STEAM REFORMATION OF DIESEL

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STEAM REFORMATION OF DIESEL FUELS

ABSTRACT

The Remote Area Power Program was created to evaluate the possible use of fuel cells and diesel reformers in residential and off-grid applications. Diesel was chosen because an infrastructure already exits in rural communities. The UAF Energy Center demonstrated the use of a reformer to convert kerosene into hydrogen, which was used in a Proton Exchange Membrane fuel cell to power an AC load.

In the summer of 1999, UAF hosted an Energy conference. At the conference Northwest Power (reformer manufacturer) indicated a diesel reformer efficiency of 65% while Plug Power promised a system efficiency (reformer, fuel cell and inverter) of 40%. After extensive experiments, the Energy Center found the current design reformer efficiency to be 30% and the system efficiency to be 15% at best. This efficiency does not compare favorably to the currently available diesel generator efficiency of 33%.
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1 INTRODUCTION

1.1 Overview

As worldwide energy consumption increases and oil reserves become exhausted, this necessitates the development of alternative energy sources to meet the emerging energy demands.

The State of Alaska covers about half a million square miles, yet has a mere population of 500,000 people. Most of these people live in three major cities, leaving just one hundred thousand people spread out over the rest of the state in small rural communities. These communities are not connected to a statewide energy grid and depend on diesel generators to provide local electrical power. These generators produced almost half a million megawatt-hours of power last year (Alaska’s Draft Energy Plan, 2000). However, electricity produced on a small scale by diesel generators in rural areas is expensive and the generators are often shut down because of routine maintenance and unexpected failures.

For every three units of fuel energy that go into a diesel engine, only one unit comes out as electricity, and the other two as waste heat. Ideally, Diesel generators are isolated from residential areas because of noise and combustion exhaust. Because of the lack of roads it is also expensive to transport fuel to these communities. This means the cost of electricity in these rural communities is very high, providing a potential niche market for alternative power sources so long as they can provide a cheaper product.

Although it is efficient to transport electricity, transport of heat over a significant distance is both inefficient and expensive. A distributed residential power generation
system with residential fuel cells could produce both electricity and recoverable heat. This would have a high co-generation efficiency, as there is a higher demand for both electricity and heat during the long, dark and cold Alaskan winters.
1.2 History/background:

Fuel cells were first invented in 1839 when William Grove, a British amateur physicist, first discovered the principle of the fuel cell (Appleby and Foulkes, 1989). Grove used four large cells, each containing hydrogen and oxygen to produce electricity. The same cell was further used for electrolysis (Thomas et al).

It was not until a hundred and twenty years later (1960s) that NASA demonstrated potential applications of fuel cells in providing power during space flight. Industry then began to realize the commercial possibilities of fuel cells. However, this new technology needed to overcome many technical barriers along with very high research and development costs. To date, these costs have prevented fuel cells from being economically competitive with the conventional technologies for terrestrial applications.

In 1970’s, the fear of exhausting the fossil reserves in conjunction with the detrimental effects of pollution and global warming increased interest in finding clean and efficient technologies. In the mid-eighties, the U.S Department of Transportation and Energy began funding the research and development of fuel cells. This led to hundreds of companies around the world trying to make this technology economically, technically and environmentally viable. Companies are currently working to make this technology cheaper, reliable, durable and environmentally friendly.

During the late 1990’s, global warming became a major international issue. More than a quarter of all man made greenhouse gasses come from internal combustion engines. Although pollutants like carbon monoxide and nitrogen oxides can be reduced with the use of catalytic converters, there is no effective way to reduce greenhouse gasses
like carbon dioxide and water vapor. Introducing highly efficient alternative technologies like fuel cells and hybrid vehicles into transportation markets and small stationary power generation sectors may significantly reduce the dependency on oil.

A PEM fuel cell requires pure hydrogen as a fuel source. While the ideal long term solution to both the fossil fuel depletion and global warming is to use hydrogen derived from renewable technologies such as wind or solar, most hydrogen produced today comes from refined hydrocarbons. Natural gas reforming is done on a large scale in petroleum refineries, but this project was designed to evaluate the feasibility of small scale diesel reforming.
1.3 Hydrogen

Hydrogen ions are mobile and very electrochemically reactive. Hydrogen also has zero emissions characteristics, with water vapor being the only by-product.

Hydrogen is the most abundant element in the universe but on Earth most of it is found in combination with other elements like oxygen (water) and carbon (fossil fuels). It also escapes from the atmosphere in its molecular form. Therefore, hydrogen has to be extracted from water or fossil fuels. Hydrogen can be produced from water by electrolysis and from fossil fuels by reforming. Hydrogen can also be produced by gasification of carbon containing materials like coal. However this method produces large amounts of carbon dioxide as a by-product. Currently the most efficient large-scale production of hydrogen is by steam reforming of natural gas, and this is used to produce 97% of the world’s commercially produced hydrogen.

One of the major issues with hydrogen involves storage. A hydrogen molecule is very small and light, therefore it is prone to leak from its container. Also, compression and cryogenic storage is expensive. Numerous new methods of storage are being explored, including metal hydride beds. Here, hydrogen is stored by absorption into a metal.

Rxn #1.1: Hydriding reaction

\[ M + \frac{x}{2} \text{H}_2 \rightleftharpoons \text{MH}_x \]

Hydrogen can cause embrittlement of metals, including steel, through the formation of hydrides. Therefore, care has to be exercised in choosing materials that
come in contact with hydrogen. Suitable infrastructure for the manufacture, distribution and storage of hydrogen does not currently exist for transportation markets.

One of the biggest hurdle in achieving a “hydrogen based” economy is the fear of it being unsafe due to its explosive nature. Much of this fear is attributed to the “Hindenburg incident”. The Hindenburg’s fire, which resulted in the death of 35 people, is commonly believed to be caused by hydrogen. Recent research into the matter has pinpointed the cause of fire to a reactive coating containing Aluminum powder, which was present on the ships structure. However, hydrogen is flammable and explosive so it must be handled with caution.

Hydrogen storage is expensive, as energy is required to compress the gas for storage and the amortization of the capital cost of the storage vessels can be significant. Hydrogen can also be stored in metal hydride beds, but this requires manipulation of pressures and temperature. In general, there are parasitic losses involved with hydrogen storage.
1.4 Fuel Cells/ Literature review:

A fuel cell is an electrochemical device that converts the chemical energy in a fuel (usually Hydrogen) into electrical energy. A Proton Exchange Membrane (PEM) fuel cell consists of an electrolyte sandwiched by two electrodes. The oxidant, (usually oxygen) passes over the cathode and the fuel (hydrogen) passes over the anode generating electricity, water and heat. Aided by a platinum catalyst the hydrogen atoms split into H\(^+\) ions (protons) and electrons. The H\(^+\) ions diffuse through the electrolyte combining with oxygen and electrons on the cathode, producing water. The electrons cannot pass through the membrane and flow to the cathode through an external circuit. This circuit contains an electric load, which consumes the power generated by the fuel cell (Appleby and Foulkes, 1989).

Figure 1.0: Schematic of a basic fuel cell.

Taken from: http://www.fuelcells.org
1.5 Types of fuel cells

Fuel cells are being developed throughout the world for a variety of power generation applications. The five major fuel cells being considered today are: Polymer Electrolyte Membrane (PEM) Fuel Cells, Alkaline (AFC) Fuel Cells, Phosphoric Acid (PAFC) Fuel Cells, Molten Carbonate (MCFC) Fuel Cells and Solid Oxide (SOFC) Fuel Cells. Each type has unique properties and applications.

1.5.1 Polymer Electrolyte Membrane Fuel Cell

The Polymer Electrolyte Membrane Fuel Cell is being developed for potential use in electric utility, portable power and transportation. This type of Fuel Cell has an operating range of 60 – 100 °C. The electrolyte consists of a solid organic polymer and poly-perfluorosulfonic acid. The chemical reactions taking place in the cell are as follows:

Anode: $\text{H}_2 \Rightarrow 2\text{H}^+ + 2\text{e}^-$

Cathode: $\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \Rightarrow \text{H}_2\text{O}$

Cell: $\text{H}_2 + \text{O}_2 \Rightarrow \text{H}_2\text{O}$

This is the only type of fuel cell evaluated at UAF Energy Center so far. However, the energy center hopes to evaluate all the different types of fuel cells. Advantages of PEM Fuel Cells include: a low operating temperature, quick start-up and use of a solid electrolyte. The quick startup along with a high power density makes PEM Fuel Cells very desirable for transportation applications. The solid electrolyte reduces corrosion problems. The drawbacks of a PEM fuel cell include: capital cost as low
temperature catalysts are expensive, and high sensitivity to fuel impurities like carbon monoxide.

1.5.2 Alkaline Fuel Cell

The Alkaline Fuel Cell (AFC) is primarily used in space and military applications. These fuel cells generated both power and potable water for space travel. They operate at 90 - 100°C. The electrolyte consists of an aqueous solution of potassium hydroxide soaked in a matrix. The electrochemical reactions that go on in an AFC are as follows:

Anode: $\text{H}_2 + 2(\text{OH})^- \rightarrow 2\text{H}_2\text{O} + 2e^-$

Cathode: $\text{O}_2 + \text{H}_2\text{O} + 2e^- \rightarrow 2(\text{OH})^-$

Cell: $\text{H}_2 + \text{O}_2 \rightarrow \text{H}_2\text{O}$

Since the AFC uses an alkaline electrolyte the cathode reaction is fast, making it a high performance fuel cell. Its drawback involves poisoning by CO$_2$ requiring scrubbing of both air and hydrogen. In space applications, tanks of pure oxygen and hydrogen are used for propulsion and are readily available, so purifying gas streams is not a problem.

1.5.3 Phosphoric Acid Fuel Cell

The Phosphoric Acid Fuel Cell (PAFC) is currently the only commercially available fuel cell. It is used in demonstrations in the electric utility industry. This fuel cell has been under development for over two decades with more than half a billion dollars invested (DOD, 2000). A PAFC operates between: 175 – 200 °C and uses liquid phosphoric acid soaked in a matrix as the electrolyte.
The electrochemical reactions that go on in a PAFC are:

Anode: \( \text{H}_2 \rightarrow 2\text{H}^+ + 2e^- \)

Cathode: \( \text{O}_2 + 2\text{H}^+ + 2e^- \rightarrow \text{H}_2\text{O} \)

Cell: \( \text{H}_2 + \text{O}_2 \rightarrow \text{H}_2\text{O} \)

A PAFC has two main advantages, which include a co-generation (electricity plus heat) efficiency of 85% and ability to use impure hydrogen (up to 1% CO) as fuel. It also has major drawbacks such as the use of a platinum catalyst (which is expensive), a relatively short stack life (<5 years), a low current and power density and finally, a large mass and volume.

1.5.4 Molten Carbonate Fuel Cell

The Molten Carbonate Fuel Cell (MCFC) is being developed primarily for use in the electric utility industry. The MCFC can use coal derived fuel gasses or natural gas. It operates at 600 - 1000°C. Its electrolyte is a solution of lithium, sodium or potassium carbonate soaked in a matrix.

Anode: \( \text{H}_2 + \text{CO}_3^{2-} \rightarrow \text{H}_2\text{O} + \text{CO}_2 + 2e^- \)

Cathode: \( \text{O}_2 + \text{CO}_2 + 2e^- \rightarrow \text{CO}_3^{2-} \)

Cell: \( \text{H}_2 + \text{O}_2 + \text{CO}_2 \rightarrow \text{H}_2\text{O} + \text{CO}_2 \)

Because the MCFC operates at higher temperature it has a higher efficiency and the ability to use more types of fuels. It also employs inexpensive catalysts, as the carbon-to-carbon bonds in larger hydrocarbon fuels break much faster as the temperature
is elevated. However, on the downside, high temperature requires heat resistant materials and leads to corrosion problems. Some of these drawbacks have contributed to MCFC problems in field demonstrations.

1.5.5 Solid Oxide Fuel Cell

The Solid Oxide Fuel Cell (SOFC), like the MCFC is primarily being developed for use in electric utility and operates at the same temperature range of 600 - 1000°C. It uses a solid ceramic as an electrolyte, which is composed of zirconium oxide to which a small amount of yttria has been added. This creates a structure that allows rapid diffusion of oxygen ions. Its electrochemical reactions are:

Anode: \( \text{H}_2 + \text{O}^{2-} \rightarrow \text{H}_2\text{O} + 2\text{e}^- \)
Cathode: \( \text{O}_2 + 2\text{e}^- \rightarrow \text{O}^{2-} \)

Cell: \( \text{H}_2 + \text{O}_2 \rightarrow \text{H}_2\text{O} \)

SOFC advantages like the MCFC include: higher efficiency and the flexibility to use more types of fuels because it operates at high temperatures. It can also employ inexpensive catalysts and does not require a catalytic converter to remove CO as it can use CO as a fuel. Using a solid electrolyte also reduces corrosion problems. However like the MCFC, high operating temperatures lead to material failure and corrosion problems. This raises major manufacturing issues.
1.6 Reformation Technology/Literature review:

Reforming reactions have been part of the petrol-chemical industry since the early twentieth century. Only with the recent emergence of the Fuel Cell industry has there been readily available published research of different reformation technologies. However, because the technology is state of the art and the industry is highly competitive, useful literature is scarce.

There are currently several reforming technologies for separating hydrogen from hydrocarbons. These include: steam reforming, partial oxidation reforming, auto-thermal reforming, fluidized bed membrane reforming, and plasma reforming. The Energy Center hopes to evaluate all of these technologies. However, due to difficulties in obtaining working devices from suppliers, the UAF Energy Center to date has only evaluated the steam reformer and is currently working on an auto-thermal reformer.

In theory, reformation of a hydrocarbon fuel should convert all the carbon in the hydrocarbon to carbon dioxide and yield pure hydrogen. In practice however, reformation leads to the production of carbon monoxide, methane, carbon dioxide and hydrogen. Some fuel cells, such as Solid Oxide, Phosphoric Acid and Molten Carbonate are tolerant to the presence of carbon monoxide, but PEM Fuel Cells are not. Carbon monoxide levels above 50 ppm result in stack (platinum catalyst) performance degradation. Therefore, it is critical to purify the hydrogen produced in a reformer if PEM fuel cells are used.
1.6.1 Steam reforming:

1.6.1.a Diesel

Diesel is a mixture of long chain hydrocarbons and is difficult to crack. Published work on diesel reforming is scarce. Steam reforming uses pure streams of steam and hydrocarbon to provide a concentrated output stream. Steam reforming of diesel can be carried out under pressure without paying a large P-V energy penalty, since the reactor feedstock are liquids, which do not require as much energy to pressurize as gasses. However, the liquid water must be turned to steam and the reformation reaction is endothermic, so heat energy must be provided externally, and transferred across a boundary.

1.6.1.b Ethanol

Hydrogen production, using steam reforming of ethanol is under development because ethanol is easily transportable and is relatively non-toxic. Hydrogen can be extracted from ethanol through steam reforming with a Rh/Al₂O₃ catalyst (S. Cavallaro 2000). The acid support (Al₂O₃), aids in the dehydration of alcohol, while the Rhodium catalyst aids in dehydrogenation and conversion of the products into methane, carbon monoxide and carbon dioxide. With an increase in Rh content there is an increase in the content of the C₁ carbons (CO, CO₂, CH₄) and a decrease in the C₂ carbons (ethylene, ethanol and acetaldehyde) from the exiting gaseous stream (Cavallaro, 2000).
The chemical equations and figure 1.1 describe the process.

Dehydrogenation of ethanol:

\[
C_2H_5OH = CH_3CHO + H_2
\]  
(1)

Dehydration of ethanol:

\[
C_2H_5OH = C_2H_4 + H_2O
\]  
(2)

Decarbonylation of acetaldehyde:

\[
CH_3CHO = CO + CH_4
\]  
(3)

Steam reforming:

\[
CH_4 + H_2O = CO + 3 H_2
\]  
(4)

\[
C_2H_4 + 2 H_2O = 2 CO + 4 H_2
\]  
(4')

Steam reforming:

\[
CH_3CHO + H_2O = 2 CO + 3 H_2
\]  
(4'')

Shift reaction:

\[
CO + H_2O = CO_2 + H_2
\]  
(5)
Figure 1.1: Pathway for steam reforming of ethanol (Cavallaro et al, 2000).
Steam reforming of methane is a well-known, commercially available process for hydrogen production. Over 90% of the hydrogen in the US is manufactured through steam reforming of natural gas, whose main component is methane. Steam reforming creates a hydrogen-rich gas mixture by reacting natural gas with steam at temperatures between 700 and 900°C (Koch et al, 1998). This mixture still has substantial amounts of carbon monoxide, which can poison a PEM fuel cell, so the mixture is further reacted with steam in catalytic converters (shift reactors), to yield more hydrogen and carbon dioxide. The reactions are as follows:

Rxn #1.2: Steam reforming

$$\text{CH}_4 + \text{H}_2\text{O} \leftrightarrow \text{CO} + 3 \text{H}_2$$

Rxn #1.3: Water-gas shift reaction

$$\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2$$

The steam reforming process is endothermic. The endothermic reforming reaction and the combustion reaction required to maintain it are housed separately. Heat is transferred through a wall from the combustion zone to the reforming zone.
Figure 1.2: Schematic of a natural gas reformer running a PEM fuel cell

Taken from Fraunhofer Institute for Solar Energy Systems.
1.6.1.d Biomass:

Biomass can be thermo-chemically converted to hydrogen by two distinct processes. The first one involves gasification followed by a shift conversion. The second involves fast pyrolysis of the biomass followed by steam reforming and shift conversion. (Wang et al, 1999).

Raw gas produced in biomass gasification in a fluidized bed must be cleaned of tars and particulates using hot gas cleaning. Hot gas cleaning methods are based on the use of calcined dolomites or on steam reforming with a nickel-based catalysts located downstream of the gasifier. Up to 98% tar conversions can be obtained using nickel-based catalysts (Corella et al, 2000).

The second method of obtaining hydrogen from biomass involves pyrolysis followed by steam reforming. Pyrolysis is the thermal degradation of biomass in the absence of oxygen. Biomass, such as wood and garbage are heated to temperatures of 450-800°C without introducing oxygen to support the combustion. Pyrolysis of biomass results in three products: gas, bio oil and charcoal. The bio oil can be efficiently reformed to yield hydrogen. Using commercially available nickel based catalysts; the hydrogen yield can be as high as 85% of the stoichiometric value (Wang et al, 1999). The steam reforming reaction of bio oil is as follows:

\[ \text{Rxn # 1.4: Steam reforming of bio oil} \]

\[ C_nH_mO_k + (2n-k)H_2O \leftrightarrow n\text{CO}_2 + (2n + m/2 - k)\text{H}_2 \]

Thus, the stoichiometric yield or ratio of hydrogen is \((2 + m/2n - k/n)\) moles per mole of carbon in the feed. This process is aided by a nickel-based catalyst, which can easily be
regenerated by steam or CO$_2$ gasification of the carbon deposits (Wang et al, 1999). Bio oil consists of many different compounds: acetic acid, m-cresol, dibenzyl ether, glucose, xylose, sucrose, etc. These compounds can be converted to hydrogen using steam reforming but the efficiency of the process depends on the fuel (Marquevich et al, 1999). Acetic acid is most readily converted to hydrogen and carbon oxides if the catalyst temperatures are above 650°C. Oxygenated aromatics (m-cresol and dibenzyl ether) are also completely converted to hydrogen and carbon oxides as long as the catalyst temperature is above 650°C. Sugars (glucose, xylose and sucrose) are difficult to process because they are easily pyrolyzed and form char very readily upon injection. The reforming of sugars also requires a very high (over six) steam to carbon ratio (Marquevich et al, 2000).
The process of biomass reforming is as follows:

![Diagram of biomass reforming process]

Figure 1.3: Hydrogen production via pyrolysis and steam reforming (Wang et al, 1999).
Partial Oxidation Reforming

Partial Oxidation (POX) reforming involves the partial burning of a fuel rich mixture over a catalyst. Here, methane or some other hydrocarbon is oxidized to produce carbon monoxide and hydrogen.

Methane is partially oxidized as follows:

Rxn # 1.5: Methane oxidation

\[
\text{CH}_4 + \frac{1}{2} \text{O}_2 \rightarrow \text{CO} + 2\text{H}_2
\]

Unlike the steam reforming process, the POX is an exothermic reaction and is usually carried out at atmospheric pressure. Therefore, no indirect heat exchanger is needed. A hydrogen plant that is based on partial oxidation involves a POX reactor, a shift reactor and finally a hydrogen purifier. POX can be used to reform heavy hydrocarbons and is better able to follow a load. However, the hydrogen concentration in the mixed gas stream is under 40% (Krumpelt) and contains large amounts of carbon monoxide and nitrogen. Since PEM fuel cells require a rich hydrogen stream and is poisoned by carbon monoxide, POX is currently used to feed high temperature fuel cells like Solid Oxide and Molten Carbonate. Large amounts of carbon monoxide can be removed with a subsequent CO shift. Here, the CO is selectively oxidized with air to remove it from the reaction gas.
The Underoxidized Burner (UOB™) generates hydrogen through a unique partial oxidation process that provides high efficiency in a compact hardware design.

Figure 1.4: Partial oxidation plant.

Taken from California Hydrogen Business Council Homepage.
1.6.3 Auto-thermal reforming

Auto-thermal reforming is essentially a Partial Oxidation process followed by steam reforming. The partial oxidation reaction generates heat and produces hydrogen. This is followed by steam injection and an endothermic reaction, which absorbs the heat from the partial oxidation process, and produces more hydrogen. This process has the advantage of being able to produce the heat required in the endothermic process from its exothermic process. It is possible to produce a higher concentration of hydrogen in the autothermal process than in the POX but not as high as steam reforming because of the nitrogen diluent. The raffinate gas stream contains high amounts of carbon monoxide which must be removed by water in a shift reaction.

1.6.4 Fluidized Bed Membrane Reforming:

Steam reforming of methane is a well-established industrial process that has been optimized at a large scale. With an increasing demand of hydrogen, efforts are underway to improve the efficiency and economics of the process, especially at a small scale. Most of the efforts undertaken have been to improve the performance of the nickel based catalyst and improving the properties of the reactor tube material, so it can withstand thermal shock/stress better. This processes started when a group of researchers from Egypt and Canada began work in the early eighties on a different process for steam reforming of methane using the fluidized bed concept.

The University of Calgary conducted studies on the Fluidized Bed Membrane Reforming (FBMR), and found it to be 12% more efficient than conventional technology at comparable operating temperature and pressure, if hydrogen was efficiently removed
from the reactor. However, the FBMR have a higher capital and operating cost than conventional steam reforming. These maybe overcome by improved membrane efficiency and more efficient heat recovery.

Figure 1.5: FBMR to reform natural gas.

Taken from University of Calgary. (http://www.ch2bc.org)
1.6.5 Plasma reforming

Plasma reforming involves direct dissociation of hydrocarbons using radio frequency electromagnetic radiation. This method, like electrolysis has the big disadvantage of requiring electricity to drive the reaction. Plasma is being considered as an ionization source for autothermal reforming.
1.7 Energy in Rural Alaskan Communities:

Electrification of rural Alaskan communities began in the early 1970’s. This was made possible from oil revenues. An infrastructure of diesel generators was set up through out rural Alaska. The cost of energy production per kilowatt-hour is very high from these generators because diesel fuel must be transported to these villages by barge or air. The State of Alaska created the Power Cost Equalization (PCE) program to offset the high cost of power production in rural Alaska. This means that rural residential users pay the same rate per kilowatt-hour as the urban communities for the first 375 KW-Hr/Month.

The Remote Area Power Program (RAPP) was created to address the electrical needs of rural Alaska. It was envisioned to be a research and development program for technologies suited for the arctic climates of Russia and Alaska. A technology of particular interest to the hydrogen community and one pursued by industry for residential power applications is the Proton Exchange Membrane Fuel Cell.

Fuel cell units placed inside homes could provide both electrical power and heat. This cogeneration devise would replace diesel generators and boilers used for space heating and domestic hot water.
Although it is relatively cheap to transport electricity, transporting heat is expensive (and can melt the permafrost). However, if heat is recovered in each household then it can be used for space heating. Also, in Alaska the summers are warm and have long day light hours, whereas the winters are cold and dark. This means households require more electricity in the winter, which coincides with maximum heat loads. A local grid system could be established in rural villages allowing for a large amount of cogeneration. This grid would allow for certain units to shut down for maintenance and repairs, or even in the case of failure without loosing power to the entire community. This would eliminate the need for a centralized power plant and make electricity/heating much more cost effective.
Figure 1.7: Micro-grid with some of the houses having fuel cells.

Taken from Witmer et al, (1999)
The goal of RAPP is to move Alaska toward an environmentally benign, carbonless and sustainable society in the following ways:

1. Accelerate the development of technologies that use hydrogen, specifically the PEMFC integrated system.

2. Establish power generation systems that increase overall efficiency of energy utilization and system reliability.

3. Significantly reduce the dependence on fossil fuels at present, while putting in place the systems necessary for the eventual transition from fossil fuels to renewables in the future.

The US Department of Energy’s Hydrogen Program is funding the Fuel Cell Project.

The project initially started with nine team members:

1> Plug Power (fuel cell development and system integration).

2> Idatech (reformer development and system integration).

3> Schatz Energy Center (fuel cell development).

4> Hydrogen Burner Technology (Reformer development).

5> Energy Partners (fuel cells).

6> Teledyne Brown Engineering (Electrolyzer and system integration).

7> Argon National Laboratory (reformer technology).

8> Sandia National Laboratories (system integration and program management).

9> UAF Energy Center (Arctic test and evaluation of fuel cells and reformer).
1.8 UAF Energy Center

The UAF Energy Center was created with the mission of evaluating renewable and alternative energy technologies that could reduce the cost of producing power in remote Alaska. The role of the Energy Center is to experiment with potential technologies in an environment where technical support is readily available and ensure that the technology is suitable for arctic conditions (Johnson et al, 2000).

The goals of the energy center are as follows:

- Develop sustainable energy systems for use in rural communities.
- Provide testing and evaluation of such systems.
- Develop ways to link electricity with utilities.
- Establish long-term training program.
- Develop control systems for on site and remote monitoring.

UAF Energy Center teamed up with Sandia National Laboratories (SNL) to begin a three-phase project that would evaluate fuel cells for use as stationary power generators in rural Alaska. Phase one involved the delivery and making operational of PEM Fuel Cells and a kerosene or diesel reformer that would produce “fuel cell quality” hydrogen. Phase two involved the delivery of second generation PEM Fuel Cells and reformers from the industrial partners. The goal was to have laboratory systems fully integrated, producing “grid” quality power in a fully automated manner. Phase three is to create third generation, fully automated systems suitable for remote locations. Phase one and two have been completed so far and phase three is on hold due to funding restrictions.
Figure 1.8: Schematic of the complete Fuel Cell System
Taken from Witmer et al (1999)
An integrated fuel cell system would consist of: a diesel reformer producing pure hydrogen, a PEM Fuel Cell producing DC power and an inverter converting the DC to AC power that can be used by household appliances. The integrated system requires the input of diesel, water and air, while producing water, waste heat and electricity.
2 EXPERIMENTAL METHODS

2.1 Reformer description:

Idatech, formerly known as Northwest Power Systems of Bend, Oregon built the reformer described in this work. It is a steam reformer with a palladium membrane assembly that permits the production of pure hydrogen. This steam reformer was a modification of the methanol reformer. Most of the work done by Ida Tech involves an integrated fuel cell stationary power system that uses methanol as the fuel. Methanol is comparatively easy to reform as the reformation reaction takes place at relatively low temperatures (350°C). However, methanol has a much lower energy density than other conventional hydrocarbon fuels. The reformer provided for this program was studied using diesel as the fuel. This is because an infrastructure of diesel already exists in rural Alaska, and would make the transition from diesel generators to fuel cells much smoother. Picture of the Idatech reformer is shown below:

of the Idatech reformer is shown below:

![Picture 2.0: Idatech Diesel Reformer.](image-url)
Reforming diesel requires significant modifications to the methanol reformer design. Methanol and water are miscible and therefore can be premixed, but diesel and water are not miscible and have to be fed separately. The catalyst used is also different since diesel is a mixture of long chain hydrocarbons and the catalyst has to aid in the break down of these chains. The operating temperature for the diesel reformer is about 450°C higher than methanol, which means more heat resistant materials have to be used. Also, when dealing with high temperatures, the design of the burner and heat transfer surfaces can have significant impact on the efficiency of the process. Idatech has implemented these changes over a series of prototype reformers that have been supplied to the RAPP Program for testing. Each new reformer has been an improvement over the previous prototype.

Vaporization of diesel fuel is difficult, but must be complete if coking (deposition of carbon) is to be avoided. In the Idatech design, steam is superheated sufficiently so that when it is mixed with diesel, the whole mixture is (hopefully) vaporized. However, since diesel is a mixture containing heavy hydrocarbon chains and is under pressure (10atm), the entire mixture may not vaporize. At atmospheric pressure, diesel should completely vaporize at 600 °C.

The mixture of diesel and water flows over the catalysts (Nickel based) that are packed into eight catalyst tubes. The catalysts facilitate the endothermic reformate reaction. Methane, Carbon dioxide, Carbon monoxide, water vapor and hydrogen are the products of the reformate reaction.
Hydrogen diffuses through a palladium membrane before exiting the reformer. This flow through is governed by the partial pressure difference of hydrogen across the membrane. The palladium membrane is selectively permeable to hydrogen, as hydrogen enters into solution and passes through while the membrane remains impervious to all other gasses. The membrane’s optimal operating temperature is 400°C. In the Idatech reformer the temperature differential between the catalyst and membrane is maintained by housing the membrane in a separate module while providing air and water flow for cooling while simultaneously preheating reactants. Palladium membranes are considered too expensive and fragile for large-scale reformers as a single defect results in failure, but may work well for a reformer scaled to meet residential applications.

Though palladium is a very effective hydrogen purifier, other gasses may pass through leaks at the seals along the edge of the membrane. These impurities are in low concentrations and can be cleaned by employing a methanization catalyst. The methanization catalyst converts carbon monoxide and carbon dioxide in the hydrogen stream into methane and water, which are inert in the fuel cell.

The catalyst used in the Idatec reformer is sensitive to sulfur. Diesel and kerosene contain significant quantities of sulfur that would poison the catalyst if not removed. Sulfur free fuel such as pure decane can be purchased but is far too expensive for use in anything but lab experiments. For most experiments de-sulfurized K-1 kerosene was used. Most of the de-sulfurization was done in the lab. The fuel, at 150PSI and a flow rate of 10ml/min was passed through a chamber containing a zinc oxide absorption bed. The chamber was placed in an oven that was heated to 450°C. The absorption bed
consists of pellets made of zinc oxide, which chemically binds to the sulfur and removes it from the fuel.

Picture 2.1: High temperature oven used for de-sulfurizing.
2.2 Instrumentation:

The primary objective of the experiment was to evaluate the performance of the Idatech steam reformer. In order to accomplish this it was important to determine a first law thermodynamic energy balance. This required knowing the amount of energy coming in and leaving the system. It also required determining the concentration of products and reactants in the reformate reaction. The reformate reaction is as follows:

\[ C_n H_{2n+2} + H_2O \rightarrow aCO + bCO_2 + cCH_4 + H_2 + H_2O \]

A variety of instruments were used on the reformer test bench to collect data. Sensors to measure temperature, pressure, flow rate and gas composition were set up at various points on the test bench. (Fig 2.1).
Figure 2.1: Location of sensors on test bench.
Since the energy coming into the system consisted of propane and hydrocarbons like diesel and kerosene, flow meters were required to determine these energy flows. The flow of diesel and water were initially measured using a paddle wheel flow meter. This device incorporates a paddle wheel, and a sensor inside the instrument that measures the frequency, which is directly correlated to the flow rate. The flow meter was used in a feedback system to control a micro pump (Fig 2.2). It was initially calibrated using a graduated cylinder and a stopwatch.

![Figure 2.2: Flow meter and pump feedback loop.](image)

However, discrepancies in the flow reading of the paddle wheel flow meter were found, and the data discarded. Some of this error could have been due to the design of the flow meter, which uses a small orifice in order to get the velocity of the flow high enough to spin the paddle wheel. This small orifice could easily have been partially blocked by a particle. Errors could have also resulted from air bubbles being trapped in the paddle wheel.
When the energy balance was first calculated it was off by a considerable margin. It became apparent that the paddle wheel flow meter was not working and two other methods to quantify water and diesel flow were used. The first method involved using a mass balance with a load cell. Knowing the density of water and diesel, the volumetric flow rate can be correlated to the corresponding weight loss. The graph shown on the next page (Fig 2.3) was used for the scale calibration. To obtain this graph a known mass was loaded on the scale and its corresponding signal (voltage) recorded.

The second method devised, involved the use of a burette to do “on the fly” measurements of flow rates (Fig 2.4). The burettes acted as a reservoir for the fluids until a valve was flipped so that all the fluid flow was from the burette only. At this point a stopwatch was used to measure the flow rate. After the measurement the valve was closed so fluid would be drained from the main reservoirs. This allowed monitoring of flow rates at will.

Also, repeated attempts to calibrate the paddle wheel flow meters resulted in very inconsistent results, and a decision was made to replace this system with a different type of pump that uses constant displacement pistons. Flow rates were estimated based on calibration curves, and measured by burette.
Figure 2.3: Load Cell calibration curve.

Figure 2.4: Schematic of Burette setup.
2.2.1 **Piston Pumps:**

The piston pumps are made by Fluid Metering Inc (FMI). In these pumps the valve-less pumping function is accomplished by the synchronous rotation and reciprocation of the piston in the precisely mated ceramic cylinder liner. A complete piston revolution is required for each suction/discharge cycle. The flow rates can be adjusted by moving the pump head position, which changes angle with respect to a rotation axis and the stroke length. A single motor can be outfitted with a pump on either end of a shaft, which means they can be used to simultaneously pump diesel and water. This allows a constant a steam to carbon ratio over a range of flow rates. The FMI pump was calibrated to better than 0.5%.

![Figure 2.5: Schematic of a FMI pump. (Taken from FMI web page).](image)

2.2.2 **Hastings Flow Meter:**

The mass flow rate of combustion air into the system was measured using a Hastings laminar flow meter made by Teledyne Brown. Laminar flow is induced inside the flow meter by passing the air stream through very small stainless steel tubes, which in
turn helps maintain a low Reynolds number. A small heating element inside provides thermal energy into the flow stream, inducing heat flow. Knowing the specific heat capacity of the gas, the temperature difference induced and the thermal energy dissipated by the heating element, mass flow rate of the gas can be calculated using the equation:

\[ Q = m c_p \Delta T \quad (2.3) \]

The Hastings flow meter came with a National Institute of Standards (NIST) calibration. The NIST certificate indicated the Hastings has a calibration error of less than one percent when the devise was delivered. The Hastings was also calibrated against another Hastings and a MKS flow meter, all agreeing to within one percent.

2.2.3 MKS Flow Meter

The hydrogen produced by the reformer was measured using two separate meters: MKS mass flow meter and a Cole Parmer volumetric flow meter, which acted as a check against each other. A MKS mass flow meter is calibrated using a specific gas, in this case hydrogen.

A volume of pure gas has a known mass at standard conditions. With a change in pressure and temperature there is a change in volume but the mass remains constant. Like the Hastings, the MKS measures mass flow by sending a portion of the gas through a sensor tube where the gas is heated with a coil and the temperature difference measured downstream.
Flow meters require clean dry gas. Any particle larger than 50μm has to be filtered out upstream. This is not a problem because better than ninety nine percent pure hydrogen is the only gas that goes through the flow meters. An advantage of using mass flow meters is that they not only measure mass directly but are also capable of handling fluctuations in temperature and pressure.

Several methods were used to calibrate the MKS. One involved filling a balloon with hydrogen gas while measuring the time needed to fill the balloon. The change in buoyancy was used to calculate the flow rate of hydrogen. Another method involved calibrating the MKS meter against the MKS meter on the fuel cell bench. Also, a bubble meter was used to verify the authenticity of the MKS reading.

Another way of measuring hydrogen flow is by correlating the stack current provided by the fuel cell, with the flow rate directly. The current is measured in amperes. Each molecule of hydrogen produces two electrons, which is equivalent to 3.2×10^{19} coulombs. There are Avogadro's (6×10^{23}) number of molecules in one mole of hydrogen which occupies 22.4 litters of space. So a direct correlation can be made between the measured current in amperes and the flow of hydrogen in standard litters per minute. Using the above procedures the error on the MKS was found to be 0.5%, which is better than the nominal factory calibration of 2%. 
The fuel cell bench MKS was calibrated using the following relationship:

\[ V = \frac{h_{HHV} \cdot m_{H_2}}{I} \]

Where:

- \( V \) = Stack voltage
- \( h_{HHV} \) = Higher heating value of hydrogen, 212.7 W/slm.
- \( M_{H_2} \) = Flow rate of hydrogen through the MKS, slm.
- \( I \) = Stack current, amperes.

Since voltage and higher heating value of hydrogen are known the flow rate of hydrogen can be correlated with the stack current for the polarization curve.

One problem with the MKS was noted on the reformer bench. Because the MKS operates by measuring a temperature difference, it is susceptible to error when placed in temperature gradients. This was observed on the reformer test bench when the MKS was placed next to the reformer. This resulted in heat being transferred to the flow meter from the reformer. The problem was corrected by moving the MKS to the bottom of the test bench where the heat flow was not an issue.

2.2.4 Temperature measurements:

Temperatures on the reformer had to be monitored. A total of 27 thermocouples were installed on the reformer bench. The catalyst tubes, burner, inlet and outlet
temperatures on the heat exchanger were monitored using type K thermocouples. The thermocouples are rated to +/-0.5 °C over their entire range but can be calibrated much more precisely at room temperature to +/-0.1 °C. This was done for the two thermocouples on the inlet and outlet of the heat exchanger. This was very important because the heat exchanger undergoes a small change in temperature and this had to be measured accurately. The thermocouples were calibrated against a fluke process meter, which comes from the factory with a NIST calibration.

2.2.5 Pressure measurements:

The reformer is operated at about 150 PSIG nominal. Pressure transducers are used to monitor these pressures. The transducers were calibrated using manual dial gauges under both vacuum and pressure. The transducers were connected in series with the pump and the pressure settings on the pump varied. The readings on the transducer were compared to the readings on the pump. These values agreed to within one percent.

2.2.6 Water Measurements:

In order to understand and verify the chemical and physical equilibrium in the system the water mass flow had to be measured. Water in the raffinate (product of reformation reaction) is difficult to measure with the FTIR because it may condense out on the sensors, causing errors, and also because of its high Infra Red absorbance.

It is relatively easy to measure the water content of the combustion exhaust, as the water can be condensed in a heat exchanger and measured. The combustion gas runs
through a heat exchanger. The water, which condenses inside the heat exchanger is collected in a collection cup and measured. The exit temperature of the combustion gas out of the heat exchanger was below the dew point of the water vapor, and so most of the water could be condensed out of the exiting gas.

![Diagram of reformer and heat exchanger]

Figure 2.6: Measurement of water in raffinate and combustion exhaust

Since the reformate gas passes through an external tube on its way to the burner, a method was devised to measure the water content. The reformate gas produced was routed through a cylinder holding a known mass of dry desiccant. The desiccant used in this case was commercial dryrite, which is a trade name for CaSO₄. It’s capable of holding a large amount of water and can be recharged.

The cylinder with the dryrite was weighed before the reformate gas is passed through it and once again after the passing. The difference in weight corresponds to the amount of water absorbed from the reformate gas. The experimentally determined flow
rate of water in the raffinate was found to be within five percent of the calculated value. While it was not practical to conduct this measurement on a continuous basis, it did serve to verify that calculations based on mass flows into the system and carbon species were relatively accurate.

2.2.7 *Calibrations and Error Analysis:*

A variety of measurements were made on the test bench. Each instrument came from the factory with a nominal error. To make the bench measurements more precise, this error could be reduced by calibrating each device carefully. The equations of the calibration curves were programmed into the control system to correct for systematic errors. The measurements made on the test bench could be crosschecked with other devices and calculated values.

All the thermocouples used on the lab bench were type K. Type K thermocouples come with a factory calibration of +/- 0.5°C. This was adequate for all the temperature measurements made on the test bench, except the heat exchanger thermocouples. In the heat exchanger; the measured ΔT is small (4 °C). The two thermocouples on the heat exchanger were calibrated to +/- 0.1°C. These thermocouples were wired to read a temperature difference, which further improved its precision to read the difference in temperature between the inlet and outlet of the heat exchanger.

The table below shows the factory calibrations along with the calibrations performed in the lab. In all cases other than the McMillan, the lab calibrations have an error range less than or equal to the factory calibrations.
Table 2.1: Instrument Calibrations

<table>
<thead>
<tr>
<th>Instrument</th>
<th>Nominal Error</th>
<th>Energy Center Calibration</th>
<th>Senses</th>
</tr>
</thead>
<tbody>
<tr>
<td>FMI Pumps</td>
<td>0.5%</td>
<td>0.5%</td>
<td>Water and diesel flow</td>
</tr>
<tr>
<td>Macmillan flow meter</td>
<td>1%</td>
<td>Found errors from 1% to 75%</td>
<td>Water and diesel flow</td>
</tr>
<tr>
<td>MKS flow meter</td>
<td>2%</td>
<td>0.5%</td>
<td>Mass flow of H₂</td>
</tr>
<tr>
<td>Hastings flow meter</td>
<td>1%</td>
<td>1%</td>
<td>Mass flow rate of combustion air.</td>
</tr>
<tr>
<td>Thermocouples (K)</td>
<td>+/- 0.5 °C</td>
<td>+/- 0.1 °C</td>
<td>Inlet and outlet temp of heat exchanger.</td>
</tr>
</tbody>
</table>
2.3 Data acquisition/control system and operation:

The Northwest Power Systems reformer was supplied to UAF without a control system. Obtaining useful data required the energy center to set up a system to acquire data and control the reformer. Since this was a laboratory experiment it was essential to maintain maximum flexibility by using a high-level control system therefore, National Instrument’s LabVIEW and compatible hardware were selected.

LabVIEW allows for a two-way interface with devices like pumps, heaters, thermocouples, valves etc. It is able to control a device by sending an output signal and at the same time acquire data by collecting and storing an input signal. Most of the devices selected for the reformer bench supplied signals of 0-5 Volts or 4-20 milliamps. LabVIEW can read the voltage signal directly. However the 4-20 milliamp signal has to be converted to voltage by using a calibrated resistor. The voltage drop across the resistor is directly proportional to the current. The advantage of the 4-20 mA signal was that line losses need not be considered since the current is small and therefore not affected by line losses. A Macintosh (G3) was used to store and process the data.

This visual instrumentation program allowed various data to be displayed on the computer monitor including:

- Single button startup
- Catalyst tube and burner temperature profile
- Water, raffinate and hydrocarbon pressure
- Water, methanol and Diesel flow rates
- Hydrogen production as recorded by the MKS and Cole Parmer instruments.
The program allowed the system to be started and shut off automatically by the click of a mouse either on the dedicated computer or from a remote site. The program also has a manual mode, which allowed for the system to be controlled manually while still recording data. The system logs the values of parameters as a function of time and stores the information in text-based files. These files can be manipulated through spreadsheets and transferred over the Internet.
2.4 Fourier Transform Infrared Spectrometer:

In order to calculate an energy balance, it was essential to quantify the carbon species in the raffinate stream.

\[ C_nH_{2n+2} + H_2O \rightarrow aCO + bCO_2 + cCH_4 + H_2 + H_2O \]

Knowing the concentration of carbon species \((a, b & c)\) in the raffinate stream is necessary to compare the change of state runs (4/17/00) with the results of equilibrium calculations. It is also necessary for attaining an energy balance for the system. The three carbon species of interest are carbon monoxide, carbon dioxide and methane. To aid in this process a Fourier Transfer Infrared Spectrometer (FTIR) was utilized.

A FTIR spectrometer has two main parts: an optical system with an interferometer and a dedicated computer. The computer is used to control the optical components, collect data, store data, manipulate the data through computations and display the spectra. The picture below shows the FTIR used in this work.
The FTIR used in this work was made by Bruker Optics. A Pentium III PC was supplied with the instrument, using OPUS software to record the spectrum of absorbance versus wavelength. The figure below shows a typical spectrum of a raffinate sample.

![Graph showing IR Spectra of Raffinate](image)

**Figure 2.7: Infrared Spectrum of a raffinate stream.**

OPUS has a built in integrator that allows for calculation of area under each peak. Each species has a unique intensity of absorbance, so the area under the peaks had to be
adjusted in order to compare the ratios of different carbon species using known adsorption coefficients.

2.4.a Advantages and disadvantages of FTIR:

A FTIR was chosen for this work because the species of interest can be simultaneously quantified rapidly and with high accuracy. This allows precise measurement of the quantity of various gasses in the raffinate stream without time constraints.

The most important disadvantages are; the FTIR cannot measure hydrogen concentrations, and water masks the absorption peaks of the carbon compounds. This is due to the massive absorption of infrared radiation by water.

2.4.b Water removal from raffinate stream:

Water is a strong absorber of infra-red energy. In order to read the ratios of the carbon species in the raffinate stream, water had to be removed before an IR spectrum was taken. To achieve this the following steps were undertaken.

At the point that the sample was taken from the reformer, raffinate was passed through a Teflon tube that was wrapped in heat tape. The tape kept the temperature of the raffinate stream above the dew point of the mixture. This was so that water could not condense out and block the flow. Teflon tubing was used because of inert properties, which means it does not react with or out-gas any species that might influence measurements of hydrocarbons in the raffinate stream. The Teflon tubing was connected to nafion tubing that was placed in a jar surrounded by desiccant. Nafion has the unique
property of allowing only water to diffuse through to the dessicant. Then the dry refformate stream flowed to a heated cell that kept the temperature at 100°C. Since, the vibration energy is a function of temperature, it is important to have a standard state in the FTIR cell.

![Diagram of raffinate stream measurement](image)

Figure 2.8: Setup of raffinate stream measurement.

The FTIR method offers the means to rapidly scan over a broad range of IR wavelengths and quantify carbon species and it is the ideal instrument for this experiment. It should be noted that the FTIR is a complex instrument and a through examination is beyond the scope of this thesis.
2.5 Operating procedure:

The production of hydrogen using the Idatech reformer requires the catalyst bed to be at a temperature of 800°C and the palladium membrane to be at 400°C. The reformation reaction is endothermic so additional heat is required for hydrogen production. When running self-sustained, the required heat is maintained by burning raffinate after product hydrogen is removed. The raffinate gas contains residual hydrogen, carbon monoxide and methane, all of which are fuels. During startup however, no raffinate is available and a supplemental fuel is required. The supplemental fuel used for this work was propane. However, this means a second fuel source has to be available and plans are under way to either use stored hydrogen or a burner capable of burning diesel fuel to solve this problem.

Whenever the reformer is not in operation and the catalyst is not completely isolated from the atmosphere, an oxide layer forms on the surface. Therefore, catalyst reduction is a necessary step in the initial start up. The oxide is removed by exposing the catalyst to a reducing environment. In this work, the catalyst was reduced using a mixture of two parts water and one part methanol starting when the average catalyst temperature reaches 625°C. This mixture was passed over the catalyst bed until a steady hydrogen flow of 12-15 slm was achieved.

After complete catalyst reduction, the flow of methanol and water was stopped, and water was fed until the hydrogen production drops close to zero. Then, hydrocarbon is introduced to the system, which results in the hydrogen flow rising quickly. Once
running on hydrocarbon the system is allowed time to come to equilibrium (10 min) before switching to raffinate, if it was to be run in the self-sustained mode.

**Hydrogen Flow 4/21/00 Self Sustained**

![Graph showing hydrogen production](image)

Figure 2.9: Production of hydrogen from reformer startup to end of run.

The figure above shows hydrogen production during a complete run. For the first 45 minutes the catalyst was reduced using a mixture of methanol and water. After stable hydrogen production was achieved, methanol was cut and the hydrogen production dropped to zero. At this point hydrocarbon was introduced.
2.6 *Overall Experimental Program:*

The premise of the experiment was to measure the thermodynamic efficiency of the reformer in diesel steam reforming. The equilibrium reaction for the reforming of diesel which is central to this experiment is:

\[
C_nH_{2n+2} + H_2O \rightarrow aCO + bCO_2 + cCH_4 + H_2 + H_2O
\]

The concentration of product species \((a, b \& c)\) in the above reaction were measured using a Fourier Infrared Spectrometer for carbon species, hydrogen flow meter for hydrogen and a mass difference method for water. The composition of the products in the above reaction is called raffinate. The measured concentrations were compared to the predicted concentrations of the mathematical (Lutz) model.

In the field it is desirable for the reformer to operate on a single fuel, and at a satisfactory efficiency (upwards of 70%). In the lab, two experiments were performed. The first was an attempt to explore the performance of the catalyst at various temperatures, pressures, flow rates and observe deviation from equilibrium. This required operation of the burner on propane so that steady state temperatures could be maintained. The flow of propane to the burner can be controlled and so the operating temperature of the reformer can be varied in a controlled manner since the two are interrelated.

The second experiment was in self-sustained mode by burning raffinate. Burning raffinate gives a more direct measure of the efficiency. The system finds its own equilibrium, giving the operator little control over the reformer temperature. The start up process still required the use of propane. In this sate the steam to carbon ratio was
maintained at a constant value while only the fuel flow rate and raffinate pressure were altered.

Reducing pressure at the membrane allowed more hydrogen to remain in the raffinate, thus increasing the heating value of the raffinate available to the burner but reducing the hydrogen produced, thus reducing the overall efficiency.

In the catalyst characterization tests; steam to carbon ratio, temperature, pressure and fuel flow were varied. Each state was allowed to equilibrate for approximately twenty minutes and the hydrogen flow was measured. FTIR spectra of the raffinate were taken in each of these states. These raffinate compositions were compared with the ChemKin results from Sandia National Laboratory.
3 RESULTS:

3.0.a History of deliveries:

The first IdaTech reformer was first tested in December of 1998 at the Sandia National Laboratories in Livermore, California. It ran for a few hours on the test bench using kerosene as the reforming fuel until the palladium membrane failed. A similar model was shipped to the UAF Energy Center seven months later.

The Energy Center publicly demonstrated the reforming of kerosene fuel feeding a PEM fuel cell stack for the first time in August of 1999. Engineers from Northwest Power Systems and Schatz Energy Center were at UAF to help with the demo. Northwest Power and Schatz Energy Center designed the reformer and fuel cell respectively. This was the first reformer run at the Energy Center and it worked for six weeks of intermittent tests totaling a run time of approximately 20 hours. The short life could be attributed to burner design problems and a leaking membrane. This reformer was delivered without a control system and most of the run time was spent trying to perfect the LabView control system. No complete data sets were collected during these six weeks of runs.

The reformer used in this work was delivered in January of 2000. This reformer was an improvement in design over the previous ones. However, the flow meters supplied with the reformer (McMillan) used to measure the flow of diesel and water did not maintain calibration and were subsequently replaced by FMI piston pumps.

Finally, in mid April two complete runs were performed. On the 17th of April 2000, a run with varied states was completed so that FTIR data could be taken and
compared to equilibrium equations. On the 21\textsuperscript{st} of April 2000, a self-sustained run was done to determine the overall efficiency of the system. This thesis is based on those two runs. The reformer failed due to a leak in early May of 2000, and no additional data was collected.
3.0.b Equilibrium calculations:

The global reaction for steam reforming of a hydrocarbon fuel can be written as follows:

\[ C_nH_m + (\frac{St}{C})n.H_2O \rightarrow \frac{(m+4n)}{2}.H_2 + n.CO_2 + ((\frac{St}{C})-2)n.H_2O \]

Where \( n \) and \( m \) define the molecular formula of the fuel and \( (\frac{St}{C}) \) stands for the steam to carbon ratio. This equation is balanced with the assumptions that there is sufficient steam to react with the fuel and the reaction goes to completion.

The assumption that the reaction goes to completion is incorrect because the final equilibrium state is determined by the minimum in the Gibbs free energy. The change in free energy, \( \Delta G \) is given by the equation:

\[ \Delta G = \Delta H - T\Delta S \]

Where \( \Delta G \), \( \Delta H \) and \( \Delta S \) stand for change in Gibbs free energy, enthalpy and entropy, respectively. It should be noted that the global reaction is not the only reaction going on within the catalyst bed and carbon dioxide is not the only carbon species formed by the global reaction. Methane and carbon monoxide are the two other carbon species formed as a product of the global reaction.

Andy Lutz, a scientist at Sandia National Laboratories helped develop a program called Chemkin, which he used to predict an equilibrium composition of gasses in the raffinate based on likely reactant products. The compositions of the gasses depend on the selection of expected species, temperature and pressure of the process.
The equilibrium analysis deals with many parameters. The model needs an input of steam to carbon ratio, formation enthalpies, partial pressure of hydrogen across membrane, reformer temperature and pressure, exhaust temperature and finally, a selection of the species in order to complete the analysis.
3.1 Experiment to compare reformer performance to Lutz data.

The first set of successful experiments were conducted on April 17, 2000. The goal of this experiment was to evaluate the gas compositions as a function of temperature, raffinate pressure, steam to carbon ratio and fuel flow in order to compare these values to equilibrium values, which provides a measurement of catalyst performance.

The experiments were started by establishing a reference state, and then proceeding to change temperature, pressure, steam to carbon ratio and fuel flow, individually. However, the steam to carbon ratio and fuel flow was actually linked since varying the fuel feed rate altered the steam to carbon ratio. The data collected in this experiment are summarized in the table below:

<table>
<thead>
<tr>
<th>State</th>
<th>Temperature (Average) °C</th>
<th>Raffinate Pressure PSI</th>
<th>Kerosene Flow ml/min</th>
<th>Steam to Carbon</th>
<th>Measured H₂ Flow SLM</th>
<th>Calculated H₂ Flow SLM</th>
</tr>
</thead>
<tbody>
<tr>
<td>T0</td>
<td>790</td>
<td>150</td>
<td>11.75</td>
<td>3.1</td>
<td>33</td>
<td>28.33</td>
</tr>
<tr>
<td>P1</td>
<td>790</td>
<td>110</td>
<td>11.75</td>
<td>3.1</td>
<td>30</td>
<td>28.5</td>
</tr>
<tr>
<td>P2</td>
<td>790</td>
<td>80</td>
<td>11.75</td>
<td>3.1</td>
<td>25</td>
<td>29.8</td>
</tr>
<tr>
<td>SC1</td>
<td>790</td>
<td>150</td>
<td>9.7</td>
<td>3.82</td>
<td>27</td>
<td>24.9</td>
</tr>
<tr>
<td>SC2</td>
<td>790</td>
<td>150</td>
<td>8.11</td>
<td>4.59</td>
<td>24</td>
<td>21.1</td>
</tr>
<tr>
<td>T1</td>
<td>740</td>
<td>150</td>
<td>11.75</td>
<td>3.1</td>
<td>30</td>
<td>25</td>
</tr>
<tr>
<td>T2</td>
<td>695</td>
<td>150</td>
<td>11.75</td>
<td>3.1</td>
<td>25</td>
<td>20.6</td>
</tr>
</tbody>
</table>
This experiment was not without problems. As can be noted from the table, the measured hydrogen production was higher than what was calculated. This problem was likely due to the hydrogen flow meter being located close to the hot reformer, causing heat flow through the MKS meter and resulting in erroneous measurements. This was corrected in later experiments (but not for April 17 & 24) by moving the hydrogen flow meter to a location out of direct heat and by conducting crosschecks with a bubble meter during subsequent runs. However, higher hydrogen production could also be explained by formation of solid carbon (coking), which is not represented in the equilibrium calculation.

The following reaction describes the reforming reaction that goes on in the catalyst bed:

\[
\text{Rxn # 3.1} \quad C_{12}H_{26} + \left( \frac{Sr}{C} \right) H_2O \ (25^\circ C) \\
\downarrow \\
[a] \ CO + [b] \ CO_2 + [c] \ CH_4 + [d] \ H_2 + [e] \ H_2O \ (800^\circ C)
\]

\((C_{12}H_{26} \text{ is frequently used as the value for diesel fuel "Moran & Shapiro, 1995"})\)

The concentrations of carbon containing species in the above reaction can be measured experimentally by using a Fourier Transfer Infrared Spectrometer (FTIR). Each of the species has signature peaks. Integrating to determine the area under each curve and compensating for absorption cross-section of each species, gives the ratios of the respective species. In the above reaction, 12 is the number of carbons in the fuel, and is
distributed according to the ratios of the respective species. Therefore, the sum of the carbon containing species is equal to 12, \(a + b + c = 12\). The molar flow rate of carbon into the system is calculated by the measured diesel flow rate. FTIR peak ratios of the gasses in the raffinate were measured for each of the states in the first experiment. Knowing the ratios of the carbon species in the raffinate allowed for the calculation of the partial pressures of each species in the raffinate. The concentration of hydrogen and water were known using other methods as described previously.

The table below summarizes the FTIR ratios and partial pressures for each of the states in the first set of experiments.

Table 3.2: FTIR peak ratios and partial pressures based on these ratios.

<table>
<thead>
<tr>
<th>State</th>
<th>Peak ratios</th>
<th>Partial Pressure</th>
<th></th>
<th>Partial Pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CO</td>
<td>CO(_2)</td>
<td>CH(_4)</td>
<td>CO(_2)</td>
</tr>
<tr>
<td>T0</td>
<td>5.71</td>
<td>4.13</td>
<td>2.16</td>
<td>0.85</td>
</tr>
<tr>
<td>P1</td>
<td>5.75</td>
<td>4.17</td>
<td>2.08</td>
<td>0.85</td>
</tr>
<tr>
<td>P2</td>
<td>6.33</td>
<td>3.99</td>
<td>1.68</td>
<td>0.84</td>
</tr>
<tr>
<td>SC1</td>
<td>2.28</td>
<td>5.59</td>
<td>2.12</td>
<td>0.98</td>
</tr>
<tr>
<td>SC2</td>
<td>2.1</td>
<td>7.35</td>
<td>2.62</td>
<td>1.07</td>
</tr>
<tr>
<td>T1</td>
<td>4.02</td>
<td>4.68</td>
<td>3.29</td>
<td>0.86</td>
</tr>
<tr>
<td>T2</td>
<td>2.6</td>
<td>4.93</td>
<td>4.47</td>
<td>0.84</td>
</tr>
</tbody>
</table>

Calculated equilibrium concentration of gasses in the raffinate were compared to what was measured in the laboratory. Data from each state that were varied in: raffinate
pressure, steam to carbon ratio and average catalyst temperature space were plotted to observe the trends.

The trend of plotted data were as follows:

Figure 3.1: Change of raffinate composition with pressure.

Figure 3.2: Trends in raffinate composition with a change in steam to carbon ratio.

(Carbon species measured, hydrogen and water calculated)
Figure 3.3: Change of raffinate composition with catalyst temperature.

The data from the experiments were compared to the equilibrium computations for various steam to carbon ratios, temperatures and pressures. While the experimental data were obtained by using kerosene, the equilibrium calculations were performed for heptane. Comparing the data in temperature space showed the same trends for the experiment and calculation. The experiment had a temperature shift from the calculation of about 60°C. The similarity between measured and calculated values indicate that the catalyst works well.
Trends in hydrogen production were observed with varying temperature, pressure and St/C ratio. Hydrogen production increased with an increase in temperature and pressure but reduced with an increase in steam to carbon ratio.

Figure 3.4: Trend observed in the parameter experiment.
The following graph shows Chemkin data along with the Experimental data.

Figure 3.5: Composition (mole fractions) of species from steam reforming of heptane at equilibrium (curves) and experiments at UAF.

The graph does not contain a line for solid carbon. Equilibrium calculations of carbon deposition have shown that carbon should only be deposited at low steam to carbon ratios therefore coking (deposition of carbon) should not be a problem in this case. However, in the laboratory we have found coking to occur frequently at higher steam to carbon ratios. This may possibly be attributed to the incomplete vaporization of fuel, which results in local high concentrations of hydrocarbon or due to contact with cold walls that favor the formation of solid carbon.
3.1.1 Thermodynamic Analysis:

In order to evaluate a new energy technology, it is important to know both the maximum theoretical and actual efficiencies of the system. The theoretical efficiency gives an upper bound on efficiency. In practice, the system encounters inefficiencies such as heat loss due to convection and radiation, incomplete chemical reactions and parasitic loads.

Efficiency can be defined in a variety of ways depending on the thermodynamic system boundary. An optimistic way of looking at reforming efficiency is the conversion efficiency of the reformer. This only looks at what is put in (hydrocarbon) versus what comes out (hydrogen), and is an appropriate indicator of catalyst performance. This is what was measured in the parameter experiment (17th April). For field use, a better way is to look at the overall efficiency, which takes into account the heat needed to carry out the chemical reactions and the heat loss to the surroundings. A total efficiency can be determined for the system while running in self sustained mode. This experiment was conducted by burning on raffinate. (21st April).
3.1.a.1 Enthalpy of reaction:

To determine the enthalpy change in the reaction 3.1, the enthalpy of the species on each side of the reaction at the temperature of the system boundary can be summed. The difference in the value of the reactants and products is the enthalpy of the reaction. If the value of the sum of the product side minus the sum of the reactant side is negative then the reaction is said to be exothermic meaning there is a release of energy. If the value is positive the reaction is said to be endothermic meaning energy has to be added to push the reaction forward.

While Diesel fuel consists of many hydrocarbon compounds, for these calculations it is assumed to be $C_{12}H_{26}$, meaning “n”=12. The FTIR ratios are based on absorbance cross-section and subsequently the actual ratios had to be calculated from the number of carbons in the fuel. In the following section, state “T0” (Temp = 790 °C, $\frac{St}{C}$ = 3.1 and raffinate pressure = 150 PSI) is used to demonstrate the calculations.

Table 3.3: Actual and FTIR ratios of carbon species in state “T0”.

<table>
<thead>
<tr>
<th>SPECIES</th>
<th>FTIR RATIO (Peak Area Ratio)</th>
<th>ACTUAL RATIO Normalized $\Sigma$=12 (Carbon Species Ratio)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>9.42</td>
<td>5.71</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>6.81</td>
<td>4.13</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>3.56</td>
<td>2.16</td>
</tr>
</tbody>
</table>
Rxn # 3.2: Chemical reaction using actual data.

\[
\begin{align*}
C_{12}H_{26} + 37.2 \text{ H}_2\text{O} & \text{ (25°C)} \\
\downarrow & \\
5.71 \text{ CO} + 4.13 \text{ CO}_2 + 2.16 \text{ CH}_4 + 22.65 \text{ H}_2 + 23.23 \text{ H}_2\text{O} & \text{ (800°C)}
\end{align*}
\]

The enthalpy of a reaction is defined as the difference between the enthalpy of the products at a specified state and the enthalpy of reactants at the same state for a complete reaction. (Moran and Shapiro, 1995)

\[
\Delta H_{\text{reaction}} = \sum (h^f + \Delta h)_{\text{products}} - \sum (h^f + \Delta h)_{\text{reactants}}
\]

Table 3.4: Heat of formation and \(\Delta h\). (Moran and Shapiro)

<table>
<thead>
<tr>
<th>SPECIES</th>
<th>(h^f + \Delta h) (kcal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO (800°C)</td>
<td>-20.6</td>
</tr>
<tr>
<td>CO(_2) (800°C)</td>
<td>-85.1</td>
</tr>
<tr>
<td>CH(_4) (800°C)</td>
<td>-7.5</td>
</tr>
<tr>
<td>H(_2) (800°C)</td>
<td>5.5</td>
</tr>
<tr>
<td>C(<em>{12}H</em>{26}) (25°C)</td>
<td>-10.85</td>
</tr>
<tr>
<td>H(<em>2)O(</em>\text{liquid}) (25°C)</td>
<td>-68</td>
</tr>
<tr>
<td>H(<em>2)O(</em>\text{gas}) (800°C)</td>
<td>-51</td>
</tr>
</tbody>
</table>

\[
\Delta H_R = [5.71 (h^f + \Delta h)\text{CO} + 4.13 (h^f + \Delta h)\text{CO}_2 + 2.16 (h^f + \Delta h)\text{CH}_4 + 22.65 (h^f + \Delta h)\text{H}_2 + 23.23 (h^f + \Delta h)\text{H}_2\text{O}] - [(h^f)\text{C}_{12}\text{H}_{26} + 37.2 (h^f)\text{H}_2\text{O}]
\]

\[
= [(-117.6) + (-351.5) + (-16.2) + (124.6) + (-1184.7)] \\
- [(-10.9) + (-2529.6)]
\]

\[
= 973.3 \text{ kcal.}
\]

\[
= 4075 \text{ KJ.}
\]
4075 KJ is required to reform one mole of diesel based on measured carbon species. The positive value for the net enthalpy change of the reaction indicates that it is endothermic. This means the reaction requires the addition of heat to make it go forward.

3.1.a.II Efficiency:

There are many ways to calculate the efficiency of a reformer. One method involves evaluating the performance of the catalyst. The most important parameter, however, is the thermal efficiency, which is a measure of the energy output divided by the energy input. In this reformer the energy input is the hydrocarbon and the energy output is hydrogen. For a complete fuel cell system the efficiency is calculated by the AC electricity output divided by the hydrocarbon input. Therefore, the definition must define the system boundary and the flux of energy in and out of the control volume.

3.1.a.III Conversion Efficiency:

Conversion efficiency refers to the effectiveness of converting diesel into hydrogen only, and does not deal with heat/energy transfer issues directly. This is an optimistic way of looking at the reformer. This efficiency only takes into account the heating value of the hydrocarbon that is being reformed and the heating value of the hydrogen gas produced in the reformate reaction.

![Figure 3.6: Conversion Efficiency.](image_url)
Conversion efficiency is defined as:

$$\eta = \left( \frac{\text{Hydrogen}_{HHV}}{\text{Fuel}_{HHV}} \right) \times \left( \frac{\text{Hydrogen}_{flow}}{\text{Fuel}_{flow}} \right)$$

where:

HHV = Higher heating value.

*Calculating Efficiency from fuel flow:*

Fuel flow (Kerosene) = 11.75 ml/min

Density = 0.8 g/ml; Fuel flow X Density = 9.4 g/ml

The chemical formula for kerosene is assumed be $\text{C}_{12}\text{H}_{26}$, giving a molecular formula weight of 170 grams. This means one mole of “kerosene” weighs 170 grams and since the flow rate of kerosene is 9.4 grams per minute, it has a flow rate of 0.0553 moles/min.

$$\left( 11.75 \frac{\text{ml}}{\text{min}} \right) \times \left( 0.8 \frac{\text{g}}{\text{ml}} \right) \times \left( \frac{1 \text{mole}}{170 \text{g}} \right) = 0.0553 \frac{\text{moles}}{\text{min}}$$

Therefore the flow rate of the hydrogen can be determined by the following:

1 mole $\text{C}_{12}\text{H}_{26}$ $\rightarrow$ 22.65 moles $\text{H}_2$

0.0553 moles/min $\rightarrow$ 1.253 moles/min $\text{H}_2$

1 mole $\text{H}_2$ $\rightarrow$ 22.4 SLM

1.253 moles $\text{H}_2$ $\rightarrow$ 28.06 SLM
Table 3.5: Higher heating values. (Taylor)

<table>
<thead>
<tr>
<th>SPECIES</th>
<th>HHV (Btu/lbm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>61045</td>
</tr>
<tr>
<td>C₁₂H₂₆</td>
<td>19750</td>
</tr>
</tbody>
</table>

Energy out = 28.06 SLM H₂ = 1.253 moles/min = 75.18 moles/hr = 0.331 lbs/hr

= 20,217.5 Btu/hr = 5.93 kw.

Energy in = 11.75 ml/min C₁₂H₂₆ = 9.4 gm/min = 1.243 lbs/hr = 24549 Btu/hr

= 7.19 kw.

\[ \eta = \frac{\text{Energy}_{\text{out}}}{\text{Energy}_{\text{in}}} = \frac{5.93\text{kw}}{7.19\text{kw}} = 82.5\% \]

This is an upper limit. It does not take into account the energy used in the burner or the hydrogen that does not diffuse through the membrane, providing an overly optimistic definition. The conversion efficiency can be greater than 100%, making it obvious that something (heat addition) has been left out of the efficiency calculation. Conversion efficiencies of 60%-110% were observed during the run on 4/17/00.

3.1.a.IV Conversion efficiency using recoverable hydrogen through membrane:

Hydrogen has to either flow through to the burner as part of raffinate or diffuse through a palladium membrane as product hydrogen before exiting the reformer. The flow through this membrane is governed by the partial pressure difference of hydrogen across the membrane. The pressure downstream of the membrane is approximately atmospheric. The pressure upstream of the membrane is the partial pressure of hydrogen.
in the raffinate. The partial pressure of a gas is defined as the pressure exerted by a gas (hydrogen) in a mixture (raffinate). Therefore, the moles of hydrogen is divided by the sum of the moles of gasses in the raffinate and multiplied by ten atmospheres, since the raffinate pressure is 150 PSI. The pressure difference, which is the driving force across the membrane, is defined as:

\[ \Delta P = \frac{P_{\text{upstream}} - P_{\text{downstream}}}{P_{\text{upstream}}} \]

The partial pressure of hydrogen and \( \Delta P \) from the above parameters in the standard state (\( P = 150 \) PSI, \( T = 790^\circ\text{C} \), S/C = 3.1) are:

\[ \text{mol of } H_2 \text{ partial} = \left( \frac{\text{mol of } H_2}{\sum \text{mol of gasses in raffinate}} \right) \times 10\text{atm} \]

\[ = \left( \frac{22.65}{57.88} \right) \times 10\text{atm} = 3.91\text{atm}. \]

\[ \Delta P = \frac{3.91 - 1}{3.91} = 0.74 \left( \frac{\text{Product } H_2}{\text{Reaction } H_2} \right). \]

= Only 74% of the hydrogen produced can be recovered.

The pressure difference across the palladium membrane can be used as an upper boundary for the production of product hydrogen. Using that definition, a maximum of 74% of the hydrogen produced in the reformate reaction can be recovered through the membrane. This corresponds to 16.76 moles of hydrogen being produced for every mole of kerosene reacted. Therefore conversion efficiency using recoverable hydrogen is:

\[ 82.5\% \times 74\% = 61\% \]
3.2 Self-sustained operation:

The second experiment involved running the reformer in self-sustained mode where the only energy input into the system was from Kerosene. In this mode supplemental heat addition via the burning of propane was not required. To operate in this mode, the fuel value of the raffinate must be sufficient to provide the heat needed in the burner to keep the endothermic reaction going. The data reported are from 4/21/00 when a successful run was made.

The raffinate from the steam reforming reaction is burned in excess air to provide heat for the endothermic steam reforming reaction. Sufficient air is added to maintain a stable flame and the flow rate of air is measured using a Hastings flow meter. The reactants are released through a throttling valve to atmospheric pressure in the burner; therefore the enthalpy before and after the valve remains unchanged. The difference in enthalpy between the product and reactants gives the magnitude of energy released. This energy is sufficient in sustaining the reformation reaction and no additional propane from an external source is required.
3.2.2 Self-sustained Efficiency:

Self-sustained refers to the reformer being run on the raffinate without the addition of any supplemental fuel such as propane. This is possible because the CO, CH₄ and residual H₂ in the raffinate can be combusted to release heat. This energy, when put back into the system results in better overall efficiency and also simplifies the fuel delivery since only one type of fuel input is required. This is also the way a real reformer must be operated in a residential power system.

However, our experiments demonstrated that if maximum hydrogen is removed, the fuel energy in the raffinate is not enough to meet the system heat requirements. Therefore, the pressure in the raffinate has to be lowered significantly in order to decrease the pressure difference across the palladium membrane and this leads to less hydrogen production for the fuel cell. This lowered pressure also reduces the ΔP across the membrane and as a result more of the hydrogen remains in the raffinate. This, while enriching the raffinate stream, reduces the hydrogen yield.

The raffinate from the steam reforming reaction is burnt in excess air to provide energy for the reaction. In the combustion reaction, the difference in enthalpy between the product and reactants give the magnitude of energy released. The self-sustained efficiency is defined as:

\[ \eta = \frac{E_{\text{out}}}{E_{\text{in}}} = \frac{(Hydrogen_{\text{HHV}})-(Elec.\text{Parasitics})}{(Fuel_{\text{HHV}})} \]

The electrical parasitics on the reformer system are required to power a variety of pumps, blowers, solenoid valves and the control system. The energy consumed by the
parasitics was measured using a wattmeter. It was estimated to be 250 watts including the blower. For a self-sustained system where the electrical power is provided by the fuel cell, this number has to be divided by the efficiency of the fuel cell and inverter. Fuel cell efficiency is approximately 45% for PEM and approximately 95% for a Trace inverter.

\[
\text{Fuel cell efficiency} = 0.45 \\
\text{Inverter efficiency} = 0.95.
\]

\[
\text{Parasitic load} = \frac{250\text{watts}}{(0.45)(0.95)} = 585 \text{ watts H}_2 \text{ equivalent.}
\]

Data taken while running in self-sustained mode on 4/21/00 showed the average diesel input into the system to be about 18.2 ml/min and the output of hydrogen about 15.5 SLM. Using HHV this gives an efficiency of:

\[
\text{Fuel energy} = 18.2 \text{ ml/min with density of 0.8} = 14.56 \text{ gm/min} = 1.926 \text{ lbs/min} \\
= 38,038 \text{ Btu/hr} = 11.15\text{kw}. \\
\text{(H}_2\text{) energy} = 15.5 \text{ SLM} = 0.692 \text{ moles/min} = 41.52 \text{ moles/hr} = 0.183 \text{ lbs/hr} \\
= 11,175 \text{ Btu/hr} = 3.28 \text{ kw.} \\
\eta = \frac{3.28\text{kw} - 0.585\text{kw}}{11.15\text{kw}} = 24.2\%.
\]

This efficiency of 24.2% is less than half of what industry was reporting. The efficiency of 65%, which Northwest Power reported at the Energy conference held at UAF, was a conversion efficiency of recoverable hydrogen through the membrane and not the true thermodynamic efficiency of a reformer system suitable for field applications.
3.2.b  *Total Energy Balance in self-sustained mode.*

An energy balance accounts for all the energy going into and coming out of the system. The two must be equal to each other, and provide a check against errors that could be made when making measurements or calculating efficiency.

For this measurement, the system boundary is drawn around the reformer. The system boundary has five energy flows across its boundary. The only energy inputs into the system are the fuel and electrical parasitics. Energy leaves the system through convection and radiation, the exhaust stream and product hydrogen. In this measurement, the raffinate composition is not important, since it does not cross the system boundary.

![Figure 3.7: Defining system boundary for self-sustained mode.](image)

Energy-in must equal energy-out. Therefore, the magnitude of the energy values of all flows across the boundary must be measured.
3.2.b.1  Convection and Radiation:

The reformer operates at relatively high temperatures (800 °C at the catalyst), and heat is lost from the external surfaces through convection and radiation. With high temperatures (especially on the non-insulated ends of the reformer) the radiation term is significant. The heat loss was calculated two ways: by the author and by Dr. R. Johnson. The more detailed calculation was carried out with the help of a program called Simulink. Simulink is a visual programming language that is run using Matlab. The calculated values of about 2.25 KW and 2.3 KW were in good agreement with each other. It should be noted that this is an estimated figure because it involved making some assumptions.

The emissivity values for the different surfaces on the reformer were textbook values, not experimentally determined. These values were taken from a table in the book “Fundamentals of Heat Transfer” by Incropera and De Witt. The air velocity, which affects convection, was measured using an anemometer. This velocity was near the lower limit of the anemometer. The velocity was also back calculated from the fan capacity of the hood above the reformer bench. The two numbers were in good agreement. Also during runs the operating parameters changed, as a result the value of the convection and radiation term would change somewhat. There is approximately a fifty percent error associated with this value. This is based on an error analysis that takes into account the uncertainties associated with: assuming “back-of-the-text-book” values for emissivity, accuracy of thermocouples and measurement of surface area.
Both natural and forced convection contribute to heat loss. The convection and radiation terms were calculated according to the following:

Figure 3.8: Reformer Design
3.2.b.1.a  Forced Convection:

Forced convection was calculated according to the following:

Hood fan capacity = 3400 cfm.

Reformer bench area = 25 ft²

\[ U_\infty = \frac{3400 \text{ cfm}}{25 \text{ sq - ft}} = 2.25 \text{ ft/sec. (Anemometer measurement was 2.2 ft/sec)} \]

\[ \text{Re}_L = \frac{U_\infty L}{v} \]

Where:

\( \text{Re}_L \) = Reynold’s number (Plate).

\( U_\infty \) = Wind velocity.

L = Characteristic length.

\( v \) = kinematic viscosity.

\( \text{Re}_d \) = Reynold’s number (Cylinder).

For a cylinder with \( \text{Re}_d < 20,000 \):

\[ \text{Nu}_d = 0.3 + \frac{0.62 \left( \frac{1}{\text{Re}_d^2} \right) \frac{1}{\text{Pr}^3}}{\left[ 1 + (0.4/\text{Pr})^{3/4} \right]} \]

For a flat plate with laminar boundary layer:

\[ \text{Nu}_L = \frac{0.6774 \text{ Pr}^{3/2} \text{ Re}^{1/2}}{\left[ 1 + (0.0468/\text{Pr})^{3/4} \right]^4} \]
\[ h = \frac{kD}{Nu_d} \]

\[ Q_{\text{Forced}} = hA(T_\infty - T_s) \]

Where:

\( Nu = \) Nusselt number.

\( Pr = \) Prandtl number.

\( k = \) Thermal conductivity.

\( h = \) Convective heat transfer coefficient.

\( A = \) surface area.

\( T_\infty = \) Ambient temperature.

\( T_s = \) Surface temperature.

\( Q = \) Heat transfer.

N.B. All properties were evaluated at \( T_{\text{film}} \) which is \( (\frac{1}{2} T_\infty - \frac{1}{2} T_s) \).

3.2.b.1.b Natural Convection:

In natural convection the Rayleigh instead of the Reynold’s number is important. The Rayleigh number can be calculated from the Grashof number and used in conjunction with the Prandlt number in the following equations to find the Nusselt number.

\[ Gr = g\beta\Delta T L^3/\nu^2 \]

\[ Ra = Gr Pr \]
For Horizontal Cylinder:

\[
\text{Nu}_d = \left[ 0.6 + \frac{0.387 \, Ra^\frac{1}{9}}{\left[ 1 + \left( \frac{0.559}{Pr} \right)^{16} \right]^{\frac{8}{9}}} \right]^2 \quad \text{For } 10^3 < Ra < 10^{13}
\]

For Vertical Plates:

\[
\text{Nu}_L = 0.68 + \frac{0.67 \, Ra^\frac{1}{4}}{\left[ 1 + \left( \frac{0.437}{Pr} \right)^{16} \right]^{\frac{9}{4}}} \quad \text{For } Ra_L < 10^9
\]

And same as forced convection;

\[
h = \frac{kD}{\text{Nu}_d}
\]

\[
Q_{\text{Natural}} = hA(T_\infty - T_s)
\]

Where:

Gr = Grashof number.

g = Gravitational acceleration. (9.8 m/s²)

\[
\beta = 1/T_{\text{film}}
\]

Ra = Rayleigh number.

3.2.b.I.c Radiation:

Heat loss due to radiation is very significant in high temperature applications. This is because temperature is raised to the fourth power in the equation that calculates radiative
heat loss. This value also has a potentially large error associated with it since the emissivities of each of the different surfaces on the reformer were estimated based on textbook values. These values were based on a table given in “Fundamentals of heat and mass transfer” by Incoropera and DeWitt.

Heat loss due to radiation was calculated as follows:

\[ Q_{\text{rad}} = \varepsilon A \sigma \left( T_{\text{Surface}}^4 - T_{\text{Ambient}}^4 \right) \]

Where:

\( \varepsilon \) = Emissivity (Material surface property).

A = Surface area.

\( \sigma \) = Stefan-Boltzmann constant. (5.67 x 10^{-8} W/m^2K^4).

T = Temperature of surface and surrounding.

Total heat loss from the Reformer is the sum of all three values.

\[ Q_{\text{tot}} = Q_{\text{Forced Conv}} + Q_{\text{Natural Conv}} + Q_{\text{Rad}} \]

Table 3.6: Heat lost from the reformer.

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Forced Convection</td>
<td>493 +/- 50 watts</td>
</tr>
<tr>
<td>Natural Convection</td>
<td>619 +/- 50 watts</td>
</tr>
<tr>
<td>Radiation</td>
<td>1179 +/- 200 watts</td>
</tr>
<tr>
<td><strong>Total heat loss</strong></td>
<td><strong>2291 +/- 300 watts</strong></td>
</tr>
</tbody>
</table>
The errors arise from uncertainties in emissivity assumptions, error associated with area measurements, temperature and flow meter reading. The uncertainties are summed to perform the error analysis. Forced and natural convection are additive in this case since a suction fan was located on top of the reformer bench.

3.2.b.II Heat Exchanger:

A heat exchanger was installed to the exhaust of the reformer to measure recoverable heat leaving the system through the exhaust. It was an “off the shelf” shell and tube exchanger where the shell was made of cast iron and the tube of copper. The shell was insulated with rock wool so as to minimize the heat loss through the shell and maximize the heat recovery by the coolant. The coolant was a 50/50 mixture of glycol and water. The flow rate of the coolant was measured using a paddle wheel flow meter and the temperature difference using thermocouples.

![Heat Exchanger](image)

Picture 3.0: Heat Exchanger installed at reformer exhaust.
The heat loss was calculated using the following:

\[ Q = mC_p\Delta T \]

Mass flow = \((0.11 \text{ gal/sec}) \times (3600 \text{ sec/hr}) \times (3.78 \text{ litters/gal}) \times (1 \text{ kg/litter}) \times (1.07)\)

= 1602 kg/hr

Table 3.7: Glycol properties. (Marks' standard handbook)

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>(m)</td>
<td>mass flow = 0.11 gal/sec</td>
</tr>
<tr>
<td>(C_p)</td>
<td>3.35 KJ/Kg°C</td>
</tr>
<tr>
<td>Specific gravity</td>
<td>1.07</td>
</tr>
<tr>
<td>(\Delta T)</td>
<td>3.4 °C</td>
</tr>
</tbody>
</table>

Heat loss = \((1602 \text{ kg/hr}) \times (3.35 \text{ KJ/Kg°C}) \times (3.4 \text{ °C})\)

= 18,247 KJ/hr = 5.07 kw.
3.3 Accounting:

Energy enters the system as Diesel fuel and electrical parasitic load, and leaves the system as heat and hydrogen. The distribution of energy leaving the system is as follows:

![DISTRIBUTION OF ENERGY LEAVING SYSTEM](image)

Figure 3.9: Outlet energy distribution

Table 3.8: Total energy distribution:

<table>
<thead>
<tr>
<th>ENERGY TYPE</th>
<th>OUT</th>
<th>IN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat Exchanger</td>
<td>5.07 kw +/- 0.25 kw</td>
<td></td>
</tr>
<tr>
<td>Convection &amp; Radiation</td>
<td>2.30 kw +/- 1.15 kw</td>
<td></td>
</tr>
<tr>
<td>Hydrogen output</td>
<td>3.28 kw +/- .015 kw</td>
<td></td>
</tr>
<tr>
<td>Fuel in</td>
<td></td>
<td>11.15 kw +/- 0.055kw</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>10.65 kw +/- 1.55 kw</strong></td>
<td><strong>11.15 kw +/- 0.055kw</strong></td>
</tr>
</tbody>
</table>

The error analysis was done by summing the instrumental errors, errors associated with measurements and the errors made in assumptions.
3.4 UAF Spreadsheet

To better understand the energy flow issues in the reformer Dr. Witmer created a spreadsheet model. This model allowed the user to adjust inputs such as fuel flow, water flow, catalyst temperature, hydrogen removed from the system, membrane temperature and also inset the gas concentrations as measured by the FTIR. Changing any of these parameters resulted in changes of energy flows through the system.

This model also calculated the overall efficiency of the reformer based on the higher heating value of the hydrocarbon going in and product hydrogen coming out of the system. This model accurately predicted the energy flows that could be measured on the bench and provided some insight into the energy balance of the system. The spreadsheet calculated the heating value of the raffinate, displayed the energy required for the endothermic reaction and the energy leaving the combustion exhaust, on the computer screen. In essence the spreadsheet served as a computer simulation of what was taking place on the lab bench. The user interface of the model is shown on the next page.
Figure 3.10: UAF Spreadsheet interface
The data collected from the runs were plotted to show a visual representation of what was occurring. Graphs for fuel flow and efficiency are shown next:

**Figure 3.11:** Running using propane

**Figure 3.12:** Running self-sustained.
Figure 3.13: Running on Propane (efficiency)

Figure 3.14: Running Self-sustained (efficiency)
Some interesting processes occur while running in self-sustained mode. It should be noted that a higher flow rate of diesel is required (18 ml instead of 12 ml). Since the steam to carbon ratio must be maintained, the water flow increases by approximately three times the difference in fuel flow. All the excess water has to be turned into steam, which requires energy.

Running in self-sustained mode requires a higher flow rate of diesel and at the same time produces a lower yield of product hydrogen. Therefore, conversion efficiency using recoverable hydrogen is much lower when running in self-sustained mode. However, the line for conversion efficiency in the parameter experiment plot is positively biased because the MKS flow meter was placed in a high temperature surrounding.

Another reason for the difference in conversion efficiency between the two experiments is because, conversion efficiency is calculated by dividing the energy value of the product hydrogen by the energy value of the hydrocarbon input into the reformer. For a self-sustained run, combustion of raffinate was used to maintain the high catalyst temperature requirements yet a lower yield of hydrogen is observed because of the excess hydrogen being diverted to the raffinate stream. Whereas, in the parameter experiment propane was used to supplement the heat in the burner.

No supplemental heat is added while running self-sustained (4/21/00), so the overall efficiency is higher than running with the addition of supplemental heat. (4/17/00). Overall efficiency which, is the co-generation efficiency (product hydrogen + recoverable heat) is labeled as total efficiency in the previous graphs.
Figure 3.11 and 3.12 show a lower yield of product hydrogen for the self-sustained run. This is because excess hydrogen in the self-sustained run is being diverted to the raffinate stream in order to increase the raffinate energy value. Also the placement of the MKS flow meter contributed to this disparity in measurement.

Figures 3.13 and 3.14 also show that the total (co-generation) efficiency of a self-sustained run is higher because the total efficiency for the parameter run is defined as:

\[
\text{Total efficiency}_{(\text{FTIR})} = \frac{(\text{Hydrogen Yield} + \text{Usable heat})}{(\text{Propane} + \text{Diesel in})}
\]

Whereas, the total efficiency for the self-sustained run is defined as:

\[
\text{Total efficiency}_{(\text{self-sustained})} = \frac{(\text{Hydrogen Yield} + \text{Usable heat})}{(\text{Diesel in})}
\]

Propane is not used in the self-sustained run and this accounts for the higher total efficiency. It should be noted that the total efficiency is actually co-generation efficiency meaning usable heat and hydrogen are both taken into account. The table on the following page summarizes the various efficiency values calculated for the reformer. The part of the curve where the values seemed to reach steady state was used to get the values in the table.
Table 3.9: Efficiency values.

<table>
<thead>
<tr>
<th>Efficiency type</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conversion</td>
<td>82.5%</td>
</tr>
<tr>
<td>Conversion using product hydrogen only</td>
<td>61%</td>
</tr>
<tr>
<td>Self-sustained</td>
<td>24.2%</td>
</tr>
<tr>
<td>Co-generation</td>
<td>75%</td>
</tr>
</tbody>
</table>
4 Discussion

The Remote Alaska Power Program (RAPP), has been provided with a series of hydrocarbon reformers built by Idatech. Each successive unit incorporated changes that were an improvement over the prior unit, which is the normal progression of technology in the prototype stage.

The basic design for the diesel reformer involved modifying a methanol reformer. The diesel reformer operates at a higher temperature (800 °C) than a methanol reformer (350 °C), which led to problems because of material issues. The first unit shipped was largely built out of 316 stainless steel. The later versions incorporated more 310 stainless steel into the burner and catalyst tube areas, which are constantly exposed to high temperatures. The 310 stainless steel is a higher nickel alloy with properties that provide better resistance to high temperature corrosion. The 316 stainless steel burner was severely oxidized by high temperature flames, which led to the loss of wall thickness and eventual failure in less than a hundred hours of operation. Replacing the burner with 310 stainless steel was successful, as it showed no noticeable corrosion after a similar amount of time.

During the course of this program, the palladium membranes failed three times. The thin palladium membrane is supported on only one side by a wire mesh and therefore is able to resist pressure from only one direction. This, although not a problem under normal operations, emergency shut downs when the reformer is connected to the fuel cell can lead to a small but damaging backpressure on the membrane. Since the membrane is a thin foil the backpressure may lead to leaks.
Another problem resulted from the spark plug failing whenever the reformer was run in a self-sustained mode. Because the raffinate contains significant amounts of hydrogen, the flame speed is much higher when burning raffinate than when burning propane. The ignition source for the burner is a spark plug that is located between two flame holders. While the burner was operating on propane both the flame holders worked and the flame was maintained at a safe distance from the spark plug. However, when the system was switched to burning raffinate the flame stabilizer did not work and the spark plug was continuously exposed to the hot flame. This led to oxidation of the metal on the spark plug and caused it to stop functioning. This meant if the burner flame went out it could not be re-ignited without the spark plug.

Consistent repeatability was not achieved in these experiments, which leads to the conclusion that the system was changing between runs. It was not possible to accurately predict the hydrogen production. This inconsistency was likely due to either the formation of carbon within the system, or to catalyst changing geometry (degrading). Over a period of time the catalyst broke down and formed powered fines increasing its surface area.

![Picture 3.2: Formation of catalyst dust.](image)
Review of the literature indicates that heavy hydrocarbon steam reformers like the diesel reformer are subject to coking. The onset of coking was observed in the Idatech reformer through an increased pressure-drop rise during a run. Equilibrium calculations done using Chem-Kin show that coking (deposition of carbon) should be limited to low steam to carbon ratio (1:1). However, coking was observed at steam to carbon ratios of 3:1 although it can be held at bay by increasing the steam to carbon ratio even higher (3.2:1).

Raising the steam to carbon ratio means having to vaporize large amounts of water, thus requiring larger amounts of energy. The excess steam also reduces the partial pressure of hydrogen across the membrane reducing product hydrogen yield. Therefore, increasing steam to carbon ratio may retard coking but also reduces efficiency.

The formation of coke using liquid hydrocarbons suggests problems with complete vaporization of the fuel. Using a fuel atomizer might solve this problem. Coking could also occur through interaction of the fuel with the vessel wall. The walls of the vessel and the tubing in the mixing region are made of stainless steel, which is an alloy of Iron and Nickel. Iron and Nickel are used to catalyze the steam reforming reaction. Cold surfaces on the vessel wall also favor coking. Once coking starts, it catalyzes the formation of more solid carbon.

Decoking is carried out by burning the solid carbon. Coke burns at relatively high temperatures and could cause local damage wherever it is deposited and burned. This results in wall failure over a period of time, as well as a breakdown of catalyst substrate and the formation of fines.
5 Conclusions

In recent years, significant effort has been put into the research and development of clean, efficient, reliable and economical power generation sources. Much of the recent attention has been focused on PEM fuel cells because of their low weight and high power density. Since hydrogen is not readily available as commercial fuel, reforming available fuels has been suggested as a possible solution.

Reforming of a light hydrocarbon like natural gas is easy when compared to diesel reforming. However, at this point in time there is no wide distribution of natural gas in Alaska. But an infrastructure for diesel already exists in rural Alaska. Therefore, reforming of diesel could be an important step in marketing fuel cell systems for remote applications.

PEM fuel cells require a very pure hydrogen source. The Energy Center has evaluated the Idatech reformer’s product hydrogen using a CO monitor to determine carbon monoxide concentrations in the product hydrogen and found the CO concentration in the product stream to be less than the ambient air, indicating much better than 99.99% pure hydrogen. The product hydrogen from the reformer was also used to fuel a PEM fuel cell. This was achieved with no noticeable degradation to the PEM fuel cell membrane, further indicating the purity of the product hydrogen. The results of the experiment also demonstrate that the catalyst works well. For these reasons it would seem that the diesel reformer is an ideal match for the PEM fuel cell. However, many issues remain before this technology is useful for remote areas.
The main issue of concern is the low efficiency of the diesel reformer (30%). The reformer in conjunction with the PEM fuel cell has an efficiency of 15%. This is less than half the efficiency of a diesel generator (35%). At these low efficiencies, the cost of needed fuel would be very high.

Other concerns are material issues that arise due to the very high operating temperatures of the reformer. The burner was initially built using 316 stainless steel and later improved to a 310 SS. The 310 SS was working well and the next step is to replace all the 316 SS used in the reformer with 310SS. Another alternative involves building the burner out of inconel. Inconel is a Nickel based alloy with a very high melting temperature. However, inconel is expensive.

Coking is a major concern and is observed regularly in the diesel reformer. One way to try and get around the problem is running the reformer at a higher steam to carbon ratio but this involves paying a high energy cost and this may not solve the problem.

One important finding is that much of the energy is leaving the system as heat in the combustion exhaust, and much of that is as water vapor. This energy can be recovered using a heat exchanger but the quality of energy is low.

At this point in time, the diesel reformer is not field ready. A lot more work has to go into development before the reformer can achieve a reliable service life and claim better efficiencies. For a small-scale hydrogen reformer to compete with traditional technologies, major breakthroughs in the technology need to take place. However ultimately, the process is limited by thermodynamics and the laws of physics, meaning a theoretical maximum efficiency exits and will not be exceeded.
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