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EFFECTS OF A NICKEL REACTOR LINER AND OTHER REACTION VARIABLES DURING SUPERCRITICAL WATER REFORMATION OF GLYCERIN

by

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A THESIS

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ABSTRACT

The non-catalytic reformation of glycerin using supercritical water was conducted in a 400-mL tubular reactor constructed of Haynes® Alloy 230. The evaluated parameters for this thesis include water-to-glycerin molar ratios ranging from 3 to 24 and reactor temperatures ranging from 500°C to 700°C. In addition, experiments were performed using the Haynes® Alloy 230 reactor both without a liner and with a Nickel 201 liner. Space time was maintained at approximately 100 seconds and the reactor pressure was kept constant at 24.1 MPa. The resultant effect on product gas composition and carbon gasification was determined. The product gases consisted of a mixture of hydrogen, carbon monoxide, carbon dioxide, methane and ethane. It was found that the greatest gas yields of hydrogen were produced at higher temperatures using more dilute glycerin solutions. Increasing the water-to-glycerin ratio and increasing temperature, up to approximately 13.5 and 600°C respectively, increased the extent of carbon gasification. Once these values were reached, 100% carbon gasification percentages were achieved. The reactor liner made of nickel was found to have a positive catalytic effect on both the reformation and water gas shift reaction. The experiments conducted with the liners produced higher carbon dioxide and hydrogen yields. The greatest hydrogen and carbon dioxide yields were obtained at 24 water-to-glycerin ratio and a temperature of 700°C using a reactor liner. In this thesis, the effects of water-to-glycerin ratios, temperature, and a reactor liner upon supercritical water reformation of glycerin are revealed based on the experimental data.

ACKNOWLEDGEMENTS

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1. INTRODUCTION

1.1 RESEARCH OBJECTIVES

The purpose of this research was to derive syngas, hydrogen in particular, via supercritical water reformation of glycerin. The effects of varying water-to-glycerin molar ratios or fuel-feed ratios on syngas production were investigated. Also, the effects of varying reactor temperatures on syngas production were studied. The effects on the extent of carbon gasification by varying these reaction variables were explored as well.

Experiments were additionally carried out both with and without a reactor liner to investigate the monolithic catalytic effects of a reactor liner upon supercritical water reformation of glycerin. For this work, the reactor liner implemented was hand-fabricated from a thin Nickel 201 sheet measuring approximately 1/100th of an inch thick. For all experiments, the space time and reactor pressure were kept constant.

1.2 MOTIVATION BEHIND RESEARCH

Biodiesel production and its glycerin byproduct have increased in recent years in response to rising demands for renewable and greener fuel technologies. While glycerin has beneficial properties for a variety of end uses, its over-abundance in the market place has rendered a new challenge of finding other economically viable and sizable uses for this commodity. This research addresses the novel process of producing gaseous hydrogen via non-catalytic supercritical water reformation of glycerin as one method to render excess glycerin into the usable alternative fuel, hydrogen.

Using a reactor liner is an additionally novel concept in itself. It has been found by Antal et al. [1,2] that metallic reactor walls catalyze some of the many reactions taking place during supercritical water reformation. After experiments have been carried out for some time on a metallic reactor, the catalytic effects become less pronounced due to a number of factors. Utilizing a reactor liner is an effective and cheaper method to provide new surfaces within the reactor which can catalyze reactions taking place during supercritical water reformation. As most gasification studies have been carried out at the micro-scale level, few have been conducted on a macro-scale. In addition, a number of studies use heterogeneous catalyst either organic such as activated carbon[3,4] or inorganic metallics[5] in their studies of biomass reforming. This study investigates the non-catalytic reformation of a particular bio-based material, glycerin, on a macro-scale.

2. BACKGROUND

2.1 SUPERCRITCAL FLUID THEORY

In 1822, Baron Charles Cagniard de la Tour first discovered critical points of substances by experimenting with various solvents at high temperatures and pressures. He heated liquids and gases inside a sealed cannon and observed that at a specific temperature splashing of the fluids inside the container ceased when perturbed. Later he went on to design a glass view cell to observe the phenomena directly.[6] In 1869, Andrews first provided an explanation of what the critical point was. Eleven years later, Hannay and Hogarth conducted an experiment dissolving cobalt chloride in supercritical ethanol to demonstrate solvent properties of supercritical fluids. In the late 1920's, Eucken, Bressler, Braune, and Strassmann investigated solubilities of various solids and liquids in supercritical carbon dioxide among other gases.[7]

A one-component fluid is deemed supercritical once its temperature and pressure have exceeded the critical values for that fluid. On a P-T phase diagram the state of a given fluid is dependent upon the temperature and pressure of the fluid. There is a terminal point on the saturation curve between liquid and vapor phases called the critical point. Once temperature and pressure have reached their critical values for a fluid, the fluid's phase can no longer be distinctly identified as a liquid or a vapor, and hence, becomes a supercritical fluid.[6,7] Figure 2-1 illustrates a three dimensional phase model for water of which projections of the P-T portion of the model are found on the left-hand side.

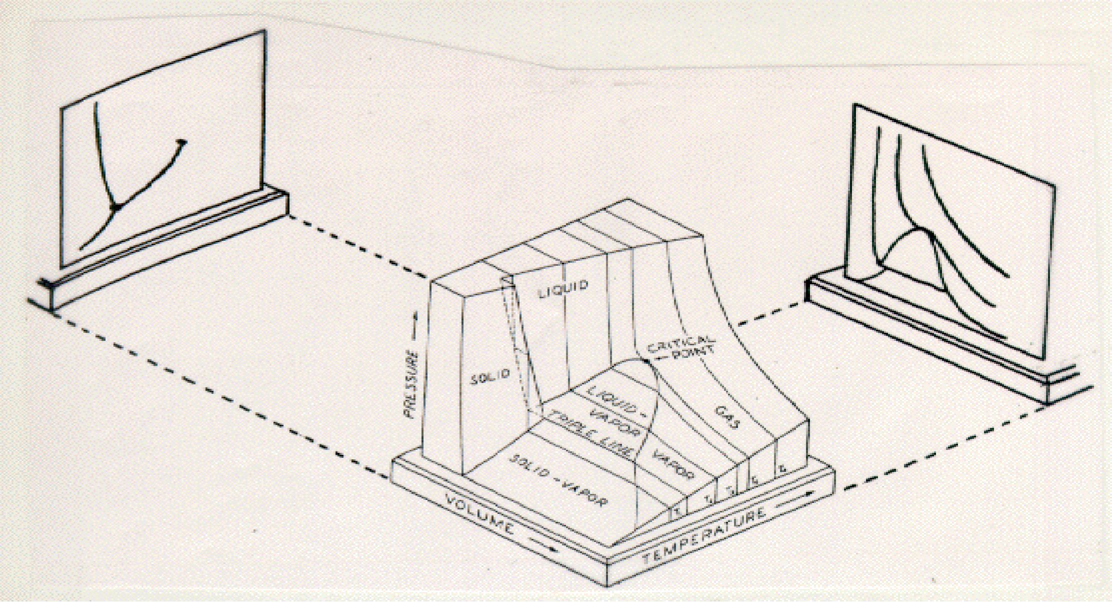

Figure 2-1. A three dimensional phase model of water with P-T and P-V projections. (Source: Eugene S. Takle, used with permission.)

One can also look at a P-V phase diagram and find the critical point of a fluid. There are two pressure curves which can be found on a P-V phase diagram, one for the liquid phase and one for the gaseous phase. Again, looking at Figure 2-1 one can see the P-V projection of the three dimensional phase model on the right-hand side of the figure. At the point where these two branches meet is the critical point and once again, distinction between gas and liquid phases disappears. It is important to note that at the critical point the isothermal compressibility of the one-phase region goes to infinity. In addition, the expansion coefficient and the isobaric heat capacity of a fluid at the critical point goes to infinity. Differences in the supercritical regions on the P-T and P-V projections can be accounted for by the fact that pressure and temperature are field variables, while volume is a density variable. These variables differ in that field variables are equal in coexisting phases, while density variables are not.[7] A list of commonly used industrial fluids and their respective critical properties are listed in Table 2-1.

Table 2-1. Commonly used industrial fluids and their critical temperature, pressure, and density values.[8]

Fluid	T_c (K)	P_c (MPa)	ρ_c (kg/m^3)
Ammonia	405	11.35	240
Benzene	562	4.90	302
Carbon Dioxide	304	7.38	468
Ethane	305	4.87	205
Ethanol	516	6.38	276
Ethylene	282	5.08	218
Fluoroform	299	4.83	525
Methane	191	4.60	162
Methanol	513	8.10	272
Naphthalene	784	4.11	314
Propane	370	4.25	217
Toluene	592	4.11	292
Water	647	22.06	322

Supercritical fluids (SCFs) are vastly different than the liquid and gaseous fluid phases of their constituents and as such have physical properties which are unique. Viscosities of SCFs are often much smaller than those of the liquid phase for a given fluid. In addition, the solubilities of SCFs are not fixed like normal fluids and can be varied by adjusting the temperature and pressure. Like solubility, the density of supercritical fluids can also be altered by making adjustments in temperature and pressure. This ability to vary densities allows SCFs to take on liquid-like, gas-like, or intermediary densities without the formation of an interface. The closer the temperatures and pressures are to the critical point, the harder it becomes to fine tune densities.[7] The fluctuation of densities when a fluid transforms to the supercritical phase leads to fluctuations in refractive index which are on the same order as the wavelength of light. This causes the supercritical fluid to take on a fog-like appearance in a phenomenon known as critical opalescence. Fluids near the critical point will also display critical opalescence; however, a meniscus can still be recognized when the temperature is below the critical temperature. Once the critical temperature is reached the meniscus completely disappears. Critical opalescence is most strongly observed at the critical temperature.[6-8]

The uniqueness and ability to fine tune properties of supercritical fluids makes them highly valued for use in a variety of scientific, engineering, and industrial settings. Supercritical fluid extraction (SFE) is used to extract desired species from natural liquid or solids by using the SCF as a solvent. Food and pharmaceutical manufactures implement SFE technologies to add or remove compounds from their product. An example of this is the extraction of caffeine from coffee beans via SFE to produce decaffeinated coffee. Properties of SCF solvents can further be manipulated by the addition of cosolvents and antisolvents.[7] Another avenue for which supercritical fluids have been employed is in chromatography. In supercritical fluid chromatography (SFC) the SCF acts as the carrier for the analyte as opposed to a gas or liquid. Since the solvation properties of SCFs vary with density, adjustments can be made simply by adjusting temperature or pressure. As a result, multi-component solutions containing constituents of vastly different solubilities can be analyzed. Analogous to SFE, SFC can also use cosolvents which are commonly referred to as an entrainer or modifier. A third area of application for SCFs has been to treat organic hazardous waste material. The method combines supercritical water and oxygen in a reactor along with the waste which is oxidized. This type of process is commonly referred to as supercritical water oxidation

(SCWO) and has the advantage that no noxious gases are produced and hence the products can be vented into the atmosphere. Polymer science is a field that has seen a great increase in the use of SCFs in recent years. Due to the high pressures needed to form polymers, the use of SCFs becomes ideal. SCFs are also used to synthesize, deconstruct, purify, and characterize polymers and to process polymer melts.[7]

2.2 SUPERCRITICAL WATER

The critical temperature and pressure of water is 647 K and 22.1 MPa respectively. As seen in Figure 2-2, once these experimental conditions have been satisfied, supercritical water will be formed. If only one critical value has been met experimentally, then subcritical water is formed which could exist either in the gaseous or liquid state.

Supercritical water has many different properties than ordinary water. First, supercritical water has a lower density than ordinary water. The lower density contributes to weaker hydrogen bonding in supercritical water than in ordinary water. The decrease in hydrogen bond strength causes supercritical water to exhibit more non-polar behavior and thus be able to dissolve non-polar organic compounds. Also, the dielectric constant for supercritical water is much smaller than normal water. At ambient temperatures and pressures water has a dielectric constant of about 78.5. This value drops to approximately 5.9 at 673.2 K and 30 MPa. In addition, the ion product of supercritical water is on the order of a billion times smaller than that for hot compressed water. These factors can greatly influence the reaction chemistry and cause some ionic reactions to turn into radical reactions.

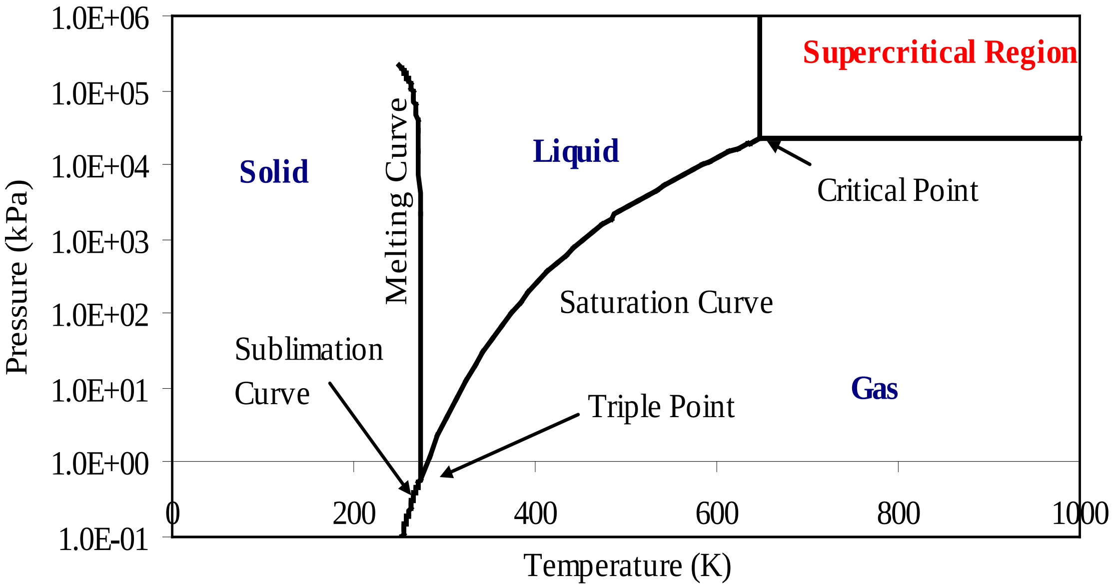

Figure 2-2. A phase diagram of water with supercritical region shown.

Perhaps the mostly greatly employed radical reaction in supercritical water is supercritical water oxidation (SCWO). In this technique, oxygen is combined with supercritical water in order to oxidize various compounds. SCWO is commonly used to destroy organic waste and toxins. An example of this is the destruction of dioxins and polychlorinated biphenyl (PCB) compounds via SCWO. There are a number of advantages to industrial processing with SCWO. Most organic compounds degrade rapidly in SCWO and residence times are generally on the order of seconds or minutes. Another advantage of SCWO is that the solute and solvent are all in the same phase which eliminates transport problems found in other processes such as “wet oxidation.” An added benefit of working with SCWO is that supercritical water is nontoxic and readily available.[8]

2.3 NICKEL AND HIGH-NICKEL ALLOYS

Although it has been used for centuries in the forging of tools and weapons, nickel was not first discovered as an element until 1751 by A. F. Cronstedt. In 1804, it was isolated as a pure species by H. T. Richter. Nickel is produced from two different types of ores. The first are sulfide ores which contain a nickel-iron sulfide mineral known as pentlandite. The nickel in these ores is recovered industrially by magnetic separation or froth flotation. The second types are lateritic nickel ores which are comprised of two different types, silicates and oxides. In lateritic silicate ores, nickel is interspersed within magnesium silicate crystal lattices. In lateritic oxide ores, nickel is found within a hydrated iron oxide mineral known as limonite. The nickel found in lateritic ores is mostly ferronickel and is processed through enrichment.[9]

Nickel consumption in the United States is as outlined in Table 2-2. In 2010, the United States consumed approximately 2.8 billion dollars worth of nickel. The United States does not currently have any active mine sites for nickel and only miniscule amounts of nickel are recovered as a byproduct in the mining of copper, palladium, and platinum ores. As a result, nickel must be either recovered from recycled materials or imported.[10]

Canada is the leading exporter of nickel to the United States, accounting for roughly 44% of the entire United States' nickel imports. Russia is the second largest nickel exporter to the U. S. with 16%. Australia and Norway combined account for 20% and the rest is imported to the U. S. from various other countries in small quantities.[10]

In 2009, Canada led the world in nickel exports and produced about 137,000 tons of nickel. This constitutes about one-tenth of the 1.33 Mt of nickel that was produced globally. Global nickel consumption for 2009 was around 1.29 Mt. Asia led the world in demand for nickel with a 54% share of the total global demand. Table 2-3 shows how nickel is consumed on a global scale.[11,12]

Table 2-2. United States nickel consumption.[10]

Use	%
Steels (including Stainless)	44
Nonferrous and Superalloys	42
Electroplating	9
Others (Catalysts, Magnets, Ceramics)	5

Table 2-3. Global nickel consumption.[12,13]

Use	%
Stainless Steel	61
Nonferrous Alloys	12
Steel Alloys	10
Electroplating	11
Others (Chemicals)	6

Nickel is a highly used industrial metal found in a number of different settings. The largest use of nickel is as an alloying element to produce ferrous and copper alloys, in addition to, stainless and specialty steels. Stainless steel production accounts for nearly half of the United States’ nickel consumption. Nickel-based alloys have been sought after for use where resistance to heat and corrosion is needed. Also, alloys comprised of nickel and iron have been implemented for use in controlled thermal expansion and soft magnetic projects. Powders composed of nickel have also been employed in the fabrication of powder-metallurgy alloys.

Nickel and nickel compounds are additionally used in the formation of catalysts, batteries, and coatings. Several reactions used to produce pesticides and fertilizers are carried out in the presence of nickel catalysts. Batteries containing nickel hybrids such as nickel-cadmium have become increasing popular. Recent technological advances have introduced nickel metal-hydride batteries which are now commonly found in high-end consumer goods such as laptops and cell phones. In addition, the ZEBRA (Zero Emission Batterie Research Activity) battery comprised of sodium and nickel is being integrated into the electric vehicle market. Another general use of nickel in industry is as a metal plating deposited on surfaces through the process of electroforming. These coatings are commonly found on electrodes.[14]

Nickel has superior metallurgical stability and has been found by Izod and Charpy impact test to be one of the strongest metals. Nickel falls between copper and iron on the electrochemical series and thus has a corrosion resistance that lies between those two metals.[15] Another property of nickel is that of its high ferromagnetic characteristics at ambient temperatures. When nickel is alloyed with other metals the magnetic characteristics are manipulated to achieve magnetic alloys with degrees of varying hardness.

Nickel 200 is an alloy which is comprised of 99.6 % pure nickel and is one of the most common nickel alloys found in industry. The balance is comprised of a variety of organic and inorganic elements as depicted in Table 2-4. It has a melting range of approximately 1435-1446°C and a density of 0.321 lb/in^3. The crystal structure of Nickel 200 is a face-centered cubic structure.[15]

Table 2-4. Elemental composition of Nickel 200.[8]

Element	Limiting Chemical Composition, %
Nickel (plus Cobalt)	99.0 min.
Copper	0.25 max.
Iron	0.40 max.
Manganese	0.35 max.
Carbon	0.15 max.
Silicon	0.35 max.
Sulfur	0.01 max

Nickel 201 is another nickel alloy that is similar in most physical properties to Nickel 200; however, it contains roughly one-tenth the carbon content which allows it to withstand higher temperatures than its Nickel 200 counterpart. Under ASME Boiler and Pressure Vessel Codes, Nickel 201 is rated for use with operating temperatures up to approximately 677 °C. The superior resistance of Nickel 201 to intergranular embrittlement as compared to Nickel 200 at elevated temperatures and pressures renders it ideal as a base material for construction of high-temperature and high-pressure reactors.[15] For this reason, Nickel 201 was selected as the material of choice for reactor liner construction.

2.4 REACTOR LINERS

The concept of reactor liners is not entirely new as demonstrated by patents from the early 1950’s. In 1953, Nebeck received U.S. Patent 2,634,194 for a lined reactor which was assigned to Universal Oil Products Company. In this patent, he describes how carbon steels are vulnerable to hydrogen attack and permeation especially when working with high temperature and high pressure reacting systems. For this reason, metal alloy liners are highly advantageous when dealing with hydrocarbon conversion processes such as dehydrogenation, reformation, and hydrocracking. In addition, he explains that the pressure difference across the liner is very small, and hence, the liner can be made very thin without fear of rupture.[16] A year later, Bergman was issued a patent for an internally insulated and liner reactor which was very similar to that of Nebeck. This patent was also assigned to Universal Oil Products Company.[17]

In 1967, Peters received a patent for a catalytic reactor tube liner which was assigned to Reichhold Chemicals, Inc. In contrast to traditional fixed liners, Peters proposed lining steel pipes with a number of different materials to produce liners suitable for different applications. One type of materials that could be used to construct liners are various metals including vanadium, molybdenum, chromium, nickel, and aluminum. Particular anodic metallic mixtures could also be deposited on reactor walls to produce a liner. A third type of materials appropriate for producing reactor liners were chelate polymeric compounds. All of these can be applied to the interior of the reactor walls via electroplating or flame jet techniques.[18]

More recent applications of reactor liners have been found in military-based settings. The U.S. Navy has implemented a supercritical water oxidation (SCWO) unit as a method to treat waste generated on ships. In their setup, they have used a platelet reactor liner which aids in resistance to degradation by thermal or corrosive means to the pressure vessel. Additionally, it allows their unit to operate at higher operating temperatures and lower residence times. Post-experimental inspections with a fiber-optic camera found no evidence of corrosion or salt-plugging to the liner.[19]

Another recent application of liners has been demonstrated in chemical processing by CTI Industries. Although these liners were not used explicitly in a reactor, their functions were similar to liners placed within a reactor. In 2006, CTI Industries was contracted by a major oil refinery to place liners in failing tubes of two overhead fin fan condensers. Retubing the old bundles would have been expensive and resulted in loss of production yielding great costs to the refinery. Instead, CTI was able to construct liners of Hastelloy C-276 and place them in the old heat-exchanger tubes. After placement, the tubes were pressurized to create a tight seal between the liners and the tubes. Excess liner material was removed and the ends punched to seam the ends of the tubes and liners. The project was completed successfully and lead to future projects of a similar nature.[20]

2.5 GLYCERIN

Glycerin was first discovered in 1779 by the Swedish chemist, K. W. Scheele while conducting an experiment in which he heated olive oil and lead monoxide together. Later, he found that glycerin could be produced by reacting a variety of different metals and glycerides, and went on to publish his techniques in *Transactions of the Royal Academy of Sweden*. In 1811, Scheele’s term for glycerin “sweet principle of fat” was changed to the name “glycerin” by a French investigator of oils and fats named M. E. Chevreul. He derived this term from the Greek work, glykys, which means sweet. Twelve years later Chevreul filed a patent on a process of treating fats with alkali substances in order to produce fatty acids. This patent also included product recovery of glycerin. The empirical formula for glycerin, $C_3H_8O_3$, was established by the French investigator Pelouze in 1836. Forty-seven years later, Berthelot and Lucea proposed the structural formula for glycerin, $C_3H_5(OH)_3$.[21]

Glycerin did not see much practical industrial use until 1846 when the Italian chemist, Ascanio Sobrero invented the highly explosive chemical known as nitroglycerin. Twenty years later, the Swedish industrialist, Alfred Nobel found that adding silica to nitroglycerin mixtures stabilized them allowing them to be formed into a paste and transported without fear of unprompted explosions. This paste was named dynamite and became the first international technological use of glycerin. Dynamite then became used in many industries from mining and drilling to construction of bridges and railroads.[21]

Glycerin is a clear, viscous fluid which is compatible with a large variety of other chemicals making it an ideal solvent for many processes. Other chemical and physical properties of glycerin at 20°C and one atmosphere are listed in Table 2-5.

Table 2.5. Chemical and physical properties of pure glycerin.[22-24]

Property	Value
Chemical Formula	$C_3H_5(OH)_3$
Molecular Weight	92.10 g/mol
Melting Point	18.17°C
Boiling Point	290°C
Freezing Point	17°C
Density	1.2636 g/cm^3
Viscosity	1499 cP
Specific Heat (26°C)	0.5795 cal / (gm • °C)
Refractive Index	1.47399
Heat of Combustion	397.0 kcal / mol
Dissociation Constant	$7x10^{-14}$
Dielectric Constant	41.14 (at $2x10^6$ Hz)
Heat of formation (25°C)	159.8 kcal/mol
Heat of Fusion	47.5 cal/gm
Heat of Vaporization (55°C)	21060 cal /mol
Surface Tension	63.0 Dynes/cm
Vapor Pressure (50°C)	0.0025 mm Hg

Among some of the most desirable properties of glycerin are its hygroscopicity, the ability to draw moisture from the environment, and its low vapor pressure. In addition, glycerin is non-toxic to both humans and the environment. These properties combine to make glycerin a versatile ingredient that can be used as a lubricant, plasticizer, humectant, and bodying agent. Also, glycerin is a trihydric alcohol which possesses two primary hydroxyl groups and one secondary hydroxyl group. One or more of these hydroxyl groups can be reacted to produce a wide variety of specialty chemicals including esters, ethers, glycols, and aldehydes. One of the largest chemical uses of glycerin-derived esters is the production of alkyd resins of fatty acids. These esters are created by reacting acids and glycerin together at high temperatures.[22]

Due to the versatility of glycerin, its properties are often exploited throughout the chemical manufacturing industry to produce a large array of consumer goods. Leffingwell wrote of over 1500 uses for glycerin in the Merck Index in 1945.[25] Table 2-6 lists the most common industries in which glycerin is currently employed.

Table 2-6. Glycerin consumption by industry.[26]

Usage	%
Cosmetics, pharmaceuticals, & soaps	26
Resale	17
Polyglycerol esters	12
Esters	11
Food and drinks	8
Alkyd resins	6
Tobacco	4
Cellulose films	3
Paper	1
Others	12

First, the hygroscopicity of glycerin is often implemented in the use of lotions and cosmetics where moisture retention prevents drying out and cracking. Glycerin also acts as a plasticizer which adds flexibility and softness to a wide variety of materials including: creams, capsules, candy, tobacco, paper, glues and textiles. Another desirable property of glycerin is stability under atmospheric conditions, in part due to the low vapor pressure of glycerin. This stability is implemented for use in films containing volatile humectants and lengthens the “shelf life” of such films. Also, glycerin does not undergo crystallization under atmospheric exposure for long periods of time which is important in maintaining product consistency. Pure glycerin is also stable to atmospheric oxygen and will not readily oxidize unless in the presence of iron or copper catalysts. The solubility and compatibility of glycerin with many different ingredients is highly valued by formulators. The hydroxyl groups of glycerin make it a good solvent which is used to make pharmaceutical preparations and flavor extracts. Alkaloids, phenol, mercuric chloride, and boric acids are more soluble in glycerin than in water and thus highly concentrated solutions of these compounds are prepared using glycerin as the solvent. Glycerin is also highly miscible with a large number of commonly used smaller chain alcohols and glycols such as methanol, ethanol, isopropanol, ethylene glycol and propylene glycol. The high viscosity of glycerin is taken advantage of for use in hydraulic fluids and lubricants, experiments carried out in laboratories studying fluid flow behavior, and as a thickening agent in the preparation of liquid solutions such as syrups and gels. A unique and interesting feature of glycerin is that pure glycerin freezes around 18°C, but when diluted with water to a 66 wt % solution, the freezing point drops to -46.5°C. This property led glycerin solutions to originally be used for automobile cooling systems until later being replaced with ethylene glycol. Some cooling systems that refrigerate food still use glycerin solutions as a coolant due to the non-toxicity of glycerin. The non-toxicity of glycerin is another property that makes it versatile and easy to work with.[22] The TLm96 value, the amount at which over half of exposed organisms would die within 96 hours, is over 1000 mg/L. The TLm96 aquatic toxicity value is over 1000 ppm. In addition, the fire hazard presented by glycerin is classified as low.[27]

Glycerin in the United States is also referred to as glycerine; however, the chief component of these products is glycerol. To be accurate, a solution containing 95 wt. % or more glycerol is called glycerin, but glycerol is actually the chemical compound 1,2,3-propanetriol. In Europe, the term glycerol applies to any grade of glycerin, including crude, similar to how glycerine and glycerin are used interchangeably in the United States.

There are a number of different grades of glycerin commonly found in industry. The first is USP glycerin which requires odor and taste to be suitable for pharmaceutical and food products, in addition to, having a high level of purity. The USP designation means that the glycerin product has met the specifications set forth in the *U.S. Pharmacopeia (1990)* monograph entitled *Glycerin*. In addition the glycerol content in aqueous solutions must be equal to or greater than 95% by weight and have a specific gravity of at least 1.249 at 25°C. Typically, glycerin of this type is found in three levels of purity in commercial markets: 96.0%, 99.0%, and 99.5%. Solutions containing greater than 99.5% glycerin can also be obtained, but may exceed the levels of purity needed depending on the application. Analogous to the American USP designation is the European PH.EUR which indicates that the guidelines for production have been met that were established in the *European Pharmacopoeia II (1986).* It is typical to see a percentage after the PH.EUR designation indicating the purity of the glycerin product.

Another glycerin grade is CP which stands for chemically pure glycerin. In the United States, this form of glycerin is considered to be generic because it has not been tested for compliance in accordance with the *U.S. Pharmacopeia*; however, it is generally of the same quality as USP grade glycerin. In Europe, requirements for production of chemically pure, CP, glycerin have been set forth by the British Standards Institution. A primary difference between the United States and European designation of CP glycerin is that European CP glycerin does meet the requirements set forth in the *European Pharmacopoeia*. Food grade glycerin is an additional type of glycerin which has requirements much like those of the USP standards. The guidelines for glycerin falling under this category must meet the standards laid out in the *Food Chemicals Codex* (FCC) monograph, *Glycerin*. In Europe, glycerin to be used as a food additive must meet the requirements in the Council Directive 78/663/EEC. This document provides purity specifications for additives to food such as emulsifiers, stabilizers and gelling agents.[22]

High gravity glycerin is an industrial grade of glycerin that conforms to the General Services Administration's Federal Specification O-G-491C. In addition, glycerin of this grade must be in compliance with the American Society for Testing and Materials (ASTM) guidelines set forth in the *Standard Specification for High-Gravity Glycerin D-1257*. The concentration of glycerin in high gravity glycerin must be at least 98.7% by weight and have a minimum specific gravity of 1.2587 at 25°C; however, it is rare to find glycerin at this particular concentration and thus most industrial suppliers offer high gravity glycerin at a glycerin concentration of 99.0% by weight with a specific gravity of 1.2595 at 25°C. In Europe, the ASTM guidelines for high gravity glycerin are accepted for glycerin to be used in industrial applications. Similar to high gravity glycerin is dynamite glycerin which adheres to all the same requirements as high gravity glycerin; however, the color of this glycerin is subjected to the Federal Color Standard and cannot be darker than the standard. In Europe, the Nobel Explosive Company Ltd. has outlined requirements for glycerin to be used in explosives in *Specification 21D*. Additionally, the British Standards Institution has defined standards for dynamite glycerin in *British Standard Specification for Dynamite Glycerol, BS2624*.

The last types of glycerin are saponification crude and soap lye crude and are generically referred to in the U.S. as crude glycerin produced from triglycerides. The former is a fat hydrolysis concentrate and has a glycerol concentration of about 88 wt %. In Europe, this type of glycerin is commonly called hydrolyser crude glycerol and is produced in accordance with the *British Standard Specification BS 2622*. The latter is a concentrated solution recovered from the spent lye of the soap kettle. In Europe, soap lye crude is only required to contain 80 wt. % glycerol as detailed in the *British Standard Specification for Soap Lye Crude Glycerol BS 2621*. Due to the lower level of purity, these types of glycerin are generally only used in refining processes.[22]

Glycerin is produced industrially via two different methods, the first being as a byproduct in both triglyceride saponification in oleochemical manufacturing and triglyceride transesterfication in biodiesel manufacturing. The second method of production is through the use of synthetic techniques. To produce soap, a triglyceride is hydrolyzed with a base such as NaOH or KOH.[28] To produce biodiesel, a triglyceride is hydrolyzed with an alcohol, commonly methanol, in the presence of a heterogeneous or homogeneous acid or base catalyst.[29,30,31] Glycerin produced in these processes is technically crude glycerol and is further purified by distillation or ion exchange techniques to produce glycerin.[22] Approximately 75% of the glycerin produced in the U.S. is made as a byproduct from these processes while the balance is produced synthetically.[32] At the time of World War I, the company, BASF had developed a method to produce glycerin from allyl alcohols. Later, many patents were developed for synthetic glycerin between 1937 and 1945 in response to greater demands for glycerin during World War II. This was due largely in part for uses in creating explosives.[29] In the 1930's, Shell Development Company opened the first U.S. synthetic glycerin plant based on their allylchloride-epichlorohydrin process. Shell later developed another glycerin production process in the 1960's using a method based on acrolein-allyl chemistry. Their success was short-lived and Shell ceased synthetic glycerin production in the mid 1980's. The Dow Chemical Company picked up where Shell left off and began producing synthetic glycerin based on epichlorohydrin chemistry in the 1980's. In the early 1990's Dow was the only U.S. producer of synthetic glycerin.[33] Their success was also short-lived and in the mid 2000's Dow shut down their glycerin plant in Texas. The rapid influx of glycerin on the market also resulted in the shut down of a Proctor and Gamble natural glycerin plant in England.[34] A third method to produce glycerin is via the fermentation of sugars called the "Protel process" which has been studied and used in Europe in times of war and economic crisis to supplement glycerin demand; however, the costs and inefficiencies involved with this process far outweigh those found in more modern, commercial glycerin production processes.[33]

Demand for biodiesel production has seen recent, rapid increases as the need for alternative and green fuels has grown in response to rising costs associated with gasoline and other petroleum-derived fuels. In additions, concerns about global warming have sparked interests in fuels which are carbon neutral and produce lower emissions than current fuel technologies. While the entire energy crisis will not be solved strictly by using biodiesel, it offers a promising alternative to conventional fuel technology for a number of reasons. First, it is derived from renewable resources and has a closed carbon cycle. Second, it will help alleviate some oil dependence and provide new markets for processing oils and fats. Third, the emissions from biodiesel are generally lower than conventional diesel fuel with the exception of nitrogen oxides. Last, its lubricating properties make it an ideal additive for ultra-low-sulfur diesel (ULSD) even in concentrations as low as 1-2%.[29] While there are a multitude of benefits related to biodiesel use, its production has caused a rapid influx of glycerin on the market. This is because biodiesel production generates approximately ten percent crude glycerol as a byproduct.[26] In 2006, the United States produced roughly 250 million lbs of glycerol from biodiesel production. DOE reports have shown that if the U.S. were to convert approximately two percent of the diesel market to biodiesel, almost one billion pounds of byproduct glycerol could be produced in the U.S alone. With current global markets for glycerin at roughly 1.3 billion pounds the potential for a glycerin surplus is highly probable. As a result, new processes and techniques to convert glycerin into higher-value products have been researched and implemented in recent years. This will aid production plants in maintaining fiscal efficiency, as well as, manage glycerol waste streams.[26]

The conversion of glycerol into higher-value chemicals can be broken down into two separate categories. The first is conversion based on oxidation/reduction chemistry to produce other compounds containing three carbon atoms. The second type of conversion is to transform glycerol into an entirely new compound. The first method can produce a wide variety of chemicals; however, the ones of greatest market potential and value are propylene glycol, isopropanol, acrylic acid, propionic acid, and acrolein. Although oxidation is easier to carry out, a majority of the aforementioned chemicals are produced with reduction techniques. The second conversion method employs the use of biological enzymes to convert glycerol into new unique species. A few of these species include: butanol, acetic acid, and hydrogen.[26]

2.6 HYDROGEN

Hydrogen was first discovered by Boyle in the latter half of the seventeenth century in an experiment dissolving iron in sulfuric acid. Cavendish published data on some physical properties of hydrogen including specific weight and density in 1766. Nearly 130 years later, the Linde-Process was used by Dewar to liquefy hydrogen. A blemish in hydrogen history occurred in 1937 with the explosion of the hydrogen-filled zeppelin, “Hindenburg” at Lake Hurst. In 1963, hydrogen reclaimed fame in the aviation industry by being used in combination with oxygen to launch a rocket at Cape Kennedy.[35]

Gaseous mixtures of hydrogen and carbon monoxide are commonly referred to as synthesis gas or syngas. Syngas may also contain other gases such as: carbon dioxide, methane, nitrogen, and other higher-boiling hydrocarbons. Synthesis gases were originally called “water gases” when discovered in 1780 by Felice Fontana. He found that by reacting water and carbon, in the form of coal, at temperatures greater than 500°C, combustible gases could be formed. In 1921, Patart produced methanol synthetically by reacting syngas mixtures at 400°C over a ZnO catalyst. Five years later, Fischer and Tropsch developed a process to produce higher-order hydrocarbons from syngas mixtures reacted with ferric catalysts. The Fischer-Tropsch process was widely used by Germany in World War II to produce synthetic fuels from coal. Since that time, syngas has been used to produce a wide array of industrial chemicals. Some of these include ammonia produced from hydrogen and nitrogen and oxo-alcohols from mixtures of hydrogen and carbon monoxide.

Hydrogen is a highly combustible, colorless, odorless gas and is the lightest of all chemical elements with one proton and one electron. Hydrogen has two isotopes, deuterium and tritium, which contain one and two neutrons in the nucleus respectively. Table 2-7 contains other physical properties of hydrogen at 0°C and one atmosphere.

Table 2-7. Physical properties of hydrogen.[35]

Property	Value
Molar mass	2.016 g/mol
Density	0.0899 kg/m^3
Thermal conductivity	0.1645 W/m K
Constant volume heat capacity	20.2 J/mol K
Constant pressure heat capacity	28.6 J/mol K
Boiling temperature	20.37 K
Density (liquid) at boiling point	70.00 kg/m^3
Density (gas) at boiling point	1.319 kg/m^3

Hydrogen is unique in that it has a very high compatibility and readily bonds with almost any other element. Metal hydrides are readily formed between many alkali and alkali-earth metals and hydrogen. Hydrogen can be used to saturate hydrocarbons containing double or triple bonds. Hydrogen is also implemented to remove oxygen from metal oxides to produce pure metal and water.

Molecular hydrogen only accounts for 0.5 vppm of the atmosphere near the ground. It is more often found bound up with other elements such as oxygen and carbon. It has been estimated that hydrogen accounts for a mass portion of 0.88% of the earth's crust, atmosphere and hydrosphere. With regards to the entire universe, hydrogen is by far the most frequent element. Roughly 84% of the mass of the sun is comprised of hydrogen which is fused into helium.[35]

There are a variety of ways that hydrogen can be produced industrially. One method to make hydrogen is via the electrolysis of water. This technique uses an electrolyser constructed of a negatively-charged cathode and a positively-charged anode. The electrolyser is suspended in an 25-30 wt % alkaline solution, typically potassium hydroxide, and the electrodes are separated with a membrane permeable to OH^- ions. After a voltage is applied, the electrochemical reactions (1) and (2) take place at the electrodes resulting in the overall reaction for the process (3):

(1) Cathode reaction: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

(2) Anode reaction: $2OH^- \rightarrow \frac{1}{2}O_2 + H_2O + 2e^-$

(3) Overall reaction: $H_2O \xrightarrow{\Delta V} H_2 + \frac{1}{2}O_2$

The process is typically carried out at temperatures around 80°C and pressures between 1-30 bar. While this process has the benefit of zero emissions there are a few drawbacks.

One is that the efficiency of the process is dependent on the corrosion resistance and conductivity of the electrodes. In addition, this process requires an inexpensive source of electricity to carry out the reactions and is only technically feasible up to production capacities of 5000 m^3/ hr at 0°C and one atmosphere.

Steam reformation is another way to produce syngas and hence, hydrogen. This process uses natural gas, liquefied petroleum gas (LPG), or naphtha as feedstock and reforms them with water vapor to produce a syngas mixture. The generalized reaction (4) taking place during steam reformation is shown below along with the specific reactions (5) and (6) taking place when steam reforming natural gas.

(4) $C_nH_m + nH_2O \leftrightarrow nCO + (n+m/2)H_2$

(5) $CH_4 + H_2O \leftrightarrow CO + 3H_2$ $\Delta H_R = 206$ kJ/mol

(6) $CO + H_2O \leftrightarrow CO_2 + H_2$ $\Delta H_R = -41$ kJ/mol

Eqn. 6 is more commonly referred to as the water-gas shift reaction and takes place in parallel with reformation. This reaction is mildly exothermic; however, the reformation reaction in eqn. 5 is endothermic and the overall conversion is limited by chemical equilibrium. Steam reformation is generally carried out in the presence of nickel catalyst at high temperatures. Due to the susceptibility of nickel to poisoning, the feedstock must be purified by removal of sulfur and chlorides contaminants.[35]

Partial oxidation (POX), sometimes referred to as gasification, is yet another method to produce syngas which is similar to reformation; but, does not require the use of catalyst. Instead, oxygen, either in pure form or in the form of air, is added to the feed in the reactor and reacted according to the reaction in eqn. 7.

$$(7)\quad C_nH_m + (n/2)O_2 \rightarrow nCO + (m/2)H_2$$

This process can accommodate heavier hydrocarbons like coal and oils, but can also be used with natural gas as illustrated in eqn. 8. The correct ratios of oxygen to carbon must be used or undesirable side reactions can occur. Eqn. 9 depicts the partial oxidation reaction taking place when too much oxygen is added leading to an unwanted heat gain from the highly exothermic reaction. Eqns. 10 and 11 show the reactions occurring when too little oxygen is used in partial oxidation leading to the formation of coke inside the reactor.

$$(8)\quad CH_4 + \tfrac{1}{2}O_2 \rightarrow CO + 2H_2 \qquad \Delta H_R = -36\text{ kJ/mol}$$

$$(9)\quad CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \qquad \Delta H_R = -803\text{ kJ/mol}$$

$$(10)\quad CH_4 \rightarrow C + 2H_2 \qquad \Delta H_R = 75\text{ kJ/mol}$$

$$(11)\quad 2CO \rightarrow C + CO_2 \qquad \Delta H_R = -173\text{ kJ/mol}$$

An additional unique feature of this process compared to steam reformation is that removal of sulfur from feedstock is not required prior to reacting; however, an acid gas removal system must be integrated into the unit for post-operative cleanup.

One last technique to produce syngas from hydrocarbons combines steam reformation with partial oxidation and is known as autothermal reformation (ATR). This process takes advantage of the heat generated by the exothermic partial oxidation reaction to supply heat to the endothermic steam reformation reaction. This method can also be modified for use as a secondary reformation process. In this secondary process, syngas mixtures which have already been reformed in a primary reactor are fed into the autothermal reactor and allowed to react with compressed air to produce more syngas.

Although syngas can be used in a variety of ways to produce many different compounds, it requires intensive product gas cleanup if hydrogen is the ultimately desired component from it. There are many different methods used to cleanup syngas exploiting both physical and chemical properties. One method used to purify syngas is through pressure swing adsorption (PSA). This method uses high pressures to adsorb all the component gases onto a surface, of which hydrogen does not highly adsorb onto. The purified hydrogen is captured and the remaining gas mixture, typically called tail or purge gases, are used as a fuel gas for the reformation unit. Another type of hydrogen separation in syngas mixtures is through the use of a polymeric membrane. These membranes are designed to exploit the diffusion and solubility of hydrogen to separate it from the rest of the syngas mixture. Another method used for hydrogen purification is cryogenic freezing. This process separates hydrogen out of the syngas mixture by utilizing the differential between the boiling point of hydrogen and the other gases in the mixture.[35]

There are a variety of current industrial applications for hydrogen. In metallurgy, hydrogen is used as a component gas for welding and annealing. It is also used as a shielding gas, or to provide a shielding atmosphere, in the production of float glass, stainless steel, and semiconductors. In the chemical industry, hydrogen is typically used to hydrogenate many different types of chemical species. For instance, it is used to hydrogenate oils to produce ointments, soaps, and margarine. Hydrogen is also used to hydrogenate sulfur compounds in fuels so that they may be removed for fuel purification. Hydrogenation is additionally used to saturate compounds and functional groups containing unsaturated bonds to produce specialty chemicals. An area for hydrogen use that has received much attention in recent years has been in fuel cells. Although first developed in 1839 by Sir William Robert Grove, fuel cells have not seen wide industrial use until recently due to high energy costs and the need for advanced technologies. The scalability of fuel cells has rendered them ideal for a wide span of applications ranging from use in vehicles and electronic devices all the way to full-scale power plants. The fuel cell operates using a combination of oxidation/reduction and polymeric chemistry. The design is relatively simple and consists of anode and cathode plates separated by a polymer electrolyte membrane (PEM). Hydrogen or hydrogen-containing gases are used as a fuel which is oxidized at the anode according to the reaction in eqn. 12:

$$(12)\quad 2H_2 \rightarrow 4H^+ + 4e^-$$

The electrical current produced by this reaction is run through a circuit to perform work before being returned to the cathode side of the fuel cell. The H^+ generated on the anode side of the fuel cell travels through the polymer electrolyte membrane and reacts with oxygen and the recovered electrical current to produce water as shown in eqn. 13:

$$(13)\quad O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$

In this manner, chemical energy is converted into electrical energy with the only product of the reactions being water. With advancements in polymer and catalysts chemistry, fuel cells are now able to react a variety of different fuels for different applications. Table 2-8 shows some different fuel cell types along with the different polymers and catalysts that are used.[35]

Table 2-8. Different fuel cells and their properties.[35]

Type	Alkaline	Polymer-electrolyte	Phosphoric acid	Molten carbonate	Solid oxide
Operation temperature (°C)	60-90	80-110	160-200	600-800	800-1000
Fuel	High purity H_2	High purity H_2	H_2, natural gas	H_2, natural gas	H_2, natural gas, LPG
Anode catalyst	Raney-Ni	Pt/C	Pt/C	Ni/Al	Ni
Cathode catalyst	Raney-Ni	Pt/C	Pt/C	NiO	La-Sr-MnO_3
Membrane electrolyte	KOH	Sulfonated PTFE	Phosphoric acid	Li/Na carbonate	Y-ZrO_2

One last area of hydrogen application has been in the field of alternative fuels and sustainable energy. World dependence on fossil fuels has resulted in a great depletion of petroleum-based reserves. As a result, new, sustainable fuels including hydrogen are being investigated to help alleviate this dependence. Hydrogen has a number of advantages that render it ideal for use as a fuel. First, it is a zero-emissions fuel which greatly reduces the carbon footprint on the environment. Hydrogen also stores well allowing surplus energy to be captured and converted for use at a later time or at a different location. Hydrogen is also a sustainable fuel which can also be produced through a variety of sources including biomass, solar, wind, and hydropower. Although there are many benefits to hydrogen use as a fuel, a number of advancements in fuel-processing technologies and global infrastructure must be made before a hydrogen-based economy can be realized.[35]

3. APPARATUS

3.1 INTRODUCTION

The supercritical water reformation (SWR) unit is comprised of six main components: reactant feed system, Haynes® Alloy 230 reactor, radiant reactor heaters, integrated heat exchanger, product sample collection/analysis system, and data acquisition and control system. A schematic process flow diagram is shown in Figure 3-1. The supercritical water reformation unit is housed inside of a 128 ft^3 enclosure constructed from 4 x 4 ft^2 steel plates measuring ¼" thick that are bolted onto a Unistrut frame. There are some additional pieces of equipment found detached from the unit which are essential for analytic and operational purposes.

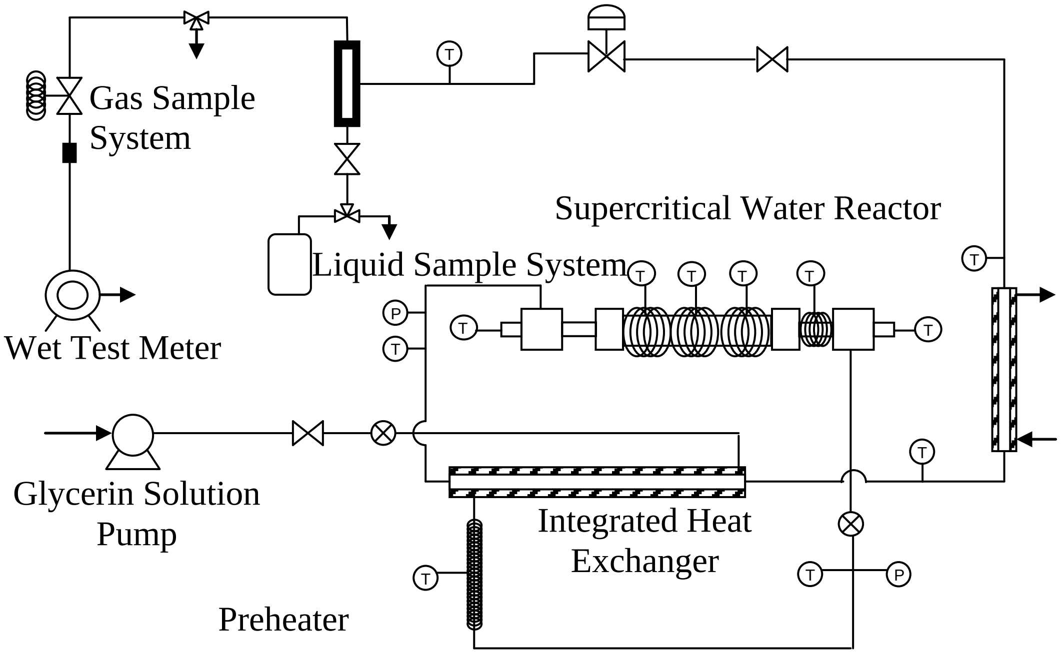

Figure 3-1. A schematic diagram of the supercritical water reformation unit.

3.2 THE SUPERCRITICAL WATER REFORMATION SYSTEM

The supercritical water reformation unit begins with the reactant feed delivery system. Reactant solutions were prepared by measuring out the desired stoichiometric amounts of pure glycerin and deionized water using an Arlyn D-620L scale with a range of 0-22.5 kg and reading increments of 0.002 kg. The solutions were then well-mixed in 5 gal. high-density polyethylene (HDPE) plastic jugs and placed back on the scale. The scale was also used to keep record of total reactant mass fed into the system. The reactant was delivered to the system by an Eldex® high-pressure reciprocating micro-metering BBB-4 pump.

Next, the reactant feed enters into the integrated heat exchanger and is heated up by the exiting reactor product stream. It has been reported by Matsumura et al.[36-38] that heat exchange is crucial to maintain sustainable thermal efficiencies in reformation systems. The heat exchanger was constructed from ½” stainless steel tubing surrounding an ¼” inner pipe made of Inconel® 625 carrying the hot product mixture leaving the reactor. The pre-mixed glycerin solutions were pumped counter-currently through the stainless steel tubing, thus cooling down the product mixture and heating the glycerin solutions before they reach the reactor. After leaving the heat exchanger the reactant solutions were further heated with Omega heat tapes before entering the reactor assembly.

The reactor assembly is comprised of a tubular HAYNES® 230 alloy reactor with heads and crosses at both the inlet and outlet. The reactor inlet cross allows for the introduction of air or other gaseous reactants which can be mixed with the fuel reactant, in this case, glycerin, before entering into the reactor. The heads on each end of the reactor were screwed onto the reactor with screw caps and fixed in places by eight bolts tourqed to 120 in-lbs. In addition, Graphoil gaskets were placed inside the heads before placing them onto the reactor to ensure a proper seal. The reactor crosses each housed a thermowell which extended to the center of the reactor. Inside each thermowell, four thermocouples of varying length were inserted to measure internal reactor temperature at fixed lengths down the reactor as shown in Figure 3-2.

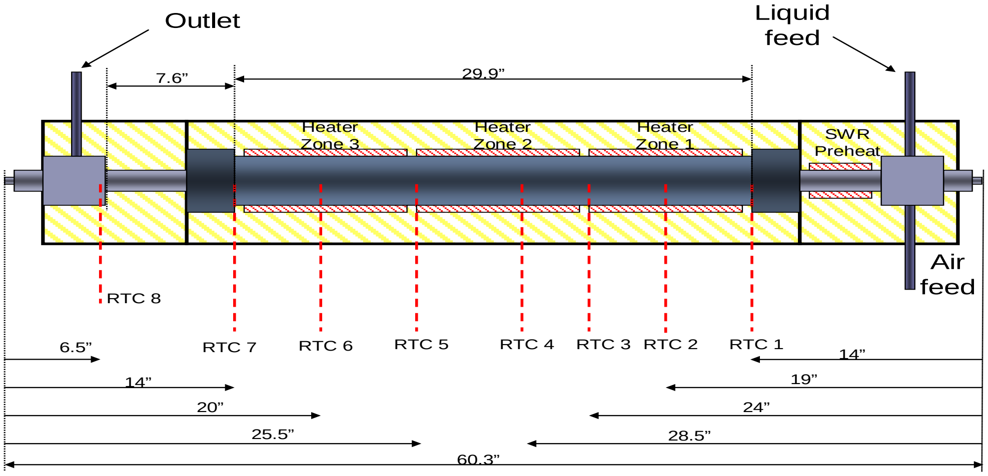

Figure 3-2. A schematic diagram of the supercritical water reactor assembly with heater and thermocouple placement.

Parr Instrument Co. manufactured the reactor and the rest of the assembly with the exception of the reactor crosses and thermowell adapters which were manufactured by the High Pressure Equipment Co. The O.D. and I.D. of the reactor are 3” and 1” respectively. The reactor body is 3’ long and has an internal volume of approximately 380 mL. The crosses for the reactor were constructed from Inconel® 625 Grade 1 while the screw caps were constructed from Inconel® 625 Grade 2. The chemical composition of Inconel® 625 is provided in Table 3-1.

Table 3-1. Elemental composition of Inconel® 625.[39]

Element	Limiting Chemical Composition, %
Nickel	58.0 min.
Chromium	20.0 - 23.0
Iron	5.0 max
Molybdenum	8.0-10.0
Niobium (Tantalum)	3.15-4.15
Carbon	0.10 max
Manganese	0.50 max
Silicon	0.50 max
Phosphorus	0.015 max
Sulfur	0.015 max
Aluminum	0.40 max
Titanium	0.40 max
Cobalt	1.0 max

Although both materials are similar in chemical composition, Grade 2 is heat-treated during production to achieve greater strength allowing it to withstand higher operating temperatures.[39] The crosses are rated for maximum operation at 650 °C at 5000 psi. The reactor and reactor heads were constructed from HAYNES® 230 alloy, the composition of which is given in Table 3-2. They are able to withstand operation conditions up to 800°C at 5250 psi.

The heaters and insulation for the reactor were custom made by Watlow Electric Manufacturing Co. and consisted of three separate parts: the inlet SWR preheat, the reactor body heater, and the outlet insulation. The SWR preheat was used to heat the SWR inlet cross and inlet reactor head. The reactor body heater was used to heat the reactor and consisted of 3 heating elements used to provide consistent heating down the length of the reactor. Each heating element heated a distinct region which was designated as a zone. The outlet insulation covered the SWR outlet cross and reactor head and did not contain any heating elements. It was used explicitly to maintain uniformity in the thermal profile of the reactor assembly.

Table 3-2. Elemental composition of HAYNES® 230 alloy.[40]

Element	Limiting Chemical Composition, %
Nickel	57.0
Cobalt	5.0 max
Chromium	22.0
Molybdenum	2.0
Tungsten	14.0
Iron	3.0 max
Silicon	0.4
Manganese	0.5
Carbon	0.1
Aluminum	0.3
Boron	0.015 max
Lanthanum	0.02

After the reactants were reformed in the reactor, the effluent was cooled by passing it through the integrated heat exchanger. Subsequent cooling was provided by a water-fed heat exchanger. Next, the effluent was filtered for particulate matter (PM) using Swagelok® 90 and 15 micron filters. In addition, a Hoke® micro-metering valve was installed after the filters to aid in the removal of fine particulate matter and provide extra pressure control. Once the particulates had been removed, the effluent was depressurized to ambient pressure via a Badger® control valve. This control valve was operated pneumatically and controlled using a computer. Next, the effluent was delivered to a Strahman® sight gauge where gaseous and liquid products were separated. The liquid product was either collected in HDPE sample bottles for further analysis or collected in a drum for waste disposal. The gas product was sent to a gas sampling system which consisted of a gas sampling port. Product gas flow rates were measured using a Precision Scientific wet test meter and the gases were then vented safely to the atmosphere.

The computer software utilized for data acquisition and process control was National Instruments Labview®. This software collected the following data: time, date, reactor thermocouple temperatures, zone heater temperatures, reactor pressure, and additional data when the air feed delivery system was being used. The software coupled with the Badger® control valve provided PID control of the reactor pressure. The thermocouples housed inside the thermowells of the reactor and the thermocouples mounted in the zone heaters were used to measure the internal and external temperature of the reactor. This software used the response from the thermocouples to keep the reactor thermal conditions consistent throughout the experiment.

3.3 ANALYTICAL INSTRUMENTS

The product gases from the reactor were analyzed using a HP 5890 Series A gas chromatograph (GC) coupled with a thermal conductivity detector (TCD). The GC employs a 2 meter, 1/16” OD ShinCarbon 100/120 packed column from Restek. It has been calibrated to identify the following gases: hydrogen, nitrogen, carbon monoxide, carbon dioxide, methane, ethane, ethylene, and acetylene. The carrier gas used for the gas chromatograph was Ultra-pure Carrier Grade Argon from Airgas and had a purity of 99.9995%.

A computer containing HP Chemstation software was integrated with the GC setup to analyze and record data. In addition, the software allowed the user to tailor the conditions of analysis to suit their needs. The gases to be analyzed were collected in-situ by a gas sample syringe via the gas sample port. To analyze the gases, programs named Restek00, Restek01, and Restek02 were implemented depending on which gases were desired for analysis. The differences in these programs are explained in greater detail in the Appendix.

The GC was calibrated using a standard reference gas for each of the aforementioned gases and was recalibrated periodically to maintain accuracy. Calibration plots for each gas are provided in the Appendix along with their respective retention times. Once analysis of the gas was complete, HP Chemstation generated a report giving retention times and area peaks for each gas. This data was then inserted into an Excel spreadsheet designed to calculate the number of moles of each gas in the sample based on area peak values.

3.4. PROCESS SAFETY

There are a number of factors that must be properly addressed when working with the SWR reformation unit. In addition to the extreme pressures and temperatures used in the reformation process, combustible and poisonous gas mixtures are formed which must be monitored and vented properly. As a result, there are safety redundancies implemented within the system to protect both the operator and the unit. The safety features utilize computer operated controls, and in the event of power loss, manual controls. First, the unit itself is housed inside of an enclosure constructed from ¼” thick steel plates which are bolted onto a Unistrut frame. Labview® control software uses a feedback control system and in the event operating temperatures or pressures exceed those set by the operator the software will shut down the system. Another safety feature that is incorporated with the Labview® software are combustion monitors, which if activated, will alert the operator and shut down the system These monitors will detect combustible gas mixtures in the parts-per-million range. Carbon monoxide detectors were also installed to protect the operator in case of gas leaks. A rupture disk assembly located at the reactor outlet offered additional protection against overpressurization. An expansion drum coupled to the exhaust ventilation was incorporated into the system as an extra safety feature should the rupture disk assembly fail. The operator can also manually depressurize the system from the inlet or outlet to the expansion drum with depressurization valves located on the exterior of the unit.

3.5 REACTOR LINER

The material for liner construction was obtained from Elgiloy Specialty Metals in Elgin, IL. A square sheet of Nickel 201 measuring approximately 12.25” long by 13” wide and 0.013” thick was obtained. From this sheet, three strips were fashioned and marked for identification and measured for dimensions as outlined in Table 3-3.

The three strips were rolled into cylinders and placed into the reactor as follows. Piece N2A was fitted to cover the reactor entrance by the inlet and extended approximately 1/3 of the length of the reactor where it was sleeved inside of piece N2B.

Piece N2B covered the middle of the reactor and was sleeved inside of piece N2C. Piece N2C covered the end portion of the reactor leading to the outlet. The reason that the pieces were sleeved in this telescopic manner was to minimize disruption in the flow regime which could affect mixing in the reactor and hence mass transport. Each overlap of the strips measured about 0.5”. In addition, approximately 0.5” of the reactor was left exposed without being covered by the liner at the entrance and exit of the reactor. This was to allow for any axial thermal expansion of the liners that may take place when operating at high temperatures.

Table 3-3. Reactor liner component identification and dimensions.

ID #	Weight (g.)	Length (in.)	Width (in.)	Thickness (in.)
N2A	84	12.13	3.75	0.013
N2B	87	12.25	3.75	0.013
N2C	86	12.25	3.75	0.013

4. EXPERIMENTAL

4.1 INTRODUCTION

This chapter will offer insight into the procedures and techniques employed for operating the supercritical water reformation unit, the design of the experimental matrix, some of the reaction taking place during reformation, and definitions for yield and gasification calculations. The operation of the reformation unit from start-up to shut-down will be covered in greater detail. The selection of experimental conditions to investigate the effects of using a nickel reactor liner, as well as, varying temperature and water-to-glycerin molar ratios will be covered in the experimental design. Although there are numerous reactions taking place during the reformation process a select few will be explored; particularly, those of greater interest in hydrogen generation.

4.2 CHEMICAL REACTIONS

In reformation of glycerin, as well as, other hydrocarbons there are numerous chemical reactions taking place along with reformation, both simultaneously and consecutively, including methanation, dehydrogenation, water-gas shift, pyrolytic decomposition, and polymerization. The aforementioned reactions are represented by eqns. 14-19.

(14) Reformation: $C_3H_8O_3 + 3H_2O \rightarrow 3CO_2 + 7H_2$

(15) Methanation: $CO + 3H_2 \rightarrow CH_4 + H_2O$

(16) Dehydrogenation: $C_aH_b \rightarrow C_aH_{b-2} + H_2$

(17) Water-gas shift: $CO + H_2O \leftrightarrow CO_2 + H_2$

(18) Pyrolytic decomposition: $C_aH_b \rightarrow C_xH_y + C_zH_w + qH_2$

(19) Polymerization/cyclization: $C_2H_4 \rightarrow$ polycyclic aromatic hydrocarbons (PAHs) → coke

The forward water-gas shift reaction has been researched widely and is often a desired reaction in energy and environmental applications. The forward water-gas shift reaction is especially advantageous in the development of hydrogen technology since carbon monoxide and water are converted to hydrogen. Since water is in excess during supercritical water reformation, a fraction of undesirable carbon monoxide product gas can be converted into desirable hydrogen product gas. Also of significance to hydrogen production are the reformation and dehydrogenation reactions. Although useful in certain application, the methanation reaction is unwanted in this particular process since valuable hydrogen product gas is consumed instead of produced.[5,41,42]

4.3 YIELD AND GASIFICATION

Gas yields are becoming an increasingly popular method for expressing product gas composition as a function of the fuel fed into the reactor. Gas yields are generally expressed as the moles of a component produced in the gas phase divided by the moles of fuel fed. For this work, gas yields were expressed as moles of gas produced per mole of glycerin fed into the reactor.

As a result of not having liquid Total Organic Carbon (TOC) and solid coke analysis, it is proper to analyze specifically carbon produced in the gas phase. Carbon gasification was calculated as grams of carbon produced in the gas phase per minute divided by the grams of carbon fed into the reactor per minute. The grams of carbon fed into the reactor per minute were calculated by multiplying the weight percent of glycerin and the solution flow for that experiment to obtain grams of glycerin fed into the reactor per minute. This value was then multiplied by the molecular weight of carbon and again by three since glycerin contains three carbon atoms. This resulted in the grams of carbon fed into the reactor per minute. The grams of carbon produced in the gas phase were calculated by multiplying the volume percent of the component gas by the molecular weight of carbon and by the number of carbon atoms found in that particular gas. The value of grams of carbon was summed from all carbon containing gases and multiplied by the volumetric flow rate of the product gas to give grams of carbon produced in the gas phase per minute. This value was then divided by the grams of carbon fed into the reactor per minute resulting in grams of carbon produced in the gas phase per gram of carbon fed into the reactor. This value was then multiplied by 100 to give the carbon gasification percentage.

4.4 OPERATIONAL PROCEDURES

Operation of the supercritical water reformation unit began by starting up the data acquisition and controls via Labview® software installed on a computer dedicated solely to the SWR unit. Set points were entered for the reactant heaters, and the solid-state relay switches, integrated with the computer, were turned on. While the reactor was brought to the desired temperature the fuel pump was primed with water. As water entered into the reformation system, the preheat tapes were turned on and the desired set pressure entered into Labview®. Also, the emergency depressurization valves were closed to allow the reactor to build up pressure accordingly. Once the desired pump flow rates and reactor temperatures and pressures were reached, the fuel, which in this case was premixed solutions of glycerin, was swapped out with the feed water and the system allowed to stabilize again. The glycerin solutions used in this work were prepared before the experiments began for the day from a 99.7% pure glycerin stock that was obtained from thechemstore.com. The solutions were diluted to the desired water to glycerin ratios and the rest of the pure glycerin was slightly diluted with water to produce a stock solution from which other experimental glycerin solutions could be prepared. This was done to prevent absorption of water from the atmosphere due to glycerin's hygroscopic nature. Absorption of water by pure glycerin could cause inaccuracies in the water-to-glycerin molar ratios for the solutions prepared for experimentation; hence, distorting the results for varying the water-to-glycerin molar ratio during supercritical water reformation of glycerin.

Samples were collected in-situ for both gas and liquid products. Liquid products were obtained via a three-way valve connected to the bottom of the Strahman® sight gauge. Two liquid samples were collected for each run which could be later analyzed with total organic carbon (TOC) analysis. Product gas samples were collected via a sample port syringe which was plumbed into the ventilation system for the unit. The sample syringes were analyzed in real time for gas composition. In addition, a wet test meter was used to measure the product gas flow rates. Once gas results from the wet test meter and the GC were consistent, the run was concluded and the operator could begin another experiment by changing any of the experimental variables. It is important to note that only the data obtained during the consistent portion of the experiment was used for calculations. This is to ensure that the results were collected and analyzed at steady-state conditions.

When the operator was finished conducting experiments for the day, the fuel was removed and the heaters turned off. Water was pumped to help eliminate both fuel from the feed line and combustible gases residing in the reactor. If it was suspect that a fair amount of coke may have been produced during the day of experiments, the heaters were left on at a lower temperature and air was slowly fed into the reactor to oxidize the coke. This procedure was carried out until sample syringe readings analyzed by the GC indicated one percent or less of carbon dioxide leaving the reactor. Once the heaters were completely shutoff, water was pumped for an additional thirty minutes. Last, the water feed was shutdown and the system slowly depressurized through the emergency depressurization valves to ensure any residual gases were properly ventilated.

4.5 EXPERIMENTAL DESIGN

A total of twenty-four experiments were performed to investigate the effects of a nickel reactor liner and varying reactor temperatures and water-to-glycerin molar ratios on product gas formation and carbon gasification during supercritical water reformation of glycerin. The space time and reactor pressure were kept constant at 100 seconds and 24.1 MPa respectively. The water-to-glycerin molar ratio was varied from 3 to 24 while the temperatures were held constant. Then, reactor temperature was varied from 500°C to 700°C while the water-to-glycerin ratio was held constant. Experiments were first conducted without a reactor liner to establish a baseline for glycerin reformation with this unit. Table 4-1 illustrates the experimental matrix design used to develop operation conditions for the set of experiments designed to investigate the effects of varying temperature and water-to-glycerin ratio without a reactor liner. Experiments were performed in the randomized order shown in Table 4-1.

Table 4-1. Experimental matrix design for glycerin reformation in supercritical water with no reactor liner. Space time was constant at 100 seconds and reactor pressure was kept at 24.1 MPa. Water-to-glycerin molar ratios and reactor temperatures were varied.

Experimental ID	Temperature	W/G molar ratio
11	500	3
8	500	13.5
7	500	24
6	600	3
10	600	3
3	600	13.5
2	600	24
5	700	3
9	700	13.5
4	700	13.5
1	700	24

The experiments carried out with a reactor liner were carried out at similar experimental operation conditions as those performed without a liner; however, the order of the experiments was randomized in a different order as shown in Table 4-2.

Table 4-2. Experimental matrix design for glycerin reformation in supercritical water with a nickel reactor liner. Space time was constant at 100 seconds and reactor pressure was kept at 24.1 MPa. Water-to-glycerin molar ratios and reactor temperatures were varied.

Experimental ID	Temperature	W/G molar ratio
18	500	3
23	500	3
21	500	13.5
15	500	24
17	600	3
22	600	3
19	600	13.5
20	600	13.5
14	600	24
24	600	24
16	700	3
12	700	13.5
13	700	24

5. RESULTS AND DISSCUSION

5.1 EXPERIMENTAL CONDITIONS

The twenty-four experiments outlined in the experimental design section were conducted at the actual experimental conditions depicted in Table 5-1 and Table 5-2. Table 5-1 shows the actual experimental conditions for the eleven experiments performed without a reactor liner while Table 5-2 shows the experimental conditions for the thirteen experiments conducted with the nickel reactor liner. Two repeat experiments were performed for the experiments conducted without a liner which are Runs 9 and 10. Four repeat experiments were conducted for the experiments conducted with a nickel reactor liner which are Runs 20, 22, 23, and 24. Deviations from the experimental set-points are a result of both operator and equipment error. Deviations also arise due to limitations of the equipment; for example, achieving a solution flow of sixty grams per minute of the most concentrated glycerin solutions pushed the boundaries of the pump's performance capabilities resulting in greater deviations in the space time.

5.2 EFFECTS OF VARYING WATER-TO-GLYCERIN MOLAR RATIO

Six sets of experiments were conducted to examine the effects of varying the water-to-glycerin molar ratio. Three sets were conducted with a reactor liner installed and three were conducted with no reactor liner. In each of the three sets, temperatures were held constant at 500°C, 600°C, and 700°C for a particular set while varying the water-to-glycerin ratio from 3 to 24. Repeat experiments were performed for two of the non-liner experiments and four of the experiments conducted with a reactor liner. For experiments where repeat runs were performed, both data points are displayed on the figure along with a 2nd-order polynomial regression line for the data trend. The gases that were analyzed for this work include hydrogen, nitrogen/oxygen, carbon monoxide, methane, carbon dioxide, ethane, ethylene, propene and propane. Propene and propane were only detected in 5 out of the 24 runs. In addition, the gas yields for propene or propane during these runs was 0.03 or less. As a result, the propene and propane gas yields are not displayed in the following figures.

Table 5-1. Experimental run conditions for supercritical water reformation of glycerin performed without a reactor liner.

Run ID	Temperature (^{o}C)	Pressure (MPa)	Solution flow (g/min)	Space time (sec)	W/G molar ratio
11	503	24.1	60.0	97.9	3
8	501	24.2	27.6	100.7	13.5
7	496	24.2	25.3	98.1	24
6	595	24.1	37.5	100.7	3
10	602	24.2	37.3	99.5	3
3	601	24.1	20.9	99.7	13.5
2	601	24.0	18.9	98.1	24
5	698	24.1	28.7	102.2	3
9	698	24.1	17.4	100.4	13.5
4	700	24.1	17.4	100.0	13.5
1	698	24.0	15.4	101.9	24

The effects of varying water-to-glycerin ratio at 500°C on product gas yields and carbon gasification are illustrated without a reactor liner in Figure 5-1 and with a reactor liner in Figure 5-2. Figure 5-3 and Figure 5-4 show product gas yields and carbon gasification with varying water-to-glycerin ratios at 600°C without and with a reactor liner respectively. Figure 5-5 and Figure 5-6 show the results of varying water-to-glycerin ratios at 700°C without and with a reactor liner. Numerical values for the product gas yields and carbon gasification can be found in Appendix B.

Table 5-2. Experimental run conditions for supercritical water reformation of glycerin performed with a reactor liner.

Run ID	Temperature (^oC)	Pressure (MPa)	Solution flow (g/min)	Space time (sec)	W/G molar ratio
18	490	24.2	58.9	111.0	3.0
23	490	24.2	56.9	114.9	3.0
21	499	24.1	27.7	100.5	13.5
15	496	24.1	24.9	98.8	24.0
17	603	24.1	35.4	104.3	3.0
22	600	24.1	35.0	106.2	3.0
19	601	24.1	20.1	103.6	13.5
20	602	24.1	20.2	102.9	13.5
14	600	24.1	18.6	100.4	24.0
24	597	24.1	18.3	103.3	24.0
16	691	24.1	28.2	105.3	3.0
12	697	24.1	16.8	104.4	13.5
13	695	24.1	14.7	107.5	24.0

In the figures that follow, there are instances where the carbon gasification exceeds 100%. Since gasification over 100% is impossible there are sources of error that need be addressed. Some error is attributed to both the operator and the analytical equipment. Another source of error in carbon gasification could result from small amounts of coke building up in the reactor. Since multiple experiments were conducted in the same day, it is possible that a previous run may have produced small amounts of coke inside the reactor. This coke could be oxidized in the subsequent run thus producing higher amounts of carbon-containing gases which increases the carbon gasification to values over 100%. In order to minimize coke effects on carbon gasification, air was fed into the reactor to oxidize the coke as described in the latter half of Section 4.4.

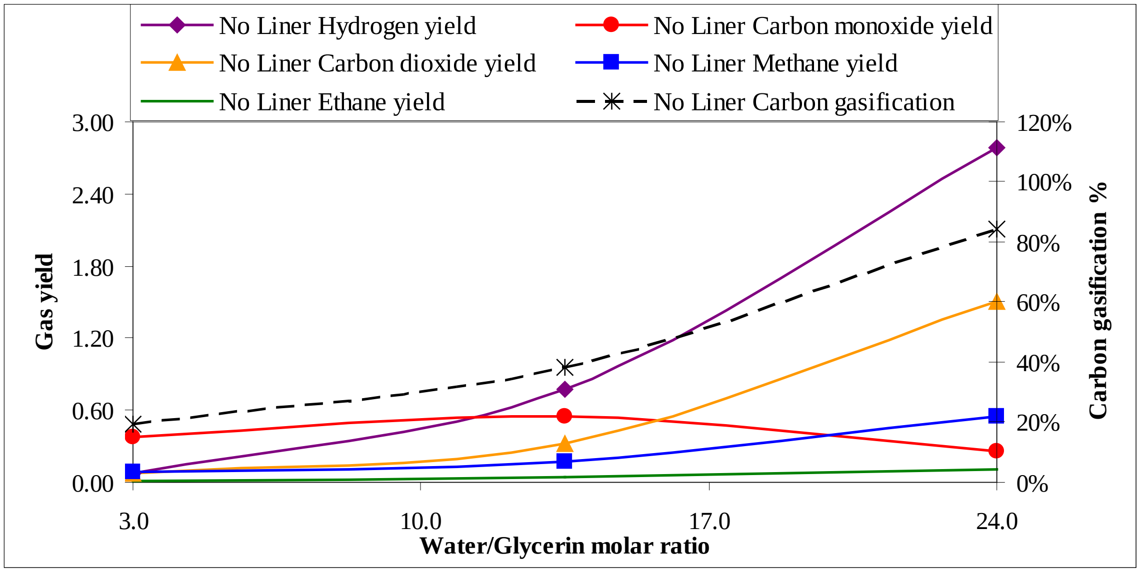

Figure 5-1. Product gas yields and carbon gasification as a function of water-to-glycerin ratio with no reactor liner installed. Experimental conditions are Temperature = 500±3°C, Pressure = 24.2±0.1 MPa, Space time = 98.9±1.5 sec.

In Figure 5-1, the hydrogen and carbon dioxide gas yields increase significantly, as did the carbon gasification, with increasing water-to-glycerin ratio. The methane gas yield increases slightly while the carbon monoxide gas yield decreases with increasing water-to-glycerin ratio. The ethane gas yield stayed relatively constant with increasing water-to-glycerin ratios. These results suggest that the forward water gas shift reaction is more active at higher water-to-glycerin ratios; however, the data do not provide much insight into activity of the methanation or pyrolytic decomposition reactions. The carbon gasification increased almost 65% in the range of water-to-glycerin ratios investigated suggesting that carbon gasification takes place to a greater extent in more dilute glycerin solutions.

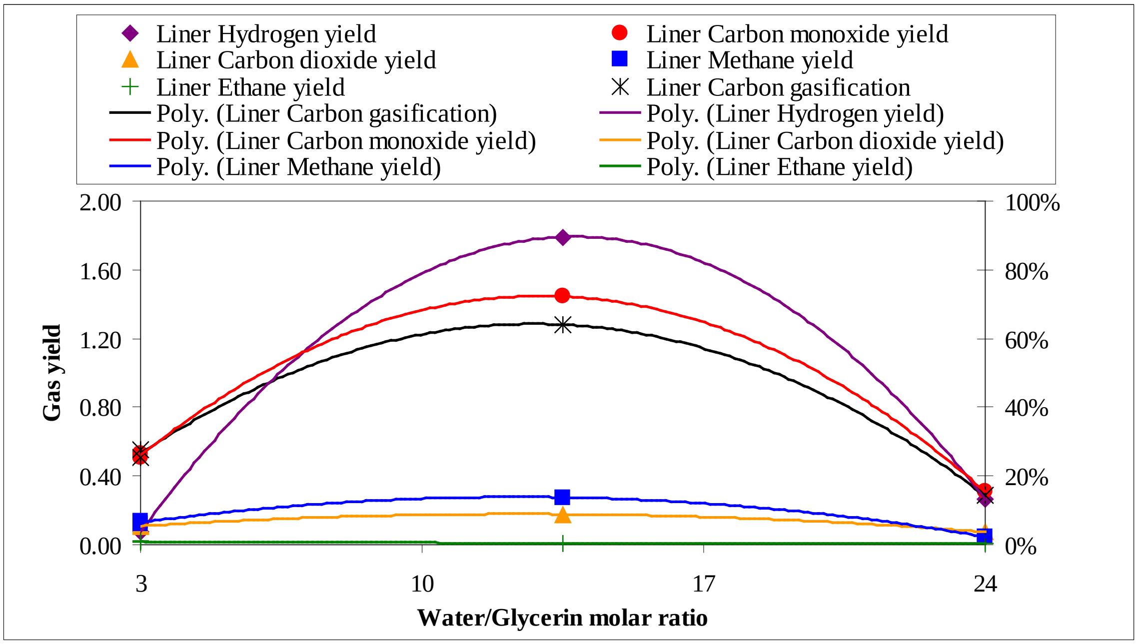

Figure 5-2. Product gas yields and carbon gasification as a function of water-to-glycerin ratio with a reactor liner installed. Experimental conditions are Temperature = 494±5°C, Pressure = 24.1±0.1 MPa, Space time = 106.3±7.9 sec.

The results of Figure 5-2 do not provide obvious trends with increasing water-to-glycerin ratios. The ethane, methane, and carbon dioxide gas yields appear constant for the most part when performing the experiments with a liner. The gas yields for hydrogen and carbon monoxide, and the carbon gasification, have a maximum at 13.5 water-to-glycerin ratio; however, the values for these results are smaller at both lower and higher water-to-glycerin ratios. From these particular results, conclusions cannot be drawn in reference to varying water-to-glycerin ratios at 500°C using a reactor liner.

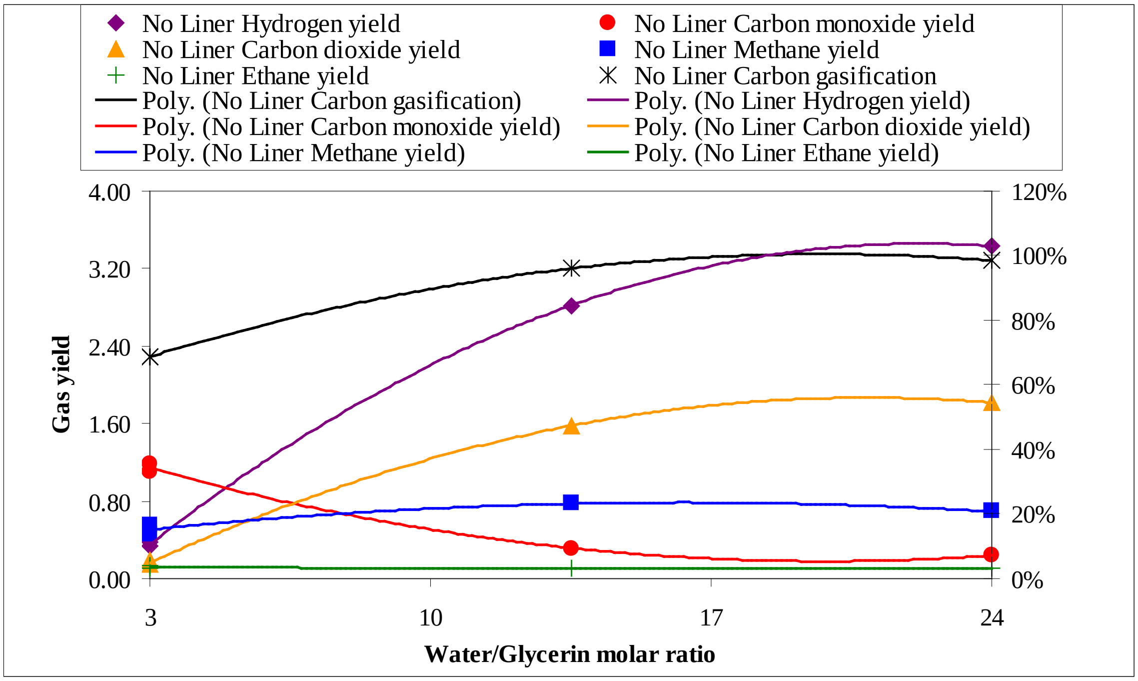

Figure 5-3. Product gas yields and carbon gasification as a function of water-to-glycerin ratio with no reactor liner installed. Experimental conditions are Temperature = 600±3°C, Pressure = 24.1±0.1 MPa, Space time = 99.5±1.1 sec.

In Figure 5-3, hydrogen and carbon dioxide gas yields greatly increased with a sharp decrease in the carbon monoxide gas yield for increasing water-to-glycerin ratios. This suggests that the forward water gas shift reaction proceeds to a greater extent at higher water-to-glycerin ratios at 600°C. Methane and ethane gas yields stayed constant with increasing water-to-glycerin ratios suggesting that the methanation and pyrolytic decomposition reactions are not taking place to a large degree at these operating conditions. The carbon gasification percentage increased with increasing water-to-glycerin ratios up to approximately 13.5 water-to-glycerin ratio. At this point, 100% carbon gasification was achieved and remained there with further increases in the water-to-glycerin ratio.

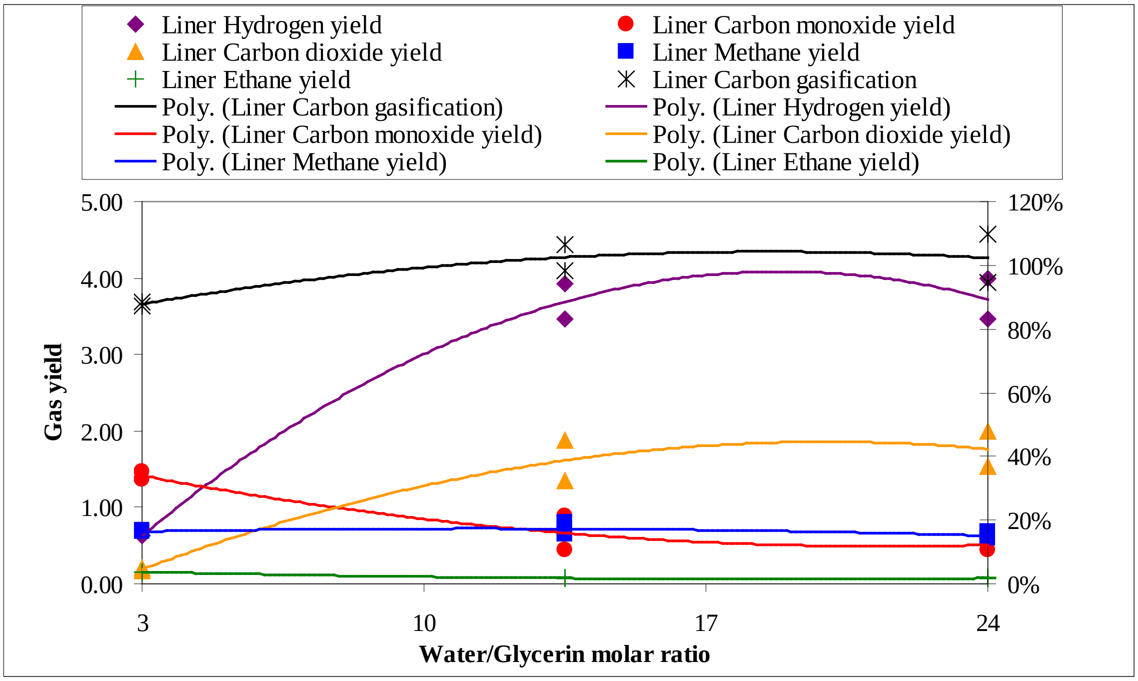

Figure 5-4. Product gas yields and carbon gasification as a function of water-to-glycerin ratio with a reactor liner installed. Experimental conditions are Temperature = 601±2°C, Pressure = 24.1±0.0 MPa, Space time = 103.4±1.9 sec.

Figure 5-4 shows similar trends for increasing water-to-glycerin ratios as those in Figure 5-3; however, the hydrogen gas yield increased from 3.43 to 3.73 in the experiments performed with a reactor liner at 24 water-to-glycerin ratios. This suggests that the liner has a positive effect with increasing water-to-glycerin ratios on gaseous hydrogen production at 600°C. The carbon monoxide gas yield was slightly higher at the 24 water-to-glycerin ratios in the experiments conducted with a reactor liner installed, but the trends were the same. The carbon gasification percentage in the liner experiments at 600°C mimics the results of the experiments performed without a liner.

In Figure 5-5, the hydrogen and carbon dioxide gas yields increase with increasing water-to-glycerin ratios, but not to the same extent as was observed at 600°C.

The carbon monoxide gas yield decreases sharply while the methane yield slightly peaks at 13.5 water-to-glycerin ratio. These results suggest that the forward water gas shift reaction is taking place at these conditions.

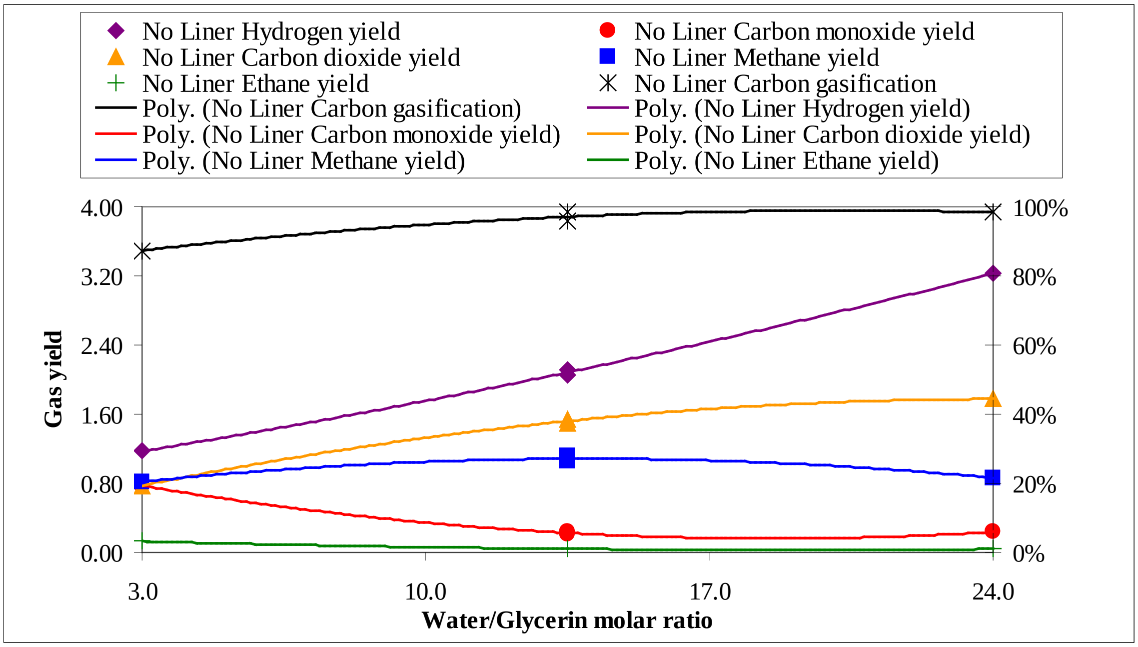

Figure 5-5. Product gas yields and carbon gasification as a function of water-to-glycerin ratio with no reactor liner installed. Experimental conditions are Temperature = 699±1°C, Pressure = 24.1±0.1 MPa, Space time = 101.1±1.1 sec.

The experiments performed with a reactor liner at 700°C produced the greatest hydrogen gas yields as seen in Figure 5-6. Hydrogen gas yields of 4.41 were achieved at 24 water-to-glycerin ratio. In addition, the carbon dioxide gas yields were greatest at these conditions achieving a value slightly over 2.00. Also, the carbon monoxide gas yields dropped to their lowest values at these conditions. This suggests that the forward water gas shift reaction is more highly favored at higher water-to-glycerin ratios or more dilute glycerin solutions.

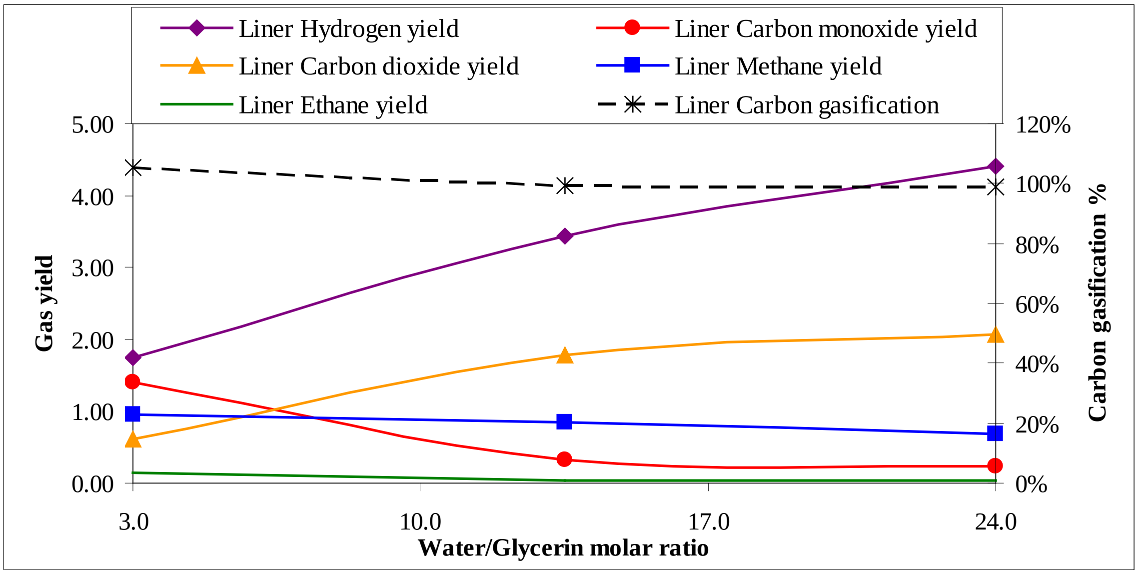

Figure 5-6. Product gas yields and carbon gasification as a function of water-to-glycerin ratio with a reactor liner installed. Experimental conditions are Temperature = 694±3°C, Pressure = 24.1±0.0 MPa, Space time = 105.7±1.6 sec.

5.3 EFFECTS OF VARYING TEMPERATURE

The experiments conducted to study the effects of varying reactor temperature on product gas formation and carbon gasification extent were conducted in a manner analogous to the experiments used to study the effects of varying water-to-glycerin molar ratios. The experiments were conducted in six sets, three of which were performed with a reactor liner and three without a reactor liner. For each of the three experimental sets, temperatures investigated ranged from 500°C to 700°C and the water-to-glycerin ratio was held constant at 3, 13.5, and 24 respectively. Repeat experiments were performed for two of the non-liner experiments and four of the experiments conducted with a reactor liner. For experiments where repeat runs were performed, both data points are displayed on the figure along with a 2nd-order polynomial regression line for the data trend. The gases that were analyzed for this work include hydrogen, nitrogen/oxygen, carbon monoxide, methane, carbon dioxide, ethane, ethylene, propene and propane. For reasons discussed in Section 5.2, propene and propane do not appear on the following figures.

Figure 5-7 and Figure 5-8 illustrate the results of varying the reactor temperature on product gas yields and carbon gasification percentage without and with a reactor liner at a fixed water-to-glycerin ratio of 3. The results of varying temperature at a water-to-glycerin ratio of 13.5 are shown without a liner in Figure 5-9 and with a liner in Figure 5-10. Figure 5-11 and Figure 5-12 show the effects of varying temperature at a water-to-glycerin ratio of 24 both without and with a reactor liner. Numerical values for the product gas yields and carbon gasification can be found in Appendix B.

As was seen in Section 5.2 there are some values for carbon gasification that exceed 100% in the following figures. Since carbon gasification over 100% is impossible to achieve there is some error in those experimental values. Sources of these errors are discussed at length in Section 5.2.

In Figure 5-7, the hydrogen, carbon dioxide, and methane gas yields increase with increasing temperature at a water-to-glycerin ratio of three when reforming without a reactor liner. This exhibits that the forward water gas shift and pyrolytic decomposition reactions are more active at higher temperatures. The decrease in carbon monoxide after reaching a temperature of 600°C along with a sharper increase in the yields for the aforementioned gases suggests that the reactions are taking place to a greater extent when reactor temperatures exceed 600°C. The formation of ethane increased with increasing temperature, but not to a large extent. Carbon gasification percentage increased rapidly with increasing temperature and achieved roughly 90% at a temperature of 700°C.

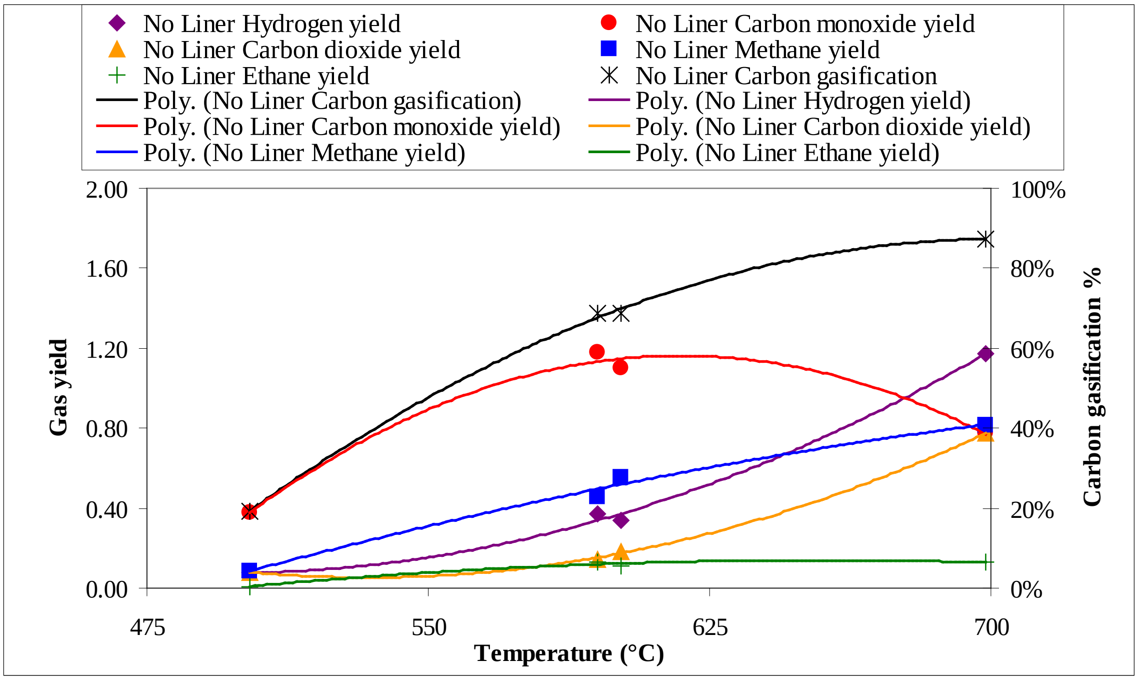

Figure 5-7. Product gas yields and carbon gasification as a function of temperature with no reactor liner installed. Experimental conditions are Water-to-glycerin ratio = 3.0, Pressure = 24.2±0.0 MPa, Space time = 100.1±1.8 sec.

Figure 5-8 depicts similar trends to those in Figure 5-7; however, the hydrogen and methane yields are greater. Carbon monoxide yield is greater as well and plateaus after reaching a temperature of 600°C. Water gas shift reaction and pyrolytic decomposition are again both active in these experiments. As found in the previous experiments, carbon gasification increased with increasing temperature, but in these experiments a carbon gasification percentage of 100% was achieved at a temperature of 700°C.

Figure 5-9 illustrates the results from the experiments performed at a fixed water-to-glycerin ratio of 13.5. The carbon dioxide and methane yields increase with increasing temperatures while the carbon monoxide yields decrease. A greater hydrogen yield was achieved at the 13.5 water-to-glycerin ratio than the experiments performed at the 3 water-to-glycerin ratio. The decrease in hydrogen yield after a temperature of 600°C suggests that the optimal reformation temperature at the imposed conditions is around 600°C and at 700°C pyrolysis is more active than reformation reaction. It appears that the forward water gas shift is not as favorable at these conditions as it is at other experimental conditions. Since water gas shift reaction is an equilibrium reaction, its slower forward reaction rate is attributable to high concentrations of CO_2 and H_2, i.e., products of the forward water gas shift reaction. Carbon gasification near 100% was achieved at reactor temperatures of 600°C.

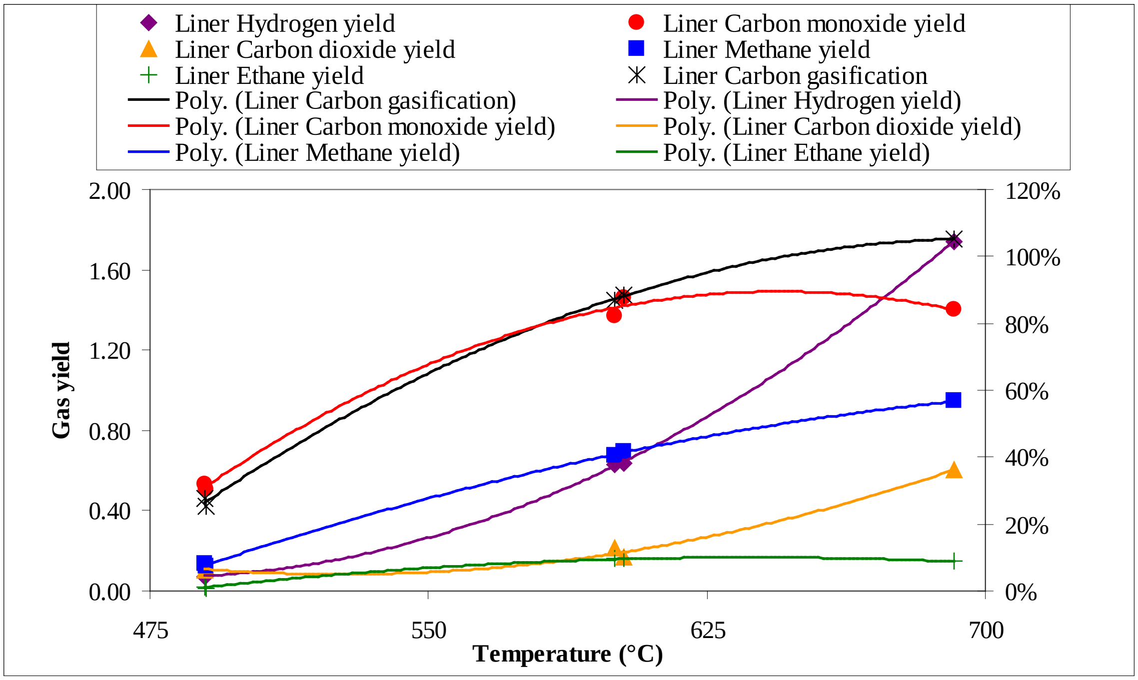

Figure 5-8. Product gas yields and carbon gasification as a function of temperature with a reactor liner installed. Experimental conditions are Water-to-glycerin ratio = 3.0, Pressure = 24.2±0.0 MPa, Space time = 108.3±4.5 sec.

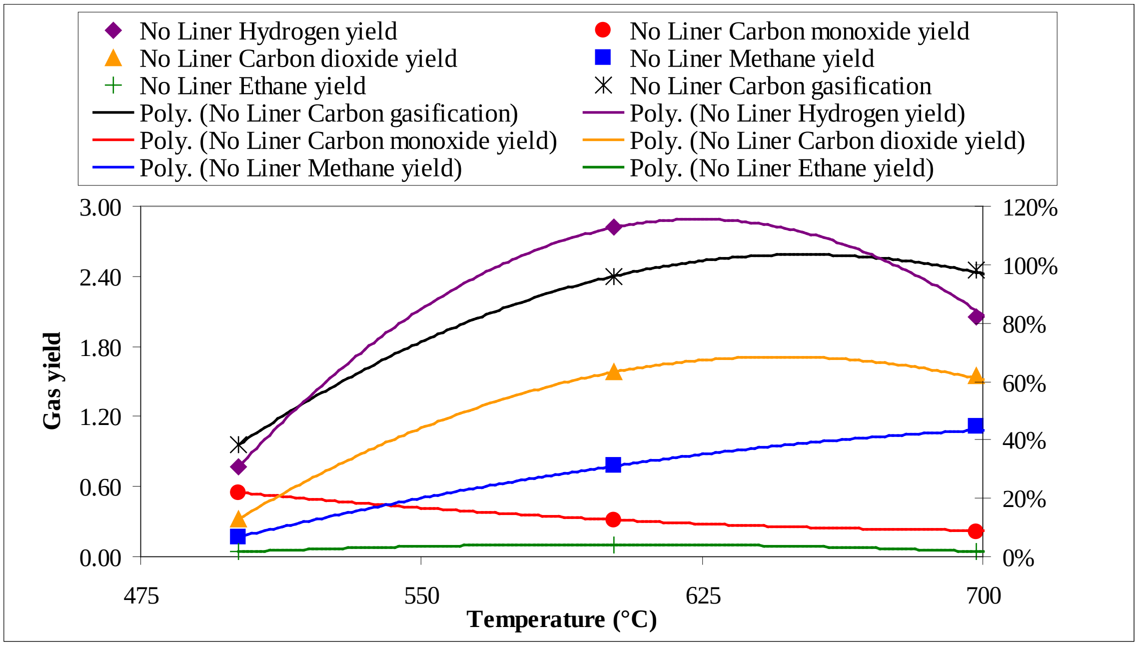

Figure 5-9. Product gas yields and carbon gasification as a function of temperature with no reactor liner installed. Experimental conditions are Water-to-glycerin ratio = 13.5, Pressure = 24.1±0.1 MPa, Space time = 100.2±0.5 sec.

Trends in Figure 5-10 mimic those in Figure 5-9 with a few subtle differences. A greater yield of hydrogen was produced and the decrease in yield when operating at temperatures greater than 600°C was less pronounced than in Figure 5-9. More carbon monoxide was produced at a temperature of 500°C, but once the temperature reached 600°C the differences between Figure 5-10 and Figure 5-9 became much smaller. The amount of methane produced increased to a lesser extent when using greater temperatures.

The trends in Figure 5-11 are much less pronounced than has been seen with more concentrated glycerin solutions. All lines are nearly parallel to each other, signifying that the temperature dependent effects are not pronounced with a high water-to-glycerin ratio of 24. Carbon gasification of 100% was achieved at 600°C. Carbon monoxide and ethane yields remained constant for the range of temperatures investigated. Hydrogen and carbon dioxide gas yields increased from 500°C to 600°C, but appear to plateau when using higher temperatures. It is also noteworthy that the hydrogen yield at 500°C is lower than the maximum case by a mere 15%. Methane yield follows a similar trend; however, it continues to increase slightly and achieves a maximum of 0.86 at 700°C. When reforming dilute glycerin solutions without a reactor liner the effect of temperature is not as prominent as when using solutions with a smaller water-to-glycerin ratio.

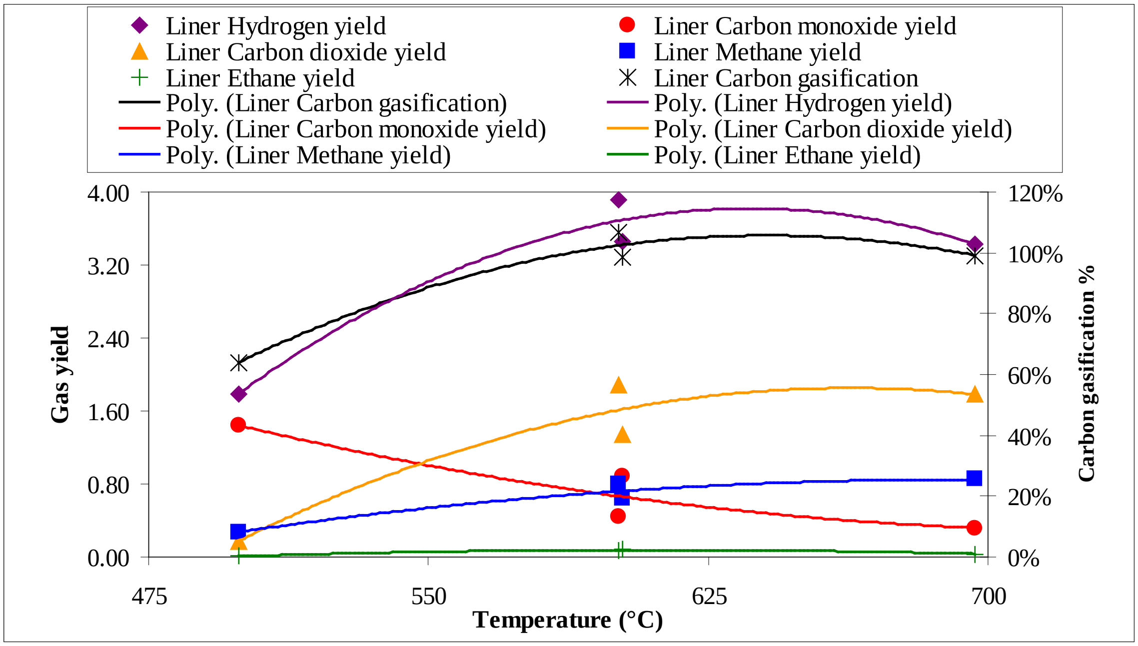

Figure 5-10. Product gas yields and carbon gasification as a function of temperature with a reactor liner installed. Experimental conditions are Water-to-glycerin ratio = 13.5, Pressure = 24.1±0.0 MPa, Space time = 102.8±1.7 sec.

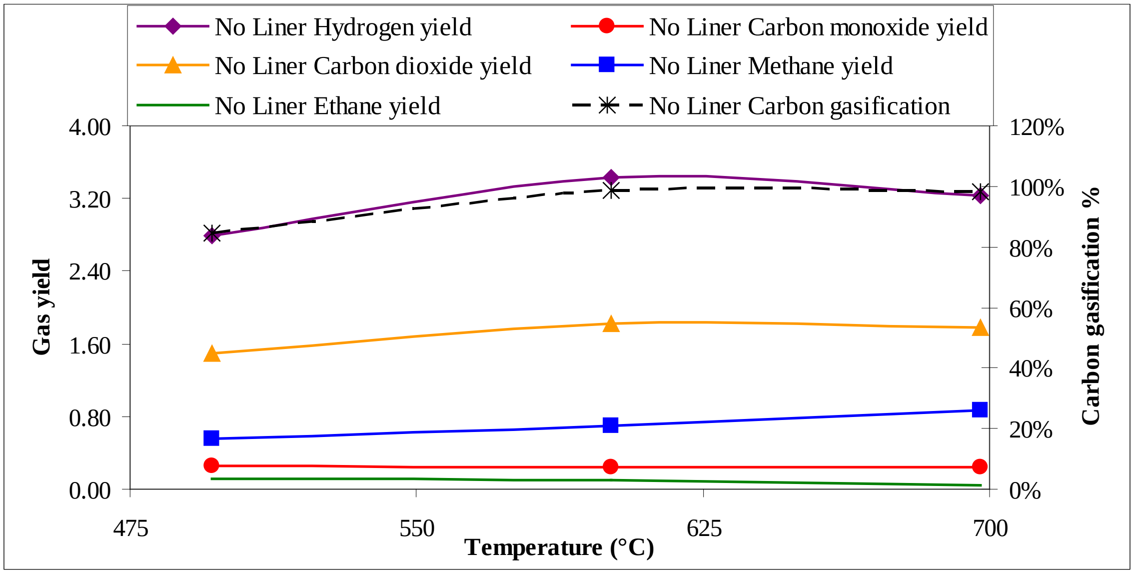

Figure 5-11. Product gas yields and carbon gasification as a function of temperature with no reactor liner installed. Experimental conditions are Water-to-glycerin ratio = 24.0, Pressure = 24.1±0.1 MPa, Space time = 99.4±2.2 sec.

Figure 5-12 shows the experimental results with a reactor liner at a water-to-glycerin ratio of 24. In comparison to Figure 5-11, all temperature-dependent trends in the product yields of Figure 5-12 are drastically different. With a liner in the reactor, the product yields at 500°C are remarkably lower than those without a liner. However, the product yields at 700°C, in particular H_2 and CO_2, are significantly higher with a liner in the reactor than those without a liner, signifying enhanced reactivity of the reformation reaction and forward water gas shift reaction in the presence of a reactor liner. The greatest hydrogen yield in all of the experiments conducted was achieved at a fixed water-to-glycerin ratio of 24 at a temperature around 700°C, in the presence of a reactor liner. A hydrogen yield of 4.41 was achieved. The greatest yield of carbon dioxide was achieved at 700°C suggesting that these conditions are highly favored for the progress of forward water gas shift reaction. Methane formation plateaus at a temperature of 600°C. A carbon gasification percentage of 100% was achievable at 600°C when using a reactor liner and dilute glycerin solutions. Ethane yields were relatively unaffected by increases in reactor temperature.

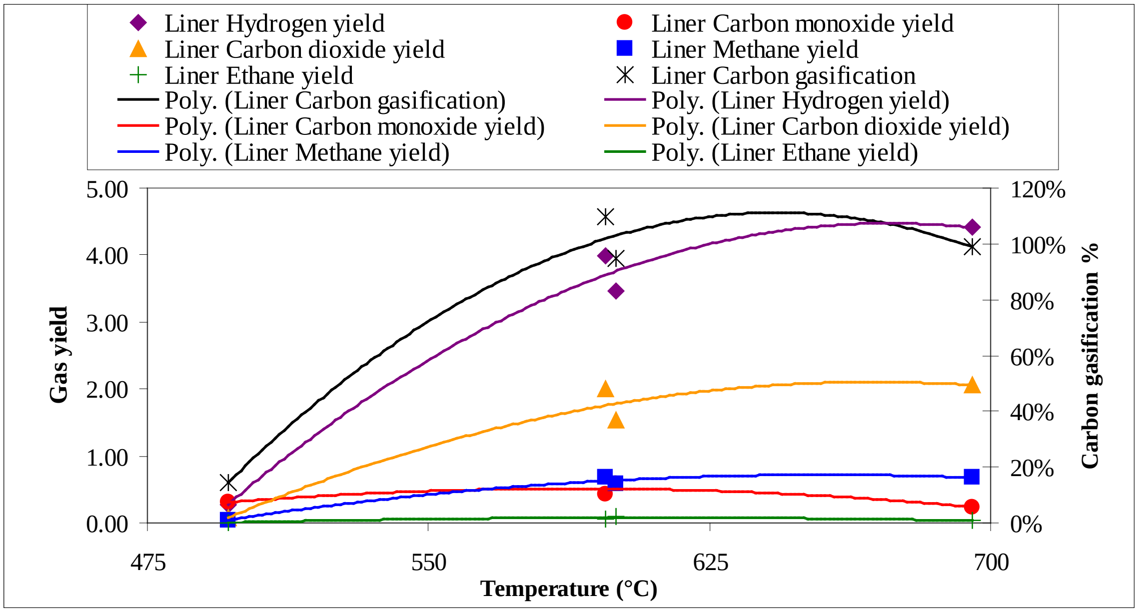

Figure 5-12. Product gas yields and carbon gasification as a function of temperature with a reactor liner installed. Experimental conditions are Water-to-glycerin ratio = 24.0, Pressure = 24.1±0.0 MPa, Space time = 102.5±3.8 sec.

5.4 EFFECTS OF A REACTOR LINER

To explore the effects of using a reactor liner on product gas composition and carbon gasification the results from the six sets of experiments conducted without a reactor liner were compared against the six sets of experiments performed with a nickel reactor liner installed. Three sets of experiments were conducted without a liner with water-to-glycerin ratio varying from 3 to 24 with fixed temperatures of 500°C, 600°C, and 700°C. Three duplicate sets of experiments were conducted with the liner in the reactor. Figure 5-1 through Figure 5-6 illustrate the results of these experiments. A different set of three experiments was conducted without a reactor liner by varying temperature from 500°C to 700°C with fixed water-to-glycerin ratios of 3, 13.5, and 24. The same experimental set was also performed with a nickel reactor liner installed. The results of these set of experiments is displayed in Figure 5-7 through 5-12.

In comparing Figure 5-1 and 5-2 it is observed that higher hydrogen and carbon monoxide yields were obtained at a water-to-glycerin ratio of 13.5; however, their was no obvious trend, hence comparisons with between liner and no liner experiments did not produce any interesting findings with respect to gas yields. The carbon gasification was much higher for the experiments conducted without a liner at a water-to-glycerin ratio of 24. Comparing Figure 5-3 and 5-4 showed greater hydrogen and carbon monoxide yields in the liner experiments when the water-to-glycerin ratio met or exceeded 13.5. The other gas yields and carbon gasification trends were similar between the two different experimental sets. Comparisons of Figure 5-5 and Figure 5-6 produced a number of interesting findings. First, 100% carbon gasification was achieved in the full range of water-to-glycerin ratios investigated in the experiments performed with a liner. In the similar experiments conducted without a liner 100% carbon gasification was only achieved at water-to-glycerin ratios meeting or exceeding 13.5. Also, at 3 water-to-glycerin ratio the carbon monoxide yield was greater for the liner experiments; however, at 24 water-to-glycerin ratio the carbon monoxide yields were 0.24 for both sets of experiments. Last, the hydrogen and carbon dioxide reached the highest values of all experiments conducted at 24 water-to-glycerin ratio for the experiments conducted with a liner. The hydrogen yield reached a value of 4.41 while the carbon dioxide yield reached a value of 2.06. This provides evidence that the water gas shift reaction is to an extent is also catalyzed by the reactor liner at these conditions. Further, the catalytic effects of a liner are most pronounced when the water-to-glycerin ratio is high, i.e., such as 24. The decrease in carbon monoxide and methane gas yields also suggest that the methanation and pyrolysis reactions are less active at these conditions as well.

In analyzing all the experiments conducted with varying water-to-glycerin ratios, the liner experiments produced greater hydrogen gas yields at temperatures above 600°C than their non-liner counterparts when the water-to-glycerin ratio met or exceeded 13.5. Carbon monoxide yields were greater in the liner experiments, but trended towards the same yield as the non-liner experiments with increasing temperature. This may be due to active transformation of CO to CO_2 via water gas shift reaction. Carbon dioxide yields were greater at 24 water-to-glycerin ratio at 500°C for the non-liner experiments; however, the yields remained similar between both experimental sets for the higher temperatures. Methane formation was greater in the non-liner experiments when water-to-glycerin ratios exceeded 13.5. This shows that the liner material has little or no catalytic effect on the pyrolytic decomposition of glycerin and its fragmented hydrocarbons. Ethane yields did not show significant variations with respect to the presence of a reactor liner or a lack thereof.

In all of the experiments performed with varying temperature, the hydrogen yield was greater in the experiments performed with a liner. The exception to this finding is found in Figure 5-12 at a temperature of 500°C; however, after the temperature reaches

550°C the liner experiments produce similar gas yields to the non-liner experiments. The carbon dioxide was also much lower at these specific conditions than the non-liner experiments at these conditions. The carbon dioxide yields became greater than the non-liner experiments once a temperature of 600°C was achieved. In comparing Figure 5-7 and Figure 5-8, the liner experiments achieved 100% gasification while the non-liner experiments did not at a fixed water-to-glycerin ratio of 3. Comparing Figure 5-9 and Figure 5-10 both showed higher hydrogen yields at 600°C which decreased at 700°C. The decrease in hydrogen yield from 600°C to 700°C was much sharper in the experiments performed without a reactor liner.

6. SUMMARY AND CONCLUSIONS

6.1 SUMMARY

The non-catalytic reformation of glycerin using supercritical water as a reaction medium was carried out in a 400-mL Haynes® Alloy 230 tubular reactor. The reactor pressure and space time were kept constant at 24.1 MPa and 100 seconds respectively. The variables under investigation were varying the water-to-glycerin molar ratio and the reactor temperature. In addition, duplicate experiments were performed both with a Nickel 201 liner installed in the reactor and without a liner. The resultant effect on product gas yields and carbon gasification percentage was then calculated. The water-to-glycerin ratios studied ranged from 3 to 24 while the temperatures were fixed at 500°C, 600°C, and 700°C. The range of temperatures investigated was from 500°C to 700°C while the water-to-glycerin ratios were fixed at 3, 13.5, and 24. Both sets of variation experiments were conducted with and without a reactor liner to investigate the direct impact of the liner on carbon gasification and product gas yields. The goal of the experiments was to produce hydrogen from a biomass-derived feedstock which could then be purified and fed to a fuel cell for electrical power generation. Also, a better understanding of reactor wall catalysis was desired to aid in the design and construction of future supercritical water reactors.

6.2 CONCLUSIONS

There are a number of conclusions that can be drawn from the data gathered in these experiments. With respect to the varying water-to-glycerin ratios it was observed that greater hydrogen and carbon dioxide yields were obtained when using more dilute glycerin solutions. This suggests that more dilute solutions promote both the water gas shift and the reformation reaction, but not the pyrolysis or methanation reactions. In addition, it was found that the carbon gasification increased with increasing water-to-glycerin ratios. This suggests that more glycerin is reacting to produce carbon and hydrogen containing gases when using larger water-to-glycerin ratios.

With respect to varying the temperature it was observed that increasing the reactor temperature increased both the hydrogen and carbon dioxide gas yields while decreasing the carbon monoxide yield. This suggests that the water gas shift reaction and to a lesser extent the reformation reaction is more favored at higher temperatures. In addition, the increase in methane gas yields with increasing temperature suggests that pyrolytic decomposition is additionally favored at higher temperatures. Carbon gasification extent was also found to increase with increasing reactor temperature. This suggests that more glycerin is reacting to produce carbon and hydrogen containing gases at higher temperatures.

Comparing duplicate experiments between those performed with and without a reactor liner provided several interesting results. It was found that the experiments performed with a liner resulted in higher hydrogen and carbon dioxide yields than the experiments performed without a liner in place. This suggests that the liner has a greater catalytic effect upon both the forward water gas shift reaction and the reformation reaction. In regards to the effects of the liner on carbon gasification the results were similar to those of the experiments conducted without a liner. There was however one important exception, being that solutions having a 3 water-to-glycerin ratio could achieve

100% carbon gasification at 700°C when using a reactor liner. In contrast, the non-liner experiment at this condition only produced a carbon gasification percentage of about 87.5%. This additionally provides evidence of the catalytic role of the liner upon the reformation reaction.

In summary, to achieve the greatest hydrogen yields during supercritical water reformation of glycerin, it is best to utilize more dilute glycerin solutions. There is a tradeoff however since the more dilute solutions will reform glycerin more efficiently, but will reform a smaller amount of glycerin in a given timeframe than would the more concentrated solutions. For most of the conditions researched, a water-to-glycerin ratio of around 17 would give significantly high hydrogen yields while maintaining an optimal concentration of glycerin in the feedstock.

It was found that reactor temperatures of 600°C or greater gave high hydrogen yields. Operating temperatures of 700°C produced the highest amounts of hydrogen, but also produced the greatest amounts of methane as well. If methane is desired in the syngas product mixture, temperature of 700°C or greater should be employed. Coupled with a separate secondary reformer or reactor, the methane could further be broken down to produce hydrogen or other alternative fuels.

Using the reactor liner had a definite positive effect on hydrogen and carbon oxide gas yields, as well as, carbon gasification. The yields of hydrogen were greater in experiments performed with a reactor liner than those without a reactor liner. The exception to this finding was reforming the most dilute solutions at the lowest temperatures. In operations where large syngas mixtures of hydrogen and carbon monoxide are desired, the liner catalyzes reactions capable of producing these product gases. The use of a liner is an inexpensive and effective method for providing clean surface reactor wall material in aged reactors.

6.3 RECOMMENDATIONS FOR FUTURE WORK

Due to the length of time necessary to properly carry out experiments and process the data only the effects of water-to-glycerin ratios, temperature, and a reactor liner were investigated. In the future, effects of pressure and space time could also be explored. In addition, various different types of high-nickel alloy reactor liners such as Inconel® 625 or Hastelloy-C276 could be experimented with. Other types of gasification could also be carried out such as partial oxidation or autothermal reformation to examine the effects of these types of gasification when using a high-nickel alloy reactor liner. Last, the liquid total organic carbon (TOC) analysis and solid carbon analysis could be carried out to achieve a global mass balance for carbon during supercritical water reformation of glycerin, as well as, to determine the molecular forms of the nongaseous carbonaceous residues.

APPENDIX A

GAS CHROMATOGRAPH CONDITIONS AND CALIBRATIONS

Product gas analysis was carried out using an HP 5890 Series A gas chromatograph (GC) coupled with a thermal conductivity detector (TCD). The column for the GC was purchased from Restek and is a two-meter long, 1/16" OD ShinCarbon 100/120 packed column. Samples were collected with a gas sample syringe via a gas sample port plumbed into the reformation system. The temperature of the injection port on the GC was kept at 120°C while the TCD temperature was kept at 220°C. Depending on the gases desired for analysis, three separate programs were used called Restek00, Restek01, and Restek02.

The oven temperature for all three programs began at 30°C and was kept there for three minutes. Following this period, the oven temperature was then raised by a rate of 8.0°C/min. The shortest program was Restek00 which raised 48°C over a period of six minutes after the initial oven heating. The final oven temperature of this program was 78°C after a total of nine minutes. The Restek01 program raised 136°C after 17 minutes producing a final oven temperature of 166°C after a total of 20 minutes. The longest program was Restek02 which raised 220°C over 27.5 minutes. Once an oven temperature of 250°C was achieved for Restek02, the oven temperature was kept there for three minutes before cooling back down to 30°C. Restek00 and Restek01 immediately began to cool back down to 30°C once their respective final oven temperatures had been reached. Once the oven temperature had cooled back down to 30°C, the oven required three additional minutes for all internal components to equilibrate.

The need for three separate GC programs was dependent on the gases desired to be analyzed. Since different gases spent different amounts of time being retained on the column we were able to characterize each gas based on retention times. A table of retention times for all gases analyzed is provided in Table A-1. The shortest program, Restek00, was capable of detecting the following gases: hydrogen, oxygen/nitrogen, methane, carbon monoxide, and carbon dioxide. This particular GC column was designed for separation of hydrocarbon gases and was thus unable to distinguish between oxygen and nitrogen resulting in overlapping peaks. Restek01 was capable of detecting all the aforementioned gases, as well as, acetylene, ethylene, and ethane. Restek02 was also able to detect each of these gases, as well as, propene and propane.

Table A-1. Gas chromatograph retention times for product gas analysis.

Species	Retention time (min)	Standard Deviation
Hydrogen	0.65	0.07
Oxygen/Nitrogen	1.3	0.2
Carbon monoxide	1.8	0.1
Methane	2.7	0.2
Carbon dioxide	6.4	0.3
Acetylene	11.4	0.3
Ethylene	13.0	0.4
Ethane	14.7	0.4
Propene	25.3	0.5
Propane	26.5	0.5

For each product gas analyzed, calibrations using standard reference gases were carried out on the GC. Various samples of each standard ranging from 0.01 mL to 1 mL were analyzed. Variation in the sample size resulted in different molar amounts of gas being analyzed. Using this data, along with the peak data obtained from the HP Chemstation report allowed for the formulation of calibration plots for each gas. The plots for each analyzed gas are shown in Figure A-1 through Figure A-10.

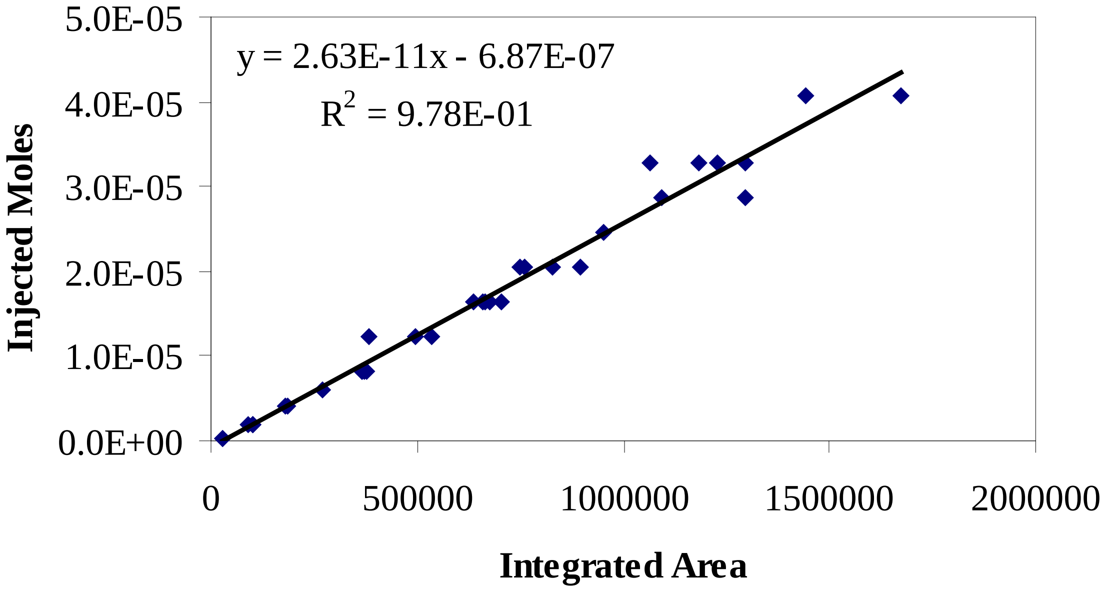

Figure A-1. Hydrogen gas calibration plot.

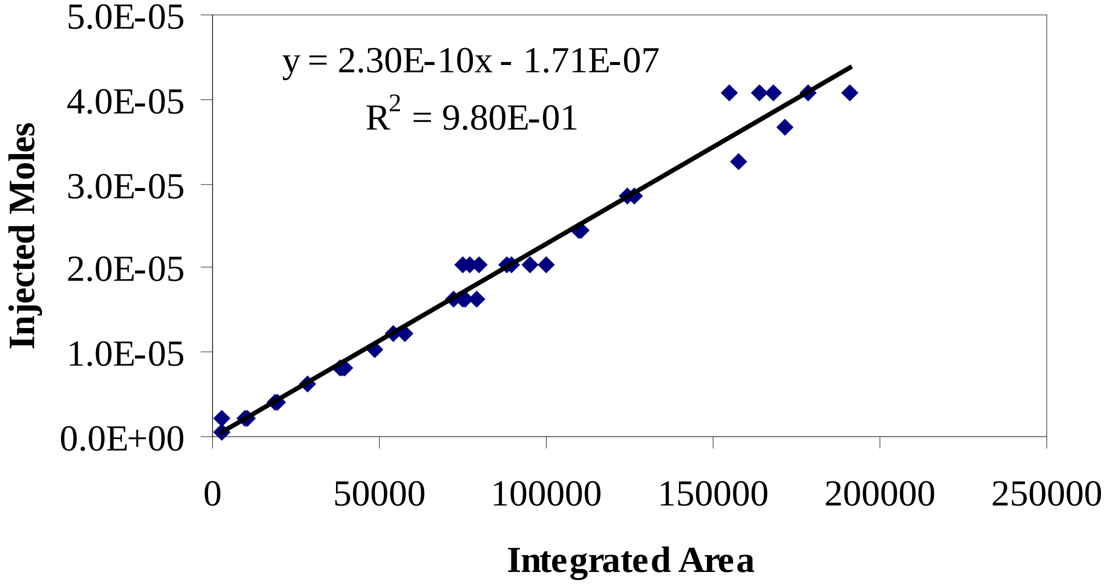

Figure A-2. Nitrogen/Oxygen gas calibration plot.

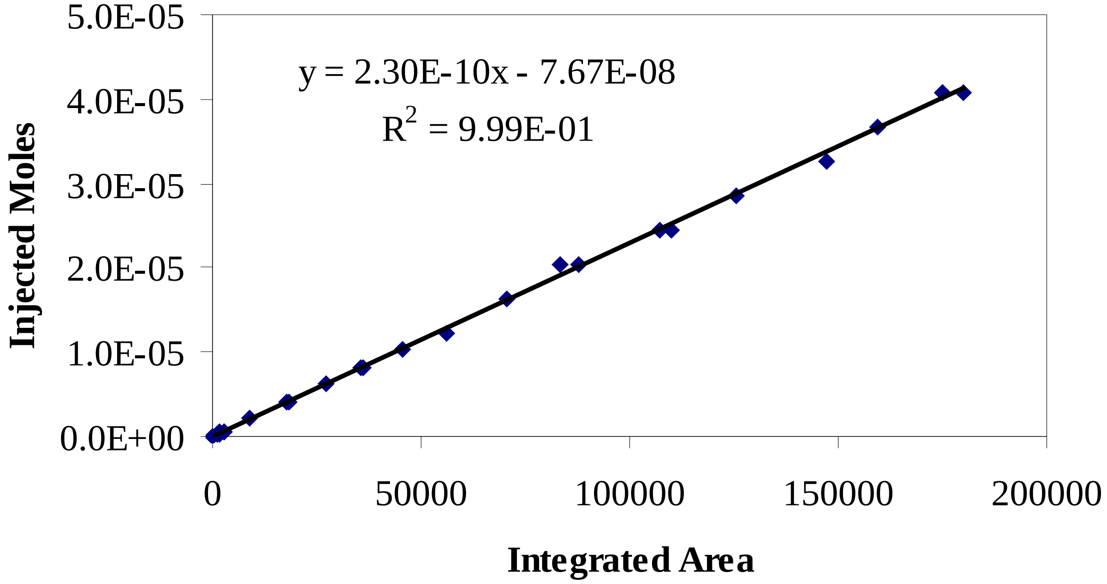

Figure A-3. Carbon monoxide gas calibration plot.

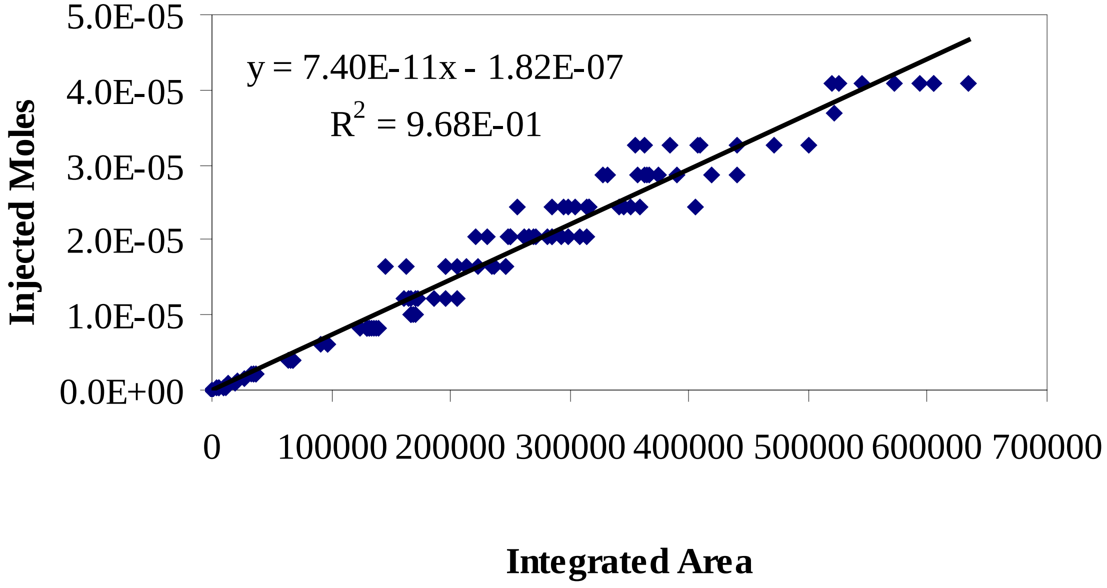

Figure A-4. Methane gas calibration plot.

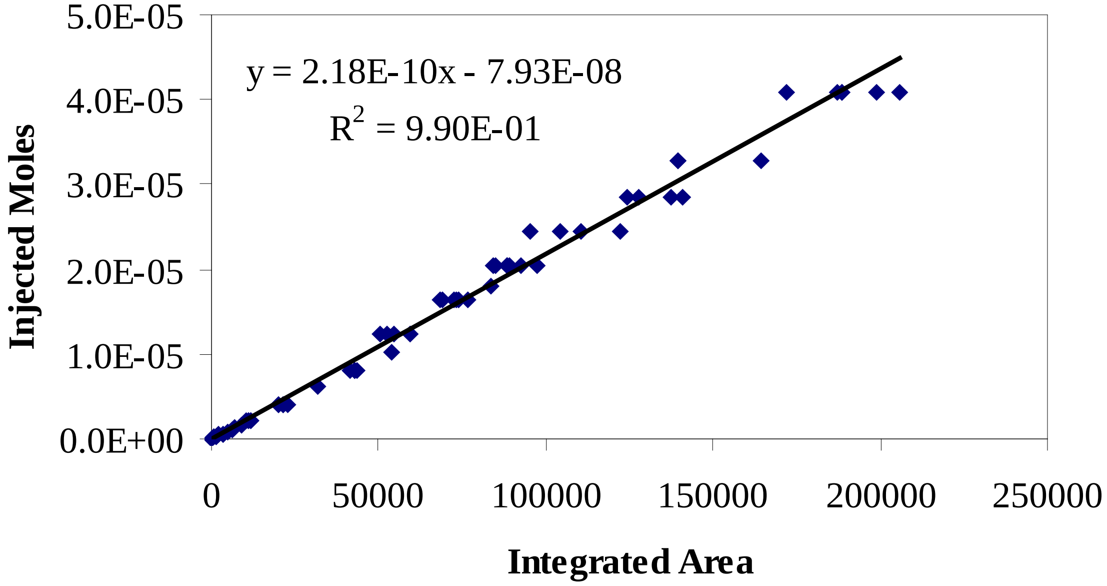

Figure A-5. Carbon dioxide gas calibration plot.

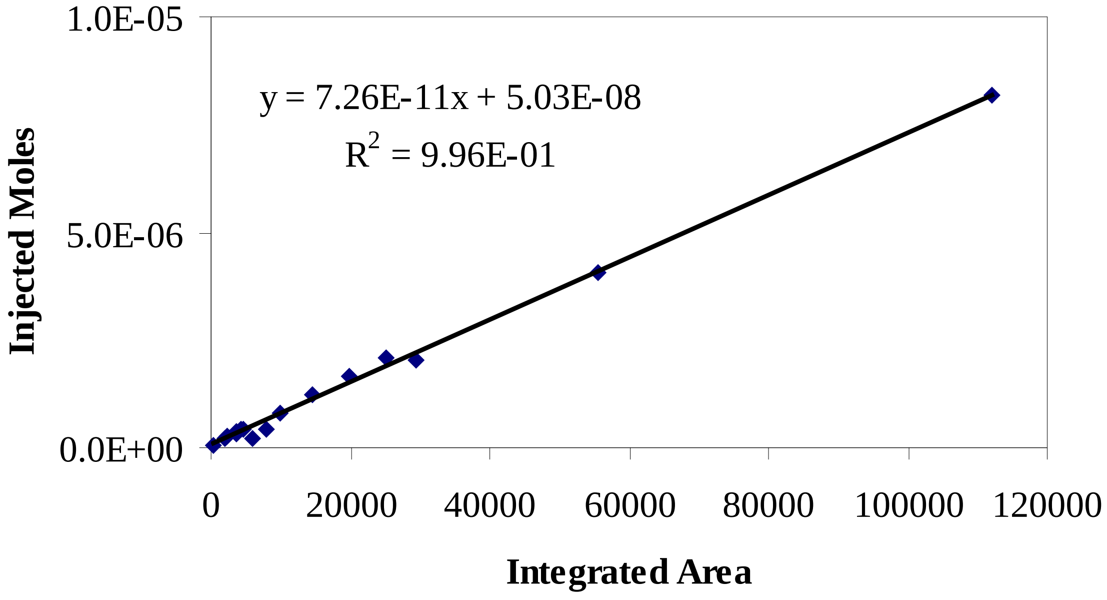

Figure A-6. Acetylene gas calibration plot.

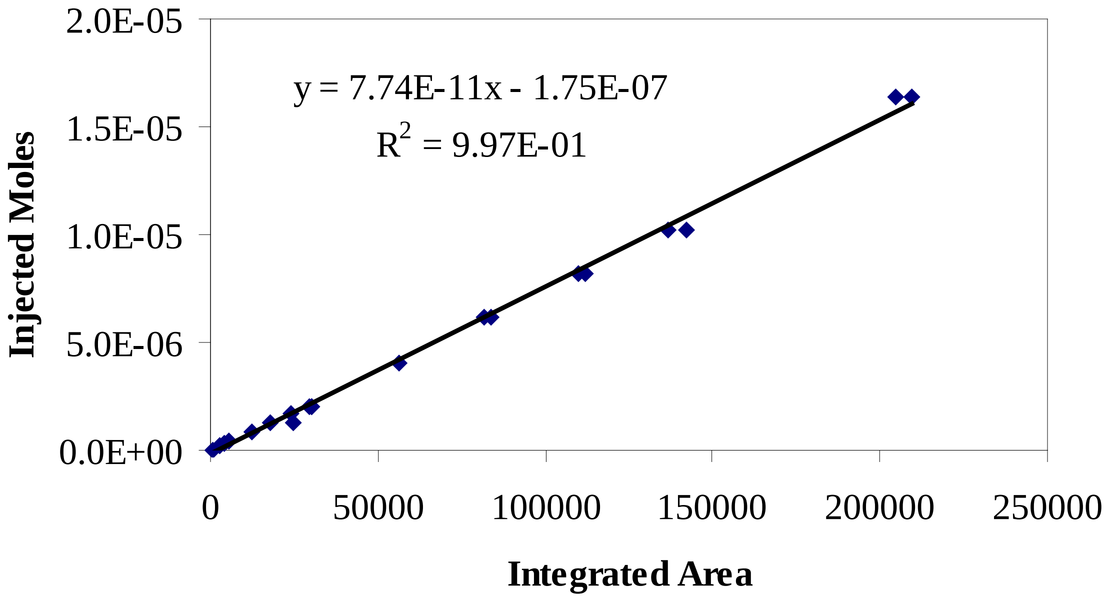

Figure A-7. Ethylene gas calibration plot.

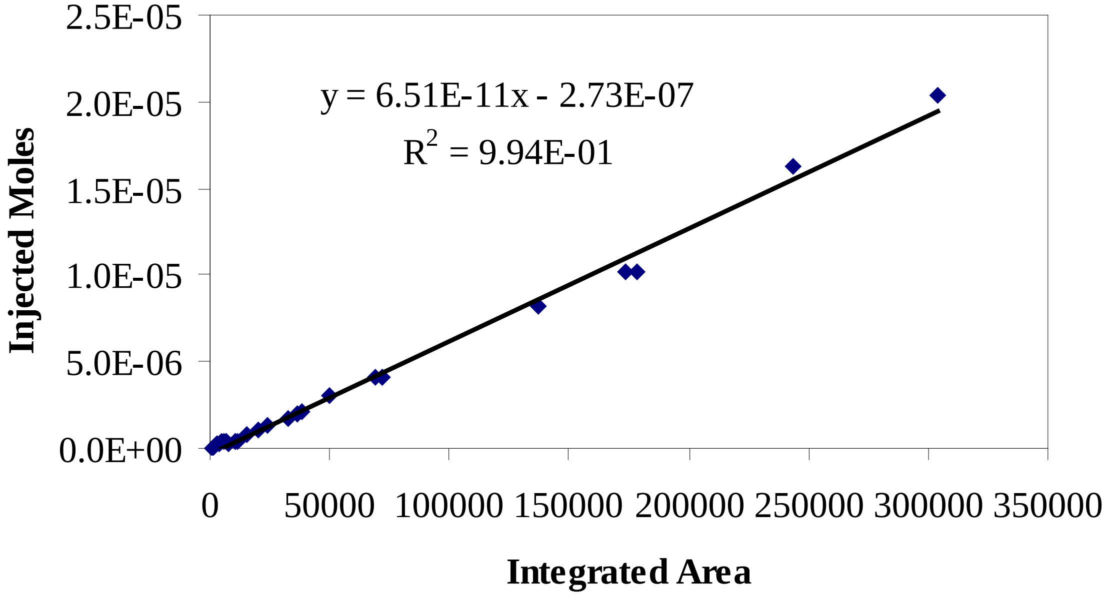

Figure A-8. Ethane gas calibration plot

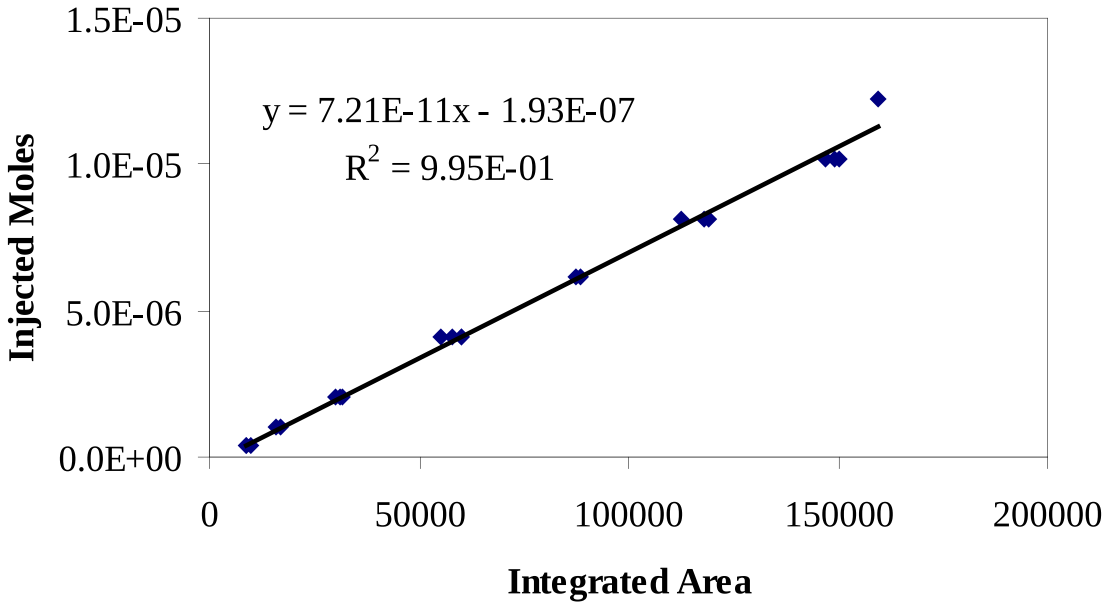

Figure A-9. Propene gas calibration plot

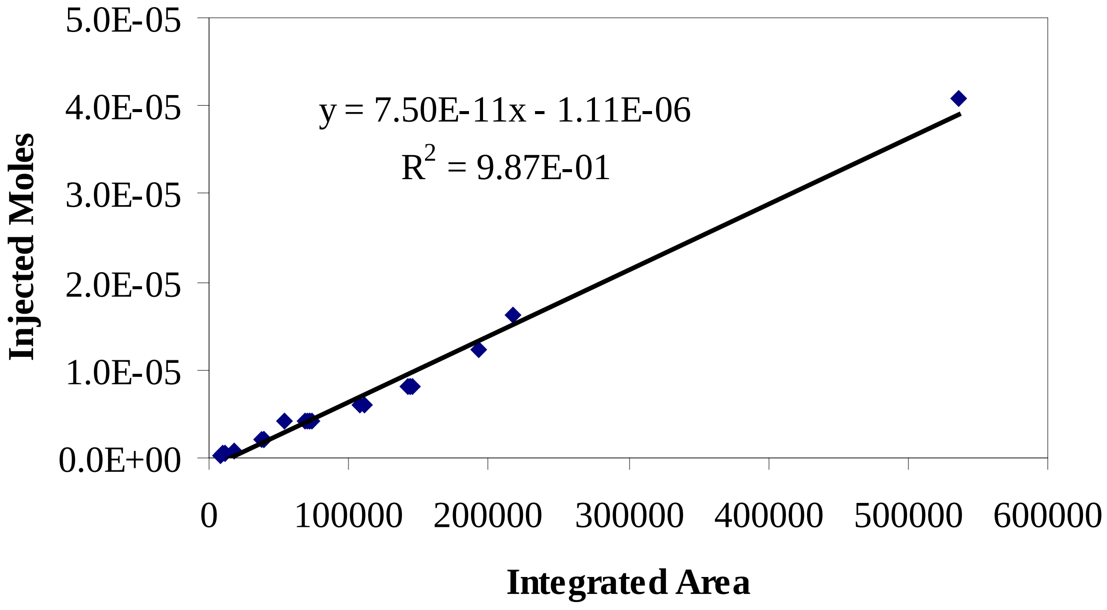

Figure A-10. Propane gas calibration plot

APPENDIX B

NUMERICAL RESULTS FOR PRODUCT GAS YIELDS AND CARBON GASIFICATION

Below are tables that display the numerical values for the product gas yields and carbon gasification obtained from all 24 experiments. The data from these tables was used to generate the graphs in Figure 5-1 through Figure 5-12. Table B-1 and Table B-2 show the results for the experiments performed without a reactor liner. Table B-3 and Table B-4 show the results for the experiments conducted with a reactor liner. In Table B-4, the propene gas yield for Experiment 12 was distorted and, as a result, there is no available data entry for that reading.

Table B-1. Numerical hydrogen, nitrogen, carbon monoxide, methane, and carbon dioxide gas yield results for experiments conducted without a reactor liner.

Experimental ID	W/G Ratio	Temperature	Gas Yield (mol gas/mol glycerin fed)				
		(°C)	H_2	N_2/O_2	CO	CH_4	CO_2
11	3	503	0.08	0.00	0.38	0.09	0.08
8	13.5	501	0.77	0.00	0.55	0.17	0.32
7	24	496	2.79	0.00	0.26	0.55	1.50
6	3	595	0.37	0.00	1.18	0.46	0.15
10	3	602	0.34	0.00	1.10	0.56	0.18
3	13.5	601	2.82	0.00	0.32	0.78	1.58
2	24	601	3.43	0.00	0.24	0.69	1.82
5	3	698	1.17	0.00	0.77	0.82	0.77
9	13.5	698	2.06	0.00	0.21	1.11	1.54
4	13.5	700	2.11	0.00	0.24	1.05	1.50
1	24	698	3.23	0.00	0.24	0.86	1.77

Table B-2. Numerical ethylene, ethane, propene, and propane gas yield and carbon gasification results for experiments conducted without a reactor liner.

Experimental ID	W/G Ratio	Temperature	Gas Yield (mol gas/ mol glycerin fed)				Carbon Gasification
		(°C)	C_2H_4	C_2H_6	C_3H_6	C_3H_8	**%**
11	3	503	0.01	0.01	0.00	0.00	19.25%
8	13.5	501	0.01	0.04	0.00	0.00	38.43%
7	24	496	0.00	0.11	0.00	0.00	84.41%
6	3	595	0.01	0.13	0.00	0.00	68.72%
10	3	602	0.00	0.11	0.00	0.02	68.83%
3	13.5	601	0.00	0.11	0.00	0.00	96.05%
2	24	601	0.00	0.10	0.00	0.00	98.53%
5	3	698	0.00	0.13	0.00	0.00	87.36%
9	13.5	698	0.00	0.04	0.00	0.00	98.32%
4	13.5	700	0.00	0.04	0.00	0.00	95.88%
1	24	698	0.00	0.04	0.00	0.00	98.39%

Table B-3. Numerical hydrogen, nitrogen, carbon monoxide, methane, and carbon dioxide gas yield results for experiments conducted with a reactor liner.

Experimental ID	W/G Ratio	Temperature	Gas Yield (mol gas/mol glycerin fed)				
		(°C)	H_2	N_2/O_2	CO	CH_4	CO_2
7	3	490	0.07	0.00	0.53	0.14	0.10
12	3	490	0.08	0.00	0.51	0.12	0.11
10	13.5	499	1.79	0.00	1.44	0.28	0.18
4	24	496	0.27	0.00	0.31	0.05	0.07
6	3	603	0.64	0.00	1.46	0.70	0.17
11	3	600	0.63	0.00	1.37	0.68	0.21
8	13.5	601	3.92	0.00	0.44	0.80	1.88
9	13.5	602	3.46	0.00	0.89	0.64	1.35
3	24	600	3.47	0.00	0.58	0.59	1.53
13	24	597	3.99	0.00	0.44	0.68	2.00
5	3	691	1.74	0.00	1.40	0.94	0.60
1	13.5	697	3.43	0.00	0.32	0.85	1.78
2	24	695	4.41	0.00	0.24	0.68	2.06

Table B-4. Numerical ethylene, ethane, propene, and propane gas yield and carbon gasification results for experiments conducted with a reactor liner.

Experimental ID	W/G Ratio	Temperature	Gas Yield (mol gas/ mol glycerin fed)				Carbon Gasification
		(°C)	C_2H_4	C_2H_6	C_3H_6	C_3H_8	%
7	3	490	0.01	0.02	0.01	0.00	27.7%
12	3	490	0.01	0.02	N/A	0.00	25.4%
10	13.5	499	0.00	0.01	0.01	0.01	64.03%
4	24	496	0.01	0.00	0.00	0.00	14.25%
6	3	603	0.00	0.16	0.03	0.00	88.6%
11	3	600	0.00	0.16	0.00	0.02	87.1%
8	13.5	601	0.00	0.07	0.00	0.00	106.6%
9	13.5	602	0.00	0.08	0.00	0.00	98.5%
3	24	600	0.00	0.09	0.00	0.00	94.7%
13	24	597	0.00	0.06	0.00	0.00	109.9%
5	3	691	0.00	0.15	0.00	0.00	105.24%
1	13.5	697	0.00	0.04	0.00	0.00	99.20%
2	24	695	0.00	0.03	0.00	0.00	98.98%

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