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HIGH PRESSURE AUTOTHERMAL REFORMING IN LOW OXYGEN
ENVIRONMENTS

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Abstract

Recent interest in fuel cells and fuel reforming has led to the conceptual design of an ocean floor, fuel cell based, power generating station fueled by methane from natural gas seeps or from the controlled decomposition of methane hydrates. Since the dissolved oxygen concentration in deep ocean water is too low to provide adequate supplies to a fuel processor and fuel cell, oxygen must be stored onboard the generating station. A lab scale experimental reformer for high pressure, 6 – 50 bar, catalytic autothermal reforming has been constructed and tested. It was of particular interest in this application to maximize H_2 production per mole of O_2 supplied. Equilibrium and kinetic models have also been used to further understand the auto thermal reforming process. This study has located optimum conditions for underwater fuel reforming and validated the use of H_2O_2 as both a stored oxidizer and steam source. Employing data from the mathematical models and experimental results, reformer performance with respect to the steam to carbon and oxygen to carbon ratios are presented. The optimal experimental conditions for maximizing the amount of H_2 produced per mole of O_2 input occurred at a S/C ratio of 3.35 and an O_2/C ratio of 0.44 at 6 bar, a S/C ratio of 3.00 and an O_2/C of 0.48 at 28 bar, and a S/C ratio of 3.00 and a O_2/C of 0.48 at 50 bar. Under these conditions 1 mole of O_2 produced 4.16 moles of H_2 at 6 bar, 3.43 moles of H_2 at 28 bar, and 2.84 moles of H_2 at 50 bar. When using H_2O_2 as oxidizer rather than bottled O_2 , $H_{2(out)}/O_{2(in)}$ yield increases of up to a 14% were observed.

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1 Introduction

The development of fuel cells and fuel cell powered vehicles has been a topic of great interest in recent years [1-3]. Fuel cells offer potential for higher efficiency and lower harmful emissions when compared to traditional combustion based power systems [4-7]. The proton exchange membrane fuel cell (PEMFC) is currently considered the most viable fuel cell technology for the near future [8-10]. As with almost all types of fuel cells, oxygen and hydrogen need to be constantly supplied to a PEMFC in order to generate electrical power. Air, which is made up of ~21% oxygen, is most often used as the oxygen source [11]. Therefore, as long as the fuel cell operates in aerobic environments, a simple air pump or blower can provide a continuous air supply. Low oxygen environments however, encountered by sub-sea or space applications, pose the additional challenge of oxidant supply [12]. Additionally, hydrogen, while abundant, is not freely present in nature as molecular hydrogen and must be produced from another source such as water or hydrocarbons. While it is likely that in the future, hydrogen will be produced by electrolysis using photovoltaic or wind power, currently the most economic way to produce hydrogen is by catalytic thermochemical reforming of hydrocarbons. In fact, reforming technology has been a heavily researched topic and has been implemented in industry for some time.

In light of the current research and development of fuel cells and fuel processing techniques, there has been recent interest by the Defense Advanced Research Projects Agency (DARPA) to construct small scale, underwater, power generating stations. In concept, these remote units, using onboard fuel cells to generate power, will be deployed

on the ocean floor where natural gas seeps or methane hydrates are present. In concept, methane released from the seeps or disassociated from the hydrates will be collected and purified to remove H_2S , a known catalyst poison. After purification, the gas stream can be reformed to produce a hydrogen rich gas for the fuel cell. Since the unit will be deployed on the ocean floor and operate at ambient pressure, design of components must accommodate the effects of elevated pressure on the physical system and reformer and fuel cell chemistry.

Oxygen supply is also a challenge. Oxygen concentrations in natural gas seeps and dissolved oxygen concentration in sea water are very low. The highest recorded molar O_2 concentration in natural gas seeps in the literature reviewed was 0.3 % [13] and the average molar O_2 concentration in sea water at depths where seeps are located is less than 0.0005 % [14]. Given the low oxygen environment, oxygen storage will be required on board the remote unit to feed both the fuel reformer and the fuel cell. Operational depths 60 to 500 m below sea level have been selected for testing. For this fuel rich, oxygen limited, reforming application it is of particular interest to maximize moles of H_2 produced per mole of O_2 supplied.

This research will provide interested parties, such as DARPA, a map of autothermal reforming (ATR) performance in pressurized oxygen-deficient environments such as the ocean floor. Possible applications include powering underwater sensory equipment and recharging unmanned submersibles.

Currently, unmanned, untethered, vehicles (UUV's) are largely powered by batteries and therefore have a limited range due to their limited energy density. The range of battery powered UUV's could be extended indefinitely if recharging could be completed underwater. Operations would benefit greatly by not having to surface, in order to recharge, thereby revealing vehicle location.

Additionally, proving it is possible to carry out ATR reforming in low oxygen environments is novel. If the technology is proven and a suitable oxygen storage method is found, other applications such as space applications, may present themselves.

2 Thesis statement

The following outlines the desired outcomes of the research.

1. Design and fabricate an experimental system that can be used to investigate autothermal reforming at elevated pressures representative of subsea conditions.
2. Optimize the performance of conventional ATR at three representative pressures (6, 30, and 50 bar) using bottled O_2 as oxidizer. (Optimization criteria and experimental design are discussed in greater detail in section 4.1.3.2.)
3. Repeat a fraction of the conditions identified by Objective 2 using H_2O_2 as an oxidizer and compare results.
4. Develop and validate a numeric model that correctly predicts trends in conventional ATR.

3 Literature Review

The following section provides a summary of literature relevant to reforming at elevated pressure in O₂ deficient environments. Fuel reforming techniques will be presented first, followed by potential hydrocarbon feedstocks for the reforming process, background on the selected oxidizer, and reformer modeling efforts which have been completed.

3.1 Fuel reforming

A fuel processor produces hydrogen from a hydrocarbon feedstock by one of three techniques: steam reforming (SR), partial oxidation reforming (POX) or autothermal reforming (ATR) [15, 16]. To provide additional project background, each of the thermochemical reforming processes is briefly discussed as it relates to the underwater application. Methane is considered as the hydrocarbon feedstock as it will be the fuel employed on the ocean floor.

3.1.1 Steam reforming

In the steam reforming process, steam reacts with fuel in the presence of a catalyst according to the global reaction,

Industrial steam reforming is normally carried out at temperatures from 700 to 900 °C [17]. It is clear from Equation (1) that SR is highly endothermic, requiring 206 kJ mol⁻¹ to drive the reaction. Due to the high thermal demands, SR can not quickly respond to

transient loads [18]. While the lack of quick response doesn't pose a problem for stationary power generating stations, the high thermal demand must still be met. Generally heat transfer is more efficient in large scale, high flow systems than in small scale systems with low flows. Therefore for large scale systems SR is attractive, but for small scale systems SR is less attractive.

3.1.2 Partial oxidation

Partial oxidation reforming provides heat for the reforming process by combusting a substoichiometric air-fuel mixture in the reformer [19]. As with SR, POX can be catalytic or non-catalytic, but the presence of a catalyst offers lower operating temperatures and a shorter residence time [20]. A shorter residence time leads to a more compact reformer design which is generally desirable. POX can be described by the following two competing reactions:

Both are exothermic and the latter can lead to extreme reactor temperatures. POX, when compared to SR or ATR, produces higher CO concentrations in the reformat [21], has a higher potential of CH₄ and CO cracking resulting in carbon deposition [9], and has a lower conversion efficiency [20].

3.1.3 Autothermal reforming

When fuel, steam, and oxygen are all fed into the reformer, the reaction can be simply described by a combination of SR and POX reactions. In fact ATR combines thermal

effects from both SR and POX reforming so that the heat required to support the endothermic steam reforming reaction (Equation (1)) is provided by oxidation reactions (Equations (2) and (3)), resulting in a lower overall temperature [22]. By varying the reactant ratios of O_2 and H_2O with respect to the fuel, the set of reactions can be net endothermic, net exothermic, or reach a thermally neutral condition. Also since ATR generates heat *in situ*, it does not require an external burner or heat exchangers like SR. In fact, when using methane as the feedstock, Takeguchi et al. stated that while the equilibrium hydrogen production of ATR is slightly less than SR, the process consumes slightly more than half the heat [23]. ATR has been selected as the most promising reforming technique for the application at hand due to its simple design and efficiency for small scale systems.

3.2 Hydrocarbon feedstock

The hydrocarbon feedstock for this specialized reforming will come from two sources: marine natural gas seeps and methane hydrates. Both sources are briefly discussed in this section.

3.2.1 Natural gas seeps

It has been estimated that 6 to 85 Tg of methane pass through the seabed of the continental shelves annually [24]. One of the most intense known seeps in the world, the Shane Seep, is located along the continental shelf just off shore from Santa Barbara, CA [25]. Other prominent seeps are found in the Caspian Sea [26] and the Gulf of Mexico [27]. Analysis of gas samples from the Shane Seep taken over a period of several months

showed a composition averaging 83.4% CH₄, 11.7% CO₂, 1.8% N₂, and 0.28% O₂, with the balance being classified as non methane hydrocarbons [13]. These seeps provide a largely untapped supply of relatively pure methane that could be potentially harvested. Shane Seep, the most likely early test site for a seafloor power generation prototype, is 21 m below sea level.

3.2.2 Methane hydrates

Methane hydrates are ice-like crystalline structures with methane molecules held within the lattice of water molecules [28]. In 1999, Kvenvolden estimated the total global resource to be greater than 10¹⁵ m³ but less than 10¹⁷ m³ [29]. When appropriate expansion factors are applied, 1 m³ of pure methane hydrate expands to approximately 164 m³ of methane and 0.8 m³ of water at standard pressure and temperature [30]. Hydrates thus provide an extremely dense source of methane which, after dissociation, could be collected in the gas phase at ambient pressures and used as a hydrocarbon feedstock for reforming.

Gas hydrates in the marine environment occur in the gas hydrate stability zone (GHSZ). The stability zone is dependent on temperature and pressure and, with favorable conditions, can begin at depths as shallow as 300m below sea level [31].

3.3 Oxidizer

While methane can be found in abundance in nature, a major limitation for operating a reformer on the seafloor is having oxygen available at sufficiently high concentrations.

Oxygen is employed in ATR to oxidize a portion of the fuel to generate heat required to sustain the endothermic reforming reactions. One source of oxygen is from the decomposition of hydrogen peroxide described by the following equation:

The decomposition of hydrogen peroxide can thus provide O₂, H₂O, and heat, all of which could be utilized to operate a reformer and fuel cell on the seafloor. Moreover, since H₂O₂ is a liquid, the oxygen available per unit volume is high. This is desirable from the perspective of minimizing the size of tanks used to transport oxidizer from the surface and to store it on the seafloor. Pure H₂O₂ has a molarity of about 42 mol/liter at 1 bar and 25°C (this will increase slightly at the higher ambient pressures and lower temperatures at the seafloor). Since the decomposition of 1 mole of hydrogen peroxide yields 0.5 mole of O₂, the oxidizer density is about 21 mol O₂/liter H₂O₂. In comparison, pure O₂ gas would have to be stored at 485 bar and 5°C to attain a density of 21 mol/liter. Additionally, H₂O₂ has a specific gravity of 1.4, which is double that of oxygen gas stored in the gas phase at 485 bar. This increase in density is beneficial as it provides negative buoyancy. Therefore, due to the favorable traits of H₂O₂ it was selected as the initial oxidizer for the system.

3.3.1 Hydrogen peroxide

Hydrogen peroxide is common in the literature; often in papers dealing with propellants and very rarely in papers dealing with reforming. A few patents, however, exist on the topic of using H₂O₂ for reforming purposes. Xiao's patent was filed in 2005 [32] and Barber's was filed in 2006 [18].

Xiao's patent deals with the possibility of feeding methanol and H_2O_2 into an ATR for methanol reforming. Reactants would first flow over a catalyst to decompose the H_2O_2 and produce steam, O_2 , and heat. The decomposition products and methanol would then flow over a reforming catalyst and reforming reactions would be sustained with heat supplied from the exothermic decomposition of H_2O_2 . It should be noted that methanol reforming can take place at a relatively low temperature; around 150°C [33].

Barber's patent is similar in nature to Xiao's but deals with ATR of ethanol and possibly other hydrocarbons. Again, the basic concept is to decompose H_2O_2 to release steam, O_2 , and heat and support ATR reactions.

In 2003, Prater and Rusek described a methanol fuel cell (MFC) which would be supplied with H_2O_2 on the cathode side [34]. Similarly Raman et al. proposed the use of H_2O_2 as an oxidant for use by a direct borohydride fuel cell (DBFC) one year later [35]. This style of fuel cell would be supplied with hydrogen by feeding borohydride on the anode side while oxygen would be supplied to the cathode via H_2O_2 . Again in 2005, Choudhury et al. advanced research into the use of H_2O_2 as the oxidizer for a DBFC.

To date, outside of the patents, no papers have appeared which deal with the use of H_2O_2 as an oxidant for use in fuel reforming.

3.4 Modeling

This section briefly describes modeling work which has been conducted covering conventional thermochemical catalytic reforming. It should be noted at the outset that SR and POX have been implemented in industry for some time [36]. As such, much literature can be found describing the thermodynamics and kinetics of relevant reactions. In comparison, relatively few papers exist on the kinetics of ATR. The following is a brief overview.

3.4.1 Steam reforming

In 1989, Xu and Froment developed kinetic parameters for methane steam reforming (MSR) and water gas shift (WGS) reactions [37]. Their study was conducted in the temperature range of 573 – 823 K with gauge pressure varying from 0.3 – 10 bar. A conventional tube reactor was used and Ni based catalyst employed. Their work formed a basis for much modeling work in the MSR field and has also carried over into POX and ATR work. Similar kinetics were developed by Hou and Ronald in 2000 [38]. Both SR models consist of three global reactions: two endothermic steam reforming reactions:

and one exothermic WGS reaction:

3.4.2 POX

Modeling the kinetics of POX was outlined by De Groote and Froment in 1996 [21]. Their model was also based on the use of a Ni catalyst and consisted of nine global reactions as shown below.

Exothermic combustion of methane:

endothermic steam reforming reactions:

exothermic WGS:

CO₂ reforming:

carbon deposition (Boudouard equation):

methane cracking:

and carbon oxidation reactions by steam and oxygen, respectively:

De Groote and Froment also provided reaction rates for all reactions although they largely were adopted from previous works. A one dimensional, heterogeneous model was proposed based on an example from Froment and Bishop [39].

Other models, such as the POX membrane reactor proposed by Basile et al. in 2001 [40], use only equations (9)-(12) laid out by De Groote et al.

3.4.3 ATR

Chan and Wang conducted a theoretical study on the chemical equilibrium of ATR in 2000 [22]. Their study gave an overview of ATR performance. As such, it can be used as a reference for determining operating conditions to obtain maximum H₂ yield with a minimum production of CO and no carbon deposition. Their study, however, was based on equilibrium values which may not be attained experimentally due to kinetic limitations. In 2003, Takeguchi et al. reported experimental results for ATR, POX, and SMR, but no modeling work was included [23].

To further the research in this field, Hoang and Chan described ATR kinetics in 2004 [41]. This would be the first of their series of papers on kinetic modeling of MSR, POX and ATR [17, 42, 43]. Their reaction scheme for ATR is a combination of SR, based on Xu and Froment [37], and POX reforming reactions. Because including all of the reactions listed for both MSR and POX would lead to a very complex model, only the reactions with significant rates were selected [17]. This led to a reaction scheme based on the following four reactions:

Exothermic combustion of methane:

Endothermic steam reforming reactions:

Exothermic WGS:

All papers by Hoang et al. used a two dimensional heterogeneous model and dealt with atmospheric pressure reforming.

In 2006, Lee et al. presented a paper based on Hoang and Chan's reaction scheme [44]. They used a 1-D pseudo-homogenous model and studied the effects of molar steam to carbon ratio (S/C) and molar oxygen to carbon ratio (O₂/C), but again, only atmospheric pressure conditions were tested.

De Groote and Froment reported simulating a 25 bar ATR condition while validating their POX model, but this was only a single run and no study involving pressure effects was presented [21].

In 1998, Olsvik and Hansen presented a paper on high pressure autothermal reforming. Their work, however, dealt primarily with fluid flow, combustion kinetics, and soot

formation. No data on product gas composition for the various reformer conditions of interest were presented [45].

Therefore, while there are many papers dealing with thermodynamics and kinetics of various reforming techniques, very few papers have been found which deal with high pressure methane ATR.

4 Materials and methods

The materials and methods used to accomplish the objectives set forth in the thesis statement are described below. This section is divided into experimental and modeling sections.

4.1 Experimental

The experimental materials and methods section includes a description of the test facility, operating procedures, and experimental design.

4.1.1 Test facility

In order to meet objectives 1 and 2 from the thesis statement, a lab scale test facility was assembled. The test facility evolved through experimentation, making it more robust and ensuring that meaningful data were acquired.

Three versions of the test facility are outlined in this section. The changes made between version one (v.1) and version two (v.2) resolved an issue encountered with the accuracy and stability of liquid reactant delivery into the reformer. Additionally, changes to the reformer insulation and heater were made. The changes made between v.2 and version three (v.3) of the test facility resolved an issue with maintaining consistent reactant temperature at the reformer inlet over a wide range of flow conditions. Additionally v.3 ensured methane was only combusted inside the reformer and not in the heated reactant delivery lines. Descriptions and schematics for each version follow.

4.1.1.1 Version 1

A schematic of the high pressure reforming system v.1 is shown below in Figure 1.

Figure 1. Schematic diagram of high pressure methane reforming test facility v.1.

The v.1 reformer was a lab-scale, fixed-bed, catalytic reactor 61.0 cm in length with a 1.1 cm inner diameter. The reformer tube was constructed from schedule XXS 3/4" stainless steel pipe with suitable geometry and material properties to withstand proposed operating temperature and pressure of 900 °C and 80 bar, respectively.

The reformer was heated by an electric tube furnace with a heating length of 30.5 cm. A nickel based steam reforming catalyst, GW-91 EW from Süd-Chemie, was crushed to produce a particle size in the range of 1.4 - 4.75 mm. Between 15 and 20 g of catalyst

Downstream of the reactor, water vapor was largely removed from the gas stream in a condenser. The gas stream was then passed through a coalescing filter (Model 31G, Balston) for further drying. The dry effluent gas was analyzed with a Shimadzu 14A gas chromatograph (GC) equipped with a thermal conductivity detector (TCD) and CarboxenTM 1000 column (45/60, SUPELCO, St. Louis, MO). A mixture of 92% helium with 8% hydrogen served as carrier gas. In each analysis the column oven temperature was held at 45° C for 1 minute, increased to 225° C over 9 minutes, held at 225° C for 2 minutes, and then decreased to 45° C over a period of 10 minutes. A graph of the GC temperature program is shown in Figure 3.

Figure 3. GC oven temperature profile for v.1.

The GC system was equipped with a six-port valve which automatically injected a dried sample from the reactor onto the GC column every 22 minutes. The concentrations of permanent gas species – H₂, N₂, CO, CH₄, and CO₂ – were determined. The analysis also

had the capability to detect higher hydrocarbons such as C_2H_4 , C_2H_6 , C_3H_6 , and C_3H_8 . ASTM standard D1946-2006 outlines the procedure for determining chemical compositions of reformed gases and gaseous mixtures containing hydrogen, oxygen, nitrogen, carbon monoxide, carbon dioxide, methane, ethane and ethylene [46]. A sample chromatogram is shown in Figure 4 and a photograph of the reforming system is shown in Figure 5.

Figure 4. Sample chromatogram

Figure 5. Photograph of the v.1 laboratory-scale reforming test bed designed to operate at pressures up to 80 bar.

4.1.1.2 Version 2

After several preliminary tests were completed, three changes to the v.1 reforming system were made. Aside from the three changes outlined below, v.2 is the same as v.1.

1) The v.1 system for delivering water and hydrogen peroxide to the reformer did not respond well to transient events and was therefore replaced. System pressure fluctuations caused the liquid reactant delivery (which was dependent on matching the pressure in the reservoir headspace with reformer operating pressure) to become unstable. To correct this, a high pressure piston pump designed for metering liquid (Optos 1HM, Eldex Inc, Napa, CA) was purchased. The pump accurately delivers 0.01 to 20 mL/min at pressures up to 200 bar with the liquid flow rate independent of system pressure.

2) The tube furnace used to bring the reformer up to temperature and also to provide supplemental heat for the reforming process, was replaced. The decision to replace the tube furnace was out of a desire to have the reformer operate autothermally; the heat in the reformer only coming from the combustion of CH_4 and not from external sources. Tests were conducted in which the furnace was used to bring the reformer up to temperature and was then turned off when the exothermic ATR reactions began to evolve heat. Reforming tests under these conditions were unsuccessful since the tube furnace provided very poor insulation. Heat loss was so great that the ATR reactions couldn't be sustained at the prescribed O_2 flowrate. Therefore the design changes to the v.1 system included vastly improved insulation for the reformer. To accomplish this, the tube furnace was replaced with high temperature insulation (Fibercraft® Board Insulation, Thermcraft Inc., Winston-Salem, NC). The insulation was formed from four layered boards 5 cm thick, 61 cm in length, and 20 cm in width, with two boards under the reformer and two on top of the reformer. A channel was cut out of the boards so the reformer could be placed into the insulation. The insulation provided minimal heat loss compared to the heat loss from the tube furnace, however, the reformer still needed to be brought up to temperature to start the ATR reactions. To accomplish this, two additional channels were cut into insulation parallel to the reformer, one on each side. These channels housed spiral wound, resistance heating wire used to bring the reformer up to temperature. When the catalyst bed reached light off temperature and the ATR reactions were able to sustain the reforming process, the heating wire was turned off. Figure 6 shows a diagram of the insulation, resistance wire and reformer. The modified schematic of the v.2 reforming system is shown in Figure 7.

Figure 6. Insulation, resistance wire, and reformer layout (bottom half shown)

Figure 7. Schematic diagram of high pressure methane reforming test facility v.2

3) The sampling interval of the GC was reduced from 22 minutes to 10 minutes. This was accomplished by increasing the initial column oven temperature from 45° C to 80° C. In each analysis the temperature was held at 80° C for 1 minute, ramped to 225° C over 5 minutes, and then decreased to 80° C over 4 minutes. Figure 8 compares the GC column oven temperature profiles of the v.1 and v.2 systems.

Figure 8. GC column oven temperature profiles used for gas analysis in v.1 (dashed line) and v.2 (solid line) systems.

4.1.1.3 Version 3

While v.2 of the reformer provided several critical upgrades to v.1, a few new problems were encountered with v.2. Other than the two modifications outlined below, reformer system v.3 is the same as v.2.

(1) The reactant temperature at the inlet of reactor was not stable over a large range of S/C ratios. This problem was resolved by adding a resistance heater tape to the tubing

that transported reactants to the reformer and controlling it with a proportional–integral–derivative (PID) controller. The settings were tuned to keep the reactants at 270° C at the inlet of the reformer. The v.3 temperature control was far superior to the previous arrangement and inlet temperatures varied only by a few degrees over a wide range of S/C ratios.

(2) Under certain S/C ratios or when using H₂O₂, the preheating lines would get hot enough to ignite the pre-mixed reactants in the transport tubing. This was solved by running a separate gas line for methane which didn't mix with oxygen and nitrogen until after the preheaters. The rest of the v.2 system features were retained. A schematic of the v.3 reforming system is shown in Figure 9.

Figure 9. Schematic diagram of high pressure methane reforming test facility v.3.

4.1.2 Operating procedure

Standard operating procedures were followed each time an experiment was conducted in order to ensure meaningful and repeatable results. The procedures are outlined in this section.

4.1.2.1 GC Startup

The GC was the first part of the system to be started up each day. It was turned on at least one hour before sampling started to allow time for preheating. During this hour, carrier gas flowed through the CG and the column oven temperature was set at 120° C. After one hour, the column temperature was set to 80° C and the GC was ready to sample calibration gas. Calibration is described in section 4.1.2.4.

4.1.2.2 Catalyst loading

At the start of each new set of experiments, fresh, pre-weighed catalyst was loaded into the reformer. Under normal circumstances the same catalyst was generally left in the reformer for several days of testing. Figure 10 shows catalyst before being loaded into the reformer. See Appendix B-2 Catalyst properties for a detailed listing of catalyst properties.

Figure 10. Unused sulfide nickel catalyst (Catalyst Ni-0309S, Engelhard, Newark NJ)

Approximately 33 grams of catalyst were loaded into the reactor for v.2 and v.3 testing of the reforming system.

4.1.2.3 Pressure test

After the reactor was loaded with catalyst it was placed into the reformer test system and all the fittings were tightened. A pressure test was conducted on the system using nitrogen. The back pressure regulator was set and the nitrogen flow turned on. When the desired system pressure was reached, about 1 bar above the highest anticipated operating pressure, gas flow into and out of the reformer was stopped and the pressure inside the system was monitored for several minutes. If the pressure decreased over a few minutes,

a detector fluid was used to locate the leak and the leak was repaired. After the system integrity was verified, the calibration procedure described in Section 4.1.2.4 was carried out.

4.1.2.4 Calibration

The calibration procedure for the reforming system was critical to obtaining accurate results. The MFCs and the GC were the most sensitive instruments requiring calibration. Calibration of pressure transducers and thermocouples were conducted by the manufacturer and their errors were used; ± 0.27 bar and $\pm 3.2^{\circ}$ C respectively. Likewise the high pressure water pump was very accurate, $\pm 0.3\%$, and daily calibration was viewed as unnecessary.

4.1.2.4.1 Flow controllers

Before each experimental run all MFCs were flow tested and if needed adjusted to ensure the desired flow was the actual flow. For calibration, regardless of gas species, a bubble flow meter (mini-BUCK Calibrator M-30, A.P. BUCK, Orlando, Fl.) was used. The BUCK is a primary flow standard suitable for calibration of mass flow controllers. A gas flow rate was set and given at least 3 minutes to stabilize. The flow was then measured by the flow meter and several readings were recorded. These readings provide an average and standard deviation for the gas flow. This procedure was repeated for each gas species, and often, for more than one gas flow rate per species. For example: if one set of experiments required three different O_2/C ratio's, the gas flow rate of O_2 would be measured and recorded at all three values prior to the test.

4.1.2.4.2 Gas chromatograph

The gas chromatograph software integrates the area under the chromatogram for each gas species. The area counts are directly related to the concentration of the gas species present in the reformat sample. A one time multipoint calibration curve, relating area counts to gas concentration (%) for each gas species was completed prior to the start of the experimental phase. Additionally, one calibration gas was analyzed before and after each day's experimental runs. The results from the daily calibration gas provided a reference point for interpreting the data and also formed a basis of comparing data from one day to another.

4.1.2.5 Reformer Startup

After completing the calibration procedure the heating wires around the reactor were energized, the N₂ flow was set to 0.5 lpm, and the backpressure regulator on the system was turned to the open position. Typically in less than half an hour the catalyst bed reached about 650° C at which temperature CH₄ and O₂ were metered into the reformer at the appropriate flow rates selected for the test. Almost immediately a temperature increase in the reactor was detected due to the partial oxidation of CH₄. When a temperature increase was observed, the reactor heating element was turned off, the water pump and the water heating element were turned on, and the system pressure was set by adjusting the back pressure regulator. Typically, within 45 minutes of turning on the water flow, the system temperatures and reformat gas composition were stabilized.

4.1.2.6 Operational Control

During the course of each experimental run, several parameters were monitored to ensure the reformer was operating as planned. These parameters include:

- (1) temperature of the reactor to ensure the exothermic reaction zone was indeed located in the catalyst bed,
- (2) pressure differential across the catalyst bed and the filter located just after the catalyst bed was monitored to ensure that catalyst bed or filter wasn't obstructed,
- (3) temperature just before the back pressure regulator was monitored to ensure that it wasn't higher than the rated temperature of the regulator seals,
- (4) flow rates of the MFC's were monitored to ensure proper gas reactant delivery,
- (5) pump operation and fluid reservoir level were monitored to ensure proper liquid reactant delivery,
- (6) reactant temperature at the entrance of the reactor was monitored to ensure the heating elements were operating and that the inlet conditions were stable, and
- (7) GC chromatograms of the reformat gas composition were monitored as an indicator of system performance.

Aside from monitoring the parameters mentioned above, another important aspect of operational control was changing conditions from one operating setpoint to another. When making a change in the S/C ratio, the volumetric flow rate of the reactor can change by over 60%. This often made it necessary to adjust the back pressure regulator to maintain constant system pressure. Changing the O₂/C ratio had a minimal effect on the volumetric flow rate in the reformer and no further adjustments were required.

4.1.2.7 GC Sampling and data collection

When the reformer was operating stably at a selected set point, the GC sampling system was switched from calibration gas to sample the reformat gas. The GC then continued to sample the reformat stream every 10 minutes thereafter. Changes between operating set points for the reforming system were made immediately after a GC sampling event.

As each GC sample was analyzed, the mole fractions of H_2 , N_2 , CO , CH_4 , and CO_2 were recorded. A screen shot of the LabView interface for each steady state operating condition was also saved.

4.1.2.8 Shut Down

When the experimental run was completed, the CH_4 flow was immediately turned off. The O_2 flow rate was then decreased to 0.5 lpm, the N_2 flow rate increased to 2 lpm., and the water flow rate left unchanged. After several minutes of flushing the system in this manner the water flow was turned off along with the water heating elements. All flows were shut off a few minutes after turning the water off. Service ports before and after the catalyst bed were then opened to allow ambient air to pass through the system by natural convection allowing the inside of the reformer to dry.

4.1.3 Experimental design

A carefully prepared experimental design is critical to obtain meaningful results and conclusions. Again, the focus of this research was to study the performance of ATR reforming at selected pressures using H_2O and O_2 to form a basis of comparison for

results obtained when H_2O_2 was used as the oxidant and steam source. Therefore the experimental design was based primarily around H_2O and O_2 ATR with the occasional performance comparison to H_2O_2 ATR reforming. The independent variables that were controlled in this research are shown in Table 1.

Table 1. Independent variables

Variable		
#	Name	Unit
1	S/C	/
2	O_2/C	/

The variables, although continuous, have defined ranges due to physical limitations of the reforming process. Note that temperature, while an extremely important factor in the reforming process, is a dependent variable in autothermal reforming.

4.1.3.1 Factorial approach

Typically, parametric studies are used to observe the response of a dependent variable while each independent variable is incrementally changed over a specified range. For this study however, a 2^2 factorial design approach was used [47]. Utilizing a two level factorial design allowed both independent variables to be changed at the same time. Among other advantages this method offered the ability to find the optimum operating conditions in fewer experiments than most other available methods.

A sub sea power generating station located on the ocean floor would be operated at a given depth and an associated operating pressure. This allows the focus of experiments to be finding the optimal operating condition at a given pressure. The approach was carried out at multiple pressures from 6 bar to 50 bar representing depths from 60 to 500

m below sea level. A sample of the two level factorial design for this study is shown in Table 2. Note that the column headings correlate to the variable numbers in Table 1. The column heading, "12", refers to a two level interaction and is used later in calculations which estimate experimental error [47].

Table 2. Variable levels for factorial experimental design

Order	Treatment	1	2	12
2	1	-1	-1	1
4	2	1	-1	-1
3	3	-1	1	-1
1	4	1	1	1

As shown in Table 2 each variable has a high (+1) and low (-1) value at which experiments were conducted. The initial high and low values for the 6 bar test are given in Table 3.

Table 3. Initial operating conditions for low pressure (6 bar) experiments.

#	Variable Name	Unit	Value		CH ₄ Flow lpm
			+	-	
1	S/C*	/	3.75	2.25	2.50
2	O ₂ /C*	/	0.58	0.46	2.50

* The value for C in all tests was 2.5 lpm

4.1.3.2 Optimization

In order to optimize a process, clear criteria must be set forth. Several possible optimization criteria exist for the sea floor reforming experiments and selection depends

on the outcome most desirable for this particular application. Some of the potential optimization criteria are listed below:

- maximize the mole fraction of H_2 in the output gas stream
- maximize the moles of H_2 produced per mole of CH_4 in the feed gas
- minimize the mole fraction of CO in the output gas stream while keeping the H_2 mole fraction above a given threshold
- minimize the mole fraction of CO in the output gas stream while keeping the CH_4 conversion above a given threshold
- maximize the moles of H_2 produced per mole of O_2 in the feed gas

Obviously there is no end to possible criteria and yet, in some cases, different optimization criteria could lead to the same operating conditions.

For the application at hand, the methane supply from the subsea gas vents is considered unlimited compared to the amount required by the reforming unit. The oxygen concentration in researched gas vents is less than 1% [13, 48]. This means oxygen isn't present in high enough concentrations to sustain the ATR reforming reactions and therefore oxygen would need to be stored onboard the system. Again, the proposed form of oxygen storage is H_2O_2 . Therefore, minimizing the consumption of O_2 is directly related to the size, and potentially, cost of the system. Additionally, since PEMFC's don't require that pure hydrogen be fed to the anode side, other gases such as CO_2 will only have a dilution effect on the cell performance [49]. The main restriction is that CO can't be present at levels above 10 ppm [49]. It is therefore proposed that the

optimization criteria for the subsea reforming application be to maximize the moles of H_2 produced per mole of O_2 consumed. CO in the reformat stream to the fuel cell would be controlled by additional, downstream unit operations.

When the optimum condition was identified at 6 bar, performance comparisons using H_2O_2 were performed. The optimization process was then repeated for reactor pressures of 28 and 50 bar. Determining optimized reformer operating conditions at a given pressure typically required 40 hours of testing.

4.1.3.3 Initial test conditions

Using data from the literature [43], previous tests, and equilibrium calculations, the initial high and low values for each variable were selected as shown in Table 3. Experiments for the four tests conditions shown in Table 2 were conducted. In addition, two tests were conducted at the center point, namely, a S/C ratio of 3.00 and an O_2/C of 0.52. Upon completing the first set of six experiments, the data were analyzed and the variables changed in order to move closer to the optimum condition. This sequence was repeated for each of the pressures of interest.

4.2 Modeling

Two numerical models were used in order to complete the fourth objective laid out in the thesis statement. The first model employed purely thermochemical equilibrium calculations as provided by the software package FACTSage™ 5.1. The second model

was a one-dimensional reactor model which included major chemical kinetics along with heat and mass transfer phenomena inside the reactor.

4.2.1 Equilibrium modeling

To generate results with FACTSageTM 5.1, the initial reactant gas species, reactant molar ratios, temperature, and pressure were specified. Equilibrium results were generated at the same pressure as the reactant pressure and at a temperature of 700° C. The final temperature is only used by the program to determine the phase of the products, the actual final temperature is calculated by the software. The final temperature entered into the program was estimated based on previous tests. Based on the input parameters, the program calculated the equilibrium products both in moles and mole fraction, and the final product temperature. Multiple input conditions were saved in tabular form and then imported into FACTSageTM 5.1 in order to calculate multiple test conditions at once. The FACTSageTM 5.1 results were then saved in a data file. A Microsoft Excel template containing post-processing functions for data was developed and the FACTSageTM 5.1 data file was imported into this existing template. The post-processed results were then saved as an Excel file. Excel and MATLAB[®] were used to generate charts from the equilibrium calculations and served as a general comparative benchmark for experimental and kinetic modeling results.

4.2.2 Kinetic modeling

A kinetic model was developed in order to further examine the conversion process inside the ATR reactor. Using a software package, COMSOL Multiphysics 3.4, several trial

models were constructed to represent the reforming process. The models were based on examples found in the literature [9, 41, 43, 50] and were used to predict spatial profiles of temperature and species concentration within the reactor. The kinetic model, therefore, provided far more insight into the actual reforming processes than did the equilibrium model.

4.2.2.1 Model description

The model was based on the four reactions:

involving six gas species: methane, oxygen, water, carbon monoxide, carbon dioxide, and hydrogen. Molecular nitrogen was also included as a nonreacting species.

4.2.2.2 Model evolution

The first model used to represent the reactor was a two dimensional pseudo-homogenous model. This approach allowed the prediction of relatively detailed temperature and conversion results inside the reactor while accounting for radial variations; the radial flux was super-imposed over the axially directed, convection transport which was assumed to be plug flow.

The model was set up with symmetry about the z -axis allowing the three dimensional geometry to be modeled in two dimensions. Below is a schematic layout of the 2-D reactor. $T_{r,z}$ represents the temperature of the catalyst bed and $C_{i,r,z}$ represent the concentration of gas species i at a given location r,z . R is the radius of the reactor and L is the length of the catalyst bed. T_a is the ambient air temperature surrounding the reactor.

Figure 11. Schematic layout of 2-D reactor

Since the actual reformer had a large aspect ratio, having a catalyst bed length of approximately 0.60 m and an inner diameter of 0.011 m, the model equations were scaled to keep from generating large numbers of nodes and elements. Each term, in the energy and mass balance equations, was multiplied by scaling factors, 'scaler' and 'scalez', of the same order as the order of derivative in the term. For example, diffusion being a second order derivative was scaled to r/scaler^2 and z/scalez^2 , while convection being a first order derivative term was scaled by r/scaler , etc.

Shortly thereafter a 2-dimensional heterogeneous model was completed which differentiated the thermal properties, heat transfer, and temperature of the catalyst bed from the gas species.

After generating some initial results from the 2-D models it was found that both temperature and gas concentration had negligible radial variations in both the homogenous and heterogeneous models. To take advantage of the negligible radial effects the model was collapsed to a 1-D heterogeneous model which dramatically reduced the computational time while preserving the main effects. A schematic layout of the 1-D reactor model is shown in Figure 12. T_z represents the gas phase temperature, $T_{s,z}$ represents the solid phase temperature, and $C_{i,z}$ represents the concentration of gas species i at a given location z . L represents the length of the catalyst bed and the nodes at which the solution is calculated are represented by dots.

Figure 12. Schematic layout of 1-D reactor

4.2.2.3 Model assumptions

The following assumptions were made while constructing the 1-D model: (1) since the reactor domain had a Péclet number ≥ 155 the diffusion coefficient in the axial direction is dominated by the convection term and can be omitted, (2) the heat conductivity of the

gas is much smaller than that of the catalyst bed and can be omitted, (3) the radial heat transfer due to heat loss through the reactor is negligible and allowing a 1-D approach, (4) changes in gas properties and concentrations with time are much smaller than those with space and are ignored within a small time step.

4.2.2.4 Model equations

The kinetic rate equations and kinetic data were obtained from literature studies that employed Engelhard's Ni-0309S catalyst [43]. The rate equations for chemical reactions as presented in equations (21)-(24):

$$R_1 = \frac{k_1 p_{CH_4} p_{O_2}^{1/2}}{(1 + K_{CH_4-c} p_{CH_4} + K_{O_2-c} p_{O_2}^{1/2})^2} \quad (25)$$

$$R_2 = \frac{k_2}{p_{H_2}^{2.5}} \left(p_{CH_4} p_{H_2O} - \frac{p_{H_2}^3 p_{CO}}{K_{e2}} \right) \times \frac{1}{Q_r^2} \quad (26)$$

$$R_3 = \frac{k_3}{p_{H_2}} \left(p_{CO} p_{H_2O} - \frac{p_{H_2} p_{CO_2}}{K_{e3}} \right) \times \frac{1}{Q_r^2} \quad (27)$$

$$R_4 = \frac{k_4}{p_{H_2}^{3.5}} \left(p_{CH_4} p_{H_2O}^2 - \frac{p_{H_2}^4 p_{CO_2}}{K_{e4}} \right) \times \frac{1}{Q_r^2} \quad (28)$$

$$Q_r = 1 + K_{CO} p_{CO} + K_{H_2} p_{H_2} + K_{CH_4} p_{CH_4} + \frac{K_{H_2O} p_{H_2O}}{p_{H_2}} \quad (29)$$

where

$$r_{CH_4} = -R_1 - R_2 - R_4 \quad (30)$$

$$r_{O_2} = -2R_1 \quad (31)$$

$$r_{CO_2} = -R_1 + R_3 + R_4 \quad (32)$$

$$r_{H_2O} = 2R_1 - R_2 - R_3 - 2R_4 \quad (33)$$

$$r_{CO} = R_2 - R_3 \quad (34)$$

$$r_{H_2} = 3R_2 - R_3 + 4R_4 \quad (35)$$

The three governing equations that describe the model are listed below:

$$\varepsilon \frac{\partial C_i}{\partial t} = D_{dpi} \left(\frac{\partial^2 C_i}{\partial r^2} + \frac{1}{r} \frac{\partial C_i}{\partial r} + \frac{\partial^2 C_i}{\partial z^2} \right) - u \frac{\partial C_i}{\partial z} + \rho_{cat} r_i \quad (36)$$

$$\rho_b c_{pcat} \frac{\partial T_s}{\partial t} = \lambda \left(\frac{\partial^2 T_s}{\partial r^2} + \frac{1}{r} \frac{\partial T_s}{\partial r} + \frac{\partial^2 T_s}{\partial z^2} \right) + \rho_{cat} \sum_{j=1}^4 (-\Delta H_j) R_j + S_h h (T - T_s) \quad (37)$$

$$\overline{\varepsilon \rho_g c_{pg}} \frac{\partial T}{\partial t} = -u \overline{\rho_g c_{pg}} \frac{\partial T}{\partial z} + S_h h (T_s - T) \quad (38)$$

Equations (36)-(38) are the mass balance for the gas phase, the energy balance for the solid phase, and the energy balance for the gas phase, respectively.

Using the assumptions listed above the Equations (36)-(38) can be simplified to the following:

$$\varepsilon \frac{\partial C_i}{\partial t} = -u \frac{\partial C_i}{\partial z} + \rho_{cat} r_i \quad (39)$$

$$\rho_b c_{pcat} \frac{\partial T_s}{\partial t} = \lambda \frac{\partial^2 T_s}{\partial z^2} + \rho_{cat} \sum_{j=1}^4 (-\Delta H_j) R_j + S_h h (T - T_s) \quad (40)$$

$$\overline{\varepsilon \rho_g c_{pg}} \frac{\partial T}{\partial t} = -u \overline{\rho_g c_{pg}} \frac{\partial T}{\partial z} + S_h h (T_s - T) \quad (41)$$

where

- i gas species (H₂, O₂, CO, CO₂, H₂O, CH₄)
- j reaction index (1-4)
- t time (s)
- z coordinate (m)
- C_i concentration of gas species i (mol m⁻³)
- D_{dpi} dispersion coefficient of gas species i
- u superficial gas velocity (m s⁻¹)
- ρ_{cat} density of catalyst bed (kg catalyst m⁻³)
- $\overline{\rho_g}$ average gas density (kg m⁻³)
- ε void fraction of the catalyst bed
- $\overline{c_{pg}}$ average specific heat of gas (J kg⁻¹ K⁻¹)
- h heat transfer coefficient between catalyst bed and gas phase (W m⁻³ K⁻¹)
- S_h heat transfer area per unit volume of catalyst bed (m⁻² m⁻³)
- T temperature of gas phase (K)
- T_s temperature of solid phase (K)
- λ effective thermal conductivity of catalyst bed (W m⁻¹ K⁻¹)
- r_i reaction rate of gas species i (mol kg⁻¹ catalyst s⁻¹)
- ΔH_j heat of reaction j (J mol⁻¹)
- R_j reaction rate of reaction j (mol kg⁻¹ catalyst s⁻¹)

$$D_{dpi} = \varepsilon \left(\frac{D_i}{\tau_{bed}} + 0.5 d_p u \right) \quad (42)$$

where

D_i gas diffusivity of species i ($\text{m}^2 \text{s}^{-1}$)

τ_{bed} tortuosity of the bed

d_p catalyst pellet diameter (m)

and

$$\tau_{bed} = \frac{1}{\sqrt{\varepsilon}} \quad (43)$$

$$D_i = 1 \times 10^6 \cdot T^{1.75} \cdot \frac{\left(\frac{1}{m_{ave}} + \frac{1}{m_i} \right)^{\frac{1}{2}}}{P \left((20.1)^{\frac{1}{3}} + (p_i * 20.1)^{\frac{1}{3}} \right)^2} \quad (44)$$

where

m_{ave} average molar mass of gas into which gas species i is
diffusing (g mol^{-1})

m_i mass of gas species i (g mol^{-1})

P system pressure (bar)

p_i partial pressure of gas species i (bar)

4.2.2.5 Boundary conditions

The following boundary conditions were specified in the model:

at the reactor inlet, $z = 0$

$$T = T^{in}; T_s = T^{in}; C_i = C_i^{in} \quad (45)$$

and at the reactor outlet, $z = L$

$$\frac{\partial T}{\partial z} = 0; \lambda \frac{\partial T_s}{\partial z} = 0; \frac{\partial C_i}{\partial z} = 0 \quad (46)$$

where

T^{in} gas inlet temperature (K)

C_i^{in} concentration of inlet gas species i (mol m⁻³)

4.2.2.6 Initial conditions

The model was started with the inlet temperature of the gas species set to the experimental inlet temperature of 270° C. The catalyst bed temperature was given a linear profile from 270° C at the reactor inlet to 700° C at the outlet. The appropriate CH₄ flow rate (2.5 lpm), S/C and O₂/C (variable) ratios and pressure (6, 28, and 50 bar) were also specified.

4.2.2.7 Solver and mesh size

A time dependent solver was used to start the reaction. Using the temperature profile assigned to the catalyst bed the reaction would start at the backend of the reactor and propagate toward the front end until the reaction zone was stabilized. After a steady state condition was thought to have been reached in the time domain the results were saved and used as the initial condition for a stationary solver. This was done to insure that the time domain solution had indeed arrived at a steady state. If the results then converged

using the stationary solver, a steady state solution for the set of operating condition was assumed to be reached. A parametric solver was then used to step to new conditions. The software used the Finite Element Method (FEM) to solve the equations representing the reactor phenomena.

The mesh size was critical to ensure accurate results from the model. If the mesh was too large, steep gradients were missed and faulty calculations made. Mesh refinement was performed to determine if the mesh size in use was small enough. This consisted of running multiple tests while doubling the number of nodes with each new test. The test results were compared and when the difference between two consecutive test results was less than 2%, the model was considered converged and the grid size considered adequate.

5 Results and discussion

The following section presents and discusses the experimental and modeling results that were obtained. Preliminary results will be discussed first and then the actual experimental and modeling results will be presented, discussed and compared.

5.1 Preliminary results and discussion (test facility v.1)

Initial testing of the experimental set up provided useful experience in operating the system and led to the system evolution that was discussed earlier. This section will describe the test conditions and results for the preliminary experiments. Test facility v.1 was used to carry out both conventional and hydrogen peroxide based ATR reforming experiments.

5.1.1 Conventional ATR reforming

Separate fuel, water, and oxygen streams are metered into the reformer for conventional ATR. Preliminary tests were conducted using reactor pressure as the primary variable ranging from 7 to 58 bar. Test conditions are shown in Table 4. It should be noted that the tests completed were not true ATR. While CH_4 , H_2O , and O_2 were fed into the reactor, supplemental heat was also supplied to the reactor from a surrounding furnace. It should also be noted that the tests conducted with v.1 didn't follow an experimental design. These tests were merely a starting point to prove system functionality.

Table 4. Reformer test conditions

Test Test No.	No. of Samples	Feed rate, ml/min				Ratio		Pressure (bar)	Temp. °C	GHSV (hr ⁻¹)
		CH ₄	O ₂	H ₂ O _(g)	N ₂	S/C	O ₂ /C			
1	4	500	80	1.8	500	4.5	0.16	7	800	5888
2	4	500	80	1.8	500	4.5	0.16	28	800	1472
3	4	500	80	1.8	500	4.5	0.16	46	800	896
4	4	500	80	1.8	500	4.5	0.16	58	800	711

Increasing pressure resulted in a decreasing (GHSV) from nearly 6000 to 700 hr⁻¹. GHSV is defined as the reactant flow rate, at the operating temperature and pressure, divided by the catalyst volume. Equilibrium calculations for the reactant mixtures and reforming conditions shown in the table were performed using the software package FACTSageTM 5.1. Products included CH₄, H₂, H₂O, CO, and CO₂. Figure 13 compares the results of the equilibrium calculations with the experimental results. Experimental values are averages of at least four measurements of gas composition. From the error bars displayed on the graph, it is clear that experimental conditions were very stable, in terms of both reactor pressure and gas composition. H₂ concentration in the gas decreased from ~75 to 68% over the range of experimental conditions. Gas phase CO concentration also declined from 10 to 7%. CO₂ concentration is relatively unaffected by pressure ranging from 12.5 to 14.5% over the test range. Note that the concentration of unreacted methane increased from 1 to 9.5% as pressure increased from 7 to 58 bar. Reduced methane conversion also resulted in reduced gas yield. Results in Table 5 show a decline in gas yield from 4.8 to 3.3 STP liter gas per STP liter of CH₄ entering the reformer, over the range of test pressures. The experimental results are in close agreement with the results of the equilibrium calculations over the range of pressures indicating that at this set of operating conditions, kinetic limitations to methane reforming do not exist. Elevated pressure can induce carbon formation and coking of the catalyst

but none was observed. Longer term tests should be conducted for verification. In general, these experiments confirmed that methane can be reformed at pressures typical of depths where hydrothermal vents or methane hydrates exist on the sea floor.

Table 5. Variation of inert free gas yield as a function of pressure

Pressure (bar)	Inert Free Gas Yield mole/mole CH ₄ (STP)
6.8	4.8 ± 0.3
28.4	3.8 ± 0.1
45.6	3.8 ± 0.3
58.2	3.3 ± 0.3

Figure 13. Comparison of methane reforming results as a function of pressure at O₂/C = 0.16, S/C = 4.5, T_{Reactor} = 800°C and 15 g of G91-EW a Ni based catalyst. (Equil=chemical equilibrium calculation, Exp=experimental result)

5.1.2 H₂O₂ based reforming

As mentioned earlier, a major limitation for operating a reformer on the sea floor is having oxygen available at usable concentrations. A second set of experiments were performed to evaluate the use of a second oxidizer, hydrogen peroxide, a liquid at ambient conditions that can be decomposed, either catalytically or thermally, to water and oxygen according to the following reaction:

Like the previous reforming tests, the liquid reactants were metered into the reformer from a high pressure tank. Prior to conducting the H₂O₂ tests, the tank and transfer lines were passivated with dilute nitric acid. Based on a 0.5 lpm CH₄ flow rate to the reformer and the decomposition reaction shown in equation (21), a mixture of 9% H₂O₂ in deionized water at a flow rate of 1.8 ml/min was calculated to provide desired oxygen to carbon (0.15) and steam to carbon (4.4) ratios. These match the reactant ratios that were used in the experiments described in section 5.1.1.

To calibrate the H₂O₂ delivery system, a mixture of 9% H₂O₂ and 91% deionized water was placed in the liquid reactant reservoir and metered into the empty reformer at a rate of 1.8 ml/min. The reactor was maintained at a temperature of 800°C using the tube furnace and the pressure was set to 8.8 bar. CO₂ was introduced to the reformer at a flow rate of 1.0 lpm to simulate the reactant gas flow expected during experiments and to act as a sweep gas that could easily be separated from the O₂ by GC. After analyzing several samples of the outlet gas, the flow of H₂O₂/H₂O mixture was stopped and replaced with a flow of O₂ from a gas cylinder. The flow was varied from 31 to 107 ml/min to provide a

series of O₂ concentrations to the GC. The calibration curve is shown in Figure 14 with an accompanying regression equation. Using this equation, the GC area counts from the earlier analysis of gas from the 9% H₂O₂ and 91% deionized water liquid flow were converted to O₂ concentrations as shown in Table 6. Eight samples were analyzed with an average O₂ concentration of 6.2% and a standard deviation of 1.9% (absolute).

Figure 14: O₂ calibration curve for GC based on O₂/CO₂ mixtures produced with calibrated mass flow controllers.

Table 6: Variability of concentration of O₂ produced from thermally decomposing H₂O₂ in an empty reformer at 800°C, 8.8 bar.

Sample No.	Area Counts	% O ₂
1	46,816	6.0
2	29,700	3.2
3	40,000	4.9
4	51,000	6.7
5	44,929	5.7
6	44,030	5.5
7	72,268	10.1
8	55,960	7.5
Average	48,088	6.2
Standard Dev.	11,655	1.9

Results of the reforming experiments using 9% H₂O₂ and 91% deionized water as a reactant are shown in Table 7. Product composition predicted by chemical equilibrium is presented for comparison. As with the earlier experiments using O₂ from gas cylinders, agreement between experiment and equilibrium is quite good, with differences being <2% (absolute) for all species. These results provided preliminary validation to the use of H₂O₂ as a liquid oxygen carrier for reforming applications.

Table 7: Comparison of gas composition from catalytic methane reforming experiments using 9% H₂O₂ / 91% H₂O at 8 bar, 800 °C with composition predicted by chemical equilibrium at the same conditions.

	Equilibrium	Experimental
	(% volume)	
H ₂	75.7	77.75
CH ₄	0.71	1.03
CO	10.88	10.04
CO ₂	12.71	11.18

See Appendix A for an overview of sample calculations used in determining the data presented in this section.

5.2 Testing at a reactor pressure of 6 bar

The following results and discussion deal specifically with tests conducted at a pressure of 6 bar. Sections 5.3 and 5.4 report results from tests conducted at 28 bar and 50 bar, respectively.

5.2.1 Test facility version 2

Test facility v.2 provided a reforming system that could be operated in a truly autothermal fashion. Only conventional reforming results were obtained with v.2 as the system encountered problems when H_2O_2 was introduced. Many of the initial conventional tests that were run with system v.2 were also unsuccessful. For example, a faulty solid state relay caused the reactor heating wires to stay energized even after combustion reactions had started and the heating wires had been turned off causing very favorable but erroneous results. After several minor problems were fixed and v.2 of the system was working consistently 15 experimental conditions were run. Table 8 summarizes the results.

Table 8. V.2 summary of 6 bar testing results (*indicates H_2O_2 was used, BT = break through of flame front)

Run	Variables		Trials					Liters per minute / liter of CH_4								Total Lpm
	S/C	O_2/C		H_2/O_2	σ %	$[H_2]$ %	σ %	H_2	σ %	CO	σ %	CH_4	σ %	CO_2	σ %	
1	3.00	0.52	6	4.06	0.6	68.75	0.1	2.12	0.5	0.20	0.4	0.19	0.9	0.61	0.4	8.25
2	2.25	0.58	8	3.83	2.5	69.79	1.0	2.23	3.3	0.31	8.0	0.11	9.0	0.58	5.2	8.53
3	3.75	0.58	6	3.99	0.4	70.70	0.1	2.33	0.2	0.20	1.3	0.12	0.8	0.68	0.2	8.77
4	3.75	0.46	6	4.10	0.5	66.05	0.1	1.90	0.4	0.11	1.4	0.29	0.7	0.60	0.2	7.67
5	2.25	0.46	5	4.12	0.8	65.65	1.9	1.90	1.0	0.18	5.7	0.27	1.5	0.55	1.6	7.70
6	3.35	0.44	5	4.14	1.1	64.86	1.9	1.84	1.4	0.12	24.4	0.29	8.2	0.56	3.0	7.50
7	3.50	0.40	BT	4.08	0.0	62.66	0.4	1.63	1.8	0.08	4.8	0.37	0.7	0.52	3.2	6.93
8	3.00	0.52	4	4.07	1.6	68.40	0.7	2.07	1.4	0.19	0.6	0.18	0.7	0.60	0.8	8.08
9	3.00	0.52	5	3.88	0.7	66.95	1.8	2.01	0.4	0.27	1.3	0.19	1.2	0.51	0.6	7.96
10	3.35	0.44	3	3.98	0.5	64.40	0.1	1.74	0.8	0.09	1.2	0.33	0.5	0.55	0.8	7.27
11	2.60	0.48	4	3.99	1.0	66.48	0.4	1.90	1.1	0.16	1.9	0.26	2.2	0.55	1.2	7.67
12	4.10	0.48	BT													
13	2.60	0.40	BT	3.96	1.1	62.08	0.5	1.60	1.4	0.12	8.0	0.38	0.5	0.48	2.4	6.94
14	4.10	0.40	BT													
15	3.35	0.44	3	4.02	0.5	64.57	0.1	1.76	1.1	0.10	1.5	0.33	0.5	0.55	0.9	7.32

5.2.1.1 First factorial

Testing started by conducting a 2^2 factorial experiment around the center point condition of $S/C = 3.00$ and $O_2/C = 0.52$ (Refer to Tables 2 and 3 for experimental design). The center point condition, run #1, was run first and was followed by the four corner conditions: run #2 through #5.

The data from run #2 through #5 was used to determine the effects of both O_2/C and S/C ratios on H_2 production per mole of O_2 in the feed gas. The results of the four runs are shown below in Table 9.

Table 9. Initial factorial showing test conditions and results.

Run	S/C A	O ₂ /C B	AB	Mole Ratio H ₂ /O ₂
5	-1	-1	1	4.12
4	1	-1	-1	4.10
2	-1	1	-1	3.83
3	1	1	1	3.99

Run #5 had the highest H_{2(out)}/O_{2(in)} ratio with a value of 4.12. The lowest H_{2(out)}/O_{2(in)} ratio was only 7% lower than run #5 and was from run #2.

Although large differences were not found between the results from the four tests, it was still possible to calculate the effects of the independent variables on the H_{2(out)}/O_{2(in)} ratio and therefore propose conditions that would offer a greater yield. Table 10 shows the individual effect that the S/C and O₂/C ratio had on the moles of H_{2(out)}/O_{2(in)}. The table also shows the two factor interaction effects which, if no experimental error was present is assumed to be negligible. Therefore according to Box et al.[47] the two-factor interactions provide a reasonable approximation of variance and an estimate of experimental error.

Table 10. The effect changing the S/C and O₂/C ratio from +1 to -1 had on the H₂/O₂.

Main effects	H _{2(out)} /O _{2(in)}	Error
S/C	0.037	±0.045
O ₂ /C	-0.102	±0.045
Interaction effect		
S/C x O ₂ /C	0.045	

From the first factorial it is clear that increasing the O₂/C ratio from the low value to the high value resulted in a decrease in the moles of H_{2(out)}/O_{2(in)} by 0.102. By comparison,

increasing the S/C ratio from the low value to the high value produced an increase in the moles of $H_{2(out)}O_{2(in)}$ by 0.037. Since the effect of changing the S/C ratio by one step was less than the estimated experimental error of the tests (0.045), it isn't a significant effect.

5.2.1.2 Path of steepest ascent

Based on the calculated effects and the step size used in the first factorial, a proposed path was calculated in which the predicted $H_{2(out)}/O_{2(in)}$ yield increased. The "path of steepest ascent" is shown in Figure 15 by a dashed line which passes through the center point of the first factorial. Two runs were completed along this path; the first run showed a slight increase in yield while the 2nd run showed a decrease before the high temperature reaction zone blew out of the backend of the reformer. The first test point along the path, having a S/C = 3.35 and an $O_2/C = 0.44$, was considered the new best test condition and would become the center point for a new factorial design. The new factorial would confirm if this new condition offered the highest yield or if there was another path of steepest ascent that would lead to a better condition.

The center point of the first factorial was replicated in run #8 to confirm system performance over time; that is the time between run #1 and run #8 (7 hours). The results from run #1 to run #8 are nearly identical as can be seen by comparing the results in Table 8. The consistency of the reformat gas concentrations over time suggested that the catalyst was not experiencing deactivation over the course of an experiment and that the instrumentation such as the mass flow controllers and the GC were truly operating in a stable fashion.

Four days after the first 8 runs were completed runs #9 – #15 were completed. The same catalyst was reused. Run #9 was run at the same condition as the center point of the first factorial in order to compare the yield from the previous tests. This time the reactor had a 4.67% lower $H_{2(out)}/O_{2(in)}$ yield. The difference is likely due to slight deactivation of the catalyst as the reforming process was stopped and then restarted. The first factorial and the path of steepest ascent (runs #1 - #8) made up test group 1.

5.2.1.3 Second factorial

A second factorial was run using a new center point. This time the center point was the condition with the maximum yield from test group 1. This center point used was the same condition as run #6 which had a $S/C = 3.35$ and $O_2/C = 0.44$, and was found along the path of steepest ascent.

To start the new factorial the center point was tested first. This center point, run #10, had also been tested in run #6 of the previous tests. The $H_{2(out)}/O_{2(in)}$ yield of run #10 was 3.98; a 3.86% drop from run #6. This difference in yield is nearly the same as the decrease in yield from the run #7 to #8 and showed that the runs from the second day were consistently lower than those from the first.

It was only possible to attain steady state operations for one of the four corner runs of the 2nd factorial. Run #11 was conducted at a S/C ratio of 2.6 and an O_2/C ratio of 0.48. The $H_{2(out)}/O_{2(in)}$ yield at this condition was nearly identical to the results from run #10; 3.98

and 3.99 respectively. Run #12 and #13 were attempted but in both cases the high temperature reaction zone blew out of the backend of the reactor. This was due to the high S/C ratio in run #12 and the low O₂/C ratio in run #13. Run #14 wasn't attempted as it had both the high S/C ratio of run #12 and the low O₂/C ratio of run #13.

Testing was completed by replicating the center point. The H_{2(out)}/O_{2(in)} yield for the replication in run #15 was 4.02. This marked a marginal increase of 0.75% over run #10 and again proved the stability of the reforming system over several hours of testing and various conditions. Run #9 through run #15 made up test group 2.

A graphical overview of the various conditions and their H_{2(out)}/O_{2(in)} yields is shown in Figure 15. The type of marker used to depict the conditions also shows their grouping. The number to the right of the marker is the H_{2(out)}/O_{2(in)} yield and the number in brackets following the yield is the run number as identified in Table 8. BT refers to a condition where the high temperature reaction zone blew through the backend of reactor. If a number is listed before the BT label, it refers to the yield before the high temperature reaction zone blew through.

Figure 15. V.2 experimental results from 6 bar testing

Figure 16 shows the results when the day to day variance is taken into account. This new figure was made by averaging the percent decrease in yield from group 1 to group 2 tests that were run at the same condition. This factor was then used to correct all group 2 test results. A "c" is used after the run number to indicate the results have been multiplied by this factor, an increase of 4.25 %, to remove the day to day differences. Estimated contour lines have also been added to the figure to show the H_{2(out)}/O_{2(in)} yield based on

the experimental results. See Appendix B-1 for a possible explanation of day to day differences in $H_{2(out)}/O_{2(in)}$ yield.

Figure 16. Corrected data from v.2 experimental results at 6 bar with estimated yield contours and bounding limits for blow through condition.

After the 15 runs were completed it was concluded that the optimum operating condition had been arrived at for the 6 bar condition. From Figure 16 the optimum condition appears to be a broad plateau which is bracketed to the left and to the top by a physical limitation: the inability to stabilize the high temperature reaction zone in the reactor.

Generally speaking the O_2/C ratio has a much greater effect on the $H_{2(out)}/O_{2(in)}$ yield than the S/C ratio.

5.2.1.4 Hydrogen peroxide based reforming

Hydrogen peroxide based autothermal reforming was attempted with v.2 of the system but the tests were unsuccessful. The additional heat release of the decomposing H_2O_2 in the preheated transfer lines ignited the fuel and H_2O_2 mixture well before the mixture entered the reactor. After the failed attempt, the system was modified to resolve this problem. Further tests results using H_2O_2 are given in section 5.2.2.

5.2.2 Test facility version 3

Version 3 (v.3) of the test facility expanded the testing capabilities to include H_2O_2 based reforming. Before the results are presented some additional information regarding H_2O_2 is discussed.

5.2.2.1 H_2O_2 reforming

The strength of H_2O_2 in the following discussion refers to the weight percentage of H_2O_2 in the H_2O_2 /water mixture fed to the reactor. Table 11 shows the equivalent liquid phase concentrations of H_2O_2 and molar percentages of O_2 in the mixture after the H_2O_2 has decomposed to O_2 and H_2O as a function of H_2O_2 strength in the parent solution.

Table 11. Summary of H_2O_2 liquid concentrations (volume % and mole %) and O_2 concentration after complete decomposition of H_2O_2 as a function of H_2O_2 strength (weight %).

H_2O_2 Weight %	H_2O_2 Vol % ($\varnothing$)	H_2O_2 Mol %	O_2 Mol %
50.0	41.8	34.6	14.8
47.5	39.7	32.4	14.1
45.0	37.6	30.2	13.4
42.5	35.5	28.1	12.6
40.0	33.4	26.1	11.9
37.5	31.4	24.1	11.2
35.0	29.3	22.2	10.5
32.5	27.2	20.3	9.8
30.0	25.1	18.5	9.1

The v.3 experimental apparatus allowed the use of H_2O_2 as an oxidizer and steam source for ATR within physical limitations of the system. Working with 67% (weight) H_2O_2 or greater can be dangerous as the heat of decomposition of H_2O_2 can completely vaporize the water present in the H_2O_2 solution and lead to spontaneous decomposition. Therefore, it is difficult to find H_2O_2 in a solution at a concentration greater than 50% by weight and no effort was made to exceed this limit for safety reasons.

Figure 17 shows the possible S/C and O_2 /C ratios that can be tested by using 50 % weight H_2O_2 . The bottom right hand corner of the figure shows operating space that requires higher concentration H_2O_2 . Additionally the chart shows the required flow rate as well as the required weight percent concentration. It should be noted that the flow rate required in mlpm is based on a system CH_4 flow rate of 2.5 lpm.

Figure 17. Possible testing conditions with various % weight solutions of H_2O_2 at various flow rates and the corresponding S/C ratio and O_2/C ratios.

When the reforming results from v.2 of the reforming system were examined it was clear that the operating space which yielded the most moles of H_2 per mole of O_2 was within the possible testing area. This corresponded to an H_2O_2 flow rate of 7.5 mlpm using an H_2O_2 concentration of 38% (weight).

While the heat of decomposition of high concentration H_2O_2 may lead to hazardous conditions, the heat of decomposition from lower concentration H_2O_2 solutions (<50 % weight) is beneficial to the reforming process. Figure 18 shows the heat release for the

decomposition of H_2O_2 as a function of the weight percent H_2O_2 and the flow rate of the H_2O_2 solution. As expected, the higher the flow rate and the higher the weight percentage of H_2O_2 the higher the heat release. For comparison, the heat release from a stoichiometric combustion of CH_4 with 1.1 lpm of O_2 , typical of test conditions, is 390 W. If sufficient H_2O_2 is used to produce an equivalent amount of O_2 , 40% (weight) H_2O_2 at a flow rate of 8 mlpm, the heat release from the decomposition of H_2O_2 is a little less than half of the heat released from the combustion of CH_4 (195 W).

Figure 18. Heat release from H_2O_2 solution by decomposition reaction of H_2O_2 (W)

5.2.2.2 Experimental results

The following experiments were conducted in order to compare the results from the optimum condition determined for conventional ATR with results for H_2O_2 based reforming at the same S/C and O_2/C set points. In order to have a reference point, run #16 was conducted at the optimal condition for conventional ATR at 6 bar. Table 12 summarizes results for runs #16 through #18.

Table 12. V.3 summary of 6 bar testing results using H₂O₂ as oxidizer (*indicates H₂O₂ was used).

Run	Variables					Moles per mole of CH ₄ (in)										Total
	S/C	O ₂ /C	Trials	H ₂ /O ₂	σ %	[H ₂] %	σ %	H ₂	σ %	CO	σ %	CH ₄	σ %	CO ₂	σ %	
16	3.35	0.44	6	3.95	0.6	64.54	0.3	1.75	0.8	0.09	1.9	0.33	0.8	0.55	0.3	7.30
17	3.35	0.44	5*	4.38	2.4	66.80	2.4	1.95	2.8	0.12	2.9	0.25	3.6	0.59	3.0	7.76
18	3.75	0.46	4*	4.47	1.6	68.29	0.3	2.04	1.6	0.11	3.1	0.23	2.8	0.63	1.7	8.03

Figure 19 adds experimental runs #16 through #18 to the first 15 runs previously shown in Figure 15. The operational space identified in Figure 17 has been overlaid as a cross hatched area.

Figure 19. V.3 results added to v.2 results for tests conducted at 6 bar.

Just as test group two had a lower yield than test group one, the yield from test group three is also lower than test group 1. To compensate for this day to day difference, the results for test group three were multiplied by a correction factor of 4.8%, the percentage difference between run #6 and run #16: a replicated run from test group 1 and 3 respectively. Figure 20 shows the final graphical overview of all tests conducted at 6 bar with correction factors applied.

Figure 20. Corrected v.3 results added to v.2 results 6 bar testing

It is possible to compare the experimental results for different tests that used the same operating set point using O_2 . The average moles of $H_{2(out)}/O_{2(in)}$ for a S/C of 3.35 and an O_2/C of 0.44 was 4.16. Run #17 used H_2O_2 to replace the pure O_2 and produced 4.59 (corrected) moles of H_2 per mole of O_2 , a 10% increase over the use of pure O_2 . For a S/C of 3.75 and an O_2/C of 0.46 the moles of $H_{2(out)}/O_{2(in)}$ was 4.16 under conventional reforming. Run #18 used H_2O_2 to replace the pure O_2 and produced 4.68 (corrected) moles of H_2 per mole of O_2 , a 14% increase over the use of pure O_2 .

This indicates that H_2O_2 based reforming is possible and produces an increase in the moles of $H_{2(out)}/O_{2(in)}$. The increase is driven by the higher temperatures produced by the decomposition of H_2O_2 and the resulting higher steam reforming rates.

It is clear that the $H_{2(out)}/O_{2(in)}$ yield when using H_2O_2 as the oxidizer and steam source is greater than conventional ATR, producing an average increase in yield of 12%. The reforming results are not the only effect of the use of H_2O_2 . The decomposition of H_2O_2 actually began well before it was injected into the reactor. The increased temperature in the reactant transfer lines and the reduced duty cycle of the controller for the heating tapes on the reactant transfer lines served as indicators of the heat release from H_2O_2 decomposition reactions. Table 13 compares two different test conditions conducted with O_2 (runs #16 and #4) and with H_2O_2 (runs #17 and #18). T_{in} and T_{out} are the temperatures at the inlet and outlet of the reactor catalyst bed, respectively. The heater duty cycle is the percentage of time that the pre-heater on the reactant transfer lines was

energized. The heater output is derived from the total power the resistance heater wire consumed multiplied by the duty cycle of the heater.

Table 13. Comparison of conventional ATR to H₂O₂-based ATR reforming

Variables				Tin (°C)	Tout (°C)	Heater duty cycle %	Heater output (W)	Mol H ₂ /O ₂	Mol CH ₄
Run	S/C	O ₂ /C	Trials						
16	3.35	0.44	6	271	527	54	614	4.14	0.83
17	3.35	0.44	4*	276	550	46	529	4.59	0.63
4	3.75	0.46	5	259	515	NA	NA	4.10	0.73
18	3.75	0.46	5*	278	547	45	514	4.68	0.58

5.2.2.2.1 Power balance

The complete decomposition of H₂O₂ according to Equation (46) would have provided an additional input of 163 W of thermal energy to the system for run #17 into the system compared to run #16. The decrease in pre-heater output, 614 W (run #16) to 529 W (run #17), accounts for 85 W. Using the gas flow rate, specific heats (*c_p*) of the gas components, and recorded temperatures, the change in the reactant temperature from 271° C to 276° C accounts for only 2 W. The increase in temperature of the outlet gas, 527° C to 550° C, accounts for approximately 8 W. Additionally the flow rate of CH₄ in the reformat was 0.20 lpm less in run #17 than in run #16. While several reaction pathways can account for this difference in CH₄ levels, the most likely explanation is an increase in endothermic steam reforming. The water gas shift reaction, which is exothermic, is not likely to account for this difference in CH₄ levels as the outlet temperature increased in run #17 and a temperature increase has an inverse relationship with the WGS reaction. Therefore, based on the steam reforming equation shown in Equation (21), approximately 30 W is required to convert the 0.20 lpm CH₄.

Using this analysis, and summing up the $85\text{W} + 2\text{W} + 8\text{W} + 30\text{W}$ accounted for earlier and dividing by the total of 163W provided by the decomposition of H_2O_2 , 77 % of the additional chemical energy entering the system as H_2O_2 can be accounted for. Twenty three percent or 38 W is not accounted for. The remaining 23 % may be accounted for as additional heat loss from the system. Differences between the compositions of the reactant streams may also contribute.

5.2.3 Comparison with equilibrium model

Figure 21 shows the moles of H_2 produced per mole of O_2 fed into the reactor at 6 bar predicted by thermochemical equilibrium. The initial temperature of the reactants was set to 270°C . These results are based on conventional ATR with O_2 , not ATR with H_2O_2 .

Figure 21. Moles of H_2 produced / mole of O_2 fed into reactor (equilibrium values, 6 bar, no heat loss)

The white area at the top left of the chart and the steep gradient bordering it indicates a region where it is physically impossible for the reactions to take place. According to the equilibrium calculations in this region the energy requirements to drive the reactions are

higher than the reactants supply and the reactions aren't sustained. This phenomenon was also observed experimentally although the exact location of the border differed as explained later.

Overall the equilibrium results are similar to the experimental results. However, since no heat loss is introduced into the equilibrium calculations, the physical limitations of the reforming process aren't reached until the O_2/C is lower and the S/C ratio is higher than the experimental results show. Figure 22 shows the equilibrium results, with a black line indicating the approximate boundary, above and to the right of which, the experimental reforming reactions were not sustained.

Figure 22. Comparison of reforming limitations for equilibrium calculations and experimental runs

The equilibrium calculations predict that the initial conditions and a pressure of 6 bar will produce a maximum $H_{2(out)}/O_{2(in)}$ of 4.35. While the maximum occurs at a $S/C = 3.00$ and an O_2/C ratio = 0.35, it should also be noted that there is a fairly broad plateau near the maximum. Moving away from the broad plateau leads to a steeper gradient as the $H_{2(out)}/O_{2(in)}$ yield decreases. The trends in the equilibrium model are quite similar to the

experimental trends even though they are based purely on equilibrium with no heat loss. As expected, the equilibrium model predicted a maximum $H_{2(out)}/O_{2(in)}$ yield at a lower O_2/C ratio than the experiments showed. Again this is a result of having no heat loss in the equilibrium calculations.

Table 14 compares the gas composition from run #6, the optimum experimental condition, with the same condition calculated with FACTSageTM 5.1. Fact stands for FACTSageTM 5.1, mole of CH_{4c} stands for mole of CH_4 consumed, T_{out} is the reformat gas temperature at the outlet of the reactor for the experimental run #6, and T_{out} is the final temperature of the product gas mixture for the FACTSageTM 5.1 calculation.

Table 14. Experimental and equilibrium model (Fact) reformat gas composition comparison (6 bar)

Run	Variables			H_2/O_2	$[H_2]$ %	Moles per mole of $CH_{4(in)}$				Mol CO	Mol CO_2	Tout
	S/C	O_2/C	Trials			H_2	CO	CH_4	CO_2	/ mol CH_{4c}		(°C)
6	3.35	0.44	5	4.14	64.86	1.84	0.12	0.29	0.56	0.17	0.79	512
Fact	3.35	0.44	NA	4.25	65.10	1.87	0.16	0.27	0.56	0.23	0.77	640

The predicted $H_{2(out)}/O_{2(in)}$ yield is only 2.5% greater than the experimental yield. The predicted moles of H_2 , CO, CH_4 , and CO_2 in the reformat gas per mole of CH_4 fed into the reactor were at worst 33% different from the experimental results. This worst case difference occurred for the CO yield per mole of CH_4 fed into the reactor. The difference can largely be explained by the fact the carbon balance in the experimental run was 3% from complete closure. That is, by a simple carbon balance, if one mole of CH_4 enters the reactor, then the moles of CO, CH_4 , and CO_2 exiting the reactor should also add to 1.00 assuming no other products containing carbon. In the case of run #6, the total moles

of carbon exiting the reactor summed to 0.97. If the missing 0.03 moles of carbon based species were added to the CO count the results would change from a 33% difference to a 7% difference.

The equilibrium model predicted the temperature of product gas to be 640° C compared to 512° C for the experimental results. This difference can be attributed to the fact that the equilibrium model does not take heat loss into account.

The reactor in the experimental run had a temperature profile similar to the one shown in Figure 23. The temperature profile was captured as the flame front slowly blew through the backend of the reactor and passed over a thermocouple in the process.

Figure 23. Example temperature profile from experimental run

Zone 1 primarily covers the heating of reactants from the combustion of CH_4 . Heating largely occurs by conduction through the catalyst bed from the high temperature region in Zone 2. Zone 2 is characterized by both combustion and steam reforming reactions. The majority of the combustion takes place in the region before the peak temperature. After the peak temperature is reached the steam reforming reactions consume heat and the temperature drops quickly. This high temperature zone is relatively narrow and conversion in this zone may be limited by reaction kinetics. Zone 3 covers a region where the gas temperature decreases as it flows through the backend of the reactor. The temperature decrease is due to heat loss through the reactor wall as well as continued steam reforming reactions. As the temperature decreases the WGS reaction produces additional hydrogen.

The experimental runs may produce less hydrogen than the equilibrium results due to kinetic limitations of the steam reforming reactions. However the reactor should produce additional hydrogen through the WGS which favors lower temperatures as seen on the backend of the reactor. In summary, less steam reforming would result in more CH_4 in the reformat gas, and a higher WGS reaction would result in less CO per mole of CH_4 consumed. Therefore the experimental results would be expected to include more CH_4 and less CO per mole of CH_4 consumed. A similar H_2 yield is possible depending on how much H_2 is produced by the WGS shift. The data in Table 14 seem to agree with the hypothesized difference in the reaction mechanism.

For comparison, reforming experiments are often conducted to optimize the moles of $\text{H}_{2(\text{out})}/\text{CH}_{4(\text{in})}$. Although the absolute maximum can't be seen on this graph the optimum is in a different area than the optimum for moles $\text{H}_{2(\text{out})}/\text{O}_{2(\text{in})}$. Within the limitations of the operating space, the optimum result is 2.36 moles of $\text{H}_{2(\text{out})}/\text{CH}_{4(\text{in})}$ at a S/C ratio = 5 and an O_2/C ratio = 0.65.

Figure 24. Mole of H_2 produced / mole of CH_4 fed into reactor (equilibrium values, 6 bar, no heat loss)

It is clear from the equilibrium results that optimizing the moles of $\text{H}_{2(\text{out})}/\text{O}_{2(\text{in})}$ in the reactant feed gas leads to a different optimum condition than optimizing the moles of $\text{H}_{2(\text{out})}/\text{CH}_{4(\text{in})}$.

5.2.4 Comparison with kinetic model

COMSOL Multiphysics 3.4 was used to predict gas composition and temperature throughout the reactor. Figure 25 shows the moles of H_2 produced per mole of O_2 fed into the reactor at 6 bar. Like the equilibrium model, the temperature of the reactants was

set to 270° C. This model is also based on conventional ATR rather than ATR with H_2O_2 .

Figure 25. Mole of H_2 produced / mole of CH_4 fed into reactor (kinetic model, 6 bar)

Again the white space on the top left corner of the chart indicates a region where the reformer reactions aren't stable. The kinetic model predicted that the reformer would be unable to sustain reactions at a lower S/C ratio than was experimentally observed and that the reformer would continue to operate down to lower O_2/C ratios than were experimentally possible.

Table 15 compares the gas composition of run #6, the optimum experimental condition, with a very similar condition calculated with COMSOL Multiphysics 3.4, abbreviated as COM in the table. All other variable have been previously defined.

Table 15. Experimental and kinetic model reformat gas composition comparison (6 bar)

Run	Variables			$\text{H}_{2(\text{out})}$ /		Moles per mole of $\text{CH}_{4(\text{in})}$				Mol CO	Mol CO_2	T_{out} (°C)
	S/C	O_2/C	Trials	$\text{O}_{2(\text{in})}$	$[\text{H}_2]$ %	H_2	CO	CH_4	CO_2	/ mol CH_4c		
6	3.35	0.44	5	4.14	64.86	1.84	0.12	0.29	0.56	0.17	0.79	512
COM	3.20	0.44	NA	4.20	64.78	1.84	0.14	0.28	0.58	0.19	0.81	589

While the equilibrium model predictions were very close to the experimental the kinetic model is even closer. The predicted $H_{2(out)}/O_{2(in)}$ yield using the kinetic model is only 1.5% greater than the experimental yield. The predicted flow rates (lpm) of H_2 , CO , CH_4 and CO_2 in the reformat gas per unit flow rate of CH_4 fed into the reactor were at worst 16.6% different from the experimental results. This worst case difference compares the difference in the CO yield per mole of CH_4 fed into the reactor. The difference can again largely be explained by the fact the carbon balance in the experimental run is 3% off. If the missing 0.03 moles where added to the CO and CO_2 count the results could change from a 16.6% difference to a mere 1.75% difference.

The temperature predicted at the outlet of the reactor was 589° C. This is 77° C higher than was observed during experimentation. The difference is likely due to additional heat loss by convection out of the ends of the reactor tube, a phenomenon that isn't captured by the kinetic model.

Figure 26 shows a graphical comparison of the optimum condition that was reached experimentally with the corresponding results from both the equilibrium model and the kinetic model. Run 6 is the experimental run, Fact stands for FACTSageTM 5.1, and COM stands for COMSOL Multiphysics 3.4.

Figure 26. Comparison, experimental, equilibrium (Fact), and kinetic modeling (COM) at 6 bar. * indicates moles / mole of CH_{4(in)}.

5.2.5 Comparison with relevant research

The most complete data set of experimental results presented in the literature was presented by Hoang et al. [43] Figures from this publication were analyzed to produce the comparative data shown in Figure 27. Hoang's reforming tests were conducted at a pressure of 1 bar without an accompanying inlet temperature for the reactants. It was stated that steam was introduced into the reactor so the inlet temperature of the reactor must have been at least 100° C but no further detail was provided.

Figure 27. Mole of H_2 produced per mole of reactant O_2 from experimental CH_4 reforming results at 1 bar. (Hoang et al. [42])

The maximum moles of $H_{2(out)}/O_{2(in)}$ was 3.0 and occurred at a S/C ratio = 1.8 and a O_2/C = 0.50. This is a marked difference from the present experimental and modeling results and it would appear that Hoang's reactant inlet temperature must have been significantly lower than the $270^\circ C$. This would explain why the lower O_2/C and higher S/C ratios did not produce stable reaction conditions and also why the greatest $H_{2(out)}/O_{2(in)}$ yield occurred at a much higher O_2/C ratio. Yet, while the $H_{2(out)}/O_{2(in)}$ yield is significantly lower, the trends shown in Figure 27 are very similar to the experimental results from the present study. It is also clear that the S/C ratio had a lesser effect on the yield than did the O_2/C .

5.3 Methane reforming results at 28 bar pressure

The following results and discussion deal specifically with tests conducted at a pressure of 28 bar. Fourteen runs were conducted using v.3 of the system. Table 16 lists the results for all 14 runs, both conventional and H_2O_2 based.

Table 16. V.3 summary of 28 bar testing results (*indicates H₂O₂ was used)

Run	Variables			Moles per mole of CH ₄ (in)												Total Lpm
	S/C	O ₂ /C	Trials	H ₂ /O ₂	σ %	[H ₂] %	σ %	H ₂	σ %	CO	σ %	CH ₄	σ %	CO ₂	σ %	
1	3.00	0.48	5	3.12	0.4	60.68	0.0	1.49	0.4	0.10	0.2	0.37	0.2	0.51	0.3	6.63
2	2.25	0.54	5	2.82	1.5	61.04	0.8	1.52	2.1	0.16	3.1	0.32	1.5	0.51	1.5	6.71
3	2.25	0.42	6	2.87	1.0	55.17	0.7	1.21	1.4	0.09	4.3	0.46	1.1	0.43	0.7	5.93
4	3.75	0.54	6	3.07	0.8	63.01	0.5	1.66	1.2	0.11	4.1	0.31	1.5	0.60	0.7	7.14
5	3.75	0.54	BT													
6	2.25	0.54	5	2.63	3.4	58.86	2.1	1.42	4.8	0.16	7.5	0.36	4.6	0.49	1.6	6.49
7	3.00	0.48	5	3.47	0.2	62.45	0.1	1.67	0.2	0.13	2.0	0.36	0.6	0.54	0.3	7.26
8	3.00	0.52	6*	3.82	1.2	64.50	0.5	1.83	1.5	0.15	4.3	0.31	1.9	0.59	1.9	7.72
9	3.75	0.54	5	3.35	0.7	64.12	0.5	1.80	0.4	0.12	0.4	0.32	0.8	0.61	0.6	7.63
10	3.75	0.54	5*	3.52	0.9	64.90	0.2	1.89	1.0	0.14	0.9	0.28	1.2	0.64	1.2	7.90
11	3.75	0.42	BT													
12	3.75	0.42	BT*													
13	3.00	0.54	4	3.38	0.7	65.44	0.3	1.82	0.7	0.14	0.8	0.27	2.0	0.59	0.3	7.50
14	3.00	0.48	3	3.39	1.0	62.37	0.5	1.62	1.3	0.11	2.6	0.35	1.0	0.54	0.6	6.99

Since an optimum condition had all ready been reached for a pressure of 6 bar it was possible to estimate an experimental optimum for 28 bar. Testing, therefore, started by conducting a 2² factorial around the center point condition of S/C = 3.00 and O₂/C = 0.48.. Run #1, the center point condition, was followed by the four corner conditions: runs #2 through 5. Run #2 was then replicated in run #6. The values for the four conditions mentioned are shown in Table 17 and the results are shown in Table 18.

Table 17. Initial operating conditions for mid pressure (28 bar) experiments.

#	Variable		Value	
	Name	Unit	+	-
1	S/C	/	3.75	2.25
2	O ₂ /C	/	0.58	0.46

Table 18. Test conditions and initial results for mid pressure (28 bar) factorial experiments.

Run	S/C A	O ₂ /C B	S/C x O ₂ /C AB	Mole Ratio H ₂ /O ₂
3	-1	-1	1	2.87
5	1	-1	-1	BT
2 / 6	-1	1	-1	2.82 / 2.62
4	1	1	1	3.07

After conducting the first factorial around the center point it became clear that the center point, run 1, had the highest moles of $H_{2(out)}/O_{2(in)}$. Run #1, yielding 3.12 moles of H_2 per mole of O_2 was closely followed by run #4. Since all runs around the center point had a lower yield of $H_{2(out)}/O_{2(in)}$ than the center point, it was concluded that the estimated optimum condition for 28 bar had been determined. This first set of tests made up test group 1.

After reaching an optimum condition at 28 bar, performance comparisons with H_2O_2 were conducted. These tests made up the second test group. For each test condition, the reformer was initially run in the conventional form. When the system was operating stably, it was switched from O_2 to H_2O_2 without interruption. Three conditions were compared: run #1, the center point, and runs #4 and #5. This set made up test group 2.

Lastly, two more conditions were tested which made up test group 3. These last two tests were conducted during the start-up of a 50 bar test and are included for additional comparison purposes.

A graphical summary of all the various conditions that were run at 28 bar is shown in Figure 28. The layout and symbols used in Figure 28 are the same as those used in Figure 15.

Figure 28. V.3 experimental results from 28 bar testing

Figure 29 shows the results when the day to day variance is again taken into account. Estimated contour lines have also been added to the figure to show the H₂(out)/O₂(in) yield based on the experimental results.

Figure 29. Corrected V.3 experimental results from 28 bar testing with estimated contour curves

The optimum condition at 28 bar shifted further to the right when compared to the 6 bar optimum, and therefore required additional O₂ input. Additionally, the maximum yield of H_{2(out)}/O_{2(in)} decreased from approximately 4.16 moles to approximately 3.43 moles. This is a decrease of 17.5%. Since the steam reforming reactions favor lower pressures, a decrease in the H_{2(out)}/O_{2(in)} yield was expected with increased pressure.

The following observations were made after comparing conventional reforming to H₂O₂ based reforming. At a S/C ratio of 3.00 and an O₂/C ratio of 0.48 (run #7 and #8) an

$H_{2(out)}/O_{2(in)}$ mole increase of 10% was observed when the system was switched to H_2O_2 . At a S/C ratio of 3.75 and an O_2/C ratio of 0.54 (run #9 and #10) an $H_{2(out)}/O_{2(in)}$ mole increase of only 5% was observed when the system was switched to H_2O_2 .

5.3.1 Comparison with equilibrium model

Figure 30 shows the moles of H_2 produced per mole of O_2 fed into the reactor at 28 bar predicted by thermochemical equilibrium as a function of O_2/C and S/C ratios. The initial temperature of the reactants was set to 270° C. These results are based on conventional ATR with O_2 , not ATR with H_2O_2 .

Figure 30 Mole of H_2 produced / mole of O_2 fed into reactor (equilibrium values, 28 bar, no heat loss)

Comparing the equilibrium results at 28 bar to the results at 6 bar (Figure 24) the following observations were made: (1) the maximum moles of $H_{2(out)}/O_{2(in)}$ dropped 16% from 4.35 to 3.64, (2) the optimum condition changed from a S/C ratio of 3.00 and an O_2/C ratio of 0.35 at 6 bar to a lower S/C ratio of 2.5 and a higher O_2/C ratio of 0.4 at 28 bar, (3) the large plateau of insensitive $H_{2(out)}/O_{2(in)}$ yield in response to changes in the S/C and O_2/C operating parameters near the maximum still exists.

Table 19 compares the optimal condition of the experimental results at 28 bar to equilibrium results at the same condition. The predicted $H_{2(out)}/O_{2(in)}$ yield is only 2.6% greater than the experimental yield. The predicted moles of $H_{2(out)}$ and $CO_{2(out)}$ per mole of $CH_{4(in)}$ were very close to the experimental results differing by 8% or less. The moles of $CO_{(out)}$ and $CH_{4(out)}$ per mole of $CH_{4(in)}$, however, were significantly different. The equilibrium $CO_{(out)}/CH_{4(in)}$ was 77% higher than the experimental observation. Again it appears that the experimental runs produce less hydrogen from steam reforming reactions due to kinetic limitations in the high temperature reaction zone but that this is compensated by additional hydrogen production from WGS reactions favored by the lower temperatures seen on the backend of the reactor. Therefore the experimental results should include more CH_4 and less CO per mole of CH_4 consumed. A similar H_2 yield is possible depending on how much H_2 production the WGS shift causes. The data in Table 19 seem to agree with the hypothesized difference in the reaction mechanism.

Table 19. Comparison of optimal experimental results with FactSage equilibrium model reformat gas composition at 28 bar

Run	Variables			Trials	H_2/O_2	[H_2] %	Moles per mole of $CH_{4(in)}$				Mol CO	Mol CO_2	Tout
	S/ C	O_2/ C					H_2	CO	CH_4	CO_2	/ mol CH_4c		(° C)
7	3.00	0.48		5	3.47	62.45	1.67	0.13	0.36	0.54	0.20	0.84	514
Fact	3.00	0.48		NA	3.56	63.18	1.71	0.23	0.28	0.50	0.32	0.69	743

The equilibrium model predicted the temperature of product gas to be 743° C. This is 229° C higher than the reactor exit gas temperature recorded experimentally. This difference can again be attributed to the fact that the equilibrium model does not take any heat loss into account.

5.3.2 Comparison with kinetic model

Figure 31 shows the moles of H_2 produced per mole of O_2 fed into the reactor at 28 bar. Like the equilibrium model, the temperature of the reactants was set to 270° C. This model is also based on conventional ATR rather than ATR with H_2O_2 .

Figure 31. Mole of H_2 produced / mole of CH_4 fed into reactor (kinetic model, 28 bar)

Comparing the kinetic models results at 28 bar to the results at 6 bar the following observations were made: (1) the maximum moles of $H_{2(out)}/O_{2(in)}$ dropped 12% from 4.20 to 3.70, (2) the optimum condition changed to a lower S/C ratio of 2.25 and a higher O_2/C ratio of 0.5, (3) the large plateau near the maximum still exists.

Table 20 compares the optimal condition of the experimental results at 30 bar to kinetic model results at the same condition. The predicted $H_{2(out)}/O_{2(in)}$ yield is 7% greater than the experimental yield.

Table 20. Experimental and kinetic model reformat gas composition comparison (28 bar)

	Variables					Moles per mole of CH _{4(in)}				Mol CO	Mol CO ₂	Tout
Run	S/ C	O ₂ / C	Trials	H ₂ / O ₂	[H ₂] %	H ₂	CO	CH ₄	CO ₂	/ mol CH _{4c}		(°C)
7	3.00	0.48	5	3.47	62.45	1.67	0.13	0.36	0.54	0.20	0.84	514
COM	3.00	0.48	NA	3.70	63.86	1.77	0.18	0.27	0.55	0.25	0.75	638

The predicted moles of H_{2(out)} and CO_{2(out)} per mole of CH_{4(in)} were very close to the experimental results differing by 6% or less. The moles of CO_(out) and CH_{4(out)} per mole of CH_{4(in)}, however, were significantly different. The predicted CO_(out)/CH_{4(in)} was 38% higher than experimentally observed. While that is a large error it is half of the difference predicted by the equilibrium model.

The kinetic model predicted the temperature of product gas to be 638° C. This is 124° C higher than the reactor exit gas temperature recorded experimentally. While still a large difference the kinetic model predicted the experimental temperature much more accurately than the equilibrium model.

Figure 32 shows a graphical comparison of the optimum condition that was reached experimentally with the corresponding results from both the equilibrium model and the kinetic model. Run 37 is the experimental run, Fact stands for FACTSage™ 5.1, and COM stands for COMSOL Multiphysics 3.4.

Figure 32. Comparison, experimental, equilibrium (Fact), and kinetic modeling (COM) at 28 bar. * indicates moles / mole of CH_{4(in)}.

5.4 Methane reforming results at 50 bar pressure

The following results shown in Table 21 and the discussion to follow deal specifically with tests conducted at a pressure of 50 bar. Twelve runs were conducted using v.3 of the system. Table 21 lists the results for all 12 runs including both conventional and H₂O₂ based ATR.

Table 21. V.3 summary of 50 bar test results (*indicates H₂O₂ was used)

Run	Variables							Liters per minute / liter of CH ₄								Total Lpm
	S/ C	O ₂ / C	Trials	H ₂ / O ₂	σ %	[H ₂] %	σ %	H ₂	σ %	CO	σ %	CH ₄	σ %	CO ₂	σ %	
1	3.00	0.48	5	2.75	1.0	56.67	0.0	1.31	0.4	0.08	1.0	0.43	2.2	0.50	0.8	6.24
2	3.75	0.54	5	2.77	1.2	60.05	0.9	1.49	2.2	0.09	3.3	0.36	2.2	0.56	1.1	6.70
3	2.25	0.54	4	2.21	0.9	54.48	0.6	1.19	0.6	0.10	4.9	0.41	3.1	0.48	1.2	5.90
4	2.25	0.42	3	1.89	4.0	44.70	3.6	0.80	5.4	0.06	7.7	0.53	3.3	0.37	2.0	4.85
5	3.75	0.42	BT	2.73	1.5	53.84	0.9	1.15	2.0	0.06	22.9	0.47	1.8	0.45	1.6	5.78
6	3.00	0.47	4	2.93	1.5	58.94	1.4	1.38	1.4	0.09	1.7	0.39	5.4	0.50	0.9	6.43
7	3.68	0.49	6	2.81	0.6	58.41	0.3	1.36	0.7	0.08	1.2	0.39	0.4	0.51	0.3	6.40
8	3.75	0.53	5	2.71	0.7	59.69	0.2	1.43	0.9	0.09	1.2	0.35	0.6	0.54	0.8	6.56
9	3.00	0.48	4	2.87	0.7	58.43	0.3	1.38	0.9	0.08	0.9	0.40	0.6	0.50	0.9	6.44
10	3.00	0.48	4*	3.08	2.2	59.77	0.7	1.48	1.9	0.10	1.0	0.37	4.6	0.54	2.2	6.76
11	3.75	0.54	4	2.70	0.8	59.98	0.4	1.46	1.0	0.08	1.6	0.35	0.8	0.54	0.6	6.65
12	3.75	0.54	5*	2.94	0.8	62.02	0.2	1.59	0.9	0.11	0.7	0.30	0.6	0.58	0.8	6.99

Since an optimum condition had all ready been reached at 6 and 28 bar, it was possible to estimate an experimental optimum for 50 bar. Testing, therefore, started by conducting a 2^2 factorial around a center point condition of $S/C = 3.00$ and $O_2/C = 0.48$. Run #1 was the center point condition and was followed by the four corner conditions: runs #2 through #5. The values of the operating parameters at the four latter conditions are shown in Table 22 and the results are shown in Table 23. This first set of tests made up test group 1.

Table 22. Initial operating conditions for high pressure (50 bar) experiments.

#	Variable		Value	
	Name	Unit	+	-
1	S/C	/	3.75	2.25
2	O ₂ /C	/	0.58	0.46

Table 23. Initial factorial showing test conditions and results for high pressure (50 bar) experiments.

Run	S/C A	O ₂ /C B	S/C x O ₂ /C AB	Mole Ratio H ₂ /O ₂
3	-1	-1	1	2.21
5	1	-1	-1	BT
2	-1	1	-1	2.77
4	1	1	1	1.89

After conducting the first factorial, around the center point, the path of steepest accent was calculated.

The second test group (runs #6 through #8) includes a replication of the center point followed by a line search along the path of steepest ascent followed by a replication of run #2. The line search confirmed that the original center point was indeed the optimal condition.

After reaching an optimum condition at 50 bar, performance comparisons with H_2O_2 were conducted. These tests (runs #9 through #12) made up the third test group. For each condition tested the reformer was initially run in the conventional mode. When the system stabilized the O_2 flow was shut off and H_2O_2 flow was started without interruption. Two conditions were compared: run #1 and run #2.

A graphical summary of all test conditions that were run at 50 bar is shown in Figure 33.

Figure 33. V.3 experimental results from 50 bar testing

The following observations were made by comparing conventional reforming to H_2O_2 based reforming. An increase of 7.3% was observed in $\text{H}_{2(\text{out})}/\text{O}_{2(\text{in})}$ yield when the system was switched to H_2O_2 at a S/C ratio of 3.00 and an O_2/C ratio of 0.48 (run #9 and #10). At a S/C ratio of 3.75 and an O_2/C ratio of 0.54 (run #11 and #12), a $\text{H}_{2(\text{out})}/\text{O}_{2(\text{in})}$ yield increase of 8.9% was observed when the system was switched to H_2O_2 .

5.4.1 Comparison with equilibrium model

Figure 34 shows the thermochemical equilibrium prediction of the moles of H_2 produced per mole of O_2 fed into the reactor at 30 bar. The initial temperature of the reactants was set to 270°C . These results are based on conventional ATR with O_2 , not ATR with H_2O_2 .

Figure 34. Mole of H_2 produced / mole of O_2 fed into reactor (equilibrium values, 50 bar, no heat loss)

Comparing the equilibrium results at 50 bar to the results at 28 bar (Figure 30) the following observations were made: (1) the maximum moles of $\text{H}_{2(\text{out})}/\text{O}_{2(\text{in})}$ dropped 8% from 3.64 to 3.36, (2) the optimum shifted slightly from S/C ratio of 2.5 and an O_2/C of 0.40 at 28 bar to a S/C ratio of 2.5 and an increased O_2/C ratio of 0.45 at 50 bar, (3) the

large plateau of insensitive $H_{2(out)}/O_{2(in)}$ yield in response to changes in the S/C and O_2/C operating parameters near the maximum still exists, (4) the $H_{2(out)}/O_{2(in)}$ results away from the optimum condition change very little with pressure increase.

Table 24 compares the optimal condition of the experimental results at 50 bar to equilibrium results at the same condition. The predicted $H_{2(out)}/O_{2(in)}$ yield is 12% greater than the experimental yield.

Table 24. Comparison of reformat gas composition at the optimal experimental condition and equilibrium model prediction at 50 bar

	Variables					Moles per mole of $CH_{4(in)}$				Mol CO	Mol CO_2	Tout
Run	S/ C	O_2/ C	Trials	H_2/ O_2	$[H_2] \%$	H_2	CO	CH_4	CO_2	/ mol CH_4c		(°C)
6	3.00	0.48	4	2.93	58.94	1.38	0.09	0.39	0.50	0.15	0.82	572
Fact	3.00	0.48	NA	3.29	61.25	1.58	0.22	0.31	0.47	0.32	0.68	774

As observed at lower pressures, the predicted yield of $H_{2(out)}$ and $CO_{2(out)}$ per mole of $CH_{4(in)}$ were close to the experimental results, differing by less than 15%. The moles of $CO_{(out)}$ and $CH_{4(out)}$ per mole of $CH_{4(in)}$, however, were significantly different. The predicted $CO_{(out)}/CH_{4(in)}$ was 144% higher than experimentally observed. It appears that the experimental runs produce less hydrogen through steam reforming reactions due to kinetic limitations and yet additional hydrogen through the WGS which favors lower temperatures as seen on the backend of the reactor. Increasing pressure causes an increased product gas residence time in the reactor producing a greater WGS effect experimentally. This contributes to a greater disagreement between the equilibrium model and the experimental results.

The equilibrium model predicted the temperature of product gas to be 774° C and this is 202° C higher than was observed experimentally. This difference can be attributed to the fact that the equilibrium model does not take heat loss into account.

5.4.2 Comparison with kinetic model

Figure 31 shows the moles of H₂ produced per mole of O₂ fed into the reactor at 50 bar. Like the equilibrium model, the temperature of the reactants was set to 270° C. This model is also based on conventional ATR rather than ATR with H₂O₂.

Figure 35. Mole of H₂ produced / mole of CH₄ fed into reactor (kinetic model, 50 bar)

Comparing the kinetic models results at 50 bar to the results at 28 bar the following observations were made: (1) the maximum moles of H_{2(out)}/O_{2(in)} dropped 5.4% from 3.70 to 3.50, (2) the location of the optimum condition has stayed the same at a S/C ratio of 2.25 and an O₂/C ratio of 0.5, and (3) the large plateau near the maximum still exists.

Table 25 compares the optimal condition of the experimental results at 50 bar to kinetic model results at the same condition. The predicted $H_{2(out)}/O_{2(in)}$ yield is 18% greater than the experimental yield.

Table 25. Experimental and kinetic model gas composition comparison (50 bar)

Run	Variables		Trials	H_2/O_2	[H_2] %	Liters per minute / liter of CH_4				Mol CO	Mol CO_2	Tout
	S/C	O_2/C				H_2	CO	CH_4	CO_2	/ mol CH_4 c		(°C)
6	3.00	0.48	4	2.93	58.94	1.38	0.09	0.39	0.50	0.15	0.82	572
COM	3.00	0.48	NA	3.46	62.30	1.66	0.17	0.30	0.53	0.24	0.76	656

The predicted moles of $H_{2(out)}$ and $CO_{2(out)}$ per mole of $CH_{4(in)}$ were somewhat close to the experimental results differing by 20% or less. The moles of $CO_{(out)}$ and $CH_{4(out)}$ per mole of $CH_{4(in)}$, however, were very different. The predicted $CO_{(out)}/CH_{4(in)}$ was 89% higher than experimentally observed. While that is a large error it is just over half of the difference that the equilibrium model predicted.

The kinetic model predicted the temperature of product gas to be 656° C. That temperature is 84° C higher than the experimentally observed. While still a large difference, the kinetic model estimated the experimental temperature much more accurately than the equilibrium model.

Figure 36 shows a graphical comparison of the results at the optimum experimental condition with the corresponding results from both the equilibrium and kinetic models. Run 6 is the experimental run, Fact stands for FACTSageTM 5.1, and COM stands for COMSOL Multiphysics 3.4.

Figure 36. Comparison, experimental (Run 6), equilibrium (Fact), and kinetic modeling (COM) at 50 bar.
 * Indicates moles / mole of CH_{4(in)}

6 Conclusions

A lab scale experimental facility for catalytic autothermal reforming at pressures ranging from 6 to 50 bar was constructed and tested. This pressure range was selected as a design criterion for simulating conditions typical of the sea floor where natural gas seeps or methane hydrates are present. This environment presents unique fuel reforming operating conditions in that fuel is plentiful, oxygen is a limiting resource, and maximizing the hydrogen yield, i.e. moles of $H_{2(out)}/O_{2(in)}$, is of primary importance. From the tests it was noted that the optimum condition for maximizing the moles of $H_{2(out)}/O_{2(in)}$ was significantly different then maximizing the moles of $H_{2(out)}/CH_{4(in)}$ which is a more typical goal. This study has located optimum conditions for underwater fuel reforming at pressures of 6, 28, and 50 bar. Employing data from the mathematical models and experimental results, conventional reformer performance with respect to the reactant ratios of steam to carbon and oxygen to carbon were presented. Experimentally, the optimal conditions for maximizing $H_{2(out)}/O_{2(in)}$ yield occur at a S/C ratio of 3.35 and an O_2/C ratio of 0.44 at 6 bar, a S/C ratio of 3.00 and an O_2/C ratio of 0.48 at 28 bar, and a S/C ratio of 3.00 and an O_2/C ratio of 0.48 at 50 bar. Under these conditions one mole of O_2 can produce 4.16 moles of H_2 at 6 bar, 3.43 moles of H_2 at 28 bar, and 2.84 moles of H_2 at 50 bar. Proof of concept using H_2O_2 as a steam and oxidizer source was also validated. A minimum of two conditions were rerun using H_2O_2 at each of the three test pressures. An increase in $H_{2(out)}/O_{2(in)}$ yield of up to 14% was observed when H_2O_2 was used compared to results from conventional ATR. A higher yield may have been achieved had there been a way to keep the H_2O_2 from partially decomposing before

entering the reactor. In addition to the experimental runs, equilibrium and kinetic models were used to further understand the ATR reactions and predict reforming results. Model predictions and experimental results at 6 bar pressure were in close agreement. As the pressure increased the agreement wasn't as strong but model results predicted $H_{2(out)}/O_{2(in)}$ yields within 18% of the experimental results. Both equilibrium and kinetic mathematical models predicted reforming trends that were comparable to the experimental observations. It was also noted that the kinetic model, while predicting higher $H_{2(out)}/O_{2(in)}$ yields than were experimentally observed, was a better predictor of $CO_{(out)}/CH_{4(in)}$, $CO_{2(out)}/CH_{4(in)}$, and $CH_{4(out)}/CH_{4(in)}$ yields. This indicated that the kinetic reaction mechanisms were better able to simulate the physical system. Equilibrium model results had a significantly lower correlation when comparing $CO_{(out)}/CH_{4(in)}$, $CO_{2(out)}/CH_{4(in)}$, and $CH_{4(out)}/CH_{4(in)}$ yields with the experimental. This was to be expected since the equilibrium results had no heat loss and had little to no influence from the WGS reactions.

Therefore all four objectives set forth in the thesis statement were achieved. This study provided a solid basis for identifying optimal conditions for operating an ATR reformer in a high pressure, low oxygen environment where O_2 consumption needs to be conserved, specifically subsea conditions. Additionally the use of H_2O_2 as an oxidizer for ATR is novel and may be of interest for other low oxygen environments such as space applications.

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Appendix A

This section contains a few sample calculations that were used throughout the calculation process.

A-1 Flow rates

Flow rate of reactants, temperature and pressure of reformer:

$$\begin{aligned}CH_{4(in)} &= 2.5 \text{ lpm} & p &= 5 \text{ bar} \\O_{2(in)} &= 1.25 \text{ lpm} & T &= 1073 \text{ K} \\H_2O_{(\ell)(in)} &= 5 \text{ mlpm} \\N_{2(in)} &= 0.5 \text{ lpm}\end{aligned}$$

Resulting S/C and O₂/C ratios:

$$\begin{aligned}O_2/C &= O_{2(in)} / CH_{4(in)} & (48) \\&= 1.25 \text{ lpm} / 2.5 \text{ lpm} \\&= 0.5\end{aligned}$$

$$\begin{aligned}S/C &= \left(H_2O_{(\ell)(in)} \cdot \frac{\text{gram}}{\text{mL}(H_2O)} \cdot \frac{\text{mol}}{\text{gram}(H_2O)} \cdot \frac{L}{\text{mol}(H_2O)} \right) / CH_{4(in)} & (49) \\&= \left(5 \text{ mLpm} \cdot \frac{1(g)}{1(mL)} \cdot \frac{1(mol)}{18(g)} \cdot \frac{22.4(L)}{1(mol)} \right) / 2.5 \text{ Lpm} \\&= 2.49\end{aligned}$$

GC results are exported to a tab delimited text file after analysis. A program the written to automatically read this text file and output needed data in an organized fashion such as shown in the sample below.

Table 26: Sample reformat composition (normalized)

% Composition					
Hydrogen	Nitrogen	CO	CH4	CO2	SUM
61.08	6.23	7.01	7.26	18.42	100.0

The total flow rate of the reformat is calculated based on the nitrogen flow rate into the reactor, the concentration of nitrogen in the reformat exiting the reactor, and the assumption that N₂ is inert.

$$\begin{aligned}
 Total\ flow_{(out)} &= N_{2(in)} / N_2\% \\
 &= 0.5\ lpm / 6.23\% \\
 &= 8.02\ lpm
 \end{aligned}
 \tag{50}$$

Flow rates for all gas species (H₂, CO, CH₄, and CO₂) can now also be determined. For example hydrogen flow is calculated as shown below.

$$\begin{aligned}
 H_{2(out)} &= H_2\ \% * Total\ flow_{(out)} \\
 &= 61.08\% * 8.02\ lpm \\
 &= 4.90\ lpm
 \end{aligned}
 \tag{51}$$

It is of particular interest to know how many moles of hydrogen where produced from each mole of oxygen or methane supplied.

$$\begin{aligned}
 \text{mol}(H_{2(out)}) / \text{mol}(CH_{4(in)}) &= H_{2(out)} / CH_{4(in)} & (52) \\
 &= 4.90 \text{ lpm} / 2.50 \text{ lpm} \\
 &= 1.96
 \end{aligned}$$

A-2 Methane conversion

Methane conversion may also be of interest.

$$\begin{aligned}
 CH_4 \text{ conv} &= 1 - (CH_{4(out)} / CH_{4(in)}) & (53) \\
 &= 1 - (CH_4 \% * \text{Total flow}_{(out)} / 2.5) \\
 &= 1 - (7.26\% * 8.02 / 2.5) \\
 &= 0.767 \text{ or } 76.7\%
 \end{aligned}$$

A-3 Carbon Balance

The carbon balance, a continuity of mass calculation, of the reformer system is a good indicator of how accurately system calibration has been completed. The only source of carbon into the reactor during testing was CH₄. Out of the reactor carbon is present in CH₄, CO and CO₂ which make reformat gas. Into the reactor the CH₄ was metered with a MFC, out of the reactor the gas concentrations were determined by the GC. Using the calculations from section 0 the gas flow rates for each gas species were determined allowing the carbon balance to be completed. Below is a sample balance on the system showing the error in the carbon balance as a percentage.

$$\begin{aligned}
Error_{cb} &= \{1 - ((CH_{4(out)} + CO_{(out)} + CO_{2(out)})/CH_{4(in)})\} * 100 & (54) \\
&= \{1 - [(0.286 + 0.577 + 1.569)/2.492]\} * 100 \\
&= [1 - (0.2432/2.492)] * 100 \\
&= 2.56 \% *
\end{aligned}$$

*Sample calculation data taken from run # 17

The error in the carbon balance for the reforming system averaged 2.62% with a standard deviation of 0.82%.of the average.

Appendix B

This section contains information regarding the catalyst used.

B-1 Spinelization

According to a primary reforming manual from SÜD-CHEMIE when a nickel based catalyst on an alumina support is exposed to an oxidizing atmosphere at high temperatures the formation of spinel occurs. Equation (55) describes the reaction of spinel formation.

The spinel formation is basically irreversible at the operating conditions of a reformer and can be identified by decreased effectiveness of the catalyst as well as a typical blue color which the spent catalyst takes on.

B-2 Catalyst properties

Nickel content (wt.%)	9.8
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Sulfur content (wt.%)	4.9
Alumina content (wt.%)	Balance
Surface area (m ² g ⁻¹)	155
Total pore volume (ml g ⁻¹)	0.9
Size of the sphere (mm)	1.75
Average crush strength (N)	25