70</td>
<td>1.19</td>
<td>53°F</td>
<td>Plain Tube</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.226</td>
<td>11/11/15</td>
<td>6.62</td>
<td>1.24</td>
<td>53°F</td>
<td>splash plate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.251</td>
<td>11/11/15</td>
<td>6.70</td>
<td>1.19</td>
<td>53°F</td>
<td>splash plate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.32</td>
<td>10/30/15</td>
<td>10.80</td>
<td>1.24</td>
<td>44°F</td>
<td>splash plate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.231</td>
<td>10/30/15</td>
<td>11.03</td>
<td>1.24</td>
<td>44°F</td>
<td>splash plate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.408</td>
<td>01/12/15</td>
<td>4.62</td>
<td>1.14</td>
<td>30°F</td>
<td>large pigtail</td>
<td>68%</td>
<td>85%</td>
</tr>
<tr>
<td>0.439</td>
<td>01/12/15</td>
<td>5.10</td>
<td>0.97</td>
<td>30°F</td>
<td>large pigtail</td>
<td>96%</td>
<td>39%</td>
</tr>
<tr>
<td>0.418</td>
<td>03/27/15</td>
<td>6.37</td>
<td>0.88</td>
<td>35°F</td>
<td>large pigtail</td>
<td>89%</td>
<td>67%</td>
</tr>
<tr>
<td>0.56</td>
<td>03/27/15</td>
<td>4.14</td>
<td>0.88</td>
<td>35°F</td>
<td>large pigtail</td>
<td>94%</td>
<td>63%</td>
</tr>
<tr>
<td>0.455</td>
<td>03/27/15</td>
<td>4.80</td>
<td>0.90</td>
<td>35°F</td>
<td>large pigtail</td>
<td>97%</td>
<td>76%</td>
</tr>
<tr>
<td>0.51</td>
<td>4/1/2015</td>
<td>5.36</td>
<td>0.68</td>
<td>38°F</td>
<td>large pigtail</td>
<td>97%</td>
<td>71%</td>
</tr>
<tr>
<td>0.43</td>
<td>4/1/2015</td>
<td>4.42</td>
<td>0.85</td>
<td>38°F</td>
<td>large pigtail</td>
<td>80%</td>
<td>53%</td>
</tr>
<tr>
<td>0.476</td>
<td>4/1/2015</td>
<td>4.14</td>
<td>0.95</td>
<td>38°F</td>
<td>large pigtail</td>
<td>75%</td>
<td>50%</td>
</tr>
<tr>
<td>0.346</td>
<td>4/15/2015</td>
<td>4.68</td>
<td>0.85</td>
<td>60°F</td>
<td>large pigtail</td>
<td>79%</td>
<td>45%</td>
</tr>
<tr>
<td>0.523</td>
<td>4/15/2015</td>
<td>6.68</td>
<td>0.89</td>
<td>60°F</td>
<td>large pigtail</td>
<td>94%</td>
<td>70%</td>
</tr>
<tr>
<td>0.438</td>
<td>4/15/2015</td>
<td>4.79</td>
<td>0.85</td>
<td>60°F</td>
<td>large pigtail</td>
<td>87%</td>
<td>61%</td>
</tr>
</tbody>
</table>
Higher brine flow rates yielded higher percent energy recovery in the heat exchanger and in the hot gas exhaust (Figure 7.4). This may have been due to a greater temperature differential between the brine and the walls of the heat exchanger and exhaust gas, yielding more rapid heat transfer. As brine flow rates increase, some percentage of the energy recovered from the combustor is spent on heating the fluid (4.2 kJ/kg K). The majority of the energy recovered is used to change the phase of the fluid (2.26 MJ/kg), meaning the higher the brine flow rate, the larger the energy flux into the plastic control volume. If this energy is not recovered through heat exchange, it becomes an output in the energy balance and is not recovered. Under ideal favorable conditions brine flow rate would balance percent vaporization, power utilization, total mass flow rate of water vapor out of the system, and salt collection.

Figure 7.4: Vaporization performance as a function of brine flow rate in tests utilizing the eductor and various nozzles as indicated in the figure. Vaporization performance is a function of the amount of heat captured by the fluid and used to change the phase of a unit mass of water, therefore higher brine flow rates were able to capture a higher percentage of the input heat. This may explain the trend of decreased energy usage at higher flow rates.
To evaluate the effects of solution chemistry with a focus on percent salt in solution, tests ranging from 0.2 to 0.85 GPM were conducted to observe system performance at various brine strength from tap water up to 280,000 mg/L salt (NaCl). As shown in Figure 7.5 and Table 7.2, no correlation was seen between brine strength and percent liquid phase fluid recovery showing that the system is capable of treating brines of any salt concentration up to saturation with little to no performance loss. Fuel and air flow rates were kept constant across these tests to control for changes in performance due to equivalence ratio shifts. A single downspout nozzle and control volume orientation were used to ensure comparability across all salt concentration ranges. This brine strength independent behavior is unique to the supercharged pulsed jet combustor and provides the potential for this technology to fill a gap in brine remediation technology when salt concentrations exceed 150,000 mg/L. This data also allows us to predict the behavior of the supercharged pulsed jet combustor under a variety of brine flow rates and salt concentrations, which helps to optimize operational conditions for the supercharged pulsed jet combustor in an industrial process setting.
Figure 7.5: Fluid mass recovery as a function of fluid flow rate during downspout tests utilizing brines of varying strengths.
Table 7.9: Water and Salt mass balance data for downspout tests.

<table>
<thead>
<tr>
<th>Date</th>
<th>Test #</th>
<th>Brine Flow (kg/s)</th>
<th>Brine Flow (gpm)</th>
<th>Water Flow (kg/s)</th>
<th>Water Flow (gpm)</th>
<th>% Salt, average (brine)</th>
<th>Mass Processed through System (kg)</th>
<th>Mostly Liquid</th>
<th>Mostly Solid</th>
<th>Total</th>
<th>Percent of Total Collected</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Mass Collected (kg)</td>
<td>Mostly Liquid</td>
<td>Mostly Solid</td>
<td>Total</td>
<td></td>
</tr>
<tr>
<td>8/26/2014</td>
<td>1</td>
<td>0.025</td>
<td>0.34</td>
<td>0.019</td>
<td>0.30</td>
<td>24.20%</td>
<td>14.19</td>
<td>3.41</td>
<td>10.78</td>
<td>2.30</td>
<td>5.30</td>
</tr>
<tr>
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<td>0.030</td>
<td>0.42</td>
<td>0.023</td>
<td>0.37</td>
<td></td>
<td>16.36</td>
<td>3.90</td>
<td>12.46</td>
<td>2.84</td>
<td>6.59</td>
</tr>
<tr>
<td>9/4/2014</td>
<td>1</td>
<td>0.026</td>
<td>0.35</td>
<td>0.020</td>
<td>0.31</td>
<td>24.20%</td>
<td>14.76</td>
<td>3.55</td>
<td>11.21</td>
<td>2.10</td>
<td>4.72</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.023</td>
<td>0.32</td>
<td>0.018</td>
<td>0.28</td>
<td></td>
<td>10.40</td>
<td>2.50</td>
<td>7.89</td>
<td>1.67</td>
<td>3.47</td>
</tr>
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<td>0.31</td>
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<td>0.29</td>
<td></td>
<td>12.60</td>
<td>1.67</td>
<td>10.93</td>
<td>1.33</td>
<td>5.32</td>
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<td>0.31</td>
<td>0.018</td>
<td>0.29</td>
<td></td>
<td>13.99</td>
<td>1.87</td>
<td>12.12</td>
<td>1.50</td>
<td>5.99</td>
</tr>
<tr>
<td></td>
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<td>0.31</td>
<td>0.018</td>
<td>0.29</td>
<td></td>
<td>12.66</td>
<td>1.58</td>
<td>11.08</td>
<td>1.27</td>
<td>5.50</td>
</tr>
<tr>
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<td>0.31</td>
<td>0.018</td>
<td>0.29</td>
<td></td>
<td>9.90</td>
<td>1.33</td>
<td>8.57</td>
<td>0.99</td>
<td>3.53</td>
</tr>
<tr>
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<td>0.31</td>
<td>0.018</td>
<td>0.29</td>
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<td>0.29</td>
<td></td>
<td>13.12</td>
<td>1.70</td>
<td>11.42</td>
<td>1.28</td>
<td>4.11</td>
</tr>
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<td>0.34</td>
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<td></td>
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<td>8/28/2014</td>
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<td>0.030</td>
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<td>0.023</td>
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<td>3.90</td>
<td>12.46</td>
<td>2.84</td>
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</tr>
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<td>9/4/2014</td>
<td>1</td>
<td>0.026</td>
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<td>0.020</td>
<td>0.31</td>
<td>24.20%</td>
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<td>11.21</td>
<td>2.10</td>
<td>4.72</td>
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<td>2</td>
<td>0.023</td>
<td>0.32</td>
<td>0.018</td>
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<td>2.50</td>
<td>7.89</td>
<td>1.67</td>
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<tr>
<td>9/9/2014</td>
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<td>0.021</td>
<td>0.31</td>
<td>0.018</td>
<td>0.29</td>
<td></td>
<td>12.60</td>
<td>1.67</td>
<td>10.93</td>
<td>1.33</td>
<td>5.32</td>
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<td>2</td>
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<td>0.018</td>
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<td>1.50</td>
<td>5.99</td>
</tr>
<tr>
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<td>3</td>
<td>0.021</td>
<td>0.31</td>
<td>0.018</td>
<td>0.29</td>
<td></td>
<td>12.66</td>
<td>1.58</td>
<td>11.08</td>
<td>1.27</td>
<td>5.50</td>
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<tr>
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<td>0.018</td>
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<td>1.33</td>
<td>8.57</td>
<td>0.99</td>
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<tr>
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<td>0.021</td>
<td>0.31</td>
<td>0.018</td>
<td>0.29</td>
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<td>9.42</td>
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<td>9/25/2014</td>
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<td>13.12</td>
<td>1.70</td>
<td>11.42</td>
<td>1.28</td>
<td>4.11</td>
</tr>
</tbody>
</table>
7.2 Thermodynamic and Heat Transfer Analysis

Thermodynamic analysis of the system showed that even in our most energy efficient runs, only about 70% of the available energy was being utilized to change the phase of water from the liquid state to the gaseous state (Figure 7.6). This is due to the inherent limitations of a coiled tube heat exchanger as well as energy lost due to incomplete combustion in the system. The combination of a process fluid heat exchanger, which is already in production for a pilot scale unit as well as a steam condensation heat exchanger can theoretically reduce our energy usage from a typical value of 4.5 MJ/kg to much lower energy usage levels. The steam generated during vaporization in the exhaust region of the supercharged pulse jet combustor contains more than 50% of the total energy input to the system. This high energy stream represents a large opportunity for energy recovery with the proper peripheral heat exchange systems.

Figure 7.6: Energy balance tracking per unit time of inputs and outputs from and to the system by enthalpy and mass flow rate tracking assuming complete consumption of the limiting reactant. Test utilized the downspout nozzle and tap water into the control volume. Values for Incomplete Combustion and Heat Loss are unknown but represent a sum total of 19.4kW.

Energy In: 64.71 kW  
Energy out: 45.3 kW  
19.4 kW Unaccounted for
One major advantage of the supercharged pulsed jet combustor is the prevalence of fluid-to-fluid heat exchange in the hot exhaust gas region. Not only does this heat transfer exhibit high rates of heat transfer and thermal efficiency, it mitigated the need for expensive materials able to withstand the high temperature, pressure, and corrosive environments generated in conventional thermal desalination processes [7] [8] [9] [10].

To understand the heat transfer behavior from an energy balance perspective, several tests were performed to quantify heat and mass transfer in the exhaust gas region. Sonic drying phenomena and turbulent heat transfer advantages are a major point of interest in system characterization. Tests were run using the downspout nozzle and plastic control volume.

Downspout testing revealed that utilizing the hot gas stream by injecting fluid into this region using the downspout nozzle yielded an increase in average power recovery of 22% as compared to not injecting into the hot gas stream using the same nozzle. Tests where the nozzle was not introduced into the hot gas stream recovered 30.52% of the liquid water, nearly twice as much liquid water as compared to the 15.83% recovered during tests where the nozzle was in the hot gas stream. By not injected the fluid into the hot gas stream, no convective heat transfer from the exhaust gas was utilized. This caused 48% more fluid to not vaporize and be collected as liquid water in the plastic container.

Conditions such as fuel, air, and fluid flow rates were held as steady as allowed by the system controls. Power recovery was calculated by assuming that during both tests, the fluid not recovered as a liquid in the pool was instead vaporized. The mass flow rate of vaporized fluid could then be multiplied by the latent heat of vaporization of water (2.26 MJ/kg) and divided by total system input energy to find power utilization percentage during each test. Comparing similar tests, between 5.5 and 6.1kW of total power are recovered through turbulent heat
exchange phenomena in the hot gas region, representing a 10% total energy gain as compared to only using the coiled tube body heat exchanger which is representative of a conventional thermal vaporization process. It is clear injection into the hot gas region increases not only power utilization percentage but also the percent of fluid vaporized by the system. This result allowed us to compare and quantify the effects of the exhaust region of the supercharged pulsed jet combustor with a simple conductive heat exchanger. Tables 7.4 and 7.5 and Figure 7.7 summarize these findings.
Table 7.10: Power recovery when comparing tests with the downspout nozzle ‘In’ and ‘Out’ of the hot exhaust gas region

<table>
<thead>
<tr>
<th>Direction</th>
<th>Test #</th>
<th>Water Flow Rate (kg/s)</th>
<th>Fuel Flow Rate (g/s)</th>
<th>Fuel – Air Equivalence Ratio (φ)</th>
<th>Input Power (kW)</th>
<th>Mass Collected (%)</th>
<th>Mass Vaporization Rate (kg/s)</th>
<th>Power for vaporization (kW)</th>
<th>ΔT across body heat exchanger (K)</th>
<th>Power for raising fluid temperature (kW)</th>
<th>Power Recovery (%)</th>
<th>Average (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>In</td>
<td>1</td>
<td>0.011</td>
<td>1.20</td>
<td>1.52</td>
<td>56.3</td>
<td>16.7</td>
<td>0.00891</td>
<td>20.3</td>
<td>65</td>
<td>2.91</td>
<td>41.24</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.010</td>
<td>1.47</td>
<td>1.86</td>
<td>68.9</td>
<td>12.3</td>
<td>0.00877</td>
<td>19.9</td>
<td>65</td>
<td>2.72</td>
<td>32.81</td>
<td>36.6</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.010</td>
<td>1.23</td>
<td>1.55</td>
<td>57.7</td>
<td>18.5</td>
<td>0.00785</td>
<td>17.9</td>
<td>68</td>
<td>2.73</td>
<td>35.76</td>
<td></td>
</tr>
<tr>
<td>Out</td>
<td>1</td>
<td>0.009</td>
<td>1.19</td>
<td>1.50</td>
<td>55.8</td>
<td>29.1</td>
<td>0.00638</td>
<td>14.5</td>
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<td>2.52</td>
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<td>1.55</td>
<td>57.7</td>
<td>21.8</td>
<td>0.00759</td>
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<td>2.72</td>
<td>34.70</td>
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<td>4</td>
<td>0.010</td>
<td>1.14</td>
<td>1.44</td>
<td>53.5</td>
<td>38.2</td>
<td>0.00595</td>
<td>13.5</td>
<td>67</td>
<td>2.69</td>
<td>30.28</td>
<td>29.9</td>
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<td>5</td>
<td>0.009</td>
<td>1.49</td>
<td>1.88</td>
<td>69.9</td>
<td>32.3</td>
<td>0.00633</td>
<td>14.4</td>
<td>67</td>
<td>2.63</td>
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<td></td>
<td>6</td>
<td>0.009</td>
<td>1.21</td>
<td>1.53</td>
<td>56.7</td>
<td>33.1</td>
<td>0.00625</td>
<td>14.2</td>
<td>68</td>
<td>2.67</td>
<td>29.73</td>
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</table>

2 0.017 1.16 1.47 54.4 29.1 0.01169 26.6 65 4.48 57.13
Table 7.11: Mass balance and fluid temperatures comparing tests with the downspout nozzle ‘In’ and ‘Out’ of the hot exhaust gas region

<table>
<thead>
<tr>
<th>Direction</th>
<th>Test Number</th>
<th>Water Flow Rate (kg/s)</th>
<th>Water Flow Rate (gpm)</th>
<th>Fuel Flow Rate (g/s)</th>
<th>Influent Water Temperature (°C)</th>
<th>Effluent Water Temperature (°C)</th>
<th>Water Mass Processed (kg)</th>
<th>Water Mass Collected (kg)</th>
<th>Percent of total water mass collected</th>
</tr>
</thead>
<tbody>
<tr>
<td>In</td>
<td>1</td>
<td>0.0107</td>
<td>0.17</td>
<td>1.20</td>
<td>28.7 ±0.1</td>
<td>93.4 ±0.6</td>
<td>8.98</td>
<td>1.50</td>
<td>16.7</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.0100</td>
<td>0.16</td>
<td>1.47</td>
<td>29.8 ±0.2</td>
<td>94.8 ±0.6</td>
<td>8.48</td>
<td>1.05</td>
<td>12.3</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.0096</td>
<td>0.15</td>
<td>1.23</td>
<td>25.4 ±0.1</td>
<td>93.6 ±0.7</td>
<td>8.10</td>
<td>1.50</td>
<td>18.5</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>0.0090</td>
<td>0.14</td>
<td>1.19</td>
<td>26.8 ±0.1</td>
<td>93.9 ±0.7</td>
<td>7.55</td>
<td>2.20</td>
<td>29.1</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>0.0097</td>
<td>0.15</td>
<td>1.23</td>
<td>27.2 ±0.1</td>
<td>94.4 ±0.6</td>
<td>8.73</td>
<td>1.90</td>
<td>21.8</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>0.0096</td>
<td>0.15</td>
<td>1.14</td>
<td>26.9 ±0.1</td>
<td>93.5 ±0.7</td>
<td>8.08</td>
<td>3.09</td>
<td>38.2</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.0165</td>
<td>0.26</td>
<td>1.16</td>
<td>29.8 ±0.2</td>
<td>94.3 ±0.7</td>
<td>7.93</td>
<td>2.31</td>
<td>29.1</td>
</tr>
</tbody>
</table>

Out

|           | 1           | 0.0090                 | 0.14                  | 1.19                 | 26.8 ±0.1                     | 93.9 ±0.7                     | 7.55                   | 2.20                     | 29.1                                |
|           | 3           | 0.0097                 | 0.15                  | 1.23                 | 27.2 ±0.1                     | 94.4 ±0.6                     | 8.73                   | 1.90                     | 21.8                                |
|           | 4           | 0.0096                 | 0.15                  | 1.14                 | 26.9 ±0.1                     | 93.5 ±0.7                     | 8.08                   | 3.09                     | 38.2                                |
|           | 5           | 0.0094                 | 0.15                  | 1.49                 | 26.8 ±0.1                     | 94.1 ±0.9                     | 7.75                   | 2.50                     | 32.3                                |
|           | 6           | 0.0094                 | 0.15                  | 1.21                 | 26.5 ±0.1                     | 94.1 ±0.9                     | 7.85                   | 2.60                     | 33.1                                |
Figure 7.7: Brine mass recovery (on average) comparing exhaust gas utilization vs coiled body heat exchanger only during downspout nozzle tests

The front end coil was designed to compare heat transfer from the hot gas to a coiled tube heat exchanger (front end coil in the hot gas flow) to heat transfer directly from the hot gas to the fluid (downspout nozzle). This allowed the team to analyze and quantify the effects of turbulent hot gas and possible sonic drying phenomena. When comparing front end coil tests to downspout tests injecting into the hot gas stream, power recovery in the exhaust region increased by a factor of 1.6-2.5 for downspout tests vs front end coil tests (Table 7.5). Power recovery is a function of fluid flow rate, as a higher fluid flow rate maintains a larger temperature gradient, meaning for a given unit of time (the time needed for the fluid to flow through the heat exchanger) more heat is
transferred. Front end coil tests were performed to ensure minimal vaporization, meaning very high fluid flow rates (on the order of 1.5-2.5 gallons per minute) relative to the maximum theoretical vaporization capacity of the system (0.4-0.5 gallons per minute), as much as 15 times the typical flow rate for downspout testing. Because of this, actual power recovery increases between the front end coil and downspout nozzle would theoretically be even greater for similar flow rates. This shows that turbulent gas phenomena play a large role in heat transfer in the hot gas exhaust region of the combustor.

Table 7.12: Power recovery during front end coil testing.

<table>
<thead>
<tr>
<th>Test #</th>
<th>Water Flow Rate (kg/s)</th>
<th>Water Flow Rate (gpm)</th>
<th>Propane Flow Rate (g/s)</th>
<th>Power Recovered Across Heat Exchanger (kW)</th>
<th>Power Recovered Across Front End Coil (kW)</th>
<th>Total Power Recovered (kW)</th>
<th>Combustor Power (kW)</th>
<th>Percent of Input Power Recovered (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.1614</td>
<td>2.57</td>
<td>1.26</td>
<td>27.0</td>
<td>3.2</td>
<td>30.2</td>
<td>59.09</td>
<td>51.1</td>
</tr>
<tr>
<td>1</td>
<td>0.0913</td>
<td>1.45</td>
<td>0.86</td>
<td>9.9</td>
<td>1.6</td>
<td>11.5</td>
<td>40.33</td>
<td>28.5</td>
</tr>
<tr>
<td>2</td>
<td>0.0957</td>
<td>1.52</td>
<td>1.90</td>
<td>15.0</td>
<td>3.2</td>
<td>18.2</td>
<td>89.11</td>
<td>20.4</td>
</tr>
<tr>
<td>3</td>
<td>0.0945</td>
<td>1.50</td>
<td>1.18</td>
<td>13.1</td>
<td>2.4</td>
<td>15.5</td>
<td>55.34</td>
<td>28.0</td>
</tr>
</tbody>
</table>

Power recovery by the coiled tube body heat exchanger ranged from 46% to as little as 17%. This is a function of fluid flow rate through the heat exchanger. As mass flow rate of the fluid increased, the average temperature difference between the body of the combustor and the fluid increased, allowing more heat to be drawn off of the body which can be calculated using the equation

\[ Q = \dot{m} \times C_p \times (T - T_0) \]

Eq. 7.2
where $Q$ is the rate of heat transfer from the heat exchanger to the fluid, $\dot{m}$ is the mass flow rate of fluid, $C_p$ is the constant pressure specific heat of the fluid, $T$ is the outlet temperature of the fluid, and $T_0$ is the initial fluid temperature at the inlet of the heat exchanger. The relatively low efficiency of this heat exchanger means there is a large opportunity for energy recovery in this region.

### 7.3 Conclusions

The supercharged pulsed jet combustor has proven capable of separating salt from water out of brine solutions that exceeded saturation concentrations while recovering as much as 97% of the salt processed through the system. During favorable tests the system was able operate at a steady state condition of 4.14 MJ/kg of water evaporated. Much of the success of the system is due to heat and mass transfer phenomena in the hot gas exhaust region of the combustor, which was found to provide an additional 22% power recovery. By utilizing hot gas-to-brine heat exchange the need for expensive highly corrosion resistant materials such as in a mechanical vapor recompression system is greatly diminished as the salt is able to precipitate in open air at relatively low temperatures and close to ambient pressure. This makes the use of thermal plastics rather than metallic pressure vessels possible. The system is relatively inexpensive and fills a gap in the desalination technology market focused on high strength brines with TDS concentrations exceeding 150,000 mg/L. Performance data show that the supercharged pulsed jet combustor utilizing the large pigtail nozzle could be operated consistently and predictably with a moderate confidence interval to achieve a desired percent vaporization (from 35-62%), energy efficiency (4.14 MJ/kg), and salt collection percentage (from 75-97%).
Another important factor to consider is that all currently operating desalination technologies create an increased strength brine stream as solvent water is removed from solution [11]. One possible and promising application of this technology is as a secondary treatment system for a reverse osmosis or conventional thermal distillation system. The supercharged pulse jet combustor experiences negligible changes in performance based on salinity, while all other competing technologies either become increasingly more expensive as salinity increases, or simply run into physical or operational problems due to large amounts of salt precipitate. This technology may be able to greatly reduce the volume of expelled water from already existing desalination facilities. Typical reverse osmosis systems reject 50% of the feed flow as a high strength retentate, with thermal desalination systems rejecting 70% or more [11]. The supercharged pulsed jet combustor can be operated at conditions where less than 40% of the feed fluid is rejected, allowing even fluids approaching saturation concentrations of salt to be treated. Because of the brine strength insensitivity of the system and the ability of pulse combustors to handle high viscosity fluids, there are very few concerns about continuously circulating fluid even beyond the saturation concentration of salt [6] [12]. The supercharged pulsed jet combustor has proven that it is a novel technology that offers promise to accommodate a clear market need in industrial drying.
Chapter 7 References


Chapter 8
Discussion and Future Research

Continued research may focus on continuing to experiment with equivalence ratio testing by varying fuel, air, and brine flow rates and salt concentrations to create a set of equations that will allow us to accurately predict system behavior at a wide variety of conditions. Active mass flow rate tracking can allow real-time equivalence ratio adjustments based on a continuously reported value. This will allow an operator to use a previously generated curve to optimize the system for a given batch of fluid to be treated. This will also help standardize operation for emissions testing for consistent system output. Tuning of the supercharged pulsed jet combustor to run at a resonant condition may also be explored so as to observe how maximizing pressure waves affects system performance.

A major area of potential system improvement is in the implementation of peripheral heat exchange and heat recovery systems. While other thermal technologies can operate well below 1 MJ/kg, the current system configuration under optimum conditions operated around 4 MJ/kg. Both technologies operate by breaking the hydrogen bonds between water molecules and solute ions meaning that the theoretical minimum energy ignoring entropy inherent to the process is simply the latent heat of vaporization of water, 2.257 MJ/kg. Thermal desalination systems are able to circumvent this limit by careful process control, heat exchange, and power recovery systems. Steam generating processes such as multi-stage flash evaporation and multi-effect distillation couple a steam power plant to the evaporators as well as using treated brines to heat incoming fluid, thereby making their only energy losses those intrinsic to the process, namely the
efficiency of pumps and heat exchangers. The supercharged pulsed jet combustor currently employs no systems for waste heat recovery and discharges a very high energy stream into the form of steam into the open atmosphere. This stream contains more than 50% of the energy input into the system, and conventional steam heat exchangers could readily be coupled to a closed system to greatly improve system performance. [1] [2]

Another area of potential improvement related to peripheral systems is advances in the design of the heat exchanger coupled to the body of the pulse combustor. Currently a single coiled tube heat exchanger preheats the fluid before it is discharged to the exhaust region of the supercharged pulsed jet combustor. This system is inherently inefficient, and could be greatly improved upon by the implementation of a process fluid heat exchanger. A fluid jacket heat exchanger would maximize the contact surface area between the body of the combustor and the fluid being heated. This fluid could be a silicon based high temperature thermal fluid. Although silicon fluids have a lower specific heat than water, the increased boiling point, decreased viscosity, decreased density, non-corrosive nature, and extremely high boiling point allow for much more precise control of temperatures [3]. The pilot-scale system to be installed soon for testing employs this type of heat exchanger. The excess heat being lost through the body of the combustor may also be utilized to heat an enclosed control volume or preheat the incoming fluid for methanol removal.

A complete enclosed control volume was constructed by Furness-Newburge Inc. and is currently being prepared for implementation on a pilot-scale unit that will be tested by our industrial partners. The control volume will provide a way to test the emissions of the system, including particulate matter such as salt, products of incomplete combustion, and any compounds
generated during the treatment process resulting from heat and aerosolizing interaction with compounds found in hydrofracturing fluid.

A minor area of improvement that will improve process control is the implementation of a high-pressure positive displacement pump. Some tests ran into the issue of pressure buildup in the heat exchanger as water turned to steam in the heat exchanger tube, depositing solid salt in the lines. This interrupted testing as fluid could no longer pass through the heat exchanger. A dilute acid was employed to clear the lines. This procedure is not conducive to a continuous operation industrial process as it requires considerable time and the handling of hazardous chemicals as well as shortens the life of the heat exchanger and any other components subjected to the acid solution. This problem was remedied by increasing the diameter of the opening of the nozzle that introduced the brine to the hot gas stream. With a higher pressure pump the fluid could be forced through the heat exchanger despite steam formation, and behave similarly to a flash evaporation system, where the fluid instantly vaporizes as it reaches a region of pressure lower than its vapor pressure. This problem is better solved by the process fluid jacketed heat exchanger, as the temperature of the brine being treated and the temperature of the jet are decoupled, allowing independent control of either variable whereas a direct coiled heat exchanger couples the two temperatures.

Another area of future research involves the use of shadowgraphy, a type of high-speed photography that visualizes fluid flow fields by creating a shadow image based on spatially varying density. This will allow researchers to investigate regions of recurring high and low pressure in the flow field of the supercharged pulsed jet combustor that may be utilized to induce salt precipitation or enhance evaporation. This would allow for more precise and informed
testing on fluid injection location, and will likely shed some light on difficult to quantify phenomena in the hot gas exhaust region.

While continued research has many challenges to overcome and questions to answer, the research presented here outlines the potential benefits of the system, the success with drying high strength brines, rapid improvements to energy efficiency, and clear opportunity for fundamental design improvements. A pilot scale unit will be implemented at a treatment facility of Hydro Recovery LP during the summer of 2015.
Chapter 8 References


Appendix A

Methanol Removal by Air Sparging

A-1: Introduction

As discussed in chapter 1, hydraulic fracturing requires a well stimulation fluid to allow applied pressure to be transferred into rock formations in order to facilitate the extraction of resources that would otherwise be unattainable. One compound frequently used as an additive and of environmental health concern is the VOC methanol (CH$_3$OH) [41] [2] [3]. Methanol serves many purposes in hydrofracturing fluids and it has even been used as a primary fluid in place of water [41]. Reported concentrations of methanol in hydrofracturing fluid range from 24 mg/L to 690 mg/L [41]. While the Clean Air Act, Clean Water Act, and Safe Drinking Water Act do not establish criteria for methanol monitoring, human exposure and toxicity is well documented, exhibiting toxic concentrations slightly lower than gasoline [4] [5]. Removal of methanol from flowback waters is a major concern related to permitting and discharge requirements for fluids being treated by the supercharged pulsed jet combustor or other thermal evaporative systems.

Air stripping of methanol by use of a bubbled reactor has been suggested as a possible treatment technology to remediate methanol from flowback fluids. Air stripping is commonly used to sparge VOCs found in groundwater and surface water [6] [7] [8] [9]. The Penn State team designed and built a bubbled reactor air stripping unit and used it to sparge water samples that contained an initial concentration of 950 to 1250 mg/L methanol. Initial testing shows that at operating fluid temperatures of the supercharged pulsed jet combustor, methanol is highly
volatile, with a maximum rate of methanol removal from solution of 50 mg/L in 1 minute at 50.6°C. The vaporization rate of methanol out of solution is strongly a function of temperature, with increased vapor pressure and Henry’s Law Constant as temperature increases.

**A-2: Literature Review**

**A-2-1: Methanol Overview**

Methanol, the simplest alcohol, is a VOC and is used in a wide variety of industrial applications [4] [10]. Methanol is created through steam reformation of natural gas and is used as a building block for the production of a wide variety of organic compounds as well as a fuel source in the form of M100 (100% methanol) or M85 (85% methanol, 15% petrol) [4] [11] [5]. The highest volume demand for methanol is as an additive for gasoline as methyl t-butyl ether. Methanol is a colorless, flammable liquid with a boiling point of 64.7°C, a density of 0.792 g/mL, and is completely miscible in water. Air stripping is generally considered favorable for compounds with a Henry’s Law Constant of 0.01 atm·m³/mol or higher. Methanol displays a vapor pressure of 0.168 bar at 25°C and a Henry’s Law Constant of 4.55×10⁻⁶ atm·m³/mol at 25°C, 4 orders of magnitude lower than the recommended Henry’s Law Constant for air stripping [5] [10]. Despite its low Henry’s Law Constant, methanol exerts a relatively high vapor pressure, over 2 times the vapor pressure of trichloroethane (TCE), a common contaminant treated using air stripping [12]. This means that to effectively remove methanol from solution, the concentration in the air phase of incoming air must be kept very low, or equilibrium with the air phase will be reached, preventing further mass transfer out of solution. Henry’s Law Constant and vapor pressure are also both highly dependent on temperature, increasing as heat is added
Regression data based on equations generated by Goodwin and Warneck and shown in Figures A-1 and A-2 suggest an exponential relationship between vapor pressure, Henry’s Law Constant, and temperature [13] [14]. By this model, a pure solution of methanol would reach a Henry’s Law Constant of 0.01 atm m$^3$/mol at 251°C. According to an EPA handbook on air sparging, however, compounds with vapor pressures above 0.5 mmHg (0.00066 atm) and boiling points below 250-300°C are favorable for air sparging. Methanol at 85°C has a vapor pressure more than 3000 times that of the recommended minimum, and a boiling point 200°C lower than the effective reported range [15].

Figure A-1: Vapor pressure vs temperature for methanol as generated from regression equations developed by Goodwin and Warneck [14] [13]
Figure A-2: Henry’s Law Constant vs temperature for methanol as generated from regression equations developed by Goodwin and Warneck [14] [13]

The regressions in Figures A-1 and A-2 were generated based on pure methanol for the vapor pressure data and methanol as the lone solute for Henry’s Law Constant data. Actual behavior of methanol in solutions is a function of not only temperature, but also of the activity of methanol in solution due to the interaction of other dissolved species. Activity is a measure of the non-ideality of a compound in solution and accounts for a wide variety of effects impacting thermodynamic equilibrium. Because of the extremely elevated dissolved solid concentration in produced waters, the effects of dissolved inorganic salts must be considered. The general trend among most organic compounds is that as the concentration of an ionic salt increases, the solubility of organic compounds decreases. The general equation

\[ a = \gamma x \]  

(A-1)
where \( a \) = the activity of a compound in solution, \( \gamma \) = the activity coefficient, and \( x \) = the mole fraction, relates the activity coefficient to the molar concentration of a compound. Wilcox and Schrier found that the activity coefficient of alcohols in water can be approximated by the function

\[
\log \left( \frac{\gamma_2}{\gamma_0} \right) = A m_1 \tag{A-2}
\]

where \( \gamma_2^0 \) = the activity coefficient of methanol in water at a given temperature and pressure, \( \gamma_2 \) = the activity coefficient of methanol in water at a given temperature and pressure with salt added, \( A \) = a compound-specific coefficient, and \( m_1 \) = molality of salt in solution. The value \( A \) can be compared to the salting constant as reported by Schwarzenbach, which relates the saturation concentration of a compound in water compared to the saturation concentration of that same compound in water with salt as a function of the salt concentration in the water as

\[
\log \left( \frac{C_{w, sat}}{C_{w, sat, salt}} \right) = K^s m_1 \tag{A-3}
\]

where \( K^s \) is the salting coefficient, \( C_{w, sat} \) is the saturation concentration of a compound in aqueous solution, and \( C_{w, sat, salt} \) is the saturation concentration of that same compound in a saline aqueous solution. A \( K^s \) value of 0.0658 was reported for methanol solutions with sodium chloride as the ionic salt in solution. This means that the saturation concentration of methanol as a function of salt concentration in solution should drop exponentially as salinity increases. [15] [16]

Another effect to consider is the influence of co-solvents in solutions. The introduction of organic compounds to solution may act as an additional solvent allowing a higher concentration
of methanol to dissolve into solution than would dissolve into water alone. Because methanol is a small, polar molecule the addition of nonpolar organics would not act as co-solvents for methanol, but the addition of other small polar organics such as other alcohols may increase its solubility [16]. This effect is most notable in solutions where the co-solvent is around 10% of the solution by volume [16]. Isopropyl alcohol and ethylene glycol are common additives to hyrdrofracturing fluid, but their total concentration is less than 0.1% by mass, far less than 10% by volume [17] [18] [19]. Despite this, the effects of co-solvents may be important for the careful understanding of methanol mass transfer behavior.

**A-2-2: Air Stripping and Bubbled Reactors**

Air stripping was chosen as the remediation technology to address the issue of methanol contamination in flowback water due to its history of effectively treating VOCs from various water sources [9] [6] [7] [8]. Air stripping relies on the concept of Henry’s Law, which states that the equilibrium concentration of a compound between the liquid and gas phase is directly proportional to the partial pressure exerted by that gas [20] [21]. Mass transfer theory dictates that concentration gradients in a solution and equilibrium laws at interfacial phase boundaries will always travel towards equilibrium, meaning that high concentrations of a compound in solution will change phase when introduced to a gas flow with low concentrations of that gas according its Henry’s Law Constant [22]. By allowing a solution to interact with a large volume of air, compounds in solution may be partitioned into the gas phase for further treatment, transport, or utilization.
There are generally 3 types of air strippers: packed column, sieve tray, and diffused aeration. Packed column air strippers are column-shaped reactors with a porous packing media inside. Water is introduced at the top of the tower and allowed to trickle down the porous media where it interacts with air that is pumped into the base of the tower. The media provides a large surface area for water-air interaction, and the height of the tower determines residence time. Off-gas emissions may be treated using activated carbon or thermal oxidation. The methanol stripping system at Penn State was designed with the intention of the final iteration of the design using the methanol-rich air as an added source of fuel for the pulse jet, completely oxidizing the methanol.

Sieve tray air strippers, as shown in Figure A-3, flow water over perforated trays, with air being pumped through the holes. Trays are staggered at equal distances along the height of the reactor, and the weir ends alternate, providing longer fluid contact time inherent to the circuitous route as well as good surface area interaction with incoming air. Sieve tray and packed column air strippers but can achieve high levels of contaminant removal (>99%), but they may have issues with clogging from suspended solids or fouling due to biological growth on trays and packing media. Backwashing and media cleaning are required for optimal continuous operation [20].

Figure A-3. Sieve tray air stripper flow diagram [20]
Diffused aeration strippers are flow-through reactors with air diffusers/air spargers located in the base of the reactor. Bubbles are introduced by pumping clean air through a bubble diffuser. Diffused aeration was chosen for this project as it is relatively simple and inexpensive to construct, is low operating cost, requires little ongoing maintenance, can handle high suspended solids concentrations, residence time can be varied easily, and is resistant to fouling [20] [23]. As the bubbles rise through the solution, the concentration gradient of a compound in solution drives that compound into the gas phase and the compound is transported out of solution by the bubble. Total mass transfer to the bubbles is a function of temperature, the Henry’s Law Constant of the contaminant of concern, the concentration of the contaminant in solution, the residence time of the bubble, and the total interfacial area provided by the bubbles. Of the three types of reactors, bubbled reactors provide the greatest surface area per unit volume of air pumped [23]. An important design parameter for increasing mass transfer is maximizing the total interfacial surface area per unit volume of air pumped, which in a bubbled reactor is done by minimizing bubble size as generated by the diffuser and maximizing the time the bubble is in the reactor. By creating small bubbles, a bubble swarm is generated, meaning the rise velocity of a single bubble is approximately half of the rise velocity of a similar size bubble that is rising freely through solution. Total area $a_t$ may be calculated by

$$a_t = \frac{3Q_a t_b}{V R_b}$$  \hspace{1cm} (A-4)

where $Q_a =$ air volumetric flow rate, $t_b =$ time the bubble is in the reactor, $V =$ total reactor volume, and $R_b =$ the average bubble radius. The bubble residence time $t_b$ is calculated by
integrating the rise velocity over the height of the reactor, but this is very difficult to accurately measure in a bubble swarm, so often the parameter of gas holdup is used, which is defined as

\[
H = \frac{\text{Volume of Gas}}{\text{Volume of Gas} + \text{Volume of Liquid}}
\]  

(A-5)

This value can be manually measured by observing the change in fluid height in the reactor during air bubbling. [22] [20]

There are many different types of bubbled reactors, with each design attempting to take advantage of some type of flow regime within the reactor. One major function of bubbles in a reactor is to provide mixing by shear and turbulence, creating chemical dispersion, which distributes a compound in solution much more quickly than diffusion alone. Shear gradients exist at the surface of any bubbles with velocity relative to the liquid. The three major types of bubbled flow regimes pictured in Figure A-4 are homogenous bubbly flow, churn turbulent flow, and slug flow. Bubbly flow, which occurs mainly at low gas velocities (<0.05 m/s), provides the least total shear in the reactor, as bubble velocities are uniform and relatively low, most similar to laminar flow. Churn turbulent flow provides a wide range of bubble diameters in an unsteady flow regime, with high rise velocities and small bubbles. This condition provides high shear as well as high interfacial area for mass transfer to the bubbles. Slug flow occurs at high gas flow rates in relatively small reactors. As

![Figure A-4: Flow regimes found in bubbled reactors](image)
bubbles rise through the reactor, the increased shear between the bubbles and wall of the reactor stabilize its rise, and large air pockets form along the sides of the reactor. This decreases total surface area per unit volume of air, but may increase air residence time. Various reactor configurations are shown in Figure A-5 [22] [20] 

Figure A-3: Various bubbled reactor configurations selecting for different kinetic attributes such as fluid residence time or bubble rise velocity. [23]
Of all design parameters controlling mass transfer and reaction kinetics in bubbled reactors, gas holdup encompasses the most criteria in a single value. Gas holdup provides a measure of total residence time of both phases in the reactor, and combined with knowing bubble diameter, gives a good sense of mass transfer rates. This is calculated by

\[ H = \frac{a_t \times R_b}{3} \]  

(A-6)

which allows for a direct calculation of interfacial area, \(a_t\) as long as bubble radius \(R_b\) is known. Gas holdup is also a function of superficial gas velocity and remains relatively constant across scaled reactors but decreases slightly with reactor diameter. Gas holdup remains difficult to predict, as it is very dependent on parameters such as liquid viscosity, temperature, and chemical composition of the liquid. Once design parameters such as kinetic rate constants, interfacial area, bubble flow regime, and equilibrium concentrations are determined, one can begin to predict and model the behavior of a bubble reactor using mass transfer and mass balance equations.

Once a bubbled reactor is created, it can either be operated in batch mode or as a continuous steady-state system. Assuming no chemical reaction and a continuously stirred tank reactor (CSTR, uniform concentration), the rate of change of concentration per unit time in a bubbled reactor can be modeled by

\[ \frac{dC_{xw}}{dt} = \frac{Q_{w, in} \times C_{xw, in}}{V} - \frac{Q_{w, out} \times C_{xw, out}}{V} - \left[ \int_0^t (K_{x,a} \times a_s + K_{x,a} \times a_{ib}) dt \right] \times \left[ C_{xw, eq} - C_{xw, out} \right] \]  

(A-7)

In words, the rate of change of concentration of x in the water phase (w) in the reactor \(\frac{dC_{xw}}{dt}\) is equal to the mass flow rate of compound into the reactor \(\frac{Q_{w} \times C_{xw, in}}{V}\) minus the mass flow rate of
the compound out of the reactor \( \frac{Q_w \times C_{xw \text{ out}}}{V} \), minus the time-average mass transfer to the gas phase occurring at both the surface of the reactor \( K_{x,a} \times a_s \) and at the total surface area of all of the bubbles in the reactor \( K_{x,a} \times a_{tb} \). The subscript \( x \) is used to denote a generic compound.

For batch systems \( Q_w = 0 \) so the equation becomes

\[
\frac{dC_{xw}}{dt} = - \left[ \int_0^t \left( \frac{K_{x,a} \times a_s}{t} + K_{x,a} \times a_{tb} \right) dt \right] \times \left[ C_{xw \text{ eq}} - C(t)_{xw} \right]
\]

By the assumption of CSTR, \( C(t)_{xw} = C_{xw} \) and is a function of time, thus the equation is in the form of a first-order non-linear ordinary differential equation.

For a steady-state \( \frac{dC_{xw}}{dt} = 0, C(t)_{xw \text{ out}} = \text{Const.} \) flow-through system \( Q_{win} = Q_{wout} \), assuming a known time averaged total interfacial area and knowing that typically \( [K_{x,a} \times a_{tb}] > [K_{x,a} \times a_s] \), the equation can be re-written as

\[
\frac{Q_w \times (C_{xw \text{ in}} - C_{xw \text{ out}})}{V} = (K_{x,a} \times a_{tb}) \times \left[ C_{xw \text{ eq}} - C_{xw \text{ out}} \right]
\]

Solving for \( C_{xw \text{ out}} \) and recalling that the fluid residence time in a reactor, \( \tau \) is defined as

\[
\frac{V}{Q_w} \text{ gives}
\]

\[
C_{xw \text{ out}} = \frac{1}{\tau} \times C_{xw \text{ in}} - (K_{x,a} \times a_{tb} \times C_{xw \text{ eq}}) \left( \frac{1}{\tau} - K_{x,a} \times a_{tb} \right)
\]
This means that the final concentration leaving the reactor based on these assumptions is a function of fluid residence time $\tau$, the total interfacial area $a_{tb}$, the incoming concentration $C_{xw\text{ in}}$, the equilibrium concentration $C_{xw\text{ eq}}$, and the kinetic rate constant for compound $x$ to the air phase $K_{x,a}$.

The kinetic rate constant is constant for a system at specified operational conditions and is unique to a given set of compounds, phases, temperatures, and pressures. It represents the sum total resistance to mass transfer felt by a compound transferring from one region to another and is calculated by

$$\frac{1}{K_{wa} \times a} = \sum \frac{1}{k_p \times a_p}$$

(A-11)

where $K_{wa}$ is the total mass transfer coefficient between the water and air phase, $a$ is the total interfacial area, $k_p$ represents a mass transfer coefficient for a given phase $p$ and $a_p$ likewise represents an interfacial area of a given phase. For a bubbled reactor the resistance to mass transfer due to air and water must be considered.

Determining an overall mass transfer coefficient encompassing resistances to mass transfer and total interfacial area is complicated by the fact that diffusivity, total interfacial area, and equilibrium concentration all change as a function of temperature. Ordinarily a parameter such as $K_t$ would be used to denote a total mass transfer kinetics coefficient, which accounts for resistance to mass transfer as well as interfacial area, but this parameter is still a function of time, therefore a value for $K_t$ must be developed for every temperature. Using a batch system and
simplifying the equations for a batch reactor we can model the time rate of change of concentration in this system can be modeled as

\[ \frac{dC_{xw}}{dt} = -[K_t(T)] \times [C_{xw\text{eq}}(T) - C(t)_{xw}] \]  

where \( K_t(T) \) is the overall kinetic rate constant as a function of temperature, \( C_{xw\text{eq}}(T) \) is the equilibrium concentration of the compound between the liquid phase and the gas phase in the bubble at a given temperature, and \( C(t)_{xw} \) is the bulk concentration of the compound in the reactor at a given time. Knowing this, \( K_t(T) \) can be found by running a batch system in which concentration vs time, temperature vs time, and rate of change of concentration are all tracked. An equation for \( C_{xw\text{eq}}(T) \) was generated by combining the data from Goodwin and Warneck, which developed equations for Henry’s Law Constant and Vapor Pressure vs temperature. This method allows the complex parameter \( K_t(T) \) to be both simplified and easily calculable for a given reactor design, including reactor geometry, air flow rate, temperature, air sparger type, bubble size, and bubble flow regime. This method was used to calculate a \( K_t(T) \) for the Penn State system.

(Fundamental equation (A-9) was taken from Environmental Transport Processes by Dr. Bruce Logan for the modeling of oxygen transfer from air into solution. Subsequent equations were derived based on this governing equation and considering methanol transfer from solution to air. Many thanks to Dr. Logan for his instruction during his mass transfer course, and to Dr. Bill Burgos for his instruction during his organic chemistry course and consultation on this problem.)
A-3: Materials and Methods

Due to the time dependence nature of the project, the high level of complexity associated with reactor design and mass transport modeling, and uncertainty regarding chemical behavior at high temperatures and salinity, many design criteria were simplified using an empirical approach. The system was designed conceptually as a bubbled column reactor, with a constant inflow and outflow, making the residence time a function of liquid flow rate and reactor volume. A column was chosen as it maximizes the residence time of bubbles in the reactor by creating the longest travel distance from the air sparger to the fluid surface.

A 15 gallon high temperature plastic drum was used as the reactor vessel for the bubbled reactor. Air was supplied by a 5 horsepower compressor feeding into an air flow meter, needle valve, and pressure gauge to monitor air flow rate. Flow was set to the maximum setting of the compressor, which provided 8.9-9.1 SCFM of air at 16.7-18.7 psia (2-4 psig). Air injection during initial tests occurred in the base of the bubbled reactor by way of a PVC air sparger consisting of four 90° pipes each with four 1/32” openings. A ½” ball valve at the base of reactor was used for taking liquid samples. A ¼” Swagelok fitting on the lid of the reactor fed into a 3 way ball valve for gas exhaust and sampling for Gas-Chromatography Flame Ionization Detection.

When the compressor was attached to the bubbled reactor, a flow regime of majorly churn turbulent bubble behavior was observed. The reactor was large enough to prevent slug flow, and gas velocity and volume where high enough to surpass bubbly flow. The depth of the
reactor allowed for residence times at typical system flow rates of between 10 and 30 minutes as dictated by the initial fluid height in the reactor.

For initial tests, 15 kg of water was heated using an immersion heater to 50°C, then 15 g of methanol was added to achieve approximately 1000 mg/L of methanol. Background chemical oxygen demand (COD) for tap water at the combustion lab was tested and found to be between 0.5 and 1 mg/L making it less than 0.5% of the total COD. This allowed the omission of background values from calculations. The water-methanol mixture was then transferred to the bubbled reactor and air sparging began. 20 ml samples were taken immediately after fluid transfer to the reactor and at standard time intervals during the test to develop a residence time vs methanol concentration curve. All samples were taken via a ball valve in the base of the reactor.

It was observed in initial tests that the flow-through immersion heater was unable to heat the brine to a temperature greater than 50°C after 30 minutes. It was also noted that fluid began to cool very rapidly after air sparging began. To remedy this, in subsequent testing a second immersion heater was added to the heating bath and also added to the reactor before bubbling began to simulate the constant temperature of a steady state flow-through reactor as would be present in the final system design for the supercharged pulsed jet combustor. Despite these efforts, the fluid temperature dropped rapidly during the first several minutes of sparging.

To offset the effect of heat transfer from the fluid to the incoming air, an in line air heater was set up in the air line to preheat the air before introduction into the reactor. While this remedied the temperature gradient between the water in the reactor and the bubbles, much of the heat being lost from the liquid in the reactor to the surroundings was through the loss of energy
due to the enthalpy of vaporization of methanol and water being drawn out of the system. One way to remedy this situation is to couple a steam heat exchanger shell on the body of the reactor, allowing the gas phase methanol and water mixture to condense on its surface and recover the heat used to change the phase of the water and methanol solution.

COD testing was used to determine methanol concentration in each sample. Starting solutions were mixed to approximately 1000 mg/L of methanol and 20 mL sample vials were filled at each time interval for further analysis. 2 ml samples were taken from each vial and allowed to incubate in COD broth vials for 2 hours then allowed to settle before COD concentrations were determined by spectrophotometer. COD was then converted to methanol concentration assuming 100% of the COD present was as methanol and using the stoichiometric relationship of the methanol oxidation reaction.
A-4: Results

Testing showed that mass transfer of methanol was strongly a function of temperature in the reactor. Mass transfer theory dictates that the difference in methanol concentration in solution vs the equilibrium concentration must also be a factor governing rate of mass transfer, but because ambient methanol concentrations in air are so low, the equilibrium concentration of methanol in water with ambient air can be approximated as zero with no effect on the kinetic rate constant. The maximum kinetic rate constants of 0.003616 (1/sec) by theoretical model and 0.003023 (1/sec) by experiment were achieved at a temperature of 60.5 °C with an initial concentration difference of 1121.5 mg/L. The ability of this system to remove methanol is a function of fluid temperature, volume of the reactor, steady-state fluid flow rate, and starting methanol concentration. Assuming a starting concentration of 1000 mg/L, a 300 gallon reactor, 0.5 GPM flow rate, and a fluid temperature of 80°C, solutions to the model predict a 99.78% reduction in aqueous methanol concentration. As seen in Figure A-6 this solution uses a highly conservative linear fit to estimate the kinetic rate constant beyond the 60°C achieved in testing. When paired with the supercharged pulsed jet combustor as a heat source, the bubbled reactor is inexpensive, simple to operate, and effective for methanol removal.
Initial proof of concept testing showed that methanol was able to be drawn out of solution into the gas phase by air sparging, and was especially effective at high methanol concentrations and high temperatures. The strongest $R^2$ value for an equation to model the data set generated by the first test was logarithmic (as was expected due to the nature of mass transfer) with a half-life of 85.6 minutes and a time to 1-log removal of 5.88 days. These data did not have active temperature tracking and started at a low temperature relative to the maximum vapor pressure of methanol and the working fluid temperature conditions of the actual supercharged pulsed jet combustor system.

These data, shown Figure A-7, exhibited a very steep drop in initial methanol concentration, followed by a very slow decline. This was in part due to rapidly falling temperatures in the reactor caused by both heat transfer to the incoming bubbles, heat loss
through the walls of the reactor, and the latent heat of vaporization of both methanol and water being drawn out of the fluid.

These data was similarly produced in a subsequent test with a very fast initial drop in concentration followed by a rapid slowing of methanol removal with time (Figure A-8). It was theorized that perhaps mixing had not completely occurred at the start of testing and that the first data point was artificially high due to sampling error. Including the first data point, the test gave a half-life of 861 minutes. By excluding the first data point, the half-life dropped to 445 minutes. This test was run with the lid of the reactor tightly sealed and exhaust gas passing only out of the \( \frac{1}{4} \)” exhaust line. This may have caused re-condensation of methanol in this line, as the ambient temperature and fluid temperature were well below the boiling point of methanol.
Further testing, in an attempt to address the issue of temperature drop in the system, employed an immersion heater suspended in the reactor that actively heated the fluid during the experiment. Active temperature tracking allowed a relationship to be established between temperature and methanol removal rates, as well as looking at temperature drop as a function of time in the system. The immersion heater was unable to maintain a constant temperature, but it was able to hold the temperature above 34°C during the duration of the test. Based on the logarithmic regression data ($R^2 = 0.891$) a methanol half-life of 114 minutes was determined. The results of this test are presented in Figures A-9, 10, 11, and 12.

Figure A-8: Methanol concentration in solution vs residence time in the sealed top bubbled reactor
Figure A-9: Methanol concentration in solution vs residence time in the bubbled reactor with constant immersion heating

\[ y = -102.3 \ln(x) + 984.7 \]
\[ R^2 = 0.891 \]

Figure A-10: Mass flow rate of methanol out of solution as a function of residence time calculated in discreet intervals using the difference in COD values per unit time during constant immersion heating testing.
Figure A-11: Mass flow rate of methanol out of solution as a function of temperature calculated in discreet intervals using the difference in COD values per unit time during constant immersion heating testing.

Figure A-12: Temperature drop as a function of time in the bubbled reactor measured by an immersed thermocouple.
Mass flow rate of methanol out of solution is the most important parameter for this system, as the final analysis metric is total concentration reduction of methanol in solution. Using regression data for both methanol concentration and temperature vs time ($R^2 = 0.891$ and $0.9217$, respectively) mass flow rate of methanol out of solution and liquid temperature can be compared as both parameters relate to residence time of the liquid in the reactor as it cools due to heat transfer from the liquid to the bubbles and energy loss to the environment. By differentiating the methanol concentration vs time regression function, a function for methanol mass flow rate in mg/L*sec can be generated. Results shown in Figure A-13 suggest that an extreme drop in mass transfer rate occurs in the temperature region between 45 and 60°C, dropping more than an order of magnitude, from 6.58 mg/L*sec to 0.218 mg/L*sec. This means that establishing a constant elevated temperature in the reactor is vital for stimulating significant mass transfer of methanol out of solution.

Figure A-13: Mass flow rate of methanol out of solution as calculated by differentiation of the concentration vs time regression equation as compared to the change in bulk liquid temperature with time.
A final round of testing looked to quantify the combined interfacial area and kinetic rate constant of the system by achieving a steady state temperature in the system. This was not achieved by the inline air heater, but further manipulation of the relevant equations allowed for this parameter to be determined by generating regression equations for the relevant parameters. Rearranging equation A-12 to solve for \( K_t(T) \) gives:

\[
K_t(T, t) = \frac{dC_{xw}}{dt} \left[ C_{xw_{eq}}(T) - C(t)_{xw} \right]
\]

As seen in Figure A-14 and A-15, for the final round of testing \( C(t)_{xw} \) can be approximated as

\[
C(t)_{xw} = -101.7 \ln(t) + 1467.4
\]

Where \( t \) is time in seconds. By derivation it can be found that

\[
\frac{dC_{xw}}{dt} = \frac{-101.7}{t}
\]

where \( t \) is time in seconds.
Figure A-14: Methanol concentration vs time in the bubbled reactor using the inline air heater and ceramic fine bubble diffuser.

Figure A-15: Mass Flow rate of methanol out of solution, determined by first order derivative of the regression equation in Figure A-13
An equation for $C_{xw \, eq}(T)$ was developed from vapor pressure and Henry’s Law Constant equations given by Warneck and Goodwin based on the following fundamental equation:

\[ H_{p,c} = \frac{P_{x,0}}{C_{x,w \, eq}} \]  \hspace{1cm} (A-16)

Because the Henry’s Law Constant is known as a function of temperature, $P_{x,0}$ can be used to determine the equilibrium concentration of methanol in water with the incoming air. From fugacity relationships it can be shown that:

\[ P_x = \gamma_{x,w} \times x_{x,w} \times P^*_{x,w} \]  \hspace{1cm} (A-17)

where $x_{x,w}$ is the mole fraction of methanol in water, $P^*_{x,w}$ is the partial pressure of the neat liquid and is a known function of temperature as developed by Goodwin et al., and $\gamma_{x,w}$ is the activity coefficient of methanol in water. The reported numbers for this value vary drastically with technique and even using the same technique, this number varies between researchers. An average value in the temperature range in question is approximately 1.95, with maximum values around 2.7 and minimum values around 1.45. The value for $\gamma_{x,w}$ must be considered the aqueous concentration of methanol in ambient fluids in equilibrium with the air, but because this concentration would need to be measured to a high degree of accuracy and continuously with time, as well as adjusted due to the temperature and pressure found in the air line due to the compressor, an average ambient methanol partial pressure must be used. The EPA found an average concentration of 23.1 µg/L. By the ideal gas law, the partial pressure is then $1.77 \times 10^{-8}$ atm [24]. Therefore the concentration of methanol in solution at equilibrium with ambient air in mg/L is
\[ C_{x,w \text{ eq}} = \frac{5.65 \times 10^{-10}}{3.00 \times 10^{-6} \times e^{0.04117}} \]  

(A-18)

Plugging these values back into equation A-15 an equation for \( K_t(T, t) \) becomes

\[
K_t(T,t) = \frac{-101.7}{t} \left[ \frac{1.88 \times 10^{-4}}{e^{0.04117}} - (-101.7 \ln(t) + 1467.4) \right]
\]

(A-19)

This provides a semi-empirical solution for \( K_t(T, t) \) for a given round of testing. Alternately, by solving differential equation A-14, \( K_t(T, t) \) can be solved for as

\[
K_t(T,t) = -\frac{\ln \left( \frac{C_{x,w \text{ eq}}(T) - C_{x,w}(t)}{C_{x,w \text{ eq}}(T) - C_0} \right)}{t}
\]

(A-20)

Equation A-19 is specific to this test as it relies on the measured concentration in the reactor with time, while equations A-20 can be applied to a general batch reactor. The kinetic rate constant can therefore be solved for with a known initial concentration, final concentration, and equilibrium concentration. Empirical results predict a lower average value of \( K_t(T, t) \), but both values are within an order of magnitude of each other. The estimated value for ambient methanol concentration has very little effect on the model until the ambient concentration is 1 million times more concentrated, at 0.0177 atm which corresponds to an air concentration of 23.1 g/m³. At this concentration \( K_t(T, t) \) increases by 1.4%. Considering no test used more than 23 g of methanol total, this number can be approximated to be 0 and have no noticeable effect on the system kinetics. Regardless of its effect on the model, the ambient concentration as reported by the EPA was used. The results of each solution can be seen in Figures A-16 and A-17.
Figure A-16: Comparing empirical and theoretical values for the kinetic rate constant vs time assuming an ambient partial pressure of methanol of $1.77 \times 10^{-8}$ atm.

Figure A-17: Comparing empirical and theoretical values for the kinetic rate constant vs temperature assuming an ambient partial pressure of methanol of $1.77 \times 10^{-8}$ atm.
The non-dependence of the kinetic rate constant on the ambient concentration of methanol means that running this system in the field, even with an exceedingly high ambient methanol concentration, will be quite nearly as effective as running the system with an ambient methanol concentration of 0. Observing the temperature profile vs time when correlated with concentration values will allow a kinetic rate constant vs temperature equation to be generated empirically (Figure A-18). Taking these solutions we can then predict the behavior of a steady-state flow-through system given an initial and final methanol concentration and a steady-state temperature. This will allow us to determine a necessary reactor volume to supply an adequate residence time to achieve desired methanol concentrations.

Figure A-18: Temperature vs time in the bubbled reactor during tests using the inline air heater and ceramic fine bubble diffuser, noting the noticeable deviation from the trend line at the beginning and end of testing.
While the $R^2$ value for the regression modeling temperature vs time for the entire run was quite good at 0.989, significant deviation from the trend line was observed in Figure A-18 at the beginning and near the end of the test. To account for this in the final equation, two regressions as seen in Figures A-19 and A-20 were developed for discreet time intervals: From the start of testing to 8 minutes, and from 8 minutes to the end of testing. This improved $R^2$ values and removed the obvious deviation seen at the beginning and end of the test.

Figure A-19: Temperature vs time in the bubbled reactor for times between the start of testing and 480 seconds (8 minutes) using the inline air heater and ceramic fine bubble diffuser, noting the improved $R^2$ value as compared to Figure A-14.
A-5: Discussion

It is clear that at high temperatures, methanol readily transfers into the gas phase, and air sparging is an efficient mass transfer process to remove elevated methanol concentrations from solution. Mass transfer of methanol out of solution is strongly dependent on the kinetic rate constant, which is a function both temperature and interfacial area. The current system utilized a ceramic diffuser to maximize interfacial area. The diffuser was a standard part, and not designed specifically for this system. A larger fine bubble diffuser with a more even bubble flow and smaller bubbles could potentially increase the interfacial area by a large margin. The overall kinetic rate constant is comprised of a large number of variables, but it is a direct function of the
interfacial area, so increasing the interfacial area by a given factor would also increase the kinetic rate constant by the same factor. The total interfacial area is a direct inverse function of bubble size, so to increase the interfacial area by a factor of X, the bubble size must be changed by a factor of 1/X.

Another consideration for increasing mass flow rate out of the system is controlling bubble flow regime to prevent high amounts of slug flow, which could greatly decrease interfacial area. A mixture of churn turbulent and homogenous bubble flow will produce the largest interfacial area as well as facilitate mixing in the reactor. Tests performed on the current system utilized a churn turbulent flow regime, allowing the assumption of spatially uniform concentration to be valid.

Finally, proof of concept testing must be performed to validate the presented model. While the current large-scale configuration was not able to be held at a constant temperature, scaling is built into the model. A small-scale unit with drastically less overall thermal mass and a much lower flow rate could be temperature-controlled much more easily, allowing simple and direct calculations of the kinetic rate constant as well as observing reactor behavior at a wide variety of temperatures and starting concentrations.

The proposed model and experimental testing confirm that as long as high temperatures are maintained, air sparging for the removal of methanol from solution is a simple and effective solution. Scaling this type of system up for industry is much simpler than scaling involving complex flow parameters such as those found in the supercharged pulsed jet combustor. At a flow rate of 1 GPM and a sustained temperature of 85°C, a 250 gallon (945 L) tank could
achieve 3-log removal with a 4.2 hour retention time. It is clear that while methanol is very
difficult to remove from water due to its high solubility, an air sparging system operating at the
temperature and flow rate of the supercharged pulsed jet combustor is capable of high levels of
methanol removal. Improvements to sparger and reactor geometry may continue to improve the
performance of this type of system, as current geometries are far from optimized. The model
generated by the testing in this appendix shows that air sparging in a bubbled reactor may be
viable on an industrial scale for use in the hydrofracturing industry for methanol removal.
Appendix A References


