Hydrogen Production by Supercritical Water Reforming of Bio-oil Components

by

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Abstract

The concept of a hydrogen economy is gaining traction with an ever increasing body of work focusing on all aspects of the overall process which consists of converting a fuel source to hydrogen followed by storage and distribution. Among the several fossil fuel and non-fossil fuel based resources that are being considered for hydrogen production, biomass is considered to be an abundant, CO_2 neutral and ultimately viable alternative. Biomass which comprises a complex chemical structure needs to be processed to convert it into the simple molecule that is $H_{2.}$ One technique is to treat the biomass hydrothermally with rapid heating to produce a liquid called Bio-oil. There are several issues in directly using the bio-oil as a fuel; the high oxygen content implies lower energy intensity and furthermore, it is not stable over time and degrades into a viscous mixture that would make its application as a fuel difficult. One solution to circumvent this issue is to convert the variety of oxygenated compounds present to hydrogen by the reforming reaction. Carrying out the reforming reaction in the supercritical water phase allows for complete miscibility of gases and provides a homogenous reaction medium to carry out the reaction with the additional advantages of enhanced mass and heat transfer. The sheer number of compounds (typically over 300) present in bio-oil significantly increases the complexity of the reforming process.

Acetic acid is thought of as a model oxygenate of bio-oil. Therefore, supercritical water reforming of acetic acid is examined as a first step in the overall goal of converting crude bio-oil to H_2. AspenPlus© software was used to carry out a Gibb's free energy minimization to determine the effect of different thermodynamic conditions on the equilibrium composition of product gas obtained in the process. The parametric effect of reaction temperature (400 – 900^{o}C) and feed concentration (Steam to carbon mole ratio from 1:1 to 9:1) on the selectivity and yield of different gases was examined. It was found that temperatures greater than 700 ^{o}C and steam to carbon ratio in excess of 6:1 gave high hydrogen yield. It was also found that no graphitic coke formation was observed at temperatures > 500 ^{o}C when the steam to carbon ratio was 6 or higher. Thermal decomposition of acetic acid (given by a feed of pure acetic acid with no water entering the reactor) resulted in formation of graphitic carbon in the reactor even at temperatures as high as 900^{o}C.

Following the acetic acid study, thermodynamic analysis of the supercritical water reforming of a synthetic bio-oil mixture to simulate the aqueous phase of bio-oil compound was performed. Since the aqueous phase typically consists of organic acids, ketones, aldehydes and alcohols this study focused on model compound mixture containing methanol, acetic acid, acetaldehyde and acetol. Here again, the non-stoichiometric Gibb's free energy minimization method using the Peng-Robinson equation of state with Boston-Mathias mixing rule was used to determine the effect of temperature (500- 900 ^{o}C) and steam to carbon ratio (1:1 to 9:1) on product gas composition.

In-situ CO_2 removal leads to an increase in equilibrium H_2 yields during reforming operation which can be explained using the Le-Chatelier principle. One technique of CO_2 removal is the use of solid sorbents such as minerals of calcium and magnesium. Carbonation of magnesium silicates, called mineral carbonation, is a useful method for CO_2 sequestration due to the stable carbonate formation and the abundance of Mg-based minerals. The kinetics of direct carbonation of such minerals is very poor with reaction rates in the order of 1000's of years at standard temperature and pressures. Therefore the magnesium silicate must be activated either physically by the action of steam, by increasing the temperature or by chemically treating with strong acids to form $Mg(OH)_2$ which has a higher reactivity to CO_2 compared to other Mg-based compounds. In this work, the effect of supercritical water on the pore structure and morphology of talc is investigated. BET surface area and pore volume were obtained following activation under supercritical water at various temperatures and reaction times. The supercritical water reforming of methanol in a fixed bed packed with only sorbent and no catalyst was studied. Plugging of the reactor due to the fine powdery nature of $Mg(OH)_2$ was observed. This was overcome by loading the reactor with a mixture of $Mg(OH)_2$ and $CaCO_3$. It was found that the loading of sorbent was too low to detect the effect of in-situ CO_2 removal.

The catalytic conversion of glycerol to hydrogen was studied for two different catalyst support systems, 5% Ru/ZrO_2 and 10% Ni/TiO_2 was studied experimentally. The effect of reaction temperature and residence time was investigated and it was found that lower residence time gave higher hydrogen yield and reduced methane concentration in the product gas. Additionally, 10% Ni/TiO_2 catalyst was able to gasify close to 36 wt% of glycerol at temperatures of 600 ^{o}C and 650 ^{o}C with no reactor plugging.

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First and foremost, I would like to thank my graduate advisor, Dr. Ram B. Gupta for giving me the opportunity and providing the funding to work in his laboratory. I have gained valuable experience in the field of energy and environmental research and hope to use it to contribute to this field in some way or the other. Apart from his capacity as my advisor, he has also rekindled my love of thermodynamics due to my experience in his graduate thermodynamics class. His ability to treat difficult concepts with simple and memorable analogies is a quality I always try to emulate.

I thank my lab mates Shaima Nahreen, Courtney Ober and Hema Ramsurn for their friendship and technical advice. I would also like to thank Adam Byrd for his mentorship when I was first starting my research at Auburn.

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List of Abbreviations

BTU – British Thermal Unit

EJ – Exajoule

EOS – Equation of State

GHSV – Gas Hourly Space Velocity

PR – Peng-Robinson

PSRK – Predictive Soave-Redlich-Kwang

SR – Steam Reforming

SCWR – Supercritical Water Reforming

TGA – Thermo-Gravimetric Analysis

XPS – X-Ray Photoelectron Spectroscopy

1. Introduction

1.1 Motivation

The ever increasing population of the world represents a constantly increasing energy demand. The limited availability of fossil fuel based resources has led researchers to believe that biomass and bio-based feedstock is one possible solution for the future. There are two schools of thought on the utilization of biomass and its ultimate use as an energy fuel: one is conversion to gasoline- like bio-fuels with and the other is conversion to $H_{2.}$ Hydrogen is considered to be a simple and clean form of energy[reference 1,2,3,4]. Although there is considerable rhetoric surrounding the use of hydrogen as a fuel, there are many proponents of a so-called "H_2 economy" wherein a large infrastructure of storage, distribution and use would be setup in the country. Since several other feedstock (bio-based and fossil-fuel based) can be converted to H_2 as well it represents a kind of lowest common denominator for energy use in the future.

There are several pathways in the overall scheme of converting biomass to H_2 which include logistical issues of transport, technical difficulties in maximizing yields and final transportation and storage steps. In this work, the pathway considered is shown in Figure 1 below. Apart from the overall goal of converting biomass to hydrogen, each of the steps shown in the schematic shown in Figure 1 can be performed in myriad of ways with a wealth of literature behind each step. Furthermore, the additional advantage of using biomass is its inherent CO2 neutral nature. There has been increasing concern over greenhouse gas emissions and the concomitant global climate change associated with it. It is common knowledge among researchers that there exist several techno-economic challenges which need to be addressed before biomass energy based technology can be competitive with the mature and competitive technologies using fossil-fuel based resources.

Figure 1: Pathway of converting biomass to H_2 considered in this work

1.2 Objectives

- To perform a thermodynamic study on the supercritical water reforming of acetic acid and determine the optimal conditions of operation for maximizing hydrogen yield.
- To carry out a thermodynamic study on the supercritical water reforming of simulated bio-oil containing a mixture of methanol, acetaldehyde, acetic acid and acetol which are present in bio-oil and are representative of a class of several compounds.
- To perform an experimental study on the supercritical water reforming of glycerol over Ni and Ru based catalysts
- To investigate the activation of magnesium silicates in supercritical water conditions and characterize changes in pore morphology using BET surface area, pore size and pore volume measurements

2. Background and state of the art

2.1 Energy demands for the future and the "H_2 Economy"

As the population of the world increases, the concomitant increase in energy demand must be met with innovative strategies that are not dependent on fossil fuel reserves as the latter represents a finite and dwindling resource. According to the Annual Energy Outlook (EIA)[1], the contribution of non-fossil fuel based energy sources to the total supply is much lower when compared to conventional sources like petroleum, coal and natural gas. Of the total energy supply of 94.6 quadrillion BTU to the USA, almost 83% of the supply was met by fossil fuel sources while renewable sources which include solar, wind and biomass represented only 8% of the total energy supply. Recent discoveries of large amounts of natural gas in shale and gas hydrate deposits[2-4] are promising but the diffuse nature of the reserves and the high cost in extracting natural gas might prove to be prohibitively high. Furthermore, greenhouse gas emission during the processing of fossil fuel is a major concern. Among the renewable sources of energy, biomass is a promising candidate due to the CO2 neutral nature of the energy source and relative abundance. Therefore it is clear that investigating clean and renewable sources of energy is crucial to dealing with the energy crisis that is looming large.

Hydrogen has been touted as an important medium of providing energy for several reasons; it is a clean fuel and provides no GHG emissions at the point of use[4]. Furthermore, it represents a sustainable common denominator to which different fuel sources be it fossil or non-fossil fuel based can be converted to for easy distribution. This is the concept of a "Hydrogen Economy" wherein a large infrastructure is constructed for convenient supply across the nation[6]. The goal is to be able to provide a cost effective and sustainable energy source via the use of hydrogen as the primary fuel by encompassing all fuel sources. This broad aim can be visualized in Fig 1.1. Of interest is the case of biomass to H_2 which represents the case of net neutral CO_2 emission process. If conventional CO_2 separation techniques are applied to biomass, this implies an additional advantage of a CO_2 negative process. It must be mentioned here that there is already a vast amount of H_2 that is produced annually for purposes other than energy; a large fraction of H2 produced is used in ammonia production (49%) and in the petroleum and petrochemical industry for refining and upgrading purposes(37%). [7-9]

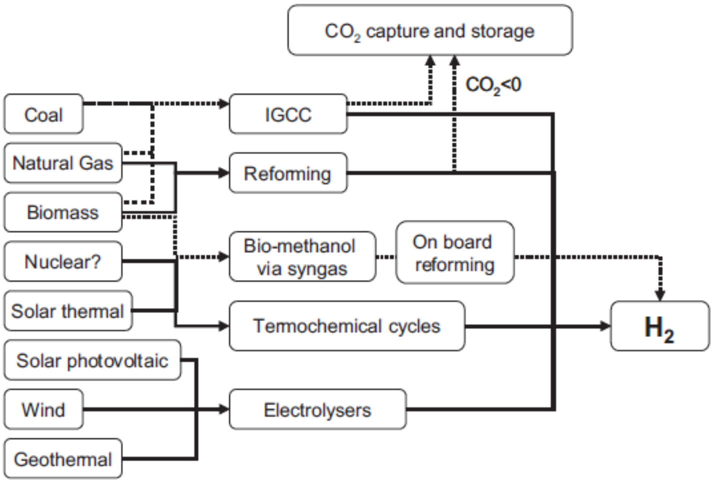

Figure 2.1 Hydrogen Production Network with both fossil fuel and non-fossil fuel resources[5]

2.2 Conversion of Biomass to Hydrogen

The sustainable production of H_2 and the net zero CO_2 emission during conversion is one of the attractive aspects of the use of biomass. Ligno-cellulosic biomass which will be referred to as biomass in this document, consists of three major components i. cellulose ii. Hemicelluloses and iii. lignin. Cellulose is a linear polymer which consist of beta 1, 4 linked D – glucose monomer units while hemicelluloses is a mixture of different mono-saccharides such as glucose, mannose and xylose. Lignin consists of aromatic polymers which form an oligomeric structure that forms a complex matrix [6]. The conversion of biomass to hydrogen can proceed in two routes namely biological and thermochemical. Biological methods utilize anaerobic bacteria to digest and/or ferment the biomass to produce a gas that can be further treated to produce hydrogen whereas thermochemical routes such as gasification and pyrolysis utilize higher temperatures and pressures to effect the conversion to H_2.[15]

2.3 Supercritical Water Background and Properties

There is a marked difference in the physical properties of water at ambient conditions (25°C, 1 atm) and at conditions of high temperature and pressure, most especially above the critical point of water. At temperatures of above 374 ^{o}C and pressure above 22 MPa, water can be said to exist in its supercritical phase.

Above the critical point, there is a drastic change in the physical constants such as dielectric constant, density and ionic product. For instance, the ionic product of supercritical water shows a large increase as compared to ambient water. Additionally, the dielectric constant decreases significantly. The ramifications of such a decrease results in a decreased hydrogen bonding network which results in supercritical water having a non-polar solvent nature - almost comparable to organic solvents such as hexane at higher temperatures. Supercritical water also exhibits enhanced heat and mass transfer properties which have significant advantages in catalyzed reactor set-ups. Apart from these properties, water also undergoes changes in viscosity, density which can be tuned by varying the temperature and pressure above the critical point. A summary of these physical properties of water are presented graphically in Fig. 1.2 at 24 MPa.

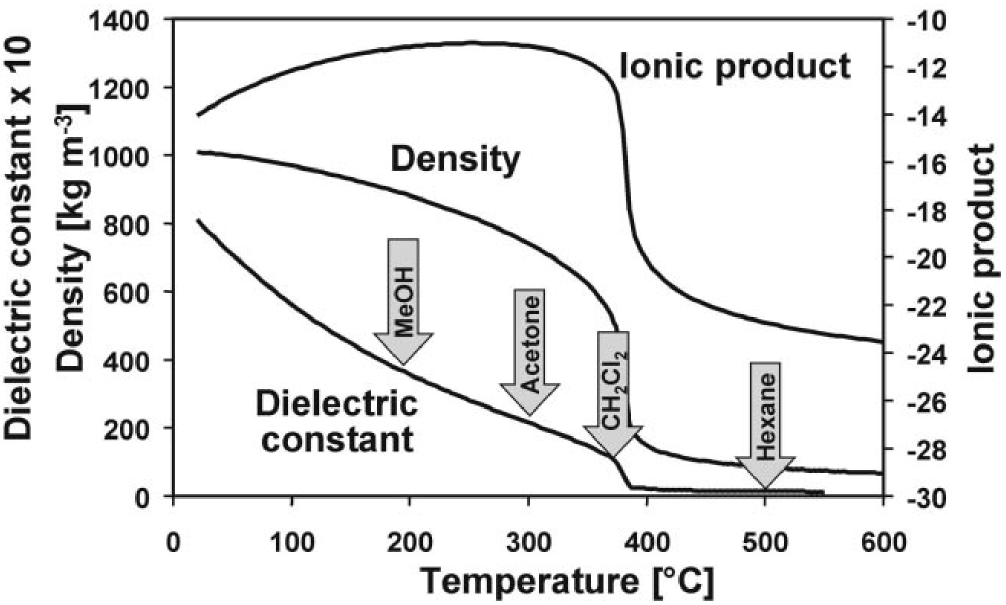

Figure 2.2: Physical properties of water at 24 MPa[14]

2.4 Reactions occurring during reforming of a carbonaceous feedstock

Steam reforming

$$C_mH_n + mH_2O = mCO + (m + \tfrac{1}{2}n)H_2 \quad \Delta H = \text{ endothermic, hydrocarbon dependent} \tag{2.1}$$

$$CH_4 + H_2O = 3H_2 + CO \quad \Delta H = +205 \text{ kJ mol}^{-1} \tag{2.2}$$

Partial oxidation

$$C_mH_n + \tfrac{1}{2}O_2 = mCO + \tfrac{1}{2}H_2 \quad \Delta H = \text{ exothermic, hydrocarbon dependent} \tag{2.3}$$

$$CH_4 + \tfrac{1}{2}O_2 = CO + 2H_2 \quad \Delta H = -35.6 \text{ kJ mol}^{-1} \tag{2.4}$$

Autothermal reforming

$$C_mH_n + \tfrac{1}{2}mH_2O + \tfrac{1}{4}mO_2 = mCO + (\tfrac{1}{2}m + \tfrac{1}{2}n)H_{2,} \quad \Delta H = 0 \tag{2.5}$$

Water-gas shift

$$CO + H_2O = CO_2 + H_2 \ \Delta H = -41.1 \text{ kJ mol}^{-1} \quad (2.6)$$

Dry reforming

$$CH_4 + CO_2 = 2CO + 2H_2 \ \ \Delta H = +247.3 \text{ kJ mol}^{-1} \quad (2.7)$$

Coke formation

$$C_mH_n = aC + C_{m-a}H_{n-2a} + aH_2 \quad (2.8)$$

$$2CO = C + CO_2 \ \ \Delta H = +172.4 \text{ kJ mol}^{-1} \quad (2.9)$$

$$CO + H_2 = C + H_2O \ \ \Delta H = -130 \text{ kJ mol}^{-1} \quad (2.10)$$

CO oxidation

$$CO + \frac{1}{2} O_2 = CO_2 \ \ \Delta H = -283 \text{ kJ mol}^{-1} \quad (2.11)$$

H_2 oxidation

$$H_2 + \frac{1}{2}O_2 = H_2O \ \ \Delta H = -242 \text{ kJ mol}^{-1} \quad (2.12)$$

Chapter 3 contains a review of thermodynamic properties and methods used in the non-stoichiometric Gibbs free energy minimization which is used in determining the equilibrium composition of the products in a given process

Chapter 4 contains the thermodynamic study of acetic acid, an important model compound in the aqueous phase of bio-oil. The effect of the reaction temperature and concentration of acetic acid in feed was investigated by examining the equilibrium composition of the product stream. AspenPlus software was used to carry out the Gibbs free minimization of the product components using the R-Gibbs module and the PR-BM equation of state.

Chapter 5 contains the thermodynamic study of a synthetic bio-oil which consists of a mixture of model compounds namely acetic acid, methanol, acetol and acetaldehyde. This mixture is representative of the aqueous phase bio-oil obtained by extracting the water soluble components from fast-pyrolysis of switchgrass by water addition. Similar to the previous chapter, the parametric effects of temperature and composition and coking was studied.

Chapter 6 contains the results from the supercritical water activation of talc in order to make the Mg more active towards carbonation. The main aim was to examine the effect of the reaction medium on the surface area and pore volume of talc. Supercritical water reforming of methanol in a fixed bed reactor packed with activated talc was performed. It was found that the loading of talc was not sufficient for a noticeable decrease in CO_2 concentration and consequent H_2 yield.

Chapter 7 contains the results from the supercritical water reforming of glycerol over two different catalyst/support systems. Ni over TiO2 and Ru over ZrO2 were studied and the effect of reaction temperature and residence time on the product gas composition and the overall hydrogen yield was determined.

Chapter 8 contains future work that can be performed to extend the work presented in this thesis.

2.5 References

1 http://www.eia.gov/neic/speeches/newell_12162010.pdf, Annual Energy Reviews, 2009

2 Barreto, L., A. Makihira, et al. (2003). "The hydrogen economy in the 21st century: a sustainable development scenario." International Journal of Hydrogen Energy **28**(3): 267-284.

3 Sloan, E. D. and C. A. Koh (2008). Clathrate hydrates of natural gases, CRC.

4 Kvenvolden, K. A. (1988). "Methane hydrate--A major reservoir of carbon in the shallow geosphere?" Chemical Geology **71**(1-3): 41-51.

5 Marbán, G. and T. Valdés-Solís (2007). "Towards the hydrogen economy?" International Journal of Hydrogen Energy **32**(12): 1625-1637.

6 Gupta, R. B. and A. Demirbaş (2010). Gasoline, diesel, and ethanol biofuels from grasses and plants, Cambridge Univ Press

7 Navarro, R. M. P., M.A.; Fierro, J.L.G., Hydrogen Production Reactions from Carbon Feedstocks: Fossil Fuels and Biomass. *Chemical Reviews* **2007,** 107, 3952-3991.

8 Lin, S.-Y. S., Yoshizo; Hatano, Hiroyuki; Harada, Michaiki, Hydrogen Production from Hydrocarbon by Integration of Water-Carbon Reaction and Carbon Dioxide Removal (HyPr-RING Method). *Energy and Fuels* **2001,** 15, 339-343.

9 Bridgwater, A. V., Renewable fuels and chemicals by thermal processing of biomass. *Chemical Engineering Journal* **2003,** 91, 87-201.

10 Klass, D. L., *Biomass for Renewable Energy; Fuels and Chemicals*. Academic Press: San Diego, CA, 1998.

11 Yu, D. A., M.; Antal Jr., M.J., Hydrogen Production by Steam Reforming Glucose in Supercritical Water. *Energy and Fuels* **1993,** 7, 574-577.

12 Savage, P. E., Organic Chemical Reactions in Supercritical Water. *Chemical Reviews* **1999,** 99, 603-622.

13 Savage, P. E. D., J.B.; Yu, J., Recent advances in catalytic oxidation in supercritical water. *Combustion Science and Technology* **2006,** 178, 443-465.

14 Kritzer and Dinjus, Chemical Engineering Journal (2001), 83(3), 207-214

15 Thangalazhy, Gopakumar Suchitra, Bio-oil production through fast pyrolysis and upgrading to “green” transportation fuels, PhD thesis, Auburn University, 2012

3. Thermodynamic Simulation of Supercritical Water Reforming: Review

3.1 Process Modeling

Simulation models can determine and closely approximate performance of different unit operations and unit processes. Additionally, energetic bottlenecks in the process and theoretical ceiling of a process can be determined quickly and accurately without need to carry out several additional experiments. Although, it must be emphasized that there is a definite place and value for experimental work, the advantages in determining feasibility of processes make simulation software and models a powerful resource.

Simulations are mathematical models that determine elemental material balances and energy balances. Based on these balances, the effect of parameters such as temperature, pressure and concentration during a given process can be ascertained either in steady state, equilibrium conditions or unsteady state scenarios. Most simulation setups are first represented by a process flow sheet similar to a process flow diagram representing a flow of data from one block (which may be a unit operation or process or a piece of equipment) as opposed to a flow of actual chemical streams. Additionally, various unit operations and their design specifications can be specified such as heat exchangers, phase separators, distillation columns and so on.

The most important outcome of running simulations is to not only obtain theoretical limitations, but to also test the effect of different process variables and their effect on the overall outcome of the process. This reduces the need for several time intensive experiments. Apart from optimizing the overall process, each individual unit operation can be looked at separately, eliminating and correcting bottlenecks in the process. Therefore, the use of process modeling and simulations represents a good starting point for a thorough analysis of a process and a process design.

3.2 Objectives

There are several parameters that are concurrently affecting hydrogen production and yield in the in the reforming process. The objectives are:

- Discussion of thermodynamic method used in simulating the process in AspenPlus ©
- Determine equation of state that can be used to accurately predict the supercritical water state
- Using EOS to predict multi-component fugacity and perform Gibbs Free energy minimization
- Determine product composition, hydrogen yields and parametric effects of temperature, pressure and concentration

3.3 Modeling with Aspen Plus © and simulating the supercritical state of water

AspenPlus © is a commercial, process simulation software wherein large and small scale reformation processes can be simulated. AspenPlus considers a gaseous behavior for the stream in supercritical conditions and the properties of the fluid are referred to the liquid state at lower temperatures, therefore, the results provided by different thermodynamic methods need to be checked where the deviation of thermodynamic properties such as enthalpy and entropy are minimal for the liquid and vapor state [1] . The second aspect of modeling the supercritical state is the use of suitable equation of state to describe the supercritical phase. Furthermore, Gutierrez et al. who have published several relevant papers in thermodynamic simulation of supercritical water properties claim that determining properties of supercritical fluids is better obtained through fugacity calculation from EOS instead of activity coefficient models where different phases are compared. This is corroborated by Prausnitz [2] who mentions that multi-component, multi-phase systems are “most conveniently expressed in terms of fugacities”. However, the most significant step is to be able to relate fugacity to the parameters under consideration namely temperature, pressure and concentration. The expression given below is one example of relating measurable variables or in this case, input variables, to the fugacity values. This is best done by the use of an accurate equation of state.

$$d\ln f i = \frac{\partial \mathrm{n} f i}{\partial \mathrm{T}} dT\,|P,x + \frac{\partial \mathrm{n} f i}{\partial \mathrm{P}} dP|T,x + \sum_{j=1}^{m-1}\left(\frac{\partial \mathrm{n} f i}{\partial \mathrm{xj}} dxj|T,P,xk\right)$$

Where f_i = fugacity of component i

m = number of components

x_k = mole fraction of component k

There are several thermodynamic methods that can be chosen for the fugacity calculation. In the modeling of supercritical water, the predictive Suave Redlich Kwong and Peng-Robinson equation of state was shown [3, 4] to have minimum deviation when comparing the enthalpies at supercritical and sub-critical conditions at different temperatures and pressures.

3.4 Methodology for simulation and thermodynamic analysis

The equilibrium composition of the gases can be determined by a non-stoichiometric method which becomes especially useful in the case where there are several components present in the system, which is typical of reforming processes. AspenPlus has a built in Gibbs free energy minimization module which takes the user input equation of state, calculates the fugacities of the components, and iteratively calculates the condition where the Gibbs free energy of the multi-component system is minimized. Furthermore, the non-stoichiometric nature obviates the entry of all possible reactions (and their molar extents) that may take place.

In the supercritical water reforming of acetic acid, several equations of state were tested and compared. Although the Peng-Robinson and Redlich Kwong Suave EOS take into account inter molecular interaction effects, it has been suggested to incorporate more robust mixing rules or α function to obtain more accurate results for equilibrium compositions. Given below are the results of the comparison between several EOS from Withag et al.[5] From the comparison, we see that between the two EOS, the PR-BM tend to consistently over predict the H_2 concentration but the difference in mole% did not exceed 2% which decreased at higher temperatures. Based on the above results, the Peng-Robinson (PR) equation of state with Boston-Mathias mixing alpha-function has been used.

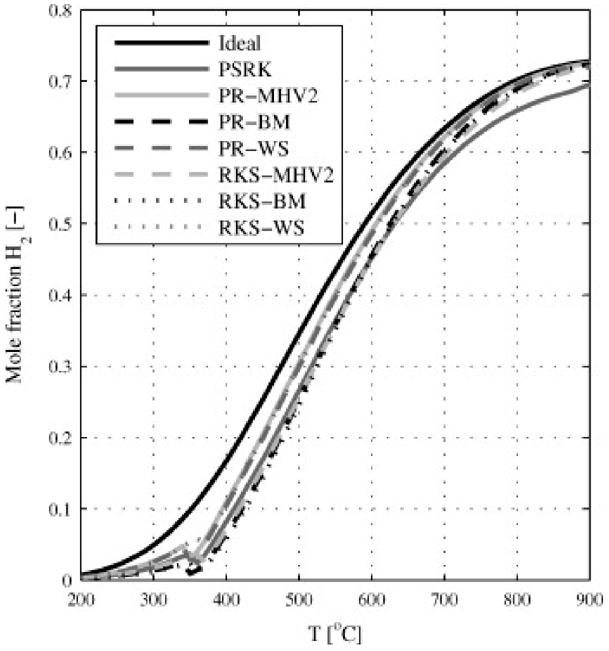

Fig 3.1 Comparison of effect of T on H_2 mole fraction for several property methods [5]

In the R-Gibbs module, all the possible products are defined and considered during the Gibb's free energy minimization. This option removes the necessity of specifying reaction stoichiometry and becomes especially useful in the scenario where a large number of reactions are taking place concurrently such as in the reforming operation where the reforming, methanation, water-gas shift and coking reaction all take place simultaneously. Apart from the compounds in the input stream, components included hydrogen, carbon monoxide, carbon dioxide, methane, ethylene and graphitic carbon (solid). By varying the input conditions of temperature and feed concentration, a picture of the parametric effect on gas composition and yield is obtained. It is important to note that kinetics of reforming also play an important role in the overall reforming operation which cannot be simulated in AspenPlus©. However, the thermodynamic conditions wherein minimal coke is formed can be determined without resorting to a kinetic study.

3.5 Process Setup

The schematic of the overall process simulated using AspenPlus© is shown in Fig 2.2. The feedstock mixes with water in the mixer. The steam to carbon ratio is varied by changing the water flowrate entering the mixer. The aqueous mixture of water and feedstock is then pumped to pressures 22.1 MPa and higher. The compressed stream is then heated using the heat exchanger module in AspenPlus©. The outlet temperature depends on the reaction temperature under study which can range from 400 to 1000^{o}C. The lower end of the temperature was taken to be 400 ^{o}C because the Tc for water is 374.1 ^{o}C. The hot, compressed mixture of acetic acid and water enters the R-Gibbs reactor where the reaction temperature and pressure are specified and all components are considered as possible products. The equilibrium composition of the reactor leaves in the exit stream depicted as "GibbsOut" in Fig 2.2

The basis of calculation is that at chemical equilibrium, the Gibbs Energy of reaction becomes zero. In other words, at equilibrium, the rate of change of free energy with the extent of the reaction is zero. The simulation continues to iterate when this term is non zero, in essence minimizing the Gibbs free energy of the multi-component system. The minimization problem is a constrained optima problem where the constraint is the conservation of elements (mass balance) at the pre-determined reactor conditions.

A comparison is made between the experimental work by Byrd and Gupta, 2007 [6] and the current work in Fig 2.3

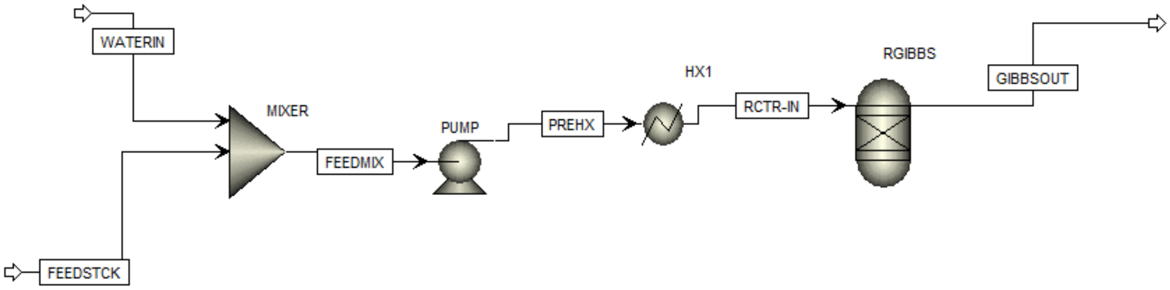

Fig 3.2 AspenPlus Flowsheet used in work

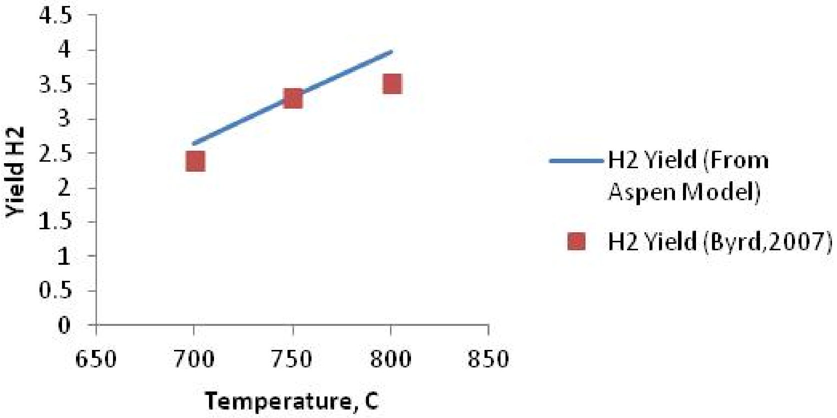

Fig 3.3 Comparison of thermodynamic model with experimental data.

3.6 References

1. Gutiérrez Ortiz, F., et al., *Thermodynamic study of the supercritical water reforming of glycerol.* International Journal of Hydrogen Energy, 2011.
2. Prausnitz, J.M., R.N. Lichtenthaler, and E.G. de Azevedo, *Molecular thermodynamics of fluid-phase equilibria*1998: Prentice Hall.
3. Gutiérrez Ortiz, F., et al., *An energy and exergy analysis of the supercritical water reforming of glycerol for power production.* International Journal of Hydrogen Energy, 2011.
4. Gutiérrez Ortiz, F., P. Ollero, and A. Serrera, *Thermodynamic analysis of the autothermal reforming of glycerol using supercritical water.* International Journal of Hydrogen Energy, 2011.
5. Withag, J.A.M., et al., *System model for gasification of biomass model compounds in supercritical water-a thermodynamic analysis.* The Journal of Supercritical Fluids, 2011.
6. Byrd, Adam. J et al. , Hydrogen production from ethanol by reforming in supercritical water using Ru/Al2O3 Catalyst, International Journal of Hydrogen Energy, 2007
7. McGlocklin Kristin, Economic analysis of various reforming techniques and fuel sources for hydrogen production, MS thesis, Auburn University, 2006

4. Thermodynamic study of Supercritical Water Reforming of Acetic acid as a bio-oil model compound

4.1 Abstract

Bio-oil that is obtained by the thermo-chemical treatment of biomass consists of a variety of oxygenated compounds that can be converted to hydrogen by supercritical water reforming. The supercritical water phase allows for complete miscibility of gases and provides a homogenous reaction medium to carry out the reforming of bio-oil. However, the presence of a diverse range of compounds in bio-oil significantly increases the complexity of the reforming process. Acetic acid is considered a model oxygenate of bio-oil due to the relatively higher number of organic acid compounds present in bio-oil and also due to the simplicity of structure. Therefore, supercritical water reforming of acetic acid is studied as a first step in the ultimate goal of converting crude bio-oil to H_2. AspenPlus© software was used to perform a Gibb's free energy minimization to determine the effect of different thermodynamic conditions on the equilibrium composition of product gas obtained in the process. The parametric effect of reaction temperature (400 – 1000^{o}C) and feed concentration (Steam to carbon ratio from 1:1 to 9:1) on the selectivity and yield of different gases was examined. It was found that temperatures greater than 700 ^{o}C and steam to carbon ratio in excess of 6:1 gave high hydrogen yield. Furthermore, it was found that no graphitic coke formation was observed at temperatures > 500 ^{o}C when the steam to carbon ratio was 6 or higher. Thermal decomposition of acetic acid resulted in formation of graphitic carbon in the reactor even at high temperatures ~ 900^{o}C. An optimal operational window for maximizing hydrogen yield during the supercritical water reforming of acetic acid and similar organic acids is suggested.

4.2 Introduction

Biomass represents an important renewable source of energy and a sustainable solution for future energy needs due to the availability of biomass reserves and the inherent lower net CO_2 emissions during its use. Hoogwijk et al[3],[4] found that the global energy potential of biomass projected up to 2050 was between 33-1130 EJ/year by considering the land available for biomass growth and productivity of biomass on such land. (1 EJ ~ 1 Quadrillion BTU of energy) However, according to the EIA outlook, 2011[5] the energy consumption projected to 2035 was found to be around 290 Quadrillion BTU. Using the same projected growth rate to 2050 it can be seen that biomass has the capability of partially meeting the energy demands of the future. [6] Furthermore, the total global CO_2 emissions are expected to increase from 13 Billion Metric tons of CO_2 in 2011 to 14.3 Billion Metric tons of CO_2 in 2035. The potential to satisfy the energy needs of the future while maintaining a net neutral CO_2 emission makes a strong case for incorporating bio-based energy resources into the energy infrastructure of the future. However the low energy density and the consequent increased transportation costs require the conversion of biomass to other forms of energy that can be easily stored and distributed. One such energy carrier is hydrogen which has attracted the attention of researchers worldwide as a clean fuel with high energy density. Conversion of biomass to hydrogen also fits in well with the goal of a hydrogen economy where the infrastructure is developed for a network of hydrogen grids that supply energy throughout the country [7, 8]. There are several thermo-chemical routes in which biomass can be converted to hydrogen[9]; in this work the fast pyrolysis of biomass wherein biomass is rapidly heated to produce a liquid called bio-oil is of focus. Current fast pyrolysis technology is significantly advanced and high liquid yields of bio oil (~75wt %) can be currently obtained through this process [10]. The remaining biomass is converted to gas and solids (10-20 wt%).

Bio-oil consists of a large number of oxygenated compounds the composition of which depends on the biomass chosen during pyrolysis. Typically, these oxygenated compounds are acids, ketones, alcohols, aldehydes, phenols, sugars and furans [11]. The high oxygen and water content from fast pyrolysis bio-oil leads to two main disadvantages in its direct use as a fuel; higher oxygen content reduces the heating value of bio-oil as a liquid fuel and high water content leads to an increased viscosity making it unsuitable as a fuel over time. In order to remedy this, it has been suggested to convert the bio oil to hydrogen which can be used as a fuel directly. Another option is to convert bio-oil to synthesis gas (or syngas) from which long chain gasoline-like liquid fuels can be produced via the Fischer Tropsch reaction [4]. The aromatic and carbohydrate derived compounds can be separated by adding water to the crude bio oil[12]. It has been suggested that the aromatic component after separation be used as a cheaper substitute for phenol-formaldehyde resins[13] and therefore the aqueous phase can be reformed to produce hydrogen. Furthermore, reforming of higher carbon containing species such as phenol, furan and sugars such as levoglucosan which are present in crude bio-oil can lead to operational difficulties due to the known formation of coke [14] and coke pre-cursors.

Supercritical water has properties that make it amenable as a homogenous reaction medium in which reforming can be carried out. Some of the relevant properties include lowered dielectric constant and the high ionic product compared to steam. A low dielectric constant reduces the polar nature of water due to less number of hydrogen bonds beyond the critical point. Therefore, supercritical water is completely miscible with organic compounds such as CO, CO_2, CH_4 and H_2 which are the main products of the reforming process. Secondly, a high ionic product gives higher [H+] and [OH-] concentrations in supercritical water which allows supercritical water to act as a catalyst for organic reactions [15]. Finally, operating the reforming process at higher pressures provides H_2 delivery at high pressure which reduces downstream compression costs [16].

4.3 Objective and scope of work

The main objective of this work is to study the conversion of acetic acid to hydrogen via reforming in supercritical water. This forms the first step of study in the overall goal of converting crude bio-oil to hydrogen in a supercritical water medium. This is accomplished by determining the parametric effects of temperature and feed concentration on equilibrium product gas composition and hydrogen yields. From this information an optimal window of operation for carrying out experimental work can be obtained where the kinetic parameters of the process including catalytic aspects, optimal residence time and coke formation can be studied. Thus, the thermodynamic analysis of converting acetic acid to hydrogen by supercritical water reforming provides an ideal set of parameters in which to carry out actual operation and is a first step towards a complete understanding of supercritical water bio-oil reforming.

4.4 Using AspenPlus to generate equilibrium data: Methodology

AspenPlus^{TM} is a simulation tool that can be used to study various facets of process engineering such as chemical and phase equilibrium, process optimization, material and energy balances of different unit operations and processes. The equilibrium composition of the gases in the reforming of bio oil model compounds can be determined by two methods; stoichiometric and non-stoichiometric.[17] In the latter case, the equilibrium composition is determined by minimizing the Gibb's free energy of the process which require only the temperature, pressure and feed concentration of reactants. This is accomplished by using the R-Gibbs reactor configuration found in AspenPlus©. The Gibbs free energy is calculated from the chemical potential which in turn is obtained from the partial fugacity of each component. The fugacity is accurately calculated by choosing the appropriate equation of state (EOS). AspenPlus contains several property methods and in-built mixing rules that can be used to obtain the desired results. The accuracy of the simulation is predicated on the accurate selection of the suitable equation of state. This becomes especially important in this study as the physical properties of water change dramatically beyond the supercritical state as the polar and non-polar interactions of the several components present complicates the calculations. From literature, typical temperature of interest during reforming lies in the 500 – 800 ^{o}C range and S/C ratios are large.

In the R-Gibbs module, all the possible products are defined and considered during the Gibb's free energy minimization. This option obviates specifying reaction stoichiometry and becomes especially useful in the scenario where a large number of reactions are taking place concurrently such as in the reforming operation where the reforming, methanation, water-gas shift and coking reaction can take place. Apart from the compounds in the input stream, components included hydrogen, carbon monoxide, carbon dioxide, methane, ethylene and graphitic carbon (solid). By varying the input conditions of temperature and feed concentration, a picture of the parametric effect on gas composition and yield is obtained. It is important to note that kinetics of reforming also play an important role in the overall reforming operation which cannot be simulated in AspenPlus©. However, the thermodynamic conditions where coke formation can be minimized can be determined.

4.5 Process Setup

The schematic of the overall process simulated using AspenPlus© is shown in Fig 2.2. The feedstock, in this case, acetic acid mixes with water in the mixer. The steam to carbon ratio is varied in these two streams. After exiting the mixer, the aqueous mixture of water and acetic is pumped to supercritical pressures above 22.1 MPa. The compressed stream is then heated using the heat exchanger module in AspenPlus©. The outlet temperature depends on the reaction temperature under study which can range from 400 to 1000^{o}C. The lower end of the temperature was taken to be 400 ^{o}C because the Tc for water is 374.1 ^{o}C. The hot, compressed mixture of acetic acid and water enters the R-Gibbs reactor where the reaction temperature and pressure are specified and all components are considered as possible products. The equilibrium composition of the reactor leaves in the exit stream depicted as “GibbsOut” in Fig 4.1

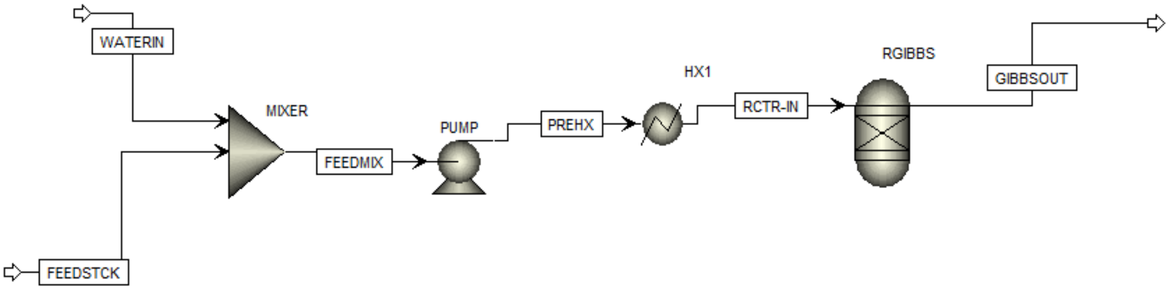

Fig 4.1 AspenPlus Flowsheet

4.6 Acetic Acid Steam Reforming : Results and Discussion:

Acetic acid is present in large amounts in bio oil (~ 12 wt%)[22] and is also regarded as a model refractory compound[23]. Catalytic steam reforming of acetic acid has been studied extensively,[14, 24-29] but there is a dearth in the literature for reforming in supercritical water medium. Oxidation of acetic acid in supercritical water has also been studied but the goal in such cases is to use supercritical water to oxidize refractory compounds such as acetic acid and to use the heat evolved for heating purposes and power generation [30]. The goal in this work is to study the express conversion of acetic acid into hydrogen.

In order to explain the trends in composition and the effect of temperature and S/C ratio, the reactions need to be considered individually [25]. (All the heats of reaction are referred to 25°C or 298 K)

1. Complete Steam Reforming of Acetic Acid (Endothermic)

$$CH_3COOH + 2H_2O \rightarrow 2CO_2 + 4H_2 \quad \Delta H = +134.77\ kJ/mol \qquad (1)$$

2. Water Gas Shift Reaction (Exothermic)

$$CO + H_2O \rightarrow CO_2 + H_2 \quad \Delta H = -41.1\ kJ/mol \qquad (2)$$

3. Methanation (Exothermic)

$$CO + 3H_2 \rightarrow CH_4 + H_2O \qquad (3)$$

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \qquad (4)$$

4. Coking Reactions

4.1 Boudouard reaction (Endothermic)

$2CO \rightarrow C(s) + CO_2 \quad \Delta H = +172.4 \text{ kJ mol}^{-1}$ (5)

4.2 CO Reduction (Exothermic)

$CO + H_2 \rightarrow C + H_2O \quad \Delta H = -130 \text{ kJ mol}^{-1}$ (6)

4.6.1 Effect of Reaction Temperature

The effect of temperature was examined by varying the temperature at fixed conditions of concentration and pressure. Unless otherwise mentioned all results represent reforming at a total reactor pressure of 250 bar. In typical supercritical water reforming, there is an excess of water present in the reactor to allow the reactions to take place in a homogenous medium. In order to illustrate examine the effect of reaction temperature on gas composition a S/C ratio of 9 was chosen which can be seen in Table 4.1 This feed composition was maintained constant.

Feed Data	Mol/hr
Acetic Acid	100
Water	1800
WAFR	18
S/C Ratio	9

Table 4.1 Feed to R-Gibbs reactor (WAFR = Water to Acetic Acid Feed Ratio)

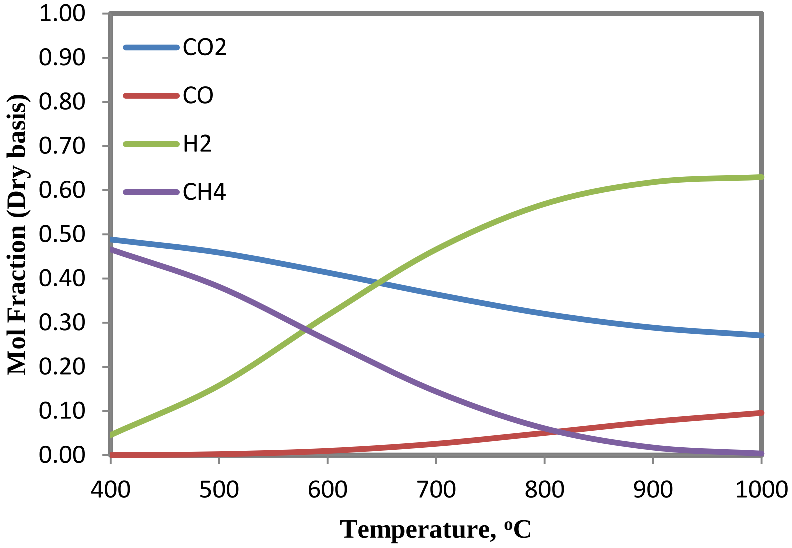

Fig 4.2 Effect of temperature on gas composition (S/C =9)

At the lowest studied temperature of 400 ^oC (slightly above water's Tc of 374.1 ^oC), the acetic acid after reforming gave a product gas consisting almost entirely of CH_4 and $CO_{2.}$ As the temperature was increased, the endothermic reforming reaction (1) starts to become favorable which increased the hydrogen mole fraction in the product gas. Secondly, the exothermic methanation reactions (3,4) start to be thermodynamically unfavorable which explains the monotonously reducing CH_4 mole fraction in the product gas stream as temperature was increased. At 900 ^oC there was negligible CH_4 present in the product stream. Furthermore at 900 ^oC, the H_2 concentration started to level off at a value of around 0.62. However, there was an increasing trend for CO mole fraction at the high temperature range (above 800 ^oC). This can be explained by the combined effect of enhanced endothermic reforming reaction and start-up of reverse water gas shift reaction which is endothermic. The molar flow rate of gases exiting the reformer reactor (in mol/hr) is shown in Fig 4.3

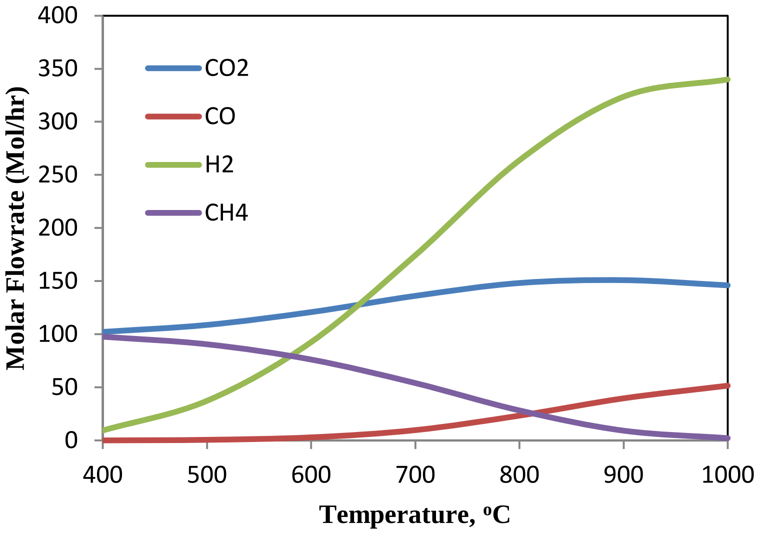

Fig 4.3 Effect of temperature on molar flow rate of gases at outlet

4.6.2 Effect of Steam/Carbon ratio (S/C)

The effect of the concentration (or S/C ratio) on the gas yield is given in the Fig 4.4 (a)-(d). As the S/C ratio was increased, there were varying effects on the different gases considered. In the case of $CO_{2,}$ the feed concentration did not have a significant effect especially at lower temperatures. For instance, at T = 600 ^{o}C, the CO_2 mole fraction in the case of S/C = 1 and S/C = 9 were 0.417 and 0.467 respectively.

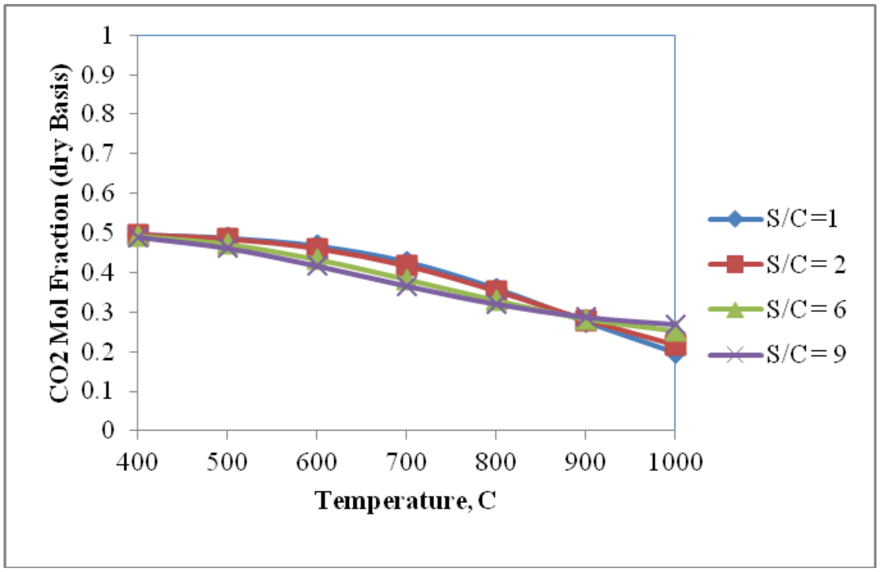

Fig 4.4 (a) Effect of Steam/Carbon ratio on CO2 concentration at equilibrium

However, for the case of CH_4, higher S/C ratios gave low methane concentrations at all the temperatures under consideration (Fig 4.4 (b)). Furthermore, CH_4 content in the product stream decreases as the temperature goes up. This is consistent with the results from the previous section which shows reducing methane concentrations with increasing temperature.

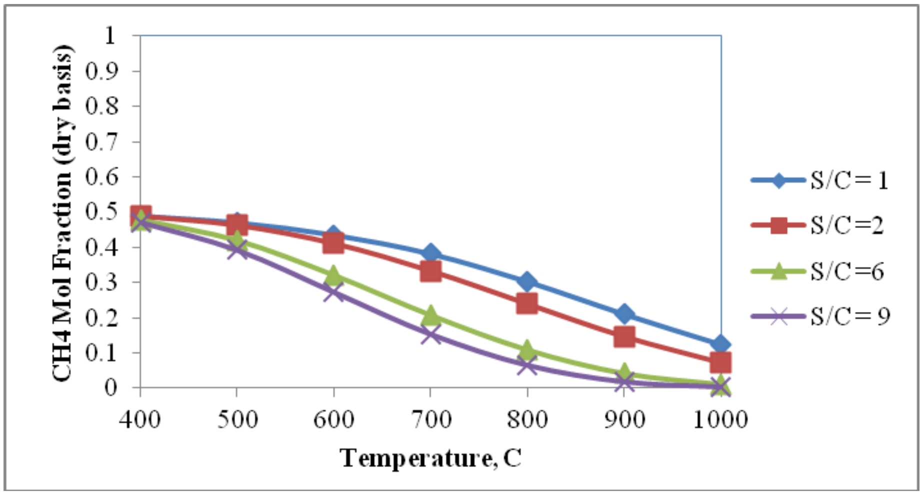

Fig 4.4 (b) Effect of Steam/Carbon ratio on CH_4 concentration at equilibrium

There was no formation of CO at all S/C ratio under consideration until a temperature of 700 ^oC was reached. Above this temperature, it was observed that increasing the water content of the stream reduced the CO formation consistently for all temperatures.

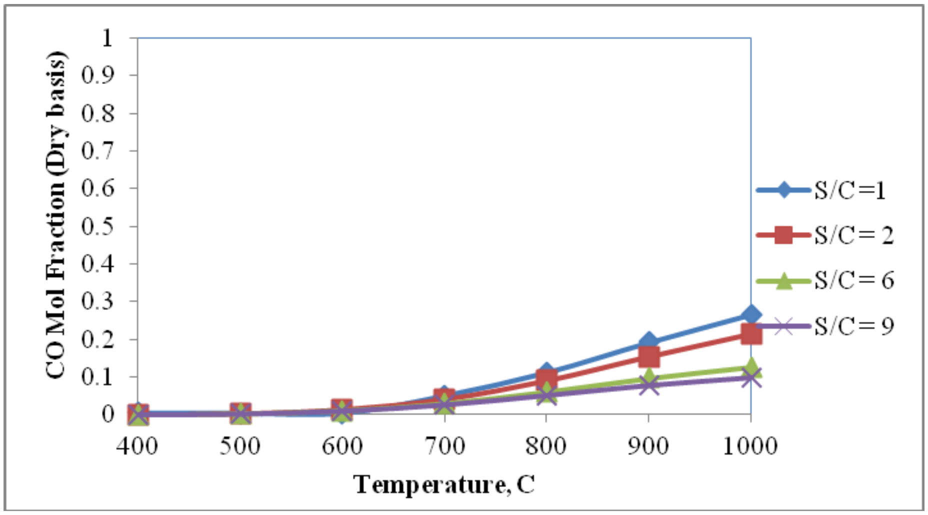

Fig 4.4 (c) Effect of Steam/Carbon ratio on CO concentration at equilibrium

Increasing S/C ratio had a positive effect on the hydrogen concentration which was found to increase monotonously with temperature for all S/C ratios. The H_2 concentration started to plateau at 62% for the case of S/C = 9 at temperatures above 900 ^oC. At the same temperature and S/C = 6:1, the H_2 mole fraction was not significantly lower at 58% mole fraction.

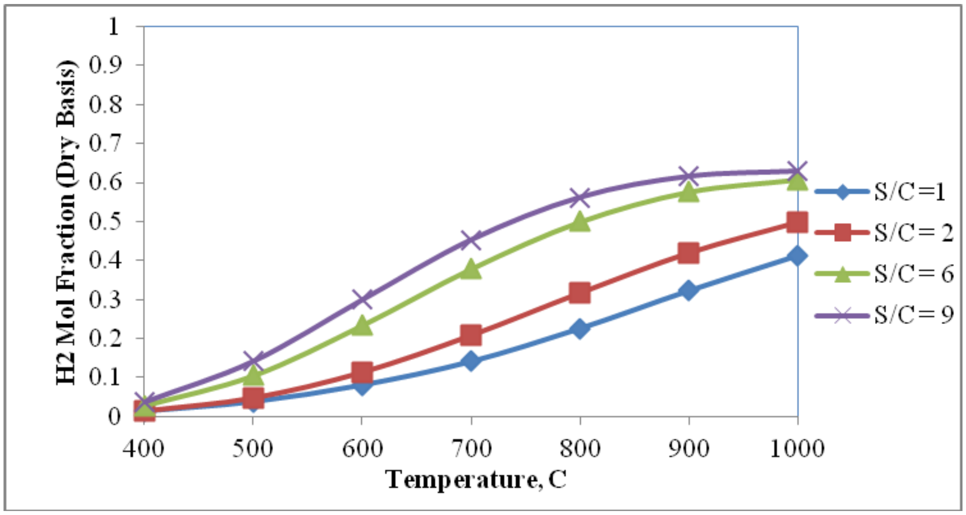

Fig 4.4 (d) Effect of Steam/Carbon ratio on H2 concentration at equilibrium

Typical reforming reaction is expected to be carried out at a maximum of 700 ^{o}C. Therefore, at 250 bar and 700 ^{o}C, the effect of S/C ratio on mole fraction of off gas was determined. The results are shown in Fig 4.5. At this condition, H_2 and CO_2 made up ~ 84% of the exiting moles from the R-Gibbs reactor. There was negligible CO with 15% CH_4 concentration.

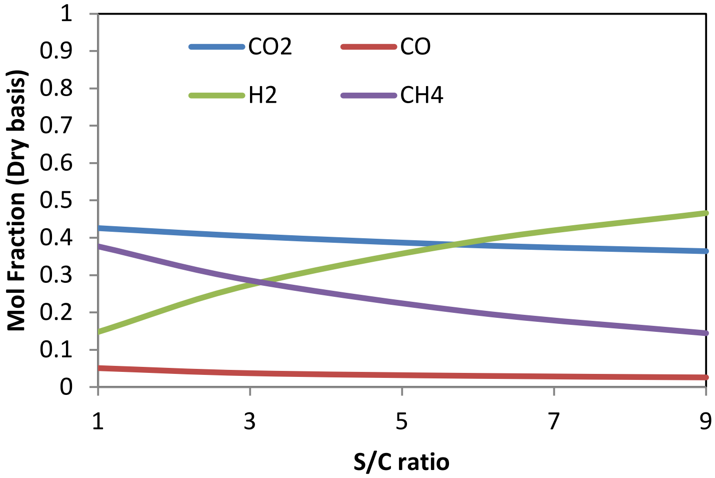

Fig 4.5 Effect of S/C ratio at 700 ^{o}C on gas composition

4.6.3 Thermodynamic prediction of coking

Coking in reforming operation is an important albeit inherently kinetic process. However, one can obtain the thermodynamic conditions that favor coking using the same R-Gibbs reactor setup in AspenPlus© as before which has the capability of predicting graphitic coke formation[29]. Coke occurs in several morphologies; pyrolytic coke, whiskers and gum formation; each of which occur in different scenarios. At low temperatures, gummy carbonaceous deposits can be observed[6]. Carbon can also form in the reactor due to Boudouard reaction (5) and thermal decomposition of acetic acid. Although one cannot determine the morphologies of coke formation using AspenPlus©, the amount of coke formed during thermal decomposition and the parametric effects on solid carbon formation can be determined.

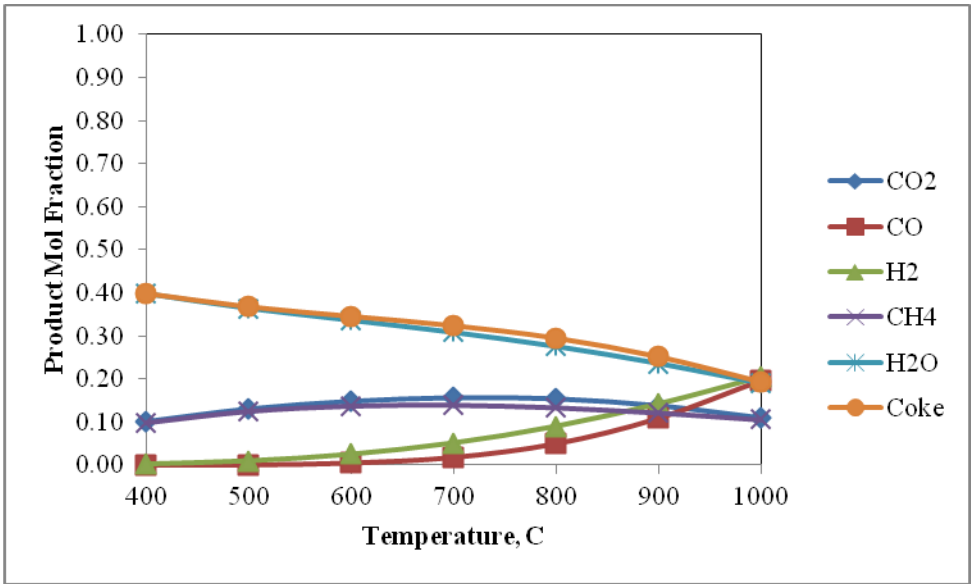

Fig 4.6 Acetic Acid decomposition in R-Gibbs reactor

Fig 4.6 shows the equilibrium composition for the case of acetic acid feed with no water present in feed. Therefore, the product stream represents the concentrations of the products by purely thermal decomposition. It is important to note that irrespective of temperature, acetic acid always showed 100% conversion in the R-Gibbs reactor[31] This can be attributed to the higher Gibbs Free Energy of acetic acid which tends to form CO_2 and H_2O at equilibrium which have lower Gibbs Free Energy. The absence of water in the feed stream showed a significantly reduced concentration of H_2 highlighting the importance of water and its role in the reforming reaction.

There is significant coke formation at lower temperatures which reduced as the temperature was increased. However, even at temperatures as high as 1000 ^{o}C coke was capable of forming highlighting the negative effect of thermal decomposition in reforming operations. When translating this information to experimental study, it implies that when a cold feed of acetic acid (or any other carbonaceous feedstock) is suddenly exposed to a high temperature increase such as the entrance of a reactor, coking can be expected and preheating the feed may prove to be useful in prolonging the inevitable plugging of the reactor. Uniform heating of reactor is also important as cold spots in the reactor could potentially serve as sites for thermal decomposition and hence coking.

When the S/C ratio was varied at different temperatures, it was found that coke formation was reduced and S/C > 3 no coke appears to form even at low temperatures. Therefore the combined effect of temperature and S/C ratio of 1:1, 2:1 and 3:1 was examined. The results are shown in Fig 4.7. At S/C = 1 significant coking was observed even at temperature of 800 ^{o}C. Coking effect showed a reducing trend with increasing S/C ratio. For S/C ratio of 3:1, no coke was seen to form at $T > 500^{o}$C. Similar results were obtained by Lemonidou et al [29]

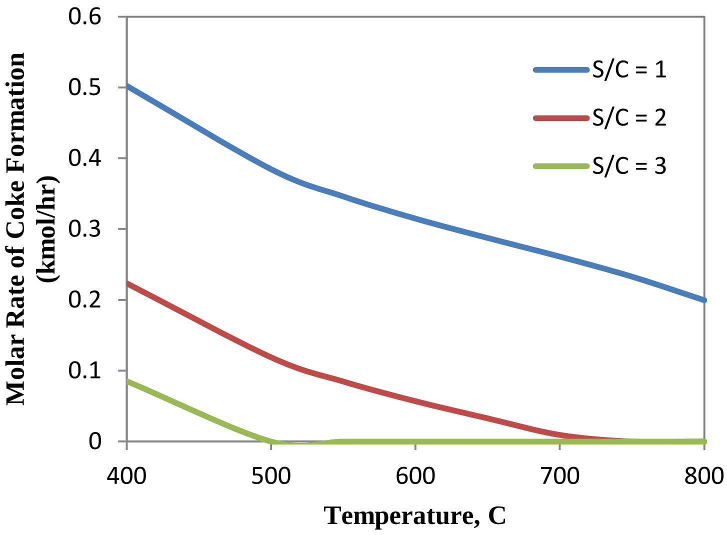

Fig 4.7 Effect of temperature on Coke formation rate at different feed concentration

4.6.4 Effect of Pressure

The critical pressure for water is 221 bar. The physical properties of water are very different between sub- and supercritical states. Therefore to study the effect of pressure, two cases arise; effect of pressure when the range of pressures is below critical pressure and the case where the pressure is above critical pressure. Based on the results from Fig. 4.8 the H_2 concentration drops (from 0.65 at atmospheric pressure to 0.49 at 200 bar) as the pressure is increased until critical pressure was. CO_2 showed an increasing trend with mol fraction increase of 5% from 1 bar to 200 bar.

However at pressures above critical pressure, almost all gas composition was nearly constant showing pressure independence in the supercritical region (Fig 4.9)

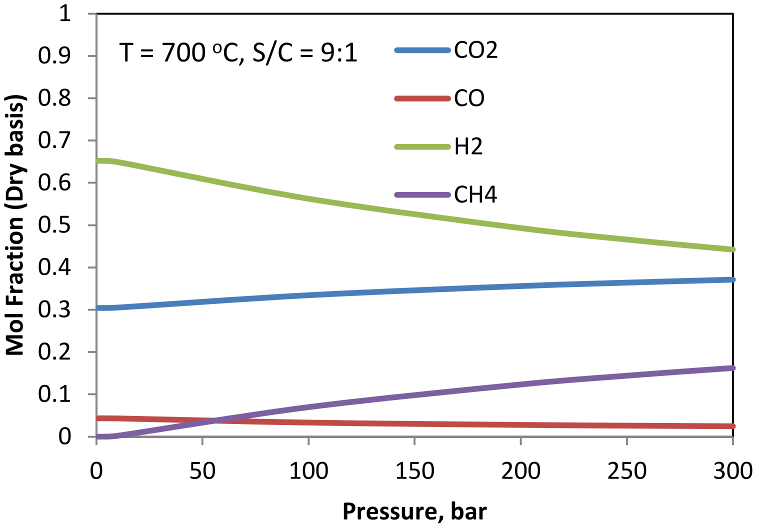

Fig 4.8 Effect of P on gas composition at 700 °C

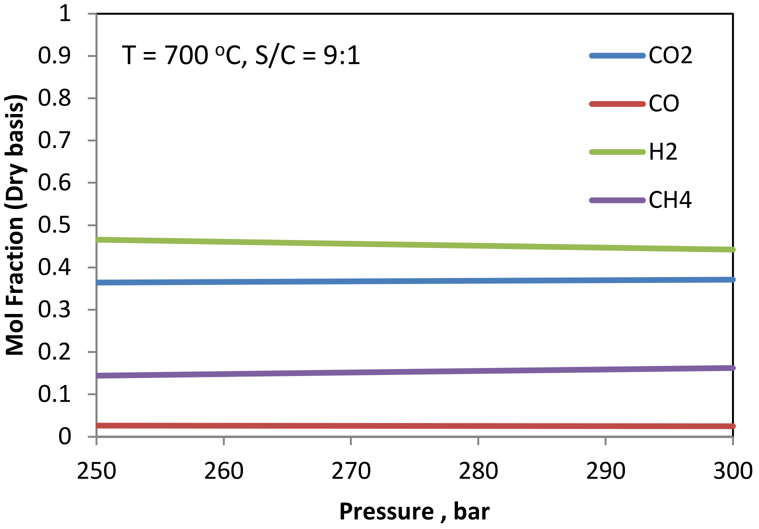

Fig 4.9 Effect of P on gas composition at 700 °C for P > Pc

4.6.5 Parametric effect on product gas selectivity and H_2 yield

The effects of temperature, pressure and feed concentration on H_2 is one of the significant factors in deciding the viability of a process. Based on Eq. (1) the theoretical H_2 yield is 4 moles of H_2 for every mole of acetic acid in the feed. Therefore the H_2 yield can be normalized and defined as

$$\%\ \text{Hydrogen Yield} = \frac{\text{Moles/hr of H2 produced}}{\text{Moles/hr of acetic acid feed x Theo. moles of H2 produced}(=4)}\ \text{x}\ 100$$

The selectivity for a flow reactor is defined as the exit molar flow rate of compound under consideration to the remaining “undesired” products flowing out of the reactor. Therefore the selectivity of CO_2, CO and CH_4 can be defined as

$$\%\ \text{Selectivity of 'x'} = \frac{\text{Moles/hr of x produced}}{\Sigma(\text{Moles/hr of CO, CO2, CH4})}\ \text{x}\ 100$$

where x can be CO, CO_2 or CH_4.

The selectivity of H_2 is defined by normalizing with respect to the reforming ratio. One mole of acetic acid gives 2 moles of CO_2 and 4 moles of H_2 in the product. Therefore, a reforming ratio (RR) or ratio of H_2/CO_2 can be defined, which in the case of acetic acid is 2/4.

$$\%\ \text{Selectivity of H2} = \frac{\text{Moles/hr of H2 produced}}{\Sigma(\text{Moles/hr of CO, CO2, CH4})}\ \text{x}\ \frac{1}{\text{RR}}\text{x}\ 100$$

Based on the above definitions, the effect of P, T and S/C ratio on selectivity is given in Figs 4.10 , 4.11 and 4.12 respectively.

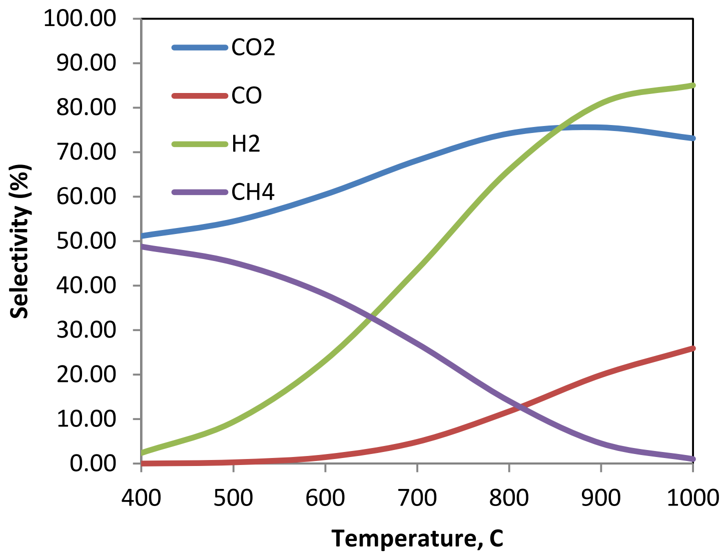

Fig 4.10 Effect of T on selectivity at 250 bar, S/C = 9:1

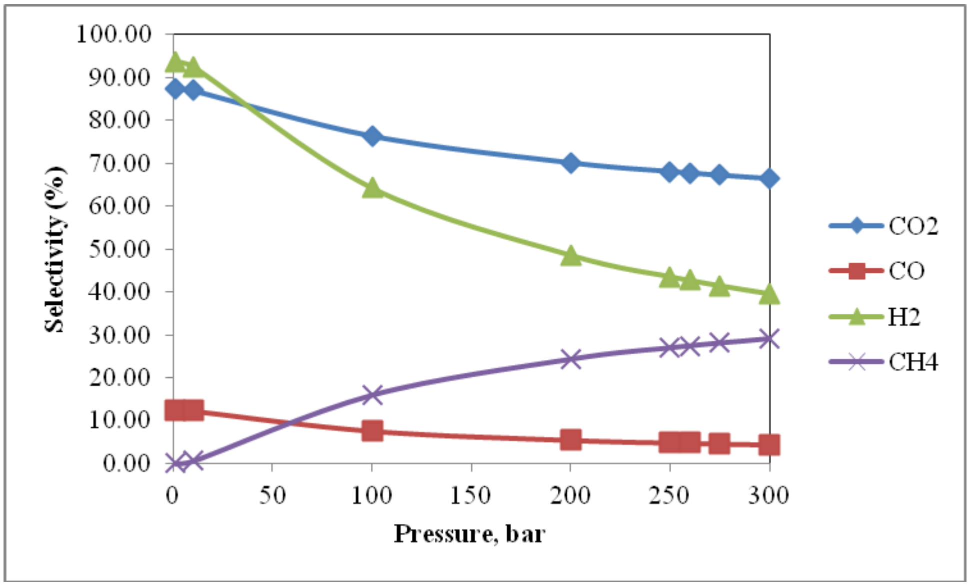

Fig 4.11 Effect of P on selectivity at 700 C, S/C = 9:1

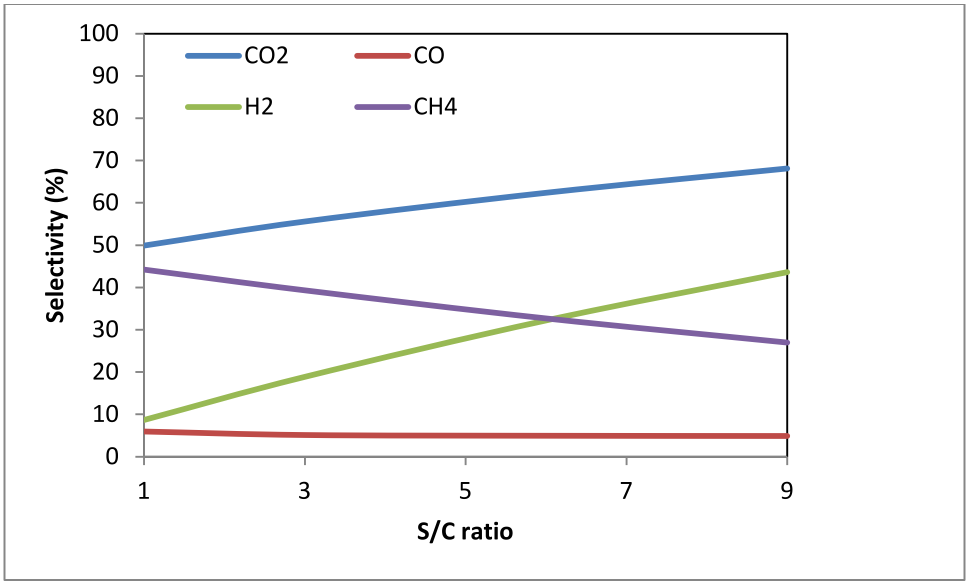

Fig 4.12 Effect of S/C ratio on selectivity at 700 C, 250 bar

From the above graphs we can make the following conclusions; high S/C ratio and temperature improves the selectivity of H_2 and CO_2. However, once above the supercritical pressure, the pressure does not affect H_2 selectivity. Furthermore, an important advantage of performing the reforming at these conditions is that the methane selectivity decreases. Therefore in the overall goal of converting acetic acid to hydrogen, high selectivity phase space can be gleaned. Also important are the H_2 yield and the effect of T, P and S/C ratio which is given in Fig 4.13, 4.14 and 4.15 respectively.

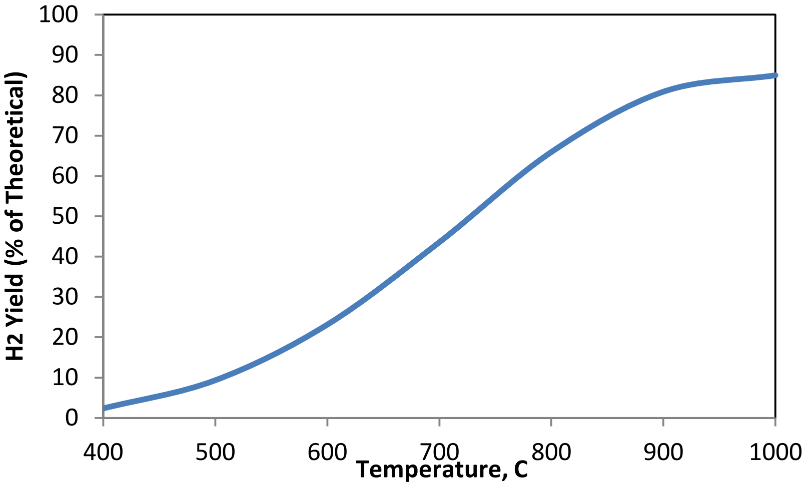

Fig 4.13 Effect of T on H_2 yield at S/C =9:1 and P = 250 bar

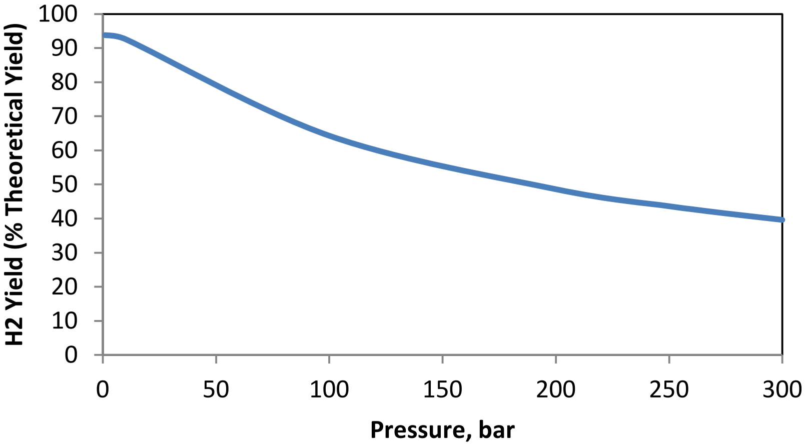

Fig 4.14 Effect of P on H_2 yield at T = 700 ^{o}C and S/C = 9:1

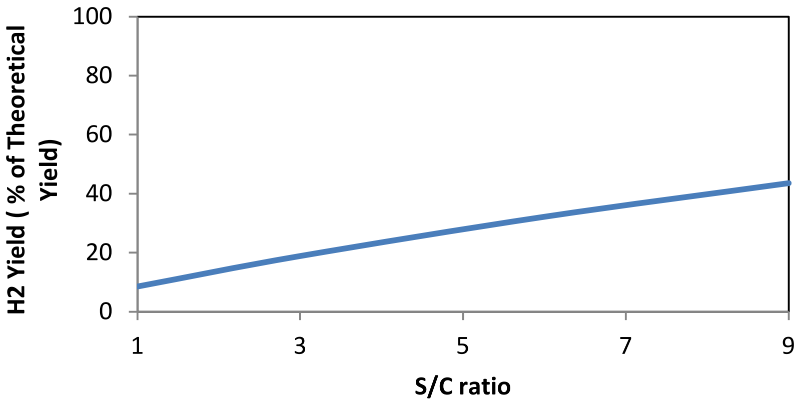

Fig 4.15 Effect of S/C ratio on H_2 yield at T = 700 ^{o}C and P = 250 bar

4.6.6 Optimal operating condition recommendations

From the above analysis, it can be gleaned that in order to maximize hydrogen production and to minimize methane and coke production during reforming, it is important to perform reforming operations at high temperatures and S/C ratio 6 or greater. Although the hydrogen yield is maximized at temperatures greater than 900^{o}C, it is recommended to run the reaction in the region of 700^{o}C. Furthermore, the use of a catalyst will improve hydrogen yield at a lower temperature and improve the overall reaction rate at a temperature lower than 900 ^{o}C. Secondly, the use of supercritical water as a reaction medium typically consists of having a high S/C ratio within the reactor. Given below in Fig 4.16 are the results from one typical scenario of 3.25 wt% feed and S/C ratio 6:1 at temperatures from 400 – 800 ^{o}C. The reason for providing this data is to mirror typical experimental conditions in the lab which will be performed to corroborate the present study.

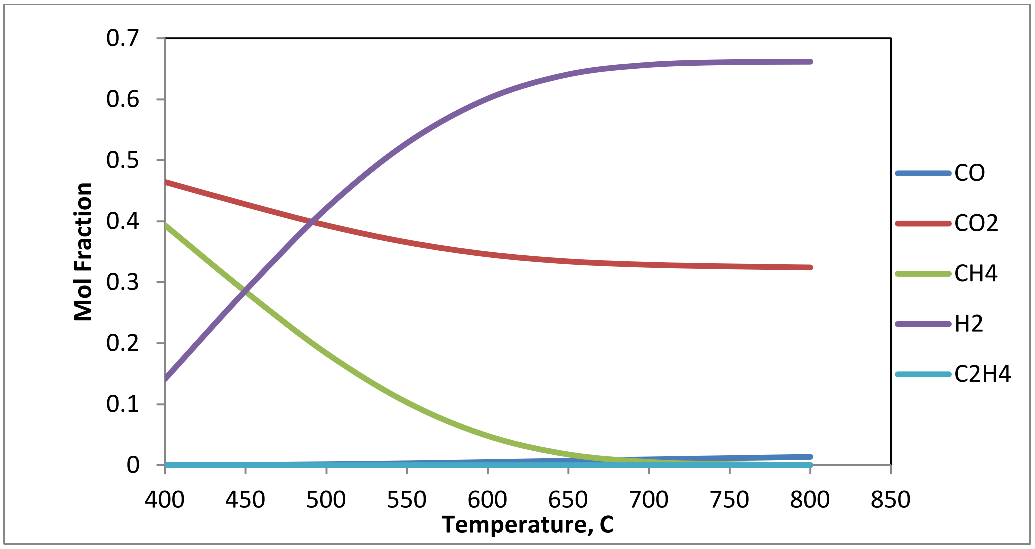

Fig 4.16 Effect of temperature on product gas composition (3.25 wt% acetic acid at 250 bar)

4.7 Conclusions:

Conversion of bio-oil to hydrogen has the potential to be an important source of CO_2 neutral and renewable energy. A thermodynamic analysis was performed by performing a Gibb's free energy minimization using R-Gibbs reactor in AspenPlus. As a first step towards ultimately having the capability to convert bio-oil to hydrogen, acetic acid, which is a model oxygenate compound of aqueous phase bio-oil was selected as a model compound. Supercritical water is a good homogenous medium to carry out organic reactions and its viability in reforming acetic acid and producing H_2 is investigated. It was found that

- a high reaction temperature favors an increased hydrogen yield in the product stream. Although higher temperatures gave slightly increased hydrogen yield, the recommended operation temperature was found to be 700 ^oC wherein maximum hydrogen yield was obtained from the R-Gibbs reactor at typical SCWR operating conditions.
- Secondly, S/C mole ratio higher than 9:1 is suitable for high hydrogen yields. Another benefit of carrying out the reaction at high temperatures and water feed is the reduced

favorability towards carbon formation in the reactor. This thermodynamic study can be combined with an experimental study of supercritical water reforming of acetic acid in the suggested optimal conditions to obtain kinetic data that can be used to determine a more accurate operating window.

4.8 References

1. Hoogwijk, M., et al., *Exploration of the ranges of the global potential of biomass for energy.* Biomass and Bioenergy, 2003. **25**(2): p. 119-133.
2. Hoogwijk, M., et al., *Potential of biomass energy out to 2100, for four IPCC SRES land-use scenarios.* Biomass and Bioenergy, 2005. **29**(4): p. 225-257.
3. Administration, U.S.E.I., *Annual Energy Review.*
4. Trane, R., et al., *Catalytic steam reforming of bio-oil.* International Journal of Hydrogen Energy, 2012. **37**(8): p. 6447-6472.
5. Marbán, G. and T. Valdés-Solís, *Towards the hydrogen economy?* International Journal of Hydrogen Energy, 2007. **32**(12): p. 1625-1637.
6. McPhail, S.J., et al., *Prospects of Hydrogen as a Future Energy Carrier Fuel Cells in the Waste-to-Energy Chain*, 2012, Springer London. p. 189-203.

7. Gupta, R.B. and A. Demirbaş, *Gasoline, diesel, and ethanol biofuels from grasses and plants*2010: Cambridge Univ Pr.

8. Venderbosch, R.H. and W. Prins, *Fast pyrolysis technology development.* Biofuels, Bioproducts and Biorefining, 2010. **4**(2): p. 178-208.

9. Thangalazhy-Gopakumar, S., et al., *Physiochemical properties of bio-oil produced at various temperatures from pine wood using an auger reactor.* Bioresource Technology, 2010. **101**(21): p. 8389-8395.

10. Czernik, S. and A.V. Bridgwater, *Overview of Applications of Biomass Fast Pyrolysis Oil.* Energy & Fuels, 2004. **18**(2): p. 590-598.

11. Effendi, A., H. Gerhauser, and A.V. Bridgwater, *Production of renewable phenolic resins by thermochemical conversion of biomass: A review.* Renewable and Sustainable Energy Reviews, 2008. **12**(8): p. 2092-2116.

12. Marquevich, M., et al., *Hydrogen from Biomass: Steam Reforming of Model Compounds of Fast-Pyrolysis Oil.* Energy & Fuels, 1999. **13**(6): p. 1160-1166.

13. Savage, P.E., *Organic chemical reactions in supercritical water.* Journal Name: Chemical Reviews; Journal Volume: 99; Journal Issue: 2; Other Information: PBD: Feb 1999, 1999: p. Medium: X; Size: pp. 603-621.

14. Byrd, A.J., K.K. Pant, and R.B. Gupta, *Hydrogen Production from Ethanol by Reforming in Supercritical Water Using* Ru/Al_2O_3 *Catalyst.* Energy & Fuels, 2007. **21**(6): p. 3541-3547.

15. Yan, Q., L. Guo, and Y. Lu, *Thermodynamic analysis of hydrogen production from biomass gasification in supercritical water.* Energy Conversion and Management, 2006. **47**(11–12): p. 1515-1528.

16. Gutiérrez Ortiz, F.J., et al., *Thermodynamic study of the supercritical water reforming of glycerol.* International Journal of Hydrogen Energy, 2011. **36**(15): p. 8994-9013.

17. Tang, H. and K. Kitagawa, *Supercritical water gasification of biomass: thermodynamic analysis with direct Gibbs free energy minimization.* Chemical Engineering Journal, 2005. **106**(3): p. 261-267.

18. Antal, M.J., et al., *Biomass Gasification in Supercritical Water†.* Industrial & Engineering Chemistry Research, 2000. **39**(11): p. 4040-4053.

19. Cocero, M.J., et al., *Supercritical water oxidation process under energetically self-sufficient operation.* The Journal of Supercritical Fluids, 2002. **24**(1): p. 37-46.

20. Diebold, J.P., I. Thermalchemie, and N.R.E. Laboratory, *A review of the chemical and physical mechanisms of the storage stability of fast pyrolysis bio-oils*2000: National Renewable Energy Laboratory Golden, CO.

21. Savage, P.E. and M.A. Smith, *Kinetics of Acetic Acid Oxidation in Supercritical Water.* Environmental Science & Technology, 1995. **29**(1): p. 216-221.

22. Basagiannis, A.C. and X.E. Verykios, *Catalytic steam reforming of acetic acid for hydrogen production.* International Journal of Hydrogen Energy, 2007. **32**(15): p. 3343-3355.

23. Basagiannis, A.C. and X.E. Verykios, *Reforming reactions of acetic acid on nickel catalysts over a wide temperature range.* Applied Catalysis A: General, 2006. **308**(0): p. 182-193.

24. Rioche, C., et al., *Steam reforming of model compounds and fast pyrolysis bio-oil on supported noble metal catalysts.* Applied Catalysis B: Environmental, 2005. **61**(1–2): p. 130-139.

25. Takanabe, K., et al., *Sustainable hydrogen from bio-oil—Steam reforming of acetic acid as a model oxygenate.* Journal of Catalysis, 2004. **227**(1): p. 101-108.
26. Watanabe, M., et al., *Catalytic decarboxylation of acetic acid with zirconia catalyst in supercritical water.* Applied Catalysis A: General, 2001. **219**(1–2): p. 149-156.
27. Wang, D., et al., *Biomass to Hydrogen via Fast Pyrolysis and Catalytic Steam Reforming of the Pyrolysis Oil or Its Fractions.* Industrial & Engineering Chemistry Research, 1997. **36**(5): p. 1507-1518.
28. Meyer, J.C., P.A. Marrone, and J.W. Tester, *Acetic acid oxidation and hydrolysis in supercritical water.* AIChE Journal, 1995. **41**(9): p. 2108-2121.
29. Vagia, E.C. and A.A. Lemonidou, *Thermodynamic analysis of hydrogen production via autothermal steam reforming of selected components of aqueous bio-oil fraction.* International Journal of Hydrogen Energy, 2008. **33**(10): p. 2489-2500.

5. Thermodynamic study of the supercritical water reforming of synthetic bio-oil

5.1 Abstract:

In this work a thermodynamic analysis of the supercritical water reforming of a synthetic bio-oil mixture representing the aqueous phase of bio-oil compound was performed. The choice of model compounds is made by picking from oxygenates found in relatively higher quantities in the bio-oil. This is done to simplify the study of the many compounds that exist in bio-oil by instead studying the behavior of entire classes of compounds. The aqueous phase typically consists of organic acids, ketones, aldehydes and alcohols. The common compounds that are used to model these compounds are formic acid, acetic acid, acetone, acetaldehyde, methanol, ethanol and acetol. The objective of this study is to examine the reforming characteristics of mixtures of model compounds that can simulate the aqueous phase of bio-oil. This study focuses on a model compound mixture containing methanol, acetic acid, acetaldehyde and acetol. A thermodynamic study of the supercritical water reforming of this mixture was carried out in AspenPlus© by a non-stoichiometric Gibb's free energy minimization method using the Peng-Robinson equation of state with Boston-Mathias mixing rule. The effect of temperature (500-900 ^{o}C) and steam to carbon ratio (1:1 to 9:1) on product gas composition, selectivity and yield of hydrogen in the off gas was studied. The trends obtained were similar to results from the study of individual compounds such as acetic acid. High hydrogen concentrations were found at high temperatures and S/C ratio. Similar trends were obtained for H_2 yields where close to 82% of theoretical hydrogen yield was obtained at T > 700 ^{o}C and S/C ratio of 9 and greater. A concern of reforming crude bio is heavy coking due to high carbon content in feed and large amounts of coke were formed when S/C ratio was low.

5.2 Introduction

Currently, H_2 is primarily produced by the reforming of fossil fuel based resources such as natural gas and naphtha. H_2 is not only foreseen as a clean and intensive energy carrier, it is also used in the upgrading of fuels and synthesis of chemicals. [32, 33] Biomass based hydrogen production has proved to be one viable method to not only supply hydrogen for a future hydrogen economy but also leads to net zero CO_2 and SO_2 emissions that are typical of fossil fuel sources.

Most of the current literature in the conversion of bio-oil to hydrogen has focused on single oxygenates such as acids[24, 25, 28, 34], aldehydes, ketones[35] and alcohols[36-38] as representative of the lighter, aqueous fraction and phenols[39], furans to signify the heavier aromatic components obtained from the decomposition of lignin. Catalytic steam reforming of whole bio-oil has been pioneered by Czernik et al [29, 40, 41] using a fluidized bed, fixed bed and micro-reactor set up. In one such study [29] it was suggested that the pyrolysis of biomass followed by catalytic reforming gave higher yields of H_2 when compared with the conventional gasification of biomass followed by WGS reaction. A thorough review of the state of the art on catalytic conversion of bio-oil to hydrogen has been provided in Chapter 1.

5.3 Objectives

The primary goal of the current chapter is to provide the first results of a thermodynamic study of the supercritical water reforming of synthetic/pseudo bio-oil mixtures and the parametric effects thereof. In the previous chapter, a thermodynamic study of the supercritical water reforming of acetic acid, a model oxygenate of bio-oil, was carried out. The results showed that higher temperatures and an excess of water in the reactor were ideal conditions to maximize hydrogen yield in the R-Gibbs reactor. In this work, mixtures of model compounds are fed into the reactor and the effect of reaction temperature and feed concentration on the overall yield and selectivity of hydrogen and other typical reforming off gases are determined. Operational window for an experimental study to determine the effect of catalysis and other kinetic aspects are suggested.

5.4 Using AspenPlus© to generate equilibrium data: Methodology

AspenPlus©[42] is a simulation tool that can be used to determine the equilibrium composition of the gases in the supercritical water reforming of different compounds. The methodology employed for mixtures of components is the same as in the study of acetic acid supercritical water reforming where it is discussed in detail. Only a brief overview is provided here. By making use of the R-Gibbs reactor module in AspenPlus© the Gibb's free energy minimization is carried out non-stoichiometrically. This is especially important in the case of studying several feed compounds entering the reactor where there are a number of reactions taking place concurrently. Apart from the compounds in the input stream, products taken into account include hydrogen, carbon monoxide, carbon dioxide, methane, ethylene and graphitic carbon. The Peng-Robinson Equation of state with Boston-Mathias mixing rule was employed and the binary interaction parameters were taken from the AspenPlus© database.

By selecting feed concentration, temperature and pressure the mole fractions of products, yield and selectivity of the various mixtures was determined. The results from such a study will provide an important starting point for experimental studies to provide a meaningful understanding of the overall process.

5.5 Process setup and operation

The process setup was similar to the case of acetic acid. In the current work, the additional carbonaceous feedstock was provided in the stream entitled “FEEDSTOCK”. The amount of organic feed into the reactor was fixed and by changing the amount of water entering the reactor through “WATERIN” stream, different S/C ratios were studied. Reaction temperature and pressure were specified in the R-Gibbs module where all components were considered to be products of the reaction. The output stream is given by “GIBBSOUT”. Based on this outlet gas composition various parameters such as mole fraction, selectivity and yield were determined.

5.6 Results and Discussion

Following the thermodynamic study of acetic acid which is a major constituent of bio-oil, the complexity of the process was increased by studying the effect of other components in the yield and selectivity of H_2, CO, CO_2 and CH_4. Typical aqueous phase bio-oil consists of several hundred constituent compounds depending on the biomass source. However, most of the components are found in very low amounts. The model mixture that was used in the study[43] is given in Table 3.1. By fixing the composition of the organic feed, the amount of Carbon is fixed therefore by varying the amount of water fed to the reactor; different S/C ratios can be investigated. From table 5.1 the total number of moles of C entering the R-Gibbs reactor is 15.26. Therefore, if a 6:1 S/C ratio was desired, 1648 kg/hr of water feed was included.

	Flowrate		
	kg/hr	kmol/hr	Kmol/hr
Component	Mass	Moles	Moles of C
Methanol	50	1.563	1.563
Acetic Acid	150	2.500	5.000
Acetaldehyde	120	2.727	5.455
Acetol	80	1.081	3.243
Water	Varied	Varied	0.000

Table 5.1 Composition of synthetic bio-oil mixture

From the acetic acid study, in the previous section, the conclusions made were that H_2 yields were high at temperatures greater than 700 ^{o}C. Secondly, H_2 yields were favored by high steam to carbon ratios with the additional benefit of thermodynamic coke formation disappearing at S/C = 6. Therefore the present parametric study was carried out in the following way: by fixing the S/C =6, the effect of temperature was studied in the range of 500 to 900 ^{o}C and the effect of S/C ratio on the gas composition was examined at a temperature of 700 ^{o}C. In order to perform a thorough analysis of the results, the representative reactions that are taking place in the reactor and need to be considered. Below are the main reactions of interest.

1. Endothermic Steam Reforming Reactions [33, 38, 44]:

Acetic Acid $CH_3COOH + 2H_2O \rightarrow 2CO_2 + 4H_2$

(1)

Acetol $C_3H_6O_2 + 4H_2O \rightarrow 3CO_2 + 7H_2$ (2)

Acetaldehyde $CH_3CHO + H_2O \rightarrow CO_2 + CH_4 + H_2$

(3)

Methanol $CH_3OH + H_2O \rightarrow CO_2 + 3H_2$ (4)

Methane $CH_4 + 2H_2O \rightarrow CO_2 + 4\ H_2$ (5)

2. Water gas Shift Reaction (Exothermic)

$CO + H_2O \Leftrightarrow CO_2 + H_2$ (6)

3. Methanation (Exothermic)

$CO + 3H_2 \Leftrightarrow CH_4 + H_2O$ (7)

$CO_2 + 4H_2 \Leftrightarrow CH_4 + 2H_2O$ (8)

4. Coking Reactions

4.1 Boudouard reaction (Endothermic)

$2CO \Leftrightarrow C(s) + CO_2$ (9)

4.2 CO Reduction (Exothermic)

$CO + H_2 = C + H_2O\ \ \Delta H = -130\ kJ\ mol^{-1}$ (10)

5.6.1 Effect of reaction temperature

The case of S/C ratio =6 represents a reasonable operating condition although higher S/C ratio may be expected in supercritical water operation. The increasing temperature improves the favorability of endothermic reforming reactions for each of the individual model compounds. The overall reforming reaction of each of the model compounds (equations 1-4) gives different hydrogen yields. However, the methanation, water gas shift and coking reactions are common to all. From the results shown in Fig 5.1 we can see that there is an upward trend for H_2 mole fraction in the product gas as the temperature increases. For instance, when comparing the H_2 mole fraction for mixture reforming with acetic acid reforming we see that at T =700 ^oC, the H_2 mole fraction was similar for acetic acid (0.39) and the synthetic bio-oil(0.38). This value increased monotonously reaching a maximum value of 0.6 at 900 ^oC.

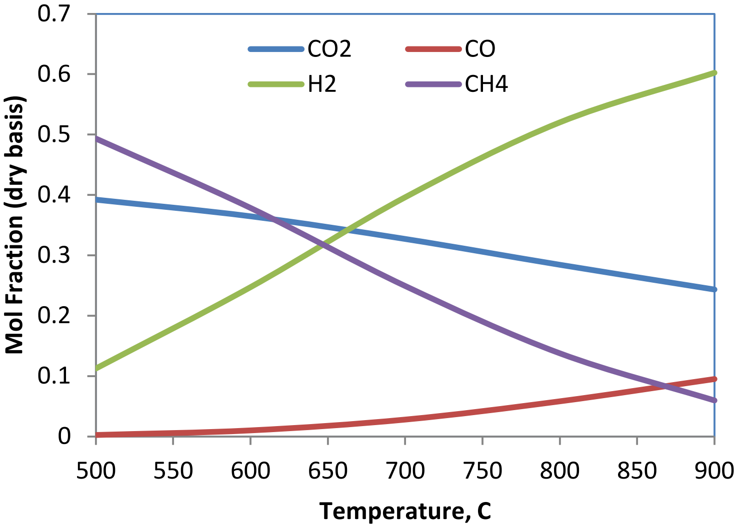

Figure 5.1 Effect of temperature on synthetic bio-oil reforming at S/C = 6

Methane concentration decreased rapidly from 0.5 mole fraction at lower temperatures of 500 ^{o}C to much reduced amounts of 0.1 at temperatures higher than 800 ^{o}C. The sharp decrease in methane concentration can be attributed to two factors. Firstly, the exothermic methanation reactions are dominant in the lower temperature range. Secondly, methane is also reformed by the supercritical water forming CO and H_2. This is evident from the increase in CO concentration as well as a reduction in the amount of water found in the product stream.

CO_2 concentration does not depend strongly on the reaction temperature and decreases in value from 0.4 to 0.26 when temperature increases from 500 to 900 ^{o}C. CO_2 is primarily formed due to the water gas shift reaction and thermal decomposition of the feed. The water gas shift reaction is an exothermic reaction which becomes less favorable at higher temperatures. Similarly, the CO concentration is negligible until temperature exceeds 800 C. The reverse water gas shift reaction which produces CO and enhanced reforming reaction contribute to the increasing CO concentration at higher temperatures.

5.6.2 Effect of S/C ratio

In order to study the effect of S/C ratio on the reforming characteristics and product gas composition, a temperature of 700 ^{o}C was fixed and S/C ratios ranging from 1:1 to 9:1 was studied. The temperature of 700 ^{o}C was chosen because at this temperature H_2 yields are high, methane concentrations are low and is not prohibitively high temperature operation-wise. The results are shown in Fig 5.2.

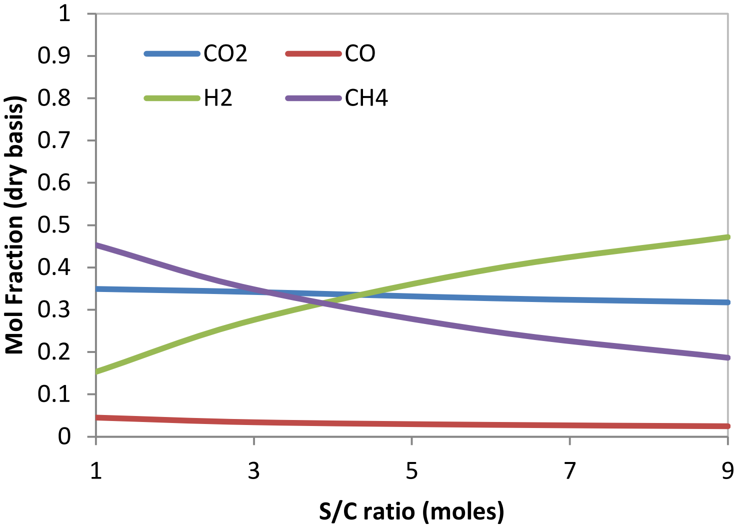

Figure 5.2 Effect of S/C ratio on synthetic bio-oil reforming at 700 ^{o}C

From the graph it can be seen that the hydrogen composition are maximized at high S/C ratios. The trend in reforming is that an excess of water represents the best condition for maximizing hydrogen yield. However, an increase in S/C ratio from 6:1 to 9:1 showed an increase from 0.39 to 0.47. It must be noted that operating the reformer at these conditions represents large water content in the exit of the reformer. Therefore recycling the water stream to make the operation more compact can be considered.

CO and CO_2 mole fractions are largely unaffected by the S/C ratio and remain constant at around 0.03 and 0.34 respectively at 700 ^{o}C. The S/C ratio has a negative effect on the CH_4 concentration which reduces from 0.45 to 0.18 when the S/C ratio increases from 1 to 9. This may be explained by the enhancement of the steam reforming of methane reaction at excess water concentrations. The only instance of coking was observed at an S/C ratio of 1:1 where the temperature was 700^{o}C. However no coke is observed in the reactor at the temperature of 700 C.

5.6.3 Thermal decomposition of synthetic bio-oil

The thermal decomposition of the bio-oil mixture was studied by feeding the reactor with pure feedstock and no water inlet in the feed. This represents an important scenario in fixed bed operation where the feedstock decomposes and causes coke formation on the catalysts reducing the catalyst time on stream. In all cases, the model compounds themselves were completely converted at equilibrium. However, there was significant amount of coke formation in the R-Gibbs reactor. A calculation of the yield of graphitic carbon relative to the moles of carbon entering the reactor showed that at lower temperatures as much as 66% of the entering carbon was converted to graphitic carbon. As expected coking was found to reduce as the temperature was increased but even at temperature as high as 800 ^{o}C significant coke yields were found (~ 52%)

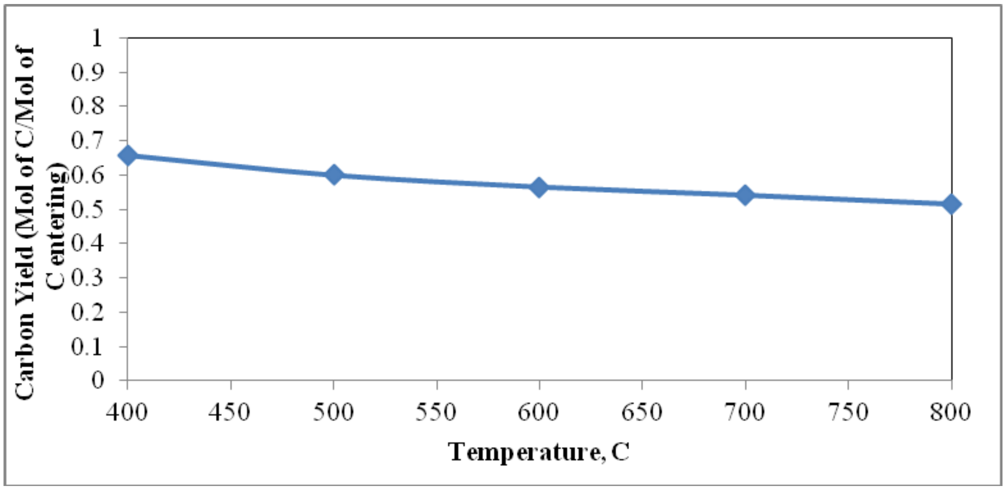

Fig 5.3 Effect of Temperature on yield of Graphitic Carbon during thermal decomposition

5.6.4 Effect of Pressure:

In all simulations carried out in this study the pressure was chosen to be 250 bar. The advantage of using supercritical water is the availability of a homogenous medium in which the reforming reaction can be carried out due to the complete miscibility of all the components. However a big disadvantage is the reduced H_2 concentration in the product gas when compared to conventional steam reforming of model compounds. However, supercritical water reforming leads to H_2 delivery at high pressures. This implies that downstream compression costs are expected to be reduced because compression and storage are economically intensive, especially so for H_2 which has a very low density.

5.7 Conclusion

Conversion of bio-oil to hydrogen has the potential to be an important source of CO_2 neutral and renewable energy. A thermodynamic analysis was performed by performing a Gibb’s free energy minimization using R-Gibbs reactor in AspenPlus. Following the study of supercritical water reforming of acetic acid, the next step in complexity is the study of a mixture of model compounds that can be used to model the aqueous phase of bio-oil. Similar to the case of supercritical water reforming of acetic acid, it was found that a high reaction temperature favors an increased hydrogen concentration in the product stream. S/C mole ratio higher than 6:1 is suitable for high hydrogen yields. The advantage of running the reaction at high temperatures and water feed is the reduced coking. This thermodynamic study can be combined with an experimental study of supercritical water reforming of acetic acid in the suggested optimal conditions to obtain a complete picture of the process.

5.8 References

1. Gupta, R.B., *Hydrogen fuel: production, transport, and storage*2008: CRC.
2. Vaidya, P.D. and A.E. Rodrigues, *Insight into steam reforming of ethanol to produce hydrogen for fuel cells.* Chemical Engineering Journal, 2006. **117**(1): p. 39-49.
3. Hu, X. and G. Lu, *Investigation of steam reforming of acetic acid to hydrogen over Ni–Co metal catalyst.* Journal of Molecular Catalysis A: Chemical, 2007. **261**(1): p. 43-48.
4. Basagiannis, A.C. and X.E. Verykios, *Catalytic steam reforming of acetic acid for hydrogen production.* International Journal of Hydrogen Energy, 2007. **32**(15): p. 3343-3355.
5. Basagiannis, A.C. and X.E. Verykios, *Reforming reactions of acetic acid on nickel catalysts over a wide temperature range.* Applied Catalysis A: General, 2006. **308**(0): p. 182-193.
6. Watanabe, M., et al., *Catalytic decarboxylation of acetic acid with zirconia catalyst in supercritical water.* Applied Catalysis A: General, 2001. **219**(1–2): p. 149-156.
7. Kechagiopoulos, P.N., et al., *Hydrogen Production via Steam Reforming of the Aqueous Phase of Bio-Oil in a Fixed Bed Reactor.* Energy & Fuels, 2006. **20**(5): p. 2155-2163.
8. Byrd, A.J., K. Pant, and R.B. Gupta, *Hydrogen production from ethanol by reforming in supercritical water using Ru/Al2O3 catalyst.* Energy & Fuels, 2007. **21**(6): p. 3541-3547.
9. Gadhe, J.B. and R.B. Gupta, *Hydrogen production by methanol reforming in supercritical water: suppression of methane formation.* Industrial & Engineering Chemistry Research, 2005. **44**(13): p. 4577-4585.

10. Boukis, N., et al., *Methanol reforming in supercritical water.* Industrial & Engineering Chemistry Research, 2003. **42**(4): p. 728-735.

11. Polychronopoulou, K., J. Fierro, and A. Efstathiou, *The phenol steam reforming reaction over MgO-based supported Rh catalysts.* Journal of Catalysis, 2004. **228**(2): p. 417-432.

12. Garcia, L.a., et al., *Catalytic steam reforming of bio-oils for the production of hydrogen: effects of catalyst composition.* Applied Catalysis A: General, 2000. **201**(2): p. 225-239.

13. Wang, D., et al., *Biomass to Hydrogen via Fast Pyrolysis and Catalytic Steam Reforming of the Pyrolysis Oil or Its Fractions.* Industrial & Engineering Chemistry Research, 1997. **36**(5): p. 1507-1518.

14. Czernik, S., R. Evans, and R. French, *Hydrogen from biomass-production by steam reforming of biomass pyrolysis oil.* Catalysis Today, 2007. **129**(3–4): p. 265-268.

15. AspenTech, L., *AspenPlus V7.3* 2011.

16. Fisk, C.A., et al., *Bio-oil upgrading over platinum catalysts using in situ generated hydrogen.* Applied Catalysis A: General, 2009. **358**(2): p. 150-156.

17. Dubey, V.R. and P.D. Vaidya, *Kinetics of steam reforming of acetol over a Pt/C catalyst.* Chemical Engineering Journal, 2012. **180**(0): p. 263-269.

6. Activation of Magnesium Silicates for CO_2 – sorption enhanced reforming

6.1 Abstract

In-situ CO_2 removal increases the H_2 yield during reforming operation. One method of CO_2 removal is the use of solid sorbents such as minerals of calcium and magnesium. Carbonation of magnesium silicates known as mineral carbonation has been known to be a useful method for CO_2 sequestration due to the stable carbonate formation. Typical magnesium silicates used in this process are serpentine, olivine and talc. Although thermodynamically feasible in the conditions under consideration, the kinetics of direct carbonation of such minerals is very poor with low reaction rates. Therefore the magnesium silicate must be activated either physically by the action of steam or temperature or chemically by treating with strong acids to form $Mg(OH)_2$ or brucite which has a high reactivity to CO_2. In this work, the effect of supercritical water on the pore structure and morphology of talc is investigated. BET surface area and pore volume were obtained following activation under supercritical water at various temperatures. Preliminary study of supercritical water reforming of methanol in a fixed bed packed with only activated talc was studied. It was found that although parts of the magnesium silicate were activated to $Mg(OH)_2$ the loading of sorbent was too low to detect the effect of in-situ CO_2 removal and consequent shift in H_2 concentration.

6.2 Introduction

6.2.1 Sorption Enhanced Reforming

Hydrogen production by the reforming of any given feedstock proceeds via a two step process; the highly endothermic reforming reaction of the feedstock producing syngas followed by the exothermic water gas shift reaction yielding higher quantities of hydrogen. The equilibrium limited nature of these reactions suggests a ceiling for the amount of hydrogen that can be produced at a given set of reaction conditions. For illustration purposes, the methane steam reforming reaction can be considered.

$$CH_4 + H_2O \Leftrightarrow CO + 3H_2 \qquad (1)$$

$$CO + H_2O \Leftrightarrow CO_2 + H_2 \qquad (2)$$

The overall reforming reaction can be written as:

$$CH_4 + H_2O \Leftrightarrow CO_2 + 4\,H_2 \qquad (3)$$

Guided by the Le-Chatelier principle, Ortiz et al [1] suggested combining a CO_2 separation step in-situ which would drive the equilibrium to the right giving rise to a hydrogen yield that is higher than the theoretical limit. The study of CO_2 separation from gas streams with multiple components has advanced independent of the sorption enhanced process. The growing concern with the increasing CO_2 emissions, especially from anthropogenic point sources such as coal fired power plants has lead to major advances in the efficacy of CO_2 separation.[2] There are several technologies that are currently present to effect the removal of CO_2 which include membranes, amine based solvents such as selexol, rectisol and the use of solid sorbents [3-5]. If we denote a CO_2 separation step in reaction (3) as CS, we have the following reaction:

$$CH_4 + H_2O + S \Leftrightarrow [S.CO_2] + 4\,H_2 \qquad (4)$$

This work focuses on the use of solid CO_2 sorbents for the in-situ CO_2 capture. Solid sorbent technology has also been used to enhance gasification processes for both biomass and coal[6, 7] and also at supercritical water conditions.[8]

6.2.2 Carbonation of Magnesium silicates: Background and state of the art

Among the different solid CO_2 sorbents, the high CO_2 capture capacities and regeneration properties of alkaline earth metals make them highly suited. In this work, the use of mineral magnesium silicates is studied. It is advantageous to use magnesium based minerals due to the large reserves of magnesium based mineral reserves that are available for carbonation as well as the very stable nature of their carbonated state which reduces the risk of the captured CO_2 escaping from the reacted solid. The carbonation of Magnesium based minerals have been primarily used for the sequestration step of the CCS or Carbon Capture and Storage scheme put forward by the IPCC. However, in this work, the main aim is to combine capture and storage while ultimate making use of the initial CO_2 capture step in the sorption enhanced reforming of bio-based feedstock which would make the production of hydrogen from biomass a net negative CO_2 emitting scenario making it a very attractive process.

The immense reserves of magnesium based minerals such as serpentine ($Mg_3Si_2O_5(OH)_4$) , olivine (Mg_2SiO_4) and talc ($Mg_3Si_4O_{12}H_2$) make for cheap raw material for the process. Ideally, one would prefer to have direct carbonation of magnesium silicates which is known to be thermodynamically feasible. However, it is limited by extremely slow reaction rates (in the order of geological time scales ~ 1000s of years). Therefore an activation step to extract the Mg from the silicates followed by carbonation of the now active Mg which typically exists as $Mg(OH)_2$ in its most active form is required. There are broadly two main methods of activation; chemical activation and physical activation.

Chemical Activation: In this method, the mineral typically serpentine, olivine or talc are treated with acid and base in a so-called pH swing process to extract the Mg out. Other methods developed by Zevenhoven [9-11] et al is the treatment of magnesium silicates with an ammonium sulphate salt followed by washing with water leading to the formation of $Mg(OH)_2$. The commonality between the above mentioned methods is the conversion of magnesium in the silicates to an ionic Mg^{2+} state. [12]

Physical Reactivation: Use of steam to reactivate calcium based sorbent is a known technique to reactivate spent sorbents[13]. Maroto valer [14] et al exposed serpentine to steam and air with heating at 300 ^{o}C and 650 ^{o}C respectively and compared the carbonation reactivity with chemical reactivation.

The significant reserves of magnesium silicate based minerals make it attractive as a CO_2 sorbent if the capture step has a high degree of conversion to carbonate. This allows the capture and sequestration step to be combined yielding a stable, carbonated solid. However, the rate of carbonation reaction is very slow and reactivation of magnesium silicates is imperative for successful implementation of the process. Most of the carbonation studies have been performed with a view towards CO_2 sequestration; therefore, there is concern among the researchers [8 15] about: a) the energy penalty in using high temperatures in the reactivation step b) presence of metal impurities such as Fe, Ni and Al. In the case of supercritical water reforming, the conditions of high temperature and pressure are favorable for the activation and carbonation of Mg-based minerals and have the potential to make it an attractive industrial process.

6.3 Objectives and scope or work

The main goals of this work are

i. To study the physical activation of magnesium silicates using supercritical water in order to improve carbonation kinetics

ii. To quantify the structural and morphological changes during supercritical water activation using BET surface area and pore volume measurements

6.4 Experimental Section

6.4.1 Experimental setup

Talc ($Mg_3Si_4O_{12}H_2$) of size 44 µm was obtained from Sigma Aldrich. About 1 gram of the powder was added to a 0.5 m long, 0.25” OD x 0.12” ID Inconel 600 reactor manufactured by Microgroup. Porous frits were added to the both ends of the reactor to prevent entrainment of the fine solid. A K-type, 1/16” thermocouple was inserted into reactor prior to filling to get accurate temperature reading within the reactor. Water was pumped into the packed bed reactor by ChromTech© Series 1500 pump. The entire apparatus was placed inside a Thermo Scientific Lindberg Blue M furnace. Exit of the reactor was connected to a double pipe heat exchanger followed by a Back Pressure Regulator to maintain supercritical pressure within the reactor. Deionized water was pumped through a pre-heater coiler also placed inside the furnace prior to entering the reactor. Pressure gauges were installed upstream and downstream of the reactor to monitor the pressure drop and to identify any plugging during operation.

6.4.2 Experimental Procedure

Activation of talc

The furnace set point was raised to the desired temperature of activation. Once the set point was reached in the thermocouple reading, de-ionized water was pumped into the reactor and the BPR was adjusted till a pressure of 3500 psi was reached. The pressure drop across the reactor when 1 gm of talc was loaded varied between 200-250 psi. Once the required temperature and pressure was reached a timer was started. Temperatures of 550 and 650 were studied. After the talc was exposed to supercritical water for the requisite time, pumping was stopped and the BPR was released. The furnace set point was dropped to 150 ^{o}C for an hour. This step is to remove any surface moisture from the talc. Any potential $Mg(OH)_2$ is unaffected at this temperature as only surface moisture is driven away. Dehydroxylation of $Mg(OH)_2$ takes place at temperatures above 300 ^{o}C [16] therefore the active $Mg(OH)_2$ is retained.

6.4.3 Solids Characterization

Following the activation step, the collected samples were characterized with a Nova 2200e BET surface area and pore volume analyzer using N_2 physisorption at -196 ^{o}C. All samples were degassed for 4 hours to remove any impurities that might be filling the pores.

6.5 Results and Discussion

6.5.1 Activation of Talc

Sample Description	Surface Area	Pore Volume	Pore Size
	(sq. m/gram)	(cc/gm)	nm
No activation	8.52	0.0411	9.65
550 C, 3750 psi, 1 hr	15.41	0.0834	10.83
550 C, 3750 psi, 2 hrs	17.82	0.0898	11.14
550 C, 3750 psi, 4 hrs	18.81	0.0902	11.02
650 C, 3750 psi, 1 hr	14.37	0.0921	9.89
650 C, 3750 psi, 2 hrs	16.34	0.0887	10.66
650 C, steam,8h *	15.8	0.035	8.8
H2SO4 treatment*	330	0.234	2.8

Table 6.1 Surface area and Pore Volume Results from activation tests. * = Maroto Valer, 2005

During the exposure of the talc to supercritical water, it was expected that the Mg would be extracted and due to the penetration of supercritical water into the pores of the talc a "popcorn effect" would cause a sufficient increase in the surface area and pore volume of the talc. The control SA and PV for sorbent prior to reactivation was 8.52 m^2/gm and 0.0411 cc/gm respectively. A large increase was not noticed after treating the talc to supercritical water. For instance, talc treated to 550 ^oC and 3750 psi for 1 hour had a pore volume of 15.41 m^2/gm and 0.0834 cc/gm respectively. As the time of the sorbents spent in these conditions was increased, an increase in the surface area and pore volume was observed. However, this increase was not substantial. When the sorbent was on stream for as long as 4 hours, the surface area and pore volume increased marginally to 18.81 m^2/gm and 0.09 cc/gm. These results are compared with Valer et al who studied the chemical activation as well as treatment with steam for extended periods of 8 hours. It was found that compared to physical reactivation, chemical reactivation had a much more substantial increase in surface area to 330 m^2/gm with an almost three-fold higher pore volume of 0.234 cc/gm.[14]

6.5.2 Carbonation of activated talc

In order to test the carbonation of solid sorbents in-situ while the reforming reaction takes place in the absence of catalyst, the supercritical water reforming of methanol was considered. Due to the absence of C-C bonds in the methanol molecule, the gasification can occur without presence of catalyst. The reactor was packed with ~ 2 grams of talc, underwent reactivation for 2 hours at 650 °C. This was followed by pumping 5 wt% methanol into the reactor which was at supercritical conditions. Runs typically lasted for 2 hours and the gas chromatography of the reaction gases showed unchanging gas phase composition. Apart from talc, 1 gm of $Mg(OH)_2$ was mixed with 1 gm of $CaCO_3$ and the same experiment was repeated. The reason for mixing was twofold: the small particle size for $Mg(OH)_2$ lead to severe pressure drop in the reactor and mixing with $CaCO_3$ which is inert towards carbonation at the given reactor conditions increases the average particle size in the reactor reducing pressure drop. Secondly, this allowed for more dispersion of $Mg(OH)_2$ particles in the reactor and better gas solid contacting, compared to a packed bed with $Mg(OH)_{2.}$

The carbonate content was determined by determining the volume of CO_2 evolved when the carbonated sorbent was treated with 6N HCl [17]. Although both sorbents underwent carbonation due to the low reactor volume (3.68 cc), sorbent loading was too small to either detect a breakthrough curve after sorbent was saturated with CO_2 or to detect a shift in the H_2 equilibrium values.

6.6 Conclusions

Magnesium silicate mineral compounds were exposed to supercritical water for different reaction times and temperatures in order to activate the Mg present to enhance reactivity with CO_2. Following reactivation, the surface area and pore volume of the sorbents were analyzed and it was found that although the surface area and pore volume doubled compared to nascent mineral, chemical reactivation of sorbents using an acid-base extraction showed a much higher increase in surface area and pore volume. Talc and $Mg(OH)_2$ were packed in an Inconel reactor where uncatalyzed methanol reforming was carried out. It was found that both sorbents were carbonated, but the loading of sorbent in the reactor was insufficient to detect a perceivable shift in the H_2 equilibrium concentration.

6.7 References

1. Lopez Ortiz, A. and D.P. Harrison, *Hydrogen Production Using Sorption-Enhanced Reaction.* Industrial & Engineering Chemistry Research, 2001. **40**(23): p. 5102-5109.
2. Metz, B., *IPCC special report on carbon dioxide capture and storage*2005: Cambridge University Press.
3. Herzog, H., *An introduction to CO2 separation and capture technologies.* Massachusetts Institute of Technology Energy Laboratory Working Paper, 1999.
4. MacDowell, N., et al., *An overview of CO2 capture technologies.* Energy Environ. Sci., 2010. **3**(11): p. 1645-1669.
5. Meisen, A. and X. Shuai, *Research and development issues in* CO_2 *capture.* Energy Conversion and Management, 1997. **38**: p. S37-S42.
6. Lin, S.Y., et al., *Developing an innovative method, HyPr-RING, to produce hydrogen from hydrocarbons.* Energy Conversion and Management, 2002. **43**(9): p. 1283-1290.
7. Wang, J. and T. Takarada, *Role of Calcium Hydroxide in Supercritical Water Gasification of Low-Rank Coal.* Energy & Fuels, 2001. **15**(2): p. 356-362.
8. Demirbas, A., *Biodiesel from sunflower oil in supercritical methanol with calcium oxide.* Energy Conversion and Management, 2007. **48**(3): p. 937-941.
9. Teir, S., et al., *Production of magnesium carbonates from serpentinite for long-term storage of CO2.* International Journal of Mineral Processing, 2007. **85**(1-3): p. 1-15.
10. Fagerlund, J. and R. Zevenhoven, *An experimental study of Mg* $(OH)_2$ *carbonation.* International Journal of Greenhouse Gas Control, 2011.

11. Fagerlund, J., et al., *Carbonation of magnesium silicate mineral using a pressurised gas/solid process.* Energy Procedia, 2009. **1**(1): p. 4907-4914.

12. Park, A.-H.A. and L.-S. Fan, *mineral sequestration: physically activated dissolution of serpentine and pH swing process.* Chemical Engineering Science, 2004. **59**(22–23): p. 5241-5247.

13. Zeman, F., *Effect of steam hydration on performance of lime sorbent for CO2 capture.* International Journal of Greenhouse Gas Control, 2008. **2**(2): p. 203-209.

14. Maroto-Valer, M.M., et al., *Activation of magnesium rich minerals as carbonation feedstock materials for CO2 sequestration.* Fuel Processing Technology, 2005. **86**(14–15): p. 1627-1645.

15. Nduagu, E., et al., *Production of magnesium hydroxide from magnesium silicate for the purpose of* CO_2 *mineralisation–Part 1: Application to Finnish serpentinite.* Minerals Engineering, 2012.

16. Yan, L., et al., *Formation of rod-like Mg(OH)2 nanocrystallites under hydrothermal conditions and the conversion to MgO nanorods by thermal dehydration.* Materials Chemistry and Physics, 2002. **76**(2): p. 119-122.

17. Pile, D.L., et al., *A Precise Method for Determining the CO2 Content of Carbonate Materials.* Journal of chemical education, 1998. **75**(12): p. 1610.

Chapter 7: Supercritical Water Reforming of Glycerol

7.1 Introduction

Dwindling fossil-fuel based resources necessitates the investigation of renewable sources of energy. Among the renewable resources under consideration, the use of biomass has seen a lot of attention due to the significant reserves across the world. Secondly, there is a large and increasing demand for H_2 and its use as an energy source in fuel cell applications as well as in several other industrial operations such as ammonia synthesis and fuel upgrading [1]. Among the several biomass derived candidates for H_2 production, glycerol ($C_3H_8O_3$) is gaining importance due to two reasons; firstly, glycerol is a model biomass derived compound and secondly, it is expected that there will be a large market in the near future as it is the by-product during the final step in bio-diesel synthesis [2].

A tremendous increase in bio-diesel production can be seen in the last decade; for instance, the annual bio-diesel production increased from 25 million gallons in 2004 to the 1 billion gallon mark in January, 2012 [3] with glycerol yields typically being 10% by weight of bio-diesel produced. [4] Therefore, glycerol is a cheap and abundant chemical that can prove to be valuable if it can be converted to H_2. Catalytic steam reforming, auto-thermal reforming and catalytic supercritical water reforming of glycerol have been carried out by several researchers with promising results [5-7]. Below is a brief review and state of the art of hydrogen production from glycerol with regard to catalysts used, typical conditions of operation and yields of hydrogen obtained.

7.2 Glycerol Reforming Process

7.2.1 Reactions

The reforming of glycerol is an endothermic reaction given by

$$C_3H_8O_3 + 3H_2O \rightarrow 7\ H_2 + 3CO_2 \qquad \Delta H = 128\ KJ/mol$$

Apart from the reforming reactions, all the other usual reforming reactions [2] such as the exothermic water gas shift reaction and methanation reaction of CO, CO_2.

$$CO + 3H_2 \rightarrow CH_4 + H_2O \qquad \Delta H = -206\ KJ/mol$$

$$CO_2 + 4\ H_2 \rightarrow CH_4 + 2\ H_2O \qquad \Delta H = -165\ KJ/mol$$

$$CO + H2O \rightarrow CO2 + H2 \qquad \Delta H = -41\ KJ/mol$$

Finally, coking occurs in catalytic and un-catalyzed operation during reforming which can form by the reactions given below,

$$2CO \rightarrow CO_2 + C \qquad \Delta H = -171.5\ KJ/mol$$

$$CH_4 \rightarrow 2H_2 + C \qquad \Delta H = 75\ KJ/mol$$

`

$$CO + H_2 \rightarrow H_2O + C \qquad \Delta H = -131\ KJ/mol$$

7.2.2 Catalysis in glycerol reforming

Catalysis during glycerol reforming is crucial as the reactions must proceed in the following specific manner; C-C bond cleavage followed by dehydrogenation resulting in the production of CO and Hydrogen [8]. The CO can further produce additional H_2 via the water gas shift reaction or react with H_2 and produce methane by the methanation reactions shown in the previous section. C-O bond cleavage followed by hydration/hydrogenation is undesirable as it leads to the formation of acrolein followed by long carbon chain (C2-C3) species and not hydrogen. A review of the mechanisms can be found in Vaidya et al. [2] Several metal species have been investigated with regard to glycerol reforming namely Ni, Co, Pt, Ru and Rh.

Adhikari et al [9] performed a thorough study of Ni catalysis for glycerol steam reforming and found that Ni/MgO, Ni/TiO2 and Ni/CeO2 gave 99% glycerol conversions at 600 ^{o}C. Ni/MgO gave the maximum H_2 yield of ~ 4 mol of H_2/mol of glycerol feed. Furthermore, Ni/Al_2O_3 also gave high conversions in another study. The typical order of metal activities for conversion of glycerol was found to be Ni> Ir> Pd> Rh>Pt>Ru[2, 9-11]. This is in agreement with the widespread use of Ni for C-C bond cleavage. Apart from Ni, results from use of Pt and Ru[8, 12-14] catalysts suggest that i. conversions are high with comparable H_2 yield as Ni based ii. Carbon deposition is significantly reduced during long term testing especially in Ru/Al_2O_3 and Ru/ZrO_2. Furthermore, they have been found to be stable under supercritical water conditions. Based on the results from previous work on catalytic reforming of Ni/TiO_2 was selected as an appropriate catalyst for testing glycerol reforming under supercritical water conditions. Although Ni/MgO gave the maximum hydrogen yields in previous work on glycerol steam reforming[15, 16], in supercritical water reforming and use of MgO or $MgO\text{-}Al_2O_3$ spinel in fixed bed reactor designs led to high pressure drops[17] and was thus not considered. Furthermore, catalyst/support stability considerations in supercritical water conditions were made in catalyst selection. To sum up we desire the following attributes in a catalyst during glycerol reforming in supercritical water:

- High activity for C-C bond cleavage
- High activity for WGS

- Low activity for C-O bond cleavage
- Stable under supercritical water conditions.

7.3 Experimental Section

7.3.1 Materials

Glyerol of 99.5% purity was obtained from Fisher Scientific Co. The catalysts used in this study were Ru/ZrO2 and Ni/TiO2 which were prepared in the lab by the standard procedure for incipient wetness impregnation. The metal loading for the two selected catalysts were 1% Ruthenium over ZrO_2 support and 5% Nickel over TiO_2 support. The ZrO2 was impregnated with ruthenium (III) nitrosyl nitrate [Ru (NO)(NO3)] purchased from Strem Chemicals. After impregnating the support with the metal pre-cursor, the solids were calcined in air at 500 ^{o}C for 6 hours. The TiO_2 support was impregnated with nickel nitrate hexahydrate [$Ni(NO3)_2 \bullet 6\ H_2O$] purchased from Sigma Aldrich and also calcined in air for 6 hours at 500 ^{o}C.

7.3.2 Experimental Setup

The setup used in carrying out experimental runs for glycerol reforming is similar to the one used in gasifying several bio-derived feedstocks and is given in the figure below. Two ChromTech 1500 HPLC pumps were used to pump DI water and glycerol into the fixed bed reactor system. The reactor was made of Inconel 600 which originally consisted of 73% Ni, 18% Cr and 9% Fe. However, the inside walls of the reactors used in the experiments can be considered to be “spent” with negligible catalytic activity offered by the reactor wall itself.

Preheated water and feedstock at room temperature were mixed at a tee fitting prior to entering the fixed bed reactor. This was done to prevent thermal degradation of the glycerol feed which leads to reactor plugging due to coke formation. The flow rates of the feed were adjusted to achieve a desired concentration of feed in the reactor as well as a pre-selected residence time. As the feed mixture enters the reactor, gasification of the feed, followed by several gas phase reactions take place following which the gases exit the reactor. The hot gases are cooled using a water-cooled double pipe heat exchanger. The pressure was maintained in the reactor using a back pressure regulator. Pressure gauges present upstream and downstream to the reactor provide the pressure drop across the reactor. 1/16" gauge K-type thermocouple is also inserted into the reactor to provide the actual reaction temperature which is different from the furnace set point.

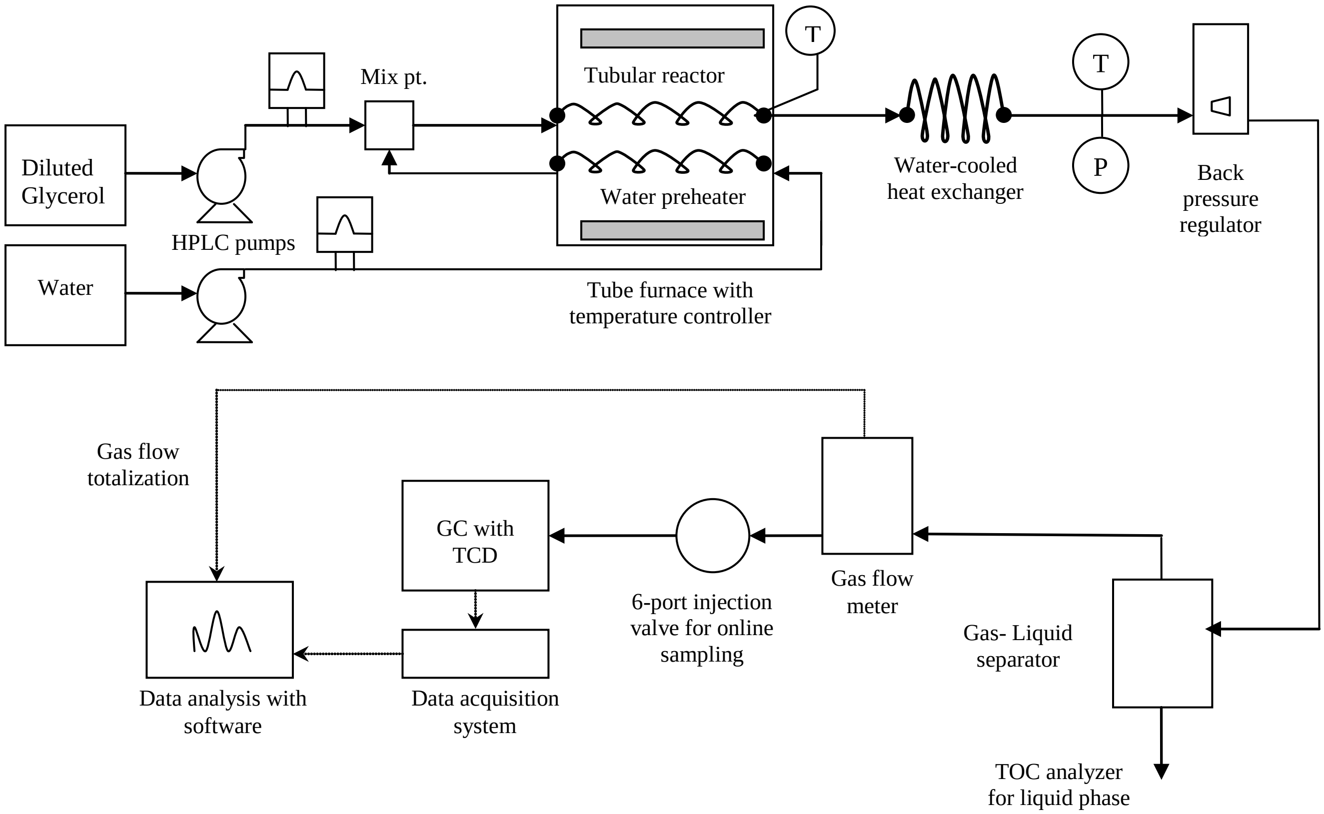

Fig 7.1 Experimental Setup for supercritical water reforming [8, 17]

Following expansion of the cooled gases through the back pressure regulator, the gas-liquid mixture was separated using a glass phase separator. The gas exiting from the phase separator was passed through a dessicator and the flow rate of this stream was measured using an Omega FMA 1600 flowmeter. The composition of this gas stream was measured using an SRI 8610 C GC which works on thermal conductivity measurements against a carrier gas. (GC-TCD) The column used for gas detection was a 60/80 Carboxen mol-sieve column. Nitrogen carrier gas was used to determine the hydrogen composition due to the wide gap in the difference of the thermal conductivity at the column temperature (200 ^{o}C). The carbon balance/closure of the gases was checked by switching to He carrier gas. Runs with carbon balance below 85% were not considered. The liquid from the phase separator was collected and its Total Organic Content (TOC) was determined using Shimadzu TOC.

The residence times was calculated by the following formula[11]

$$\tau = (V_R \,.\, \rho .\, \Phi)/ M \qquad \text{where}$$

τ = residence time in seconds

V_R = Reactor volume = 3.68 cc

ρ = Density of reaction mixture at supercritical water conditions which is taken to be the density of supercritical water

Φ = Void fraction of the bed

M = Total mass flow rate in the reactor

In the case of un-catalyzed reforming, instead of considering a truly empty bed with a void fraction of 1, the same amount of ZrO_2 was packed so that the same hydrodynamic characteristics can be compared with the case of catalytic packed bed reactors. According to May et al, ZrO_2 does not show any activity towards glycerol reforming and can be considered as inert. The void fraction of the bed was calculated by taking an equivalent amount of solids in a thin measuring cylinder and water is added carefully in a drop-wise manner till the solids were completely saturated. After repeating this experiment several times, the amount of water provided the amount of void volume present in a given mass of packing.

7.4 Results and discussion

Supercritical water reforming of glycerol was studied in different reaction conditions for two catalyst support systems; 10% Ni/TiO_2 and 5% Ru/ZrO_2. The results are shown in the table given below.

						(Dry basis)				
Catalyst	Temperature	τ	Pressure	Feed Conc.	H2	CO2	CO	CH4	H_2 Yield	Yield
	(^{o}C)	(s)	(psi)	(Wt %)	%	%	%	%		%
10% Ni/TiO2	600	2	3750	36.2	45.77	17.62	32.44	4.15	1.6	22.86
10% Ni/TiO2	650	2	3750	36.2	56.65	19.11	20.64	3.58	1.98	28.29
Uncatalyzed	510	6	3500	5	16.44	28.66	15.2	39.68	0.77	11.00
5% Ru/ZrO2	510	4	3500	5	38.14	27.76	7.2	26.8	2.32	33.14
5% Ru/ZrO2	550	2	3500	5	47.31	24.21	6.6	19.17	2.64	37.71

Table 7.1 Experimental results from supercritical water reforming of glycerol

7.4.1 Effect of reaction temperature

Due to the endothermic nature of glycerol reforming hydrogen, higher hydrogen yields are expected at higher temperatures. In the case of the un-catalyzed run where the reactor was packed with ZrO_2 and reforming was carried out at 510 C, a large TOC value was obtained which implied that a large portion of the glycerol feed remained ungasified. In order for gasification to take place there must be C-C bond scission followed by the gas phase reactions listed above. Additionally, a low H_2 yield was obtained showing that reforming reaction did not take place extensively due to the lower reaction temperature and the consequently reduced reaction rates.

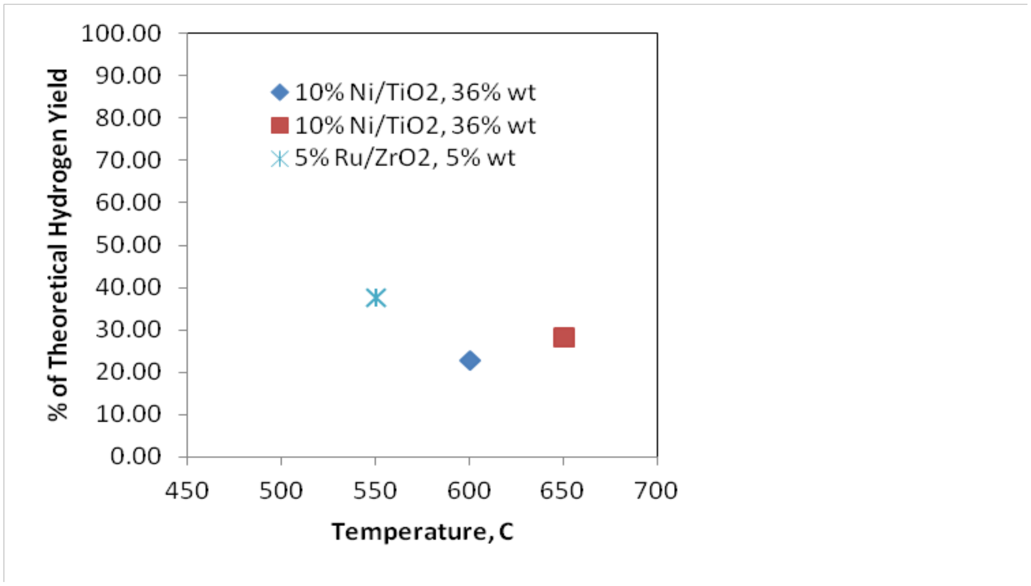

Fig 7.2 Effect of temperature on H_2 yield, 10% Ni/TiO_2, $\tau = 2$ s

In the case of the 10% Ni/TiO_2 catalyst the effect of reaction temperature can be observed by the small increase in the H_2 concentration and H_2 yield when the temperature was increased from 600 to 650 ^oC. The feed concentration of 36.2% corresponds to a water to glycerol feed ratio of 9:1. Furthermore, the low residence time of 2s implies that secondary methane formation reactions do not take place resulting in a lower methane concentration in the product gases. This is observed by the low methane concentrations of 4.15 % and 3.58% at 600 and 650 ^oC respectively.

7.4.2 Effect of residence time

From the 5% Ru/ZrO_2 system, the combined effect of higher reaction temperature and reduced residence times lead to slightly higher hydrogen yields and much lower methane concentration in the product gas. This result is in agreement with May et al who also studied the effect of residence time on a system with 5% feed concentration at 350 bar at 510 ^{o}C and 550 ^{o}C. A slightly higher hydrogen yield obtained in this work in comparison can be explained by the reduced feed concentration of 2.5% compared to the 5 wt% used in their work. As is the case with model bio-oil compounds, the same trend of improved hydrogen yields with decreasing feed concentrations is confirmed in this work. This can be seen in the figure 5.3 below.

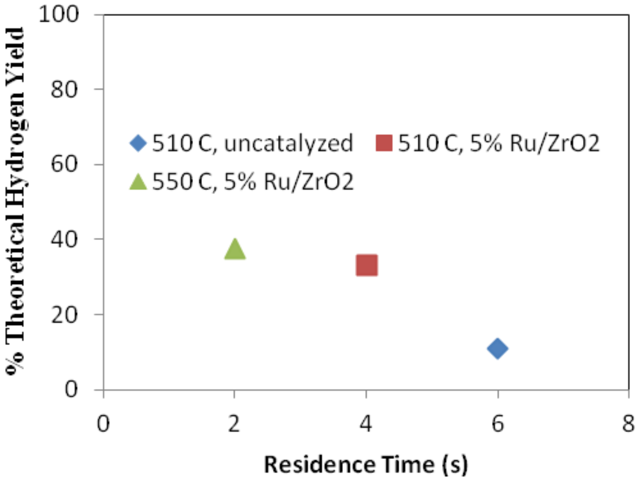

Fig 7.3 Effect of residence time on Hydrogen Yield, Ru/ZrO_2 runs at 5 wt% feed.

7.5 Conclusion

The catalytic conversion of glycerol to hydrogen was studied for two different catalyst support systems, 5% Ru/ZrO_2 and 10% Ni/TiO_2. Both Ru and Ni are known metals that can cause C-C bond scission, however Ni is a much more abundant and less expensive material which has not been studied extensively in the context of supercritical water gasification and reforming. The effect of reaction temperature and residence time was studied to maximize hydrogen yield from glycerol. It was found that lower residence time gave higher hydrogen yield and reduced methane concentration in the product gas. Additionally, 10% Ni/TiO_2 catalyst was able to gasify 36 wt% of glycerol at temperatures of 600 C and 650 C with no reactor plugging. For completeness, future work on using Ni catalysts in the supercritical water reforming of glycerol must include long term testing to determine the stability of Ni catalysts to coking and carbon deposition where Ru, Rh and Pt based catalysts have traditionally been successful.

7.6 References

1. Gupta, R.B., *Hydrogen fuel: production, transport, and storage*2008: CRC.
2. Vaidya, P.D. and A.E. Rodrigues, *Glycerol reforming for hydrogen production: a review.* Chemical engineering & technology, 2009. **32**(10): p. 1463-1469.
3. http://biodiesel.org/production/production-statistics.
4. Lang, X., et al., *Preparation and characterization of bio-diesels from various bio-oils.* Bioresource Technology, 2001. **80**(1): p. 53-62.
5. Luo, N., et al., *Thermodynamic study on hydrogen generation from different glycerol reforming processes.* Energy & Fuels, 2007. **21**(6): p. 3505-3512.
6. Chui, F., A. Elkamel, and M. Fowler, *An integrated decision support framework for the assessment and analysis of hydrogen production pathways.* Energy & Fuels, 2006. **20**(1): p. 346-352.
7. Wang, H., et al., *Thermodynamic analysis of hydrogen production from glycerol autothermal reforming.* International Journal of Hydrogen Energy, 2009. **34**(14): p. 5683-5690.

8. Byrd, A.J., K. Pant, and R.B. Gupta, *Hydrogen production from glycerol by reforming in supercritical water over Ru/Al< sub> 2</sub> O< sub> 3</sub> catalyst.* Fuel, 2008. **87**(13): p. 2956-2960.

9. Adhikari, S., S.D. Fernando, and A. Haryanto, *Hydrogen production from glycerin by steam reforming over nickel catalysts.* Renewable energy, 2008. **33**(5): p. 1097-1100.

10. Adhikari, S., S. Fernando, and A. Haryanto, *Production of hydrogen by steam reforming of glycerin over alumina-supported metal catalysts.* Catalysis Today, 2007. **129**(3-4): p. 355-364.

11. May, A., et al., *Catalytic gasification of glycerol in supercritical water.* Chemical Engineering Journal, 2010. **160**(2): p. 751-759.

12. Lehnert, K. and P. Claus, *Influence of Pt particle size and support type on the aqueous-phase reforming of glycerol.* Catalysis Communications, 2008. **9**(15): p. 2543-2546.

13. Luo, N., et al., *Glycerol aqueous phase reforming for hydrogen generation over Pt catalyst–Effect of catalyst composition and reaction conditions.* Fuel, 2008. **87**(17): p. 3483-3489.

14. Byrd, A.J., K. Pant, and R.B. Gupta, *Hydrogen production from glucose using Ru/Al2O3 catalyst in supercritical water.* Industrial & Engineering Chemistry Research, 2007. **46**(11): p. 3574-3579.

15. Adhikari, S., S. Fernando, and A. Haryanto, *A comparative thermodynamic and experimental analysis on hydrogen production by steam reforming of glycerin.* Energy & Fuels, 2007. **21**(4): p. 2306-2310.

16. Adhikari, S., S.D. Fernando, and A. Haryanto, *Hydrogen production from glycerol: An update.* Energy Conversion and Management, 2009. **50**(10): p. 2600-2604.

17. Byrd, A.J., et al., *Hydrogen production from catalytic gasification of switchgrass biocrude in supercritical water*. International Journal of Hydrogen Energy, 2011.

8: Future Work

The work in this thesis represents starting points for future work that can prove to be viable options for the increasingly pertinent and symbiotic relationship between energy and environmental solutions. That is, on the one hand there is a constantly increasing demand for energy while there is the necessity of obtaining and distributing this energy with minimal damage to environment. This is a challenging problem because we have grown accustomed to fossil fuel based resources which also have to be used in the near future. The concept of using hydrogen as a fuel is advantageous because both renewable and fossil fuel based feedstock can be converted into this common denominator.

8.1 Future experimental work suggestions

8.1.1 Catalysis in Supercritical water reforming of bio-oil

In Chapters 2 and 3, a thermodynamic analysis of the supercritical water reforming of acetic acid and mixtures of model compounds to represent actual bio-oil was conducted. The results were promising because close to theoretical hydrogen yields were obtained at high S/C ratios and temperatures. The next logical step is to perform laboratory scale experiments in this optimal operating window. There are several additional aspects that will have to be considered and from which important information can be gleaned.

A literature review of the typical catalysts that have been used in the steam reforming of bio oil and bio-oil model compounds shows that base metals such as Co, Ni, Fe and Cu as well as noble metals such as Pt, Pd, Rh and Ru have been extensively tested. The important limiting factors in the supercritical water reforming are similar to those observed in steam reforming of bio-oil; namely sintering and carbon deposition on the selected catalysts which lead to ultimate deactivation of the catalyst.

When comparing base metal and noble metal catalysts, it was found that the activity of the Ni at loadings of ~ 10% was found to be similar to the noble metals such as Pt, Ru and Rh. The catalyst must be able to break the C-C bond of the feedstock and be able to catalyze the reforming reactions taking place. Ni has the capability of not only doing these but can also catalyze the water-gas shift reaction. Further, Ni is significantly cheaper than noble metals which make its use more appreciable. However, the resistance to carbon deposition was found to be much lower in Ni than Pt and Ru. Also using a Pt based catalysts allows much lower temperatures of operation. Typical catalyst supports used for Ni in the steam reforming of bio-oil compounds have been Alumina and Silica. However, the use of a K-promoted Alumina support has been shown to increase the longevity of the catalyst. This is because one can reduce the Ni loading, high loadings of which have been known to increase sintering. Further use of Mg-Al_2O_3 spinel support has shown high yields of H_2 during steam reforming. However its use has been known to plug packed beds quickly and is not recommended.

Therefore, for the future work it is suggested to investigate Ni/ Al_2O_3 catalysts with Ni loading between 5 to 10% by weight. It will be important to compare the amount of coke formed and its morphology using TGA and XPS respectively. The amount of coke formed at different GHSV between SR and SCWR will provide valuable information on the applicability of SCWR in large scale applications. Thirdly, long term catalytic testing have not been reported in the literature for SCWR

8.1.2 Sorption enhanced supercritical water reforming

In Chapter 5 it was demonstrated how one can overcome difficulties in using $Mg(OH)_2$, an important test sorbent in fixed bed operations. To briefly summarize, during all mineral carbonation processes using Mg-rich minerals, the main aim is to extract the Mg from the silicates and convert to $Mg(OH)_2$ which has the highest reactivity to CO_2 compared to other oxides of Mg. Firstly, the sorption enhanced operation using $Mg(OH)_2$ along with the addition of an inert(at the reactor conditions) $CaCO_3$ sorbent to the $Mg(OH)_2$ which made the average particle mixture not plug as much as pure $Mg(OH)_2$. Calculations showed that there would not be sufficient loading of $Mg(OH)_2$ in the reactor to show an appreciable CO_2 capture and consequently observable improvement in H_2 yield without sorbent.

As a future work it is suggested that larger reactor volumes be used to carry out the experiments. The current volume of the Inconel reactor used was 3.6 cc which meant that enough sorbent loading was not possible to get a quantitative assessment of CO_2 capture in the process. Different gas-solid contacting may also be used to study sorption enhanced reforming. Fluidized bed reactors are conventionally used in CO_2 capture of sorbents and a smaller micro-fluidized bed has been used by Czernik et al in the study of bio-oil reforming in steam. However, the use of fluidized bed reactors results in potential problems such as attrition. Therefore, it is recommended that fixed bed reactor tests to obtain a breakthrough curve using a 50% mixture of $CaCO_3$ and $Mg(OH)_2$.

8.2 Future Simulation Work

The work done in this thesis does not include an energetic and exergetic comparison of supercritical water reforming with other competing technologies. Future work that can provide useful information in the scale up and ultimate industrial use can be:

1. Exergy balance of the process to include any bottlenecks in the process that can be improved upon to make the process more attractive.
2. Sensitivity analysis: Parametric effect of temperature, pressure and concentration on overall thermal efficiency of the process.
3. Supercritical water gasification is one technology where the large pyrolysis step is bypassed to directly gasify the biomass in supercritical water conditions wherein the same advantages prevail. It would be helpful to determine the difference in H_2 yield and determine if the pyrolysis step makes the ultimate goal of producing H_2 energetically attractive.