THEORETICAL AND EXPERIMENTAL INVESTIGATION OF HYDROGEN PRODUCTION BY GASIFICATION OF BIOMASS

By

MADHUKAR MAHISHI

A DISSERTATION PRESENTED TO THE GRADUATE SCHOOL
OF THE UNIVERSITY OF FLORIDA IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

UNIVERSITY OF FLORIDA

2006

I would like to dedicate this work to my father Shri R. K. Mahishi

ACKNOWLEDGMENTS

First of all I would like to thank my advisor, Professor D. Y. Goswami, for giving me an opportunity to work with him at the Solar Energy and Energy Conversion Laboratory and conduct research in the areas of renewable energy and hydrogen production. His guidance, advice and encouragement to work independently greatly helped in shaping my thoughts and in molding me from a graduate student to a researcher.

I would like to thank Dr. Skip Ingley, Dr. Bill Lear, Dr. S.A. Sherif and Dr. Donald Rockwood for agreeing to serve on my supervisory committee and also for their advice, comments and suggestions during the various phases of my PhD.

I would like to acknowledge the assistance and support of Dr Helena Hagelin-Weaver (Department of Chemical Engineering) during the fabrication of the experimental set-up for biomass gasification. I would like to thank all the staff members and colleagues of the Solar Energy and Energy Conversion Laboratory at UF. I would also like to acknowledge the US Department of Energy for funding our research on hydrogen production. A word of thanks goes to all my present and former room-mates (Sanjay Solanki, Viswanath Urala, Kaushal Mudaliar, Purushottam Kumar, Ashish Gupta, Sudarshan Jagannathan and others) whose enthusiasm and co-operation made graduate student life in the US a very memorable experience.

Above all I would like to thank my parents for their patience, encouragement and support all through during my PhD. Finally I would like to thank God for giving me the opportunities and challenges which, over the years, have helped me become a better person.

TABLE OF CONTENTS

page

ACKNOWLEDGMENTS 4

LIST OF TABLES 8

LIST OF FIGURES 9

ABBREVIATIONS 12

ABSTRACT 14

CHAPTER

1 INTRODUCTION 16

- Significance and Need for Hydrogen: An Overview 16
- Introduction to Present Research 19

2 HYDROGEN PRODUCTION METHODS 24

- Introduction 24
- Hydrogen Production Methods 24
  - Steam Methane Reforming (SMR) 24
  - Partial Oxidation or Autothermal Reforming of Methane 25
  - Coal Gasification 27
  - Biomass Gasification and Pyrolysis 28
  - Electrolysis 29
  - Thermochemical Hydrogen Production 30
    - Zn/ZnO cycle 31
    - UT-3 cycle 31
  - Photocatalytic Hydrogen Production 32
  - Photoelectrochemical Hydrogen Production 33
  - Biological Hydrogen Production 34
    - Fermentation of bacteria 34
    - Biophotolysis 35
- Summary 36

3 BACKGROUND AND LITERATURE REVIEW 44

- Introduction 44
  - Pyrolysis 44
  - Gasification 45
  - Combustion 45
  - Liquefaction 45
- Lab-Scale Production of Hydrogen from Biomass 46

An Overview of Biomass Gasification for Hydrogen Production 47
    Catalysis 47
        Non-Metallic Oxides 49
        Commercial Nickel Reforming Catalyst 50
        Additional Catalyst Formulations 51
    Pretreatment Technologies 53
    Chemical Kinetic Studies 54
    Experimental Studies on Biomass Gasification 57
    Thermodynamic Studies on Gasification 58
    Sorbent Enhanced Gasification 61
Scope of the Present Work 64

4 THERMODYNAMIC ANALYSIS OF BIOMASS GASIFICATION 70

Introduction 70
Fundamentals 70
Effect of Process Parameters on Equilibrium Hydrogen Yield 72
    Effect of Temperature 73
    Effect of Pressure 74
    Effect of Steam Biomass ratio 74
    Effect of Equivalence Ratio 75
    Optimum Process Parameters 75
Energy Analysis 76
    Effect of Temperature on Thermodynamic Efficiency 78
    Effect of Steam Addition on Thermodynamic Efficiency 78
    Effect of ER on Thermodynamic Efficiency 79
Comparison of Equilibrium Results with Experimental Data 80
    Summary and Conclusion 81

5 ABSORPTION ENHANCED BIOMASS GASIFICATION 95

Introduction 95
Concept of Absorption Enhanced Gasification 96
Application of SEG to Biomass Gasification 98
    Case I: Base case (no sorbent) 98
    Case II: Ethanol gasification in the presence of CaO sorbent (sorbent placed in the reformer) 100
Energy Analysis 102
Conclusion 104

6 EXPERIMENTAL STUDIES ON BIOMASS GASIFICATION 119

Objective 119
Experimental Facility 120
    Test Set-up 120
        Gasifier (Primary reactor) 120
        Secondary reactor 120

Steam generator 121
Gas cooling system (heat exchanger) 121
Heaters, insulation and tubing/fittings 121
Instrumentation 122
Gas Analysis Facility 122
GC Calibration 123
Test Methodology 123
Test Results and Analysis 125
Effect of Temperature 125
Effect of Sorbent 127
Conclusion 128

7 REGENERATION OF SPENT SORBENT 152

Introduction 152
The Reversible Calcination Carbonation Process 152
Combusting a Carbonaceous Fuel 154
Using Concentrated Solar Energy 155
Waste Heat from Gas Turbine Exhaust or from SOFC 156
Kinetics of the Reversible Calcination Carbonation Reactions 157
Sorbents other than Calcium oxide 158
Summary 160

8 SUMMARY, CONCLUSION and RECOMMENDATIONS 163

Summary 163
Conclusions 166
Recommendations for Further Work 166

APPENDIX LIST OF PUBLICATIONS 168

REFERENCES 169

BIOGRAPHICAL SKETCH 179

LIST OF TABLES

Table page

1-1 Summary of hydrogen production methods 23

3-1 Feedstock composition 67

4-1 Equilibrium gas moles at different gasification pressures 83

5-1 Reactions in SEG for some typical fuels 105

5-2 Comparison of energy consumption in biomass gasification with and without sorbent 106

5-3 Thermodynamic efficiency and energies 107

6-1 Heater ratings 130

6-2 Ultimate and proximate analyses 131

6-3 Effect of temperature on the products of biomass gasification 132

6-4 Carbon conversion efficiency (no sorbent) 133

6-5 Equilibrium yields of biomass gasification products 134

6-6 Effect of temperature on gas composition in the presence of sorbent 135

6-7 Carbon conversion efficiency (sorbent enhanced gasification) 136

LIST OF FIGURES

Figure page

2.1 Block diagram of hydrogen production by steam methane reforming 37

2.2 Block diagram of hydrogen production by partial oxidation of heavy oils 38

2.3 Principle of hydrogen production by high temperature electrolysis (HTE) 39

2.4 Block diagram of the Zn/ZnO water splitting thermochemical cycle for hydrogen production 40

2.5 UT-3 cycle reactions and flow of material 41

2.6 Photocatalytic hydrogen production 42

2.7 Principle of photoelectrochemical hydrogen production..43

3.1 Biomass gasification pilot plant..68

3.2 Schematic of biomass gasification set up for producing hydrogen 69

4.1 Variation of Gibbs energy with extent of reaction..84

4.2 Effect of temperature for P = 1 atm, β = 1, ER = 0 85

4.3 Effect of SBR on equilibrium composition 86

4.4 Effect of ER on Equilibrium composition 87

4.5 Schematic of biomass gasifier 88

4.6 Efficiency Vs temperature for various β (ER = 0.1)...89

4.7 Efficiency Vs temperature for various β (ER = 0.2)...90

4.8 Efficiency Vs temperature for various β (ER = 0.3)...91

4.9 Efficiency Vs temperature for various β (ER = 0.4)...92

4.10 Comparison of equilibrium data with experimental data o for different temperatures and residence times 93

4.11 Comparison of equilibrium data with experimental data for different β and ER 94

5.1 Concept of absorption enhanced gasification 108

5.2 Schematic of SEG (concept)...109

5.3 Flow sheet for conventional biomass gasification 110

5.4 Effect of reformer temperature on product yield 111

5.5 Effect of reformer pressure on product yield 112

5.6 Effect of steam ethanol ratio on product yield at 700^{o}C 113

5.7 Flow sheet for ethanol gasification with CaO sorbent 114

5.8 Effect of temperature on product yield for sorbent enhanced reforming.........................115

5.9 Effect of pressure on the product yield for sorbent enhanced reforming 116

5.10 Effect of steam/ethanol ratio on product yield for sorbent enhanced reforming 117

5.11 Effect of CaO/ethanol ratio on the product yield..118

6.1 Biomass gasification test set-up...137

6.2 Photograph of the test set-up..138

6.3 Gas chromatograph (SRI 8610C)..139

6.4 Set-up for GC calibration...140

6.5 Hydrogen calibration curve..141

6.6 CO calibration curve 142

6.7 CO_2 calibration curve 143

6.8 CH_4 calibration curve..144

6.9 Southern pine bark “as received”...145

6.10 Pelletized pine bark...146

6.11 Effect of temperature on gas yields (no sorbent) 147

6.12 Effect of sorbent addition at 500^{o}C...148

6.13 Effect of sorbent addition at 600^{o}C...149

6.14 Effect of sorbent addition at 700^{o}C...150

6.15 Tar laden condensate samples of plain biomass gasification (left) and sorbent enhanced gasification..151

7.1 Equilibrium CO_2 pressure as a function of temperature 161

7.2 Biomass gasification with calcination of used sorbent 162

ABBREVIATIONS

ER	Equivalence Ratio (actual air to biomass ratio divided by stoichiometric air to biomass ratio)
E_{wood}	chemical energy stored in biomass (wood) (kJ)
H	enthalpy (kJ/mol)
ΔH	enthalpy change due to temperature (kJ/mol)
$H^o{}_f$	enthalpy of formation (kJ/mol)
LHV	Lower Heating Value (kJ/mol)
n	no. of moles
P	pressure (atm)
Q_{air}	heat supplied to air-preheater (kJ)
Q_{EG}	heat input to equilibrium gasifier (kJ)
Q_{steam}	heat supplied to steam generator (kJ)
SBR	Steam Biomass Ratio (denoted by β; defined as moles of steam per mole of biomass)
SEG	Sorbent Enhanced Gasification
SMR	Steam Methane Reforming
T	Temperature (K)
WGS	Water Gas Shift reaction or Water Gas Shift reactor
g	specific Gibbs energy (kJ/kg)
q	heat transferred (kJ/kg)
s	entropy (J/kg-K)
u	specific internal energy (kJ/kg)

v	specific volume (m^3/kg)
w	work done (kJ/kg)

Greek Symbols:

β	moles of steam per mole of biomass
γ	moles of oxygen per mole of biomass
η	thermodynamic efficiency (%)
τ	residence time (s)
ξ	extent of reaction

Subscripts:

gen	generated
sys	system
surr	surrounding
NS	total number of species

Abstract of Dissertation Presented to the Graduate School
of the University of Florida in Partial Fulfillment of the
Requirements for the Degree of Doctor of Philosophy

THEORETICAL AND EXPERIMENTAL INVESTIGATION OF HYDROGEN PRODUCTION BY GASIFICATION OF BIOMASS

By

Madhukar Mahishi

December 2006

Chair: Yogi Goswami
Major Department: Mechanical and Aerospace Engineering

A detailed theoretical and experimental investigation of hydrogen production by thermochemical gasification of biomass was conducted. The thermodynamics of biomass gasification was first studied to determine the hydrogen yield at equilibrium. The gasification process is characterized by a number of endothermic and exothermic reactions. A combination of these reactions enables internal energy transfer, and therefore improved process efficiency. The maximum hydrogen yield is limited by thermodynamic equilibrium. One solution to this problem is to remove one of the co-products (CO_2) that governs the equilibrium hydrogen yield. In recent times, sorbents (such as calcium oxide) have been used for CO_2 removal from fossil fuel exhaust. The same principle was applied here to drive the reactions in favor of hydrogen. In the process the sorbent gets saturated and has to be regenerated for further use.

Process simulations were conducted using an ASPEN simulator with the end objective of determining the hydrogen yield in presence of a CO_2 sorbent. Ethanol was used as the model biomass compound and calcium oxide was the representative sorbent. The simulations showed 19% increase in hydrogen yield and about 50% reduction in product gas CO_2 while using the sorbent. The hydrogen yield in the presence of sorbent at a gasification temperature of 600°C was comparable to the hydrogen yield without the sorbent at 750°C. Hence there is a potential to

reduce the gasifier operating temperature by about 100-150^{o}C while still getting the same amount of hydrogen. The in-situ heat transfer (CO_2 absorption is exothermic) reduced the gasifier heat duty by almost 42%.

Based on the encouraging results obtained from simulations, experiments were conducted using Southern pine bark as the model biomass and calcium oxide as the representative sorbent. Hydrogen yield increased substantially (from 320 ml/g to 719 ml/g) by using sorbents at gasification temperature as low as 500^{o}C. The product gas had much less tars and particulate matter as compared to conventional gasification. The carbon conversion efficiency (a way of quantifying the effectiveness of gasification) increased from a mere 23% to 63% while using sorbent.

Sorbent enhanced biomass gasification has the potential to produce a hydrogen rich, CO_2 free and possibly tar free gas that can be sent to a fuel cell or gas turbine with minimal cleaning. Hence there is a potential to reduce the equipment needed for hydrogen production. This will lead to reduced capital and operating costs. Hence sorbent enhanced biomass gasification has the potential to become a cost effective technology for producing renewable hydrogen.

CHAPTER 1
INTRODUCTION

Significance and Need for Hydrogen: An Overview

Present day energy resources such as coal, oil and natural gas are being consumed at an accelerated rate with fear of depletion in the next few decades. It is reported that some of the oil rich countries would fail to meet the world energy demand in the next few decades. For example, United Arab Emirates is expected to exhaust its oil and natural gas reserves by 2015 and 2042 respectively [1], and fossil sources in Egypt would possibly be exhausted within the next two decades [2]. There is also a concern about the environmental pollution caused by the use of fossil fuels. According to a recent study the world CO_2 emissions from fossil sources have increased by 24.4% from 1990 to 2004 [3]. Apart from CO_2, other contaminants such as CO, NO_x, and SO_x are released during the combustion of fossil fuels. These contaminants cause acid rains, deplete the stratospheric ozone layer and are also known to be carcinogenic. According to an EPA study, vehicles in the US account for 65% of total oil consumption and result in 78% CO, 45% NOX and 37% Volatile Organic Compound (VOC) emissions [4]. Among all the air pollutants emitted by the combustion of fossil fuels, CO_2 alone accounts for 99% (by weight) of the total emissions [5]. The average surface temperature of earth has increased by 0.6^oC over the past two centuries [6]. If this trend continues it may eventually lead to higher sea levels and significant changes in global precipitation patterns. The trend in the transportation sector in industrialized countries is towards more vehicles, more freight transport by road and larger and heavier passenger vehicles. Furthermore, developing countries like China and India with large population and growing economies are expected to add to the rapid growth in vehicle usage for transportation applications [7]. This would further lead to large scale emissions which may drastically change the global weather patterns, thus affecting mankind and environment.

The world energy demand has been steadily increasing over the last few decades. According to a recent study conducted by the US Department of Energy, the world energy demand is expected to increase to 722 quads (Quadrillion BTU) by 2030 from the present demand of 421 quads (2003) [8], a 71% increase largely due to growth in developing countries. According to the same study fossil fuels will continue to supply much of the increment in projected demands; however, depletion of fossil reserves is a matter of concern. Although oil would remain an important energy source, its share in total energy consumption would decrease from 38% in 2003 to 33% in 2030. This is largely in response to the higher world oil prices which would be driven by rapid depletion of oil reserves in many parts of the world. Among all sectors, transportation and industry continue to be the major oil consumers. Alternate fossil sources such as natural gas are also limited. According to a recent study conducted by British Petroleum, the Reserves to Production ratio (R/P) of natural gas in the US is less than 10 [9]. Hence, developing alternate energy carriers is necessary. In recent years, hydrogen has gained recognition as a potential substitute to fossil fuels. Some of the factors favoring hydrogen are

- lack of green-house gas emissions when combusted or used in a fuel cell
- high energy content on a mass basis as compared to gasoline or natural gas
- easy and efficient conversion to electricity using fuel cells

Hydrogen is an important raw material for chemical, petroleum and agro-based industries. The demand for hydrogen in the hydrotreating and hydrocracking of crude petroleum is steadily increasing [10, 11]. Hydrogen is catalytically combined with various intermediate processing streams and is used in conjunction with catalytic cracking operations to convert heavy and unsaturated compounds to lighter and more stable compounds. Large quantities of hydrogen are used to purify gases such as argon that contain trace amounts of oxygen. This is done by catalytic combination of oxygen and hydrogen followed by removal of the resulting water. In the food and beverages industry, it is used for hydrogenation of unsaturated fatty acids in animal and vegetable oils, to produce solid fat and other food products. Hydrogen is also used as a carrier gas in the manufacture of semi conducting layers in integrated circuits. The pharmaceutical industry uses hydrogen to make vitamins and other pharmaceutical products. Hydrogen is mixed with inert gases to obtain a reducing atmosphere which is required for many applications in the metallurgical industry such as heat treating steel and welding. It is often used in annealing stainless steel alloys, magnetic steel alloys, sintering and for copper brazing. It is also used as a reducing agent in the float glass manufacturing industry.

Hydrogen is consumed in the production of methanol [12], synthesis of ammonia [13], methanol to gasoline synthesis [14] and also for hydrocarbon synthesis by Fischer Tropsch processes [15]. In recent times, the US government has tightened regulations on automotive tailpipe emissions, thereby cutting down the benzene and sulfur compounds in gasoline. Hence, more hydrogen is now needed in refineries for processing of heavy crudes and for desulphurization in order to meet the product quality standards. Presently, fossil fuels such as gasoline and diesel are used all over the world and have a well-established infrastructure. These fuels will continue to be in use until a long term substitute that is environmentally friendly and economically feasible is found. Hence the hydrogen demand for processing these fuels must be met.

As a fuel, hydrogen is considered to be very clean as it releases no carbon or sulfur emissions upon combustion. The energy contained in hydrogen on a mass basis (120 MJ/kg) is much higher than coal (35 MJ/kg), gasoline (47 MJ/kg) and natural gas (49.9 MJ/kg) [16].

However, on a volumetric basis hydrogen has lower energy density. Moreover chemical energy stored in hydrogen can be directly converted into electricity by a fuel cell. The conversion efficiency of a fuel cell is higher than conventional combustion engines, thereby making fuel cells attractive energy conversion devices (and hence hydrogen an attractive fuel) for transportation and stationary applications. Hydrogen has long been a fuel of choice for the jet propulsion and space industry. NASA has been using liquid hydrogen to fuel the space shuttle's main engine and hydrogen fuel cells provide onboard electric power. The space crew even drinks the water produced by the fuel cell's chemical process.

The rapid developments in fuel cells have prompted many automotive companies and the US government (through the Department of Energy) to speed up research efforts on hydrogen production. In 2003, the US government announced a $1.2 billion commitment over 5 years to accelerate hydrogen research to overcome obstacles in the commercial development of fuel cells [17].

Many experts predict that hydrogen will eventually power tomorrow's industries and thereby may replace coal, oil and natural gas [18, 19]. However it will not happen until a strong framework of hydrogen production, storage, transport and delivery is developed. All the steps must be technically feasible and economically viable.

Introduction to Present Research

Hydrogen is not found in free-state in nature. It is normally combined with other elements such as carbon, oxygen, sulfur, chlorine and so on. Hydrocarbons are a common resource, and steam reforming of hydrocarbons (methane) is a popular method of present day hydrogen production. However, producing hydrogen from hydrocarbons does not address the environmental concerns as the problem gets merely shifted from the automotive tailpipe to some remote location where hydrogen is produced. In order to have environment friendly hydrogen we must be able to produce it from renewable resources. Table 1-1 gives a summary of the various methods used for producing hydrogen. The table lists the present status of technology and the cost of producing hydrogen. Of all the renewables, biomass is a promising resource with a good potential for hydrogen production. In fact, considering the CO_2 penalty which may be imposed on fossil fuels, biomass has the potential to become cost competitive even with fossil fuels. Biomass is a resource that is abundantly available in many parts of the world.

The chemical energy stored in biomass can be converted to hydrogen by biological or thermal methods. The current research investigates the thermal pathway of converting biomass to hydrogen. Thermo-chemical biomass gasification has been used for a long time for producing syngas (a mixture of CO and H_2). Biomass when gasified in the presence of a suitable medium (such as steam) produces a gas mixture rich in CO and H_2 and containing other gases such as CH_4, CO_2 and small amounts of higher hydrocarbons. Biomass gasification is characterized by a number of reactions that are exothermic and endothermic which suggests that heat can be transferred internally to improve the process efficiency. A thermodynamic analysis would determine the necessary conditions for maximizing the process efficiency and hydrogen yield at equilibrium. A review of the literature showed us that such a thorough thermodynamic analysis has not been performed for hydrogen production from biomass. Therefore a thermodynamic analysis was conducted with the end objective of improving the process efficiency and also to determine the conditions necessary for maximizing the hydrogen yield at equilibrium. The important variables that influence the hydrogen yield are gasification temperature, gasification pressure, steam to biomass ratio and equivalence ratio. All these parameters were varied over typical range encountered in real life gasification systems. The gasifier temperature strongly influences the hydrogen yield in product gas. In actual practice, the kinetics of biomass gasification reactions are fast at temperatures above 700^{o}C. At these temperatures, lot of gases and some liquid volatiles are released. At lower temperatures, more liquids are formed and these may settle and clog the downstream equipment. At higher temperatures there is more gas in the product stream (due to reforming of all the hydrocarbons); however this would also require a high temperature heat source. At high temperatures (above 850^{o}C), the water gas shift reaction occurs in the reverse direction and reduces the hydrogen yield. The gasification pressure too affects the hydrogen yield. Most biomass gasifiers operate at atmospheric pressure. High pressure systems reduce the equilibrium hydrogen yield. Low pressure (sub-atmospheric) systems increase the hydrogen yield, but the increase is only marginal and hence the optimum pressure for hydrogen production is one atmosphere.

Steam to biomass ratio also strongly influences the amount of hydrogen produced and process efficiency. In general, when more steam is supplied the hydrogen yield is higher due to reformation of hydrocarbons. Equivalence ratio, which is a measure of the amount of air supplied during biomass gasification, is another variable that affects the amount of hydrogen produced.

The hydrogen yield in biomass gasification is limited by chemical equilibrium constraints. There is an optimum temperature, pressure, steam to biomass ratio and equivalence ratio at which the highest hydrogen yield occurs. In order to further enhance the hydrogen yield, the equilibrium constraint has to be removed. This is possible by removing one of the co-products of gasification (CO_2) that influences the equilibrium. If we can continuously remove the CO_2 as soon as it is formed, the shift reaction goes to completion and yields a hydrogen rich gas.

In the past, sorbents such as calcium oxides have been used to remove CO_2 from the fossil fuel exhaust. If the CO_2 absorption reaction can be coupled with biomass gasification and water gas shift reactions, we can produce a gas rich in hydrogen with small amounts of CO, CO_2, CH_4

and other impurities. Furthermore, the exothermic CO_2 absorption reaction can be coupled with the endothermic biomass steam gasification reaction. This would enable in-situ heat transfer and reduce the net energy consumed by the gasifier. With reduced heat duty, the gasifier will become compact and this will reduce the capital cost of the system. Process simulations were carried out in ASPEN to study the effect of sorbent addition on hydrogen yield. The temperature, pressure, steam to biomass ratio and sorbent to biomass ratio were varied over a wide range and the hydrogen yield was determined. An energy analysis was then carried out to determine the efficiency and energy consumption of the conventional and sorbent enhanced processes. An improvement in the hydrogen yield of about 19% and reduction in product gas CO_2 of about 50.2% was observed. The gasifier heat duty was reduced by about 42%.

Based on the promising results of the simulations an experimental setup was fabricated and tests were carried out. The experimental studies showed a substantial improvement in the hydrogen yield while using sorbents. A hydrogen rich product gas was obtained by steam gasifying Southern pine bark in the presence of calcium oxide. Thereafter, some studies on regeneration of used sorbent were carried out. The dissertation provides a detailed theoretical and experimental investigation of hydrogen production by steam gasification of biomass in the presence of sorbents.

Table 1-1: Summary of hydrogen production methods

Method	Energy Efficiency[1]	H_2 production Cost	Scale/Current Status	Major Advantage	Major Disadvantage
SMR	83%	$ 0.75 /kg (w/out CO_2 sequestration)	Large/ Currently available	Proven technology High Efficiency Economically favorable	CO_2 by-product Limited methane supply
Partial Oxidation	70-80%	$ 1.39 /kg (Residual oil)	Large/Available for large hydrocarbons	Proven technology Economically feasible Methane pipeline in place	CO_2 by-product Lower efficiency than SMR
Autothermal reforming	71-74%	$1.93 /kg	Large/ Currently available	Proven technology Cheaper reactor than SMR Methane pipeline in place	CO_2 by-product Limited methane supply Lower efficiency than SMR
Coal gasification	63%	$0.92/kg (w/out CO_2 sequestration)	Large/ Currently available	Proven technology Economically favorable	CO_2 by-product Less H_2 rich than SMR
Biomass Gasification	40-50%	$1.21-2.42/kg	Mid-size/Currently Available	Renewable No foreign imports	Seasonal availability Transportation problems
Biomass Pyrolysis	56%	$1.21-2.19/kg	Mid-size/Currently Available	Renewable Easily Transportable	Seasonal availability Varying H_2 content of feedstocks
Electrolysis	25%[2]	$2.56-2.97/kg (Nuke source)	Small/ Currently available	Proven technology Emission free when used with renewables	Low overall efficiency High cost Current capacities still small
Thermo-chemical	42% (850°C)	$2.01/kg (Sulfur-Iodine cycle)	Under research	Emission free No dependence on fossil fuel sources	High capital costs Severe operating conditions Highly corrosive conditions (UT-3; sulfur Iodine)
Photocatalytic	10-14% (theoretical)	$4.98/kg	Under research	Renewable No fossil dependence	Costly Low efficiency
Biological	24% (speculative)	$5.52/kg	Under research	Renewable No fossil dependence	Low efficiency High capital cost

[1] Efficiency is defined as the ratio of lower heating value of hydrogen in product gas to total energy supplied to the process

[2] Includes the efficiency of electricity production

CHAPTER 2
HYDROGEN PRODUCTION METHODS

Introduction

Hydrogen is the most abundant element found in the universe. However as compared to fossil fuels, hydrogen does not occur in free-state in nature. It normally exists in combined state with other elements. Hydrogen is bound with carbon in all hydrocarbons; it is bound with oxygen in water and is found in many other compounds such as hydrogen sulfide, hydrogen iodide, hydrochloric acid and so forth. The bound hydrogen can be separated by various methods like thermal, electrochemical, photolytic or biological methods. The next few sections describe the different methods used for producing hydrogen from various sources. Some of these methods are used commercially, others are near commercial stage development and there are still others which are at research stage.

Hydrogen Production Methods

Steam Methane Reforming (SMR)

SMR produces hydrogen in the following three steps [20]:

- methane is first catalytically reformed at elevated temperature and pressure to produce synthesis gas (synthesis gas or syngas is a mixture of H_2 and CO) (equation 2.1)
- a catalytic Water Gas Shift (WGS) reaction is then carried out to combine CO and H_2O to produce additional hydrogen (equation 2.2)
- the hydrogen product is then separated by adsorption

The reforming step occurs as per the following reaction (refer Figure 2.1). The reforming reaction is endothermic and so energy has to be supplied to the process. Methane is treated with high temperature steam to produce a mixture of H_2, CO, CO_2 and other impurities. The reaction is carried out in a reformer containing tubes filled with nickel catalyst at temperatures between 500°C and 950°C and a pressure of 30 atmospheres. Excess steam promotes the second step in the process - the conversion of syngas to the desired end product (hydrogen) as per the Water-Gas Shift reaction

$$CH_4 + H_2O \rightarrow CO + 2H_2 \quad \Delta H = \ +206\ \mathrm{kJ/mol} \tag{2.1}$$

$$CO + H_2O \rightarrow CO_2 + H_2 \quad \Delta H = -41\ \mathrm{kJ/mol} \tag{2.2}$$

The third step of hydrogen separation is conventionally accomplished by pressure swing adsorption (PSA). After removing the hydrogen, the product gas may be treated to remove CO_2 if sequestration is desired.

SMR is the most widely used method for hydrogen production. High efficiency, favorable economics and proven technology characterize the SMR process. SMR is ideal for large scale, centralized hydrogen production. A disadvantage from an economic standpoint is that capture of CO_2 may be necessary in future resulting in additional capital and operating costs. Another concern is the long-term availability of methane. For these reasons, SMR is considered as a transition technology [20]. SMR may play an important role in helping make the switch to hydrogen, but will most likely be replaced by other technologies for long term hydrogen production.

Partial Oxidation or Autothermal Reforming of Methane

Partial oxidation (POX) and Autothermal Reforming (ATR) are similar alternatives to SMR. The POX process partially oxidizes methane in a one-step reaction, while ATR combines partial oxidation and reforming reaction, catalytically reacting methane with a mixture of steam and oxygen. This differs from the steam methane reforming process which treats methane with steam only. Partial oxidation of methane produces a syngas mixture of CO and H_2 as per following the reaction:

$$CH_4 + 0.5O_2 \leftrightarrow CO + 2H_2 \qquad \Delta H = \ -36 \text{ kJ/mol} \tag{2.3}$$

A catalyst is not required but has the potential to enhance the hydrogen yield and lower the operating temperature. As the reaction is exothermic, careful design and control of special reactors to facilitate heat exchange or dilution of reactants is necessary to prevent possible explosion. An oxygen plant is usually installed on site to supply pure oxygen feed. Pure oxygen is preferable because energy is wasted in heating and compressing the additional nitrogen gas if air is used.

A more advanced partial oxidation process is autothermal reforming, a hybrid of partial oxidation and SMR processes. Both the partial oxidation and reforming reactions take place inside the autothermal reactor. The heat from the exothermic partial oxidation reaction supplies a portion of the heat required by the endothermic reforming reaction. Because a portion of the feed methane is burned within the reactor vessel as opposed to heating by an external furnace as in SMR, less energy is required in autothermal reforming. This simplifies the design of the autothermal reactor to one large vessel instead of the complex, bulky reactor design with many tubes necessary for heat exchange in SMR.

At present, commercial processes for partial oxidation using methane feedstock do not exist. This is mainly due to the lower efficiency of the partial oxidation process (70-80%) as compared to more than 80% efficiency in the case of SMR. Commercial partial oxidation is a mature technology when using other hydrocarbon feedstocks especially heavy residual oils (refer figure 2.2) (examples are Texaco and Shell gasification processes). Small scale partial oxidation units for methane are being developed for use in fuel cell systems, but are still in the research phase [22].

Coal Gasification

Coal gasification involves three steps: treatment of coal feedstock with high temperature steam (1300^{o}C) to produce syngas, a catalytic shift conversion, and purification of the hydrogen product. In the first step, coal is chemically broken down by high temperature (1330^{o}C) and high pressure steam to produce raw synthesis gas, as per the following reaction:

$$C + H_2O \rightarrow CO + H_2 + \text{impurities} \qquad \Delta H > 0 \qquad (2.4)$$

The heat required for this gasification step comes from controlled addition of oxygen, which allows partial oxidation of a small amount of the coal feedstock. Because of this, the reaction is carried out in either an air-blown or oxygen-blown gasifier. The oxygen-blown gasifier is generally used to minimize NO_x formation and make the process more compatible for carbon dioxide sequestration. In the second step, the syngas passes through a shift reactor converting a portion of the carbon-monoxide to carbon-dioxide and thereby produce additional hydrogen

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad \Delta H = -41\ \text{kJ/mol} \qquad (2.5)$$

In the third step, the hydrogen product is purified. Physical absorption removes 99% of impurities. The majority of H_2 in the shifted syngas is then removed in a Pressure Swing Adsorption (PSA) unit. In case of CO_2 sequestration, a secondary absorption tower removes CO_2 from the remaining shifted syngas. Coal is an attractive energy source due to its abundance in the United States and low and traditionally stable prices. Coal gasification is an established technology used in hydrogen production today, but additional technical and economic considerations for capture and storage of CO_2 will be necessary in future.

Biomass Gasification and Pyrolysis

Biomass refers to crops or other agricultural products including hardwood, softwood, and other plant species. It may also include municipal solid waste or sewage, a fraction of which is burned to produce steam for the process. Biomass may be used to produce hydrogen in two ways: 1) direct gasification or 2) pyrolysis to produce liquid bio-oil for reforming.

Direct biomass gasification process is similar to coal gasification. The process is carried out in three steps. First the biomass is treated with high temperature steam in an oxygen-blown or air-blown gasifier to produce syngas mixture composed of hydrocarbon gases H_2, CO, CO_2, tar and water vapor. Char (carbon residue) and ash are left behind in the gasifier. Then, a portion of the char is gasified by reaction with oxygen, steam and hydrogen while another portion is combusted to provide heat. As in the case of coal, the gasification step is followed by shift reaction and purification. Alternatively, the biomass can first be reformed to a liquid (bio-oil) by a process well known as pyrolysis. Pyrolysis is an endothermic process for thermal decomposition of biomass and is carried out at 450-550°C. The bio-oil produced is a liquid composed of oxygenated organics and water [23]. The bio-oil is steam reformed using a nickel-catalyst at 750-850°C, followed by shift reaction to convert CO to CO_2. Following are the general reactions in biomass gasification and pyrolysis:

$$\text{Biomass} + \text{steam}/O_2 \rightarrow H_2 + CO + CO_2 + C_nH_m + \text{impurities} \quad \Delta H>0 \ \text{(gasification)} \qquad (2.6)$$

$$\text{Biomass} + \text{energy} \rightarrow \text{bio-oil} + \text{char} + \text{impurities} \qquad \text{(pyrolysis)} \qquad (2.7)$$

$$\text{Bio-oil} + \text{steam} \rightarrow CO + H_2 \qquad \text{(reforming)} \qquad (2.8)$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad \Delta H = -41\ \text{kJ/mol} \qquad \text{(shift)} \qquad (2.9)$$

Biomass gasification technology has over the years progressed from small laboratory scale models to several demonstration pilot scale plants either for producing electricity or syngas. For example BIOSYN Inc. is an oxygen-blown gasification process in a bubbling fluidized bed gasifier with a bed of silica or alumina which is used for making methanol. There are several commercial gasifier manufacturers in Europe and N. America and many of these are used for producing power or syngas [24]. Biomass resource has the advantage of being renewable, sulfur-free and being locally available. Hence it has a great potential for the future “hydrogen economy”. However, there are many factors limiting commercial biomass hydrogen production, chief among them being

- high transport cost due to low energy density of biomass
- high capital cost of biomass plants
- seasonal availability

Pyrolysis is still at a relatively early stage of research and is not as mature as gasification. However, among all the renewable resources used for hydrogen production, biomass is the one which has the greatest potential for being commercialized in the near future (Table 1-1).

Electrolysis

Electrolysis uses electricity to dissociate water into diatomic molecules H_2 and O_2. An electric potential is applied across a cell with two electrodes containing a conducting medium, generally an alkaline electrolyte solution such as aqueous solution of potassium hydroxide (KOH). Electrons are absorbed and released at the electrodes, forming hydrogen at the cathode and oxygen at the anode. Under alkaline conditions, this process may be described by the following reactions [25, 26]:

Cathode: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ (2.10)

Anode: $2OH^- \rightarrow \frac{1}{2}O_2 + H_2O + 2e^-$ (2.11)

Overall: $H_2O \rightarrow H_2 + \frac{1}{2}O_2$ (2.12)

The net effect is to produce H_2 and O_2 by supplying only water and electricity (refer figure 1.3). The theoretical voltage for the decomposition at atmospheric pressure and $25^{o}C$ is 1.23 volts (V). At this voltage, reaction rates are very slow. In practice, higher voltages are applied to increase the reaction rates. However, this results in increased heat losses to the surroundings, decreasing the efficiency. The necessary voltage may be lowered by using catalysts or sophisticated electrode surfaces. Increasing temperature and pressure may also increase the efficiency at the cost of additional material needed to resist corrosion or higher pressures [27].

There are broadly two types of electrolysis technologies: (1) solid polymer using a proton exchange membrane (PEM) and (2) liquid electrolyte, most commonly potassium hydroxide. A PEM electrolyzer is literally a PEM fuel cell operating in reverse mode. When water is introduced to the PEM electrolyzer cell, hydrogen ions (protons) are drawn into and through the membrane, where they recombine with electrons to form hydrogen molecules. Oxygen gas remains behind in the water. As water is recirculated, oxygen accumulates in a separation tank and can then be removed from the system. Hydrogen gas is separately channeled from the cell stack and captured. Liquid electrolyte systems typically use a caustic solution and in those systems, oxygen ions migrate through the electrolytic material, leaving hydrogen gas dissolved in the water stream. This hydrogen is readily attracted from water when directed into a separating chamber. Electrolysis is well suited to meet early stage fuelling needs of fuel cell vehicle market. Electrolyzers scale down reasonably well; efficiency of electrolysis reaction is independent of cell size. The US DOE has predicted an electrolytic hydrogen production cost of about \$2.5/kg by 2010 for hydrogen for a plant integrated with renewable energy [28].

Thermochemical Hydrogen Production

High temperature heat (500 – $2000^{o}C$) drives a series of chemical reactions that produce hydrogen and oxygen. The chemicals used in the process are reused within each cycle. This process operates in a closed loop and consumes only water and produces hydrogen and oxygen in separate steps. The high temperature heat needed for the process can be supplied by nuclear reactors (up to 1000^{o}C) or by solar energy through concentrated solar collectors (up to 2000^{o}C). Different cycles have been identified to operate in different temperature ranges. There are more than a thousand cycles that have been proposed so far but only a few hold promise for large scale implementation [29, 30]. Two of the popular thermochemical cycles are described below.

Zn/ZnO cycle

Zinc oxide is passed through a reactor heated by solar concentrator at about 1900^{o}C (refer Figure 2.4). At this temperature zinc oxide dissociates into zinc and oxygen gases. Zinc is cooled, separated and reacted with steam (at about 300 to 400^{o}C) to produce hydrogen and solid zinc oxide. The net products are hydrogen and oxygen with water as input. Hydrogen is later separated and purified. The zinc oxide is recycled into the process to produce more hydrogen. The reactions taking place are as under:

$$\mathrm{ZnO} + \mathrm{heat} \rightarrow \mathrm{Zn} + 0.5\mathrm{O_2} \qquad (2.13)$$

$$\mathrm{Zn} + \mathrm{H_2O} \rightarrow \mathrm{ZnO} + \mathrm{H_2} \qquad (2.14)$$

$$\mathrm{H_2O} + \mathrm{heat} \rightarrow \mathrm{H_2} + 0.5\mathrm{O_2} \qquad \text{(Overall reaction)} \qquad (2.15)$$

Haueter et al have developed a solar chemical reactor for thermochemical hydrogen production based on Zn/ZnO cycle [31]

UT-3 cycle

The UT-3 cycle (University of Tokyo #3) was proposed by Kameyama and Yoshida in 1978 [32]. A UT-3 cycle is composed of a series of four thermochemical reactions. The operating temperatures are relatively lower than those found in other thermochemical cycles, the highest being 760^{o}C. When the reactions proceed in the correct order all the solid reactants are regenerated, except water which is split into hydrogen and oxygen and separated from the system. The reactions taking place are as under:

$$\text{Reaction 1: } CaBr_2 + H_2O(g) \xrightarrow{760^o C} CaO(s) + 2HBr(g) \quad (2.16)$$

$$\text{Reaction 2: } CaO(s) + Br_2(g) \xrightarrow{570^o C} CaBr_2 + 0.5O_2(g) \quad (2.17)$$

$$\text{Reaction 3: } Fe_3O_4(s) + 8HBr(g) \xrightarrow{220^o C} 3FeBr_2(s) + 4H_2O(g) + Br_2(g) \quad (2.18)$$

$$\text{Reaction 4: } 3FeBr_2 + 4H_2O(g) \xrightarrow{560^o C} Fe_3O_4 + 6HBr(g) + H_2(g) \quad (2.19)$$

The UT-3 cycle has been extensively studied in Japan. It may have the potential for commercial production of renewable hydrogen. At present investigations are going on into the chemical kinetic aspects of the reactions involved in the UT-3 cycle.

There are other cycles too (like sulfur-iodine cycle) which are being pursued. Thermochemical cycles are well suited for hydrogen production in conjunction with nuclear energy. The Department of Energy allocated $4 million research budget for select thermochemical cycles in the year 2003.

Photocatalytic Hydrogen Production

Photocatalyst materials (generally semiconductors) doped with other materials, catalyze direct water splitting using solar energy. Examples of materials that have been shown to be effective in catalyzing water splitting are oxynitirides, TaON, Ta_3N_5, and $LaTiO_2N$, nickel doped indium-tantalum-oxide catalysts, and CdS/ZnS systems. The water splitting takes place when the catalyst is irradiated with light in the presence of an electron donor and acceptor, oxidizing OH^- ions to produce O_2 and reducing H^+ ions to H_2. The semiconductor can also be paired with catalysts to promote these oxidation and reduction reactions (refer Figure 2.6).

As a photocatalytic semiconductor material immersed in water is exposed to light, the material absorbs photons causing valence electrons to jump to the conduction band (CB), leaving behind positively charged holes in the valence band (VB). If the conduction band is at a higher energy level than the reduction potential of hydrogen, the electrons in the conduction band can reduce hydrogen ions at the surface of the semiconductor to produce hydrogen gas. The valence bands are at a lower energy than the oxidation potential of hydrogen, so the positive holes accept electrons from the hydroxide ions and oxygen gas is produced as illustrated in the figure 2.6.

Effective photocatalysts are those in which the conduction and valence band levels most closely match the potential for reduction and oxidation of water. The photocatalytic hydrogen production has been demonstrated at laboratory scale [35]. However, the technology is still not feasible on commercial scale. Also, currently the process does not have the capability to produce hydrogen in sufficiently large quantities (like SMR). Further research will determine whether efficiency and cost of hydrogen production by photocatalytic water splitting will be competitive with other hydrogen production methods.

Photoelectrochemical Hydrogen Production

In its simplest form a photoelectrochemical (PEC) hydrogen production cell consists of a semiconductor electrode and a metal counter electrode immersed in an aqueous electrolyte. When light is incident on the semi-conductor electrode, it absorbs part of the light and generates electricity. This electricity is used for electrolytically splitting water. Hence a PEC cell is a combination of a photovoltaic cell and electrolysis. Fujishima and Honda first demonstrated this concept using solar energy in 1972 [37].

The cell consists of a semiconductor photoanode which is irradiated with electromagnetic radiation. The counter electrode is a metal. Following processes take place when light is incident on the semiconductor electrode.

- photogeneration of charge carriers (electron and hole pairs)

$$\hbar\nu \rightarrow h^{+} + e^{-} \tag{2.20}$$

where, $\hbar$ is the Planck's constant, ν is the frequency, h^+ is the hole and e^- is the electron.

- charge separation and migration of holes to the interface between the semiconductor and electrolyte and of the electrons to the counter electrode through the external circuit. The holes are simply vacancies in the valence band due to promotion of electrons from valence band to conduction band. However, in the study of electronic behavior of materials holes are considered to be independent entities with their own mass
- electrode processes: Water is oxidized to H^+ ions and O_2 gas by the holes at the photoanode and the H^+ ions are reduced to H_2 gas by electrons at the photocathode

At photoanode: $H_2O + h^+ \rightarrow 2H^+ + \frac{1}{2}O_2$ (2.21)

At photocathode: $2H^+ + 2e^- \rightarrow H_2$ (2.22)

The efficiency of PEC cells for hydrogen production largely depends on the efficiency of the photovoltaic cell. Due to the inherent low efficiency of PV cells, photoelectrochemical cells are not very efficient in hydrogen production as compared to conventional processes. Typical efficiency reached is around 5-6% [38] that too when multi band gap thin film PV cells are used. There are many issues other than low efficiency that need to be addressed such as corrosion resistance of the semiconductor material, optimization of the electrolyte and cost of photovoltaic cells. This method is still under research and the success of this method largely depends on the improvements made in photovoltaic materials and their performance.

Biological Hydrogen Production

Biological methods for hydrogen production have been known for over a century. Broadly there are two methods by which hydrogen can be produced:

Fermentation of bacteria

Fermentation by anaerobic bacteria as well as some microalgae (such as green algae) on carbo-hydrate rich substrates can produce hydrogen at 30 to 80 ^{o}C in the absence of sunlight and oxygen. The products of fermentation mainly include H_2 and CO_2 with small quantities of other gases such as CH_4 or H_2S depending on the reaction process and substrate used. With glucose as model substrate, a maximum of four moles of H_2 are produced per mole of glucose

$$C_6H_{12}O_6 + 2H_2O \rightarrow 2CH_3COOH + 4H_2 + 2CO_2 \tag{2.23}$$

The actual amount of hydrogen produced depends on the pH value, the hydraulic retention time as well as the gas partial pressure [39].

Biophotolysis

Biophotolysis uses the same principle found in plant and algal photosynthesis, but adapts them for the production of hydrogen instead of carbon containing biomass. Photosynthesis involves absorption of light by two distinct photosynthetic systems operating in series: a water splitting and oxygen evolving system (photosystem I or PSI) and a second photosystem (PSII) which , generates the reductant used for CO_2 reduction. In this coupled process, two photons (one per photosystem) are used for each electron removed from water and used in CO_2 reduction or H_2 formation. In green plants, only CO_2 reduction takes place, as the enzymes that catalyze H_2 formation, (the hydrogenase) are absent. Microalgae (such as cynobacteria) have hydrogenase enzyme and hence can be used to produce H_2 under certain conditions [40]. The overall reaction is given by:

$$2H_2O \xrightarrow[\text{energy}]{\text{solar}} 2H_2 + O_2 \tag{2.24}$$

Although technologies for biological hydrogen production are available, they are still not mature for commercial production. There are many technical barriers and some of them include:

- lack of characterization of microorganisms for hydrogen production
- low light conversion efficiency (less than 10%) for photolytic hydrogen production
- low hydrogen production rate to be commercially viable
- hydrogen re-oxidation by the hydrogenase enzyme

Due to the inherent technical problems the cost of hydrogen produced from biological methods is still very high as compared to conventional methods such as Steam Methane Reforming.

Summary

A summary of the different hydrogen production methods is provided in Table 1-1. It is observed that currently SMR offers the lowest hydrogen production cost. SMR is also a proven technology with very high energy efficiency. However the natural gas reserves within the US are limited and hence SMR is considered as a transition phase to the “hydrogen economy”. Partial oxidation and autothermal reforming are possible alternatives to SMR, but both these methods are less efficient. Also, the cost of hydrogen production by these methods is higher than SMR. Coal gasification is cost-competitive but CO_2 by-product removal is a matter of concern. Electrolysis is a proven technology but is currently expensive. Also, capacities are very small and hence scale-up is required for bulk hydrogen production. Thermochemical water splitting process is clean (no emissions); however it is complicated by several reactions and severe operating conditions. These methods are still under research. Biological and photocatalytic methods are both renewable but at the same time are expensive. The efficiency is also very low. Both these methods are also currently under research.

Of all the renewables, biomass is a promising resource for producing environment friendly hydrogen. In fact, considering the CO_2 penalty which may be imposed on fossil fuels, biomass has the potential to become cost competitive with fossil fuels. The drawbacks of biomass are seasonal availability, high feedstock and capital costs. Hydrogen can become a fully renewable energy carrier only if the raw materials and methods used for producing it are renewable.

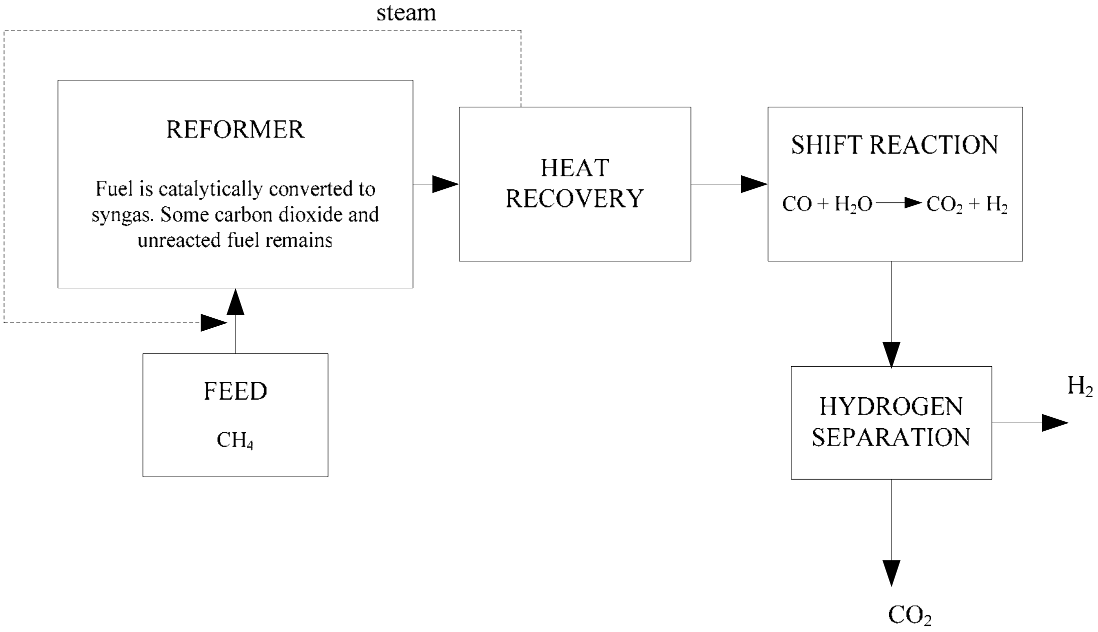

Figure 2.1: Block diagram of hydrogen production by steam methane reforming (adapted from Sherif et al [21])

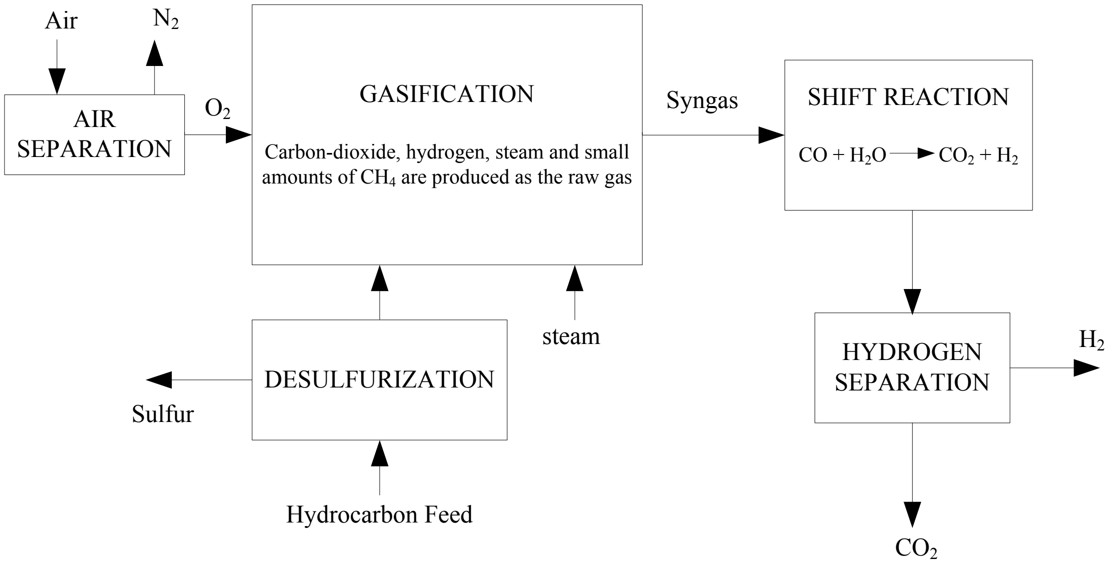

Figure 2.2: Block diagram of hydrogen production by partial oxidation of heavy oils (adapted from Sherif et al [21])

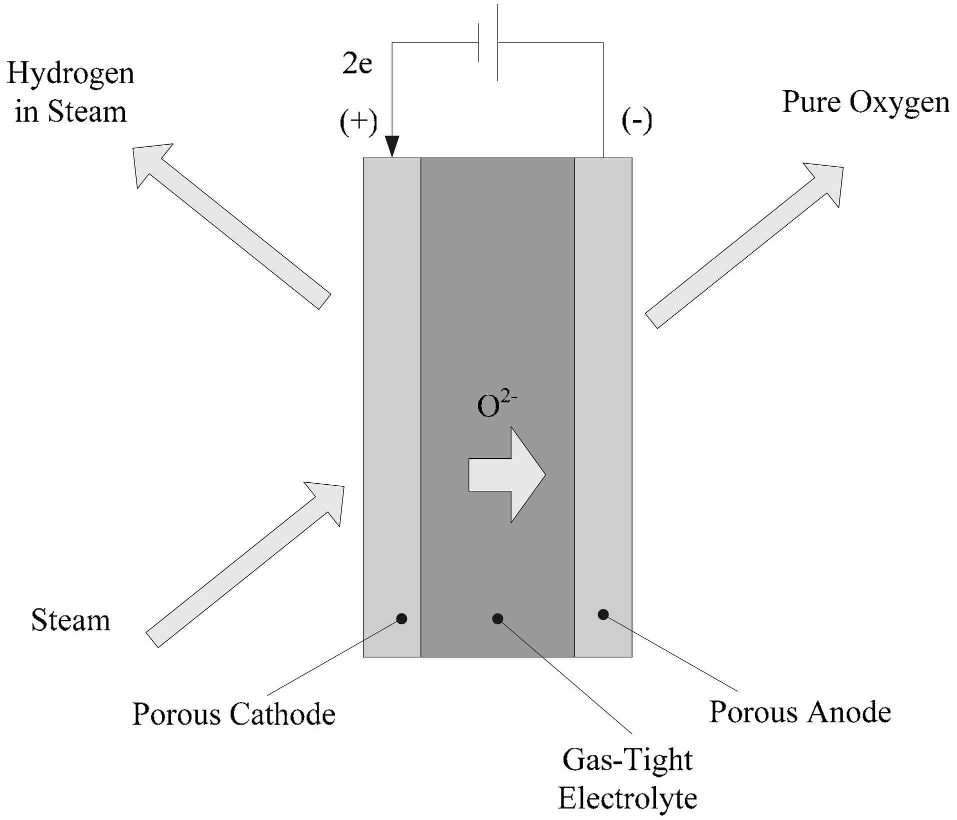

Figure 2.3: Principle of hydrogen production by high temperature electrolysis (HTE)

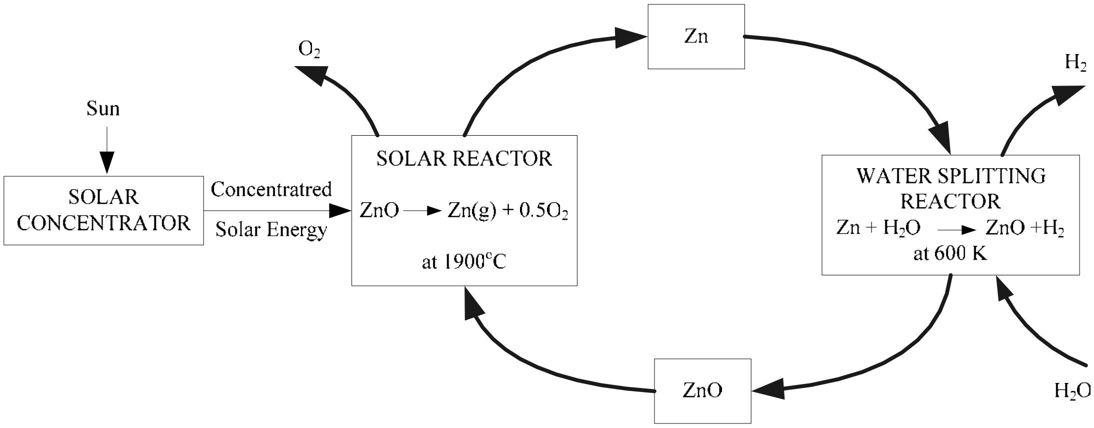

Figure 2.4: Block diagram of the Zn/ZnO water splitting thermochemical cycle for hydrogen production (adapted from Weidenkaff [33])

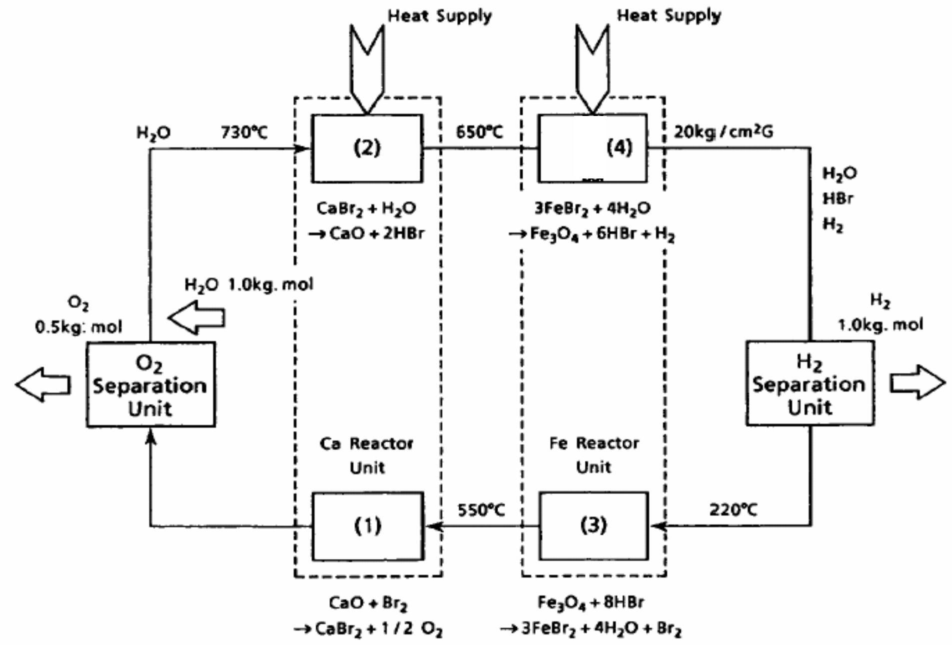

Figure 2.5 UT-3 cycle reactions and flow of material (adapted from Aochi et al [34])

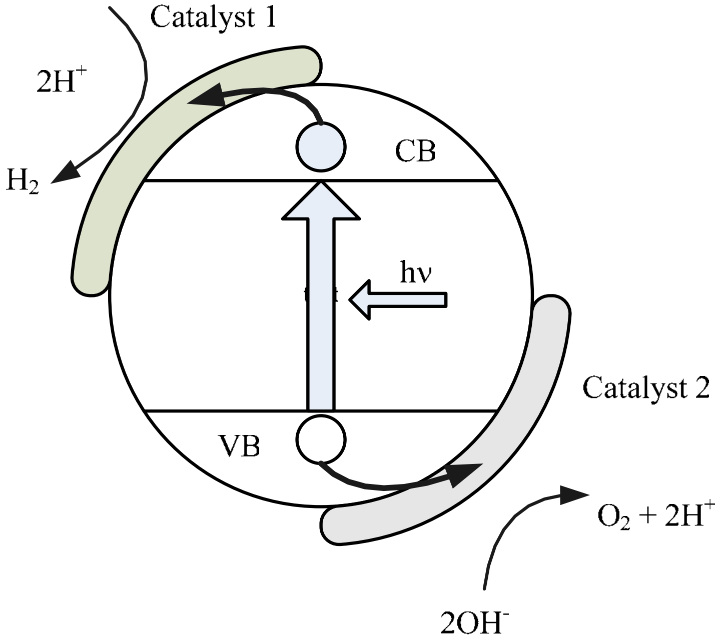

Figure 2.6: Photocatalytic hydrogen production (adapted from Oudenhoven et al [36])

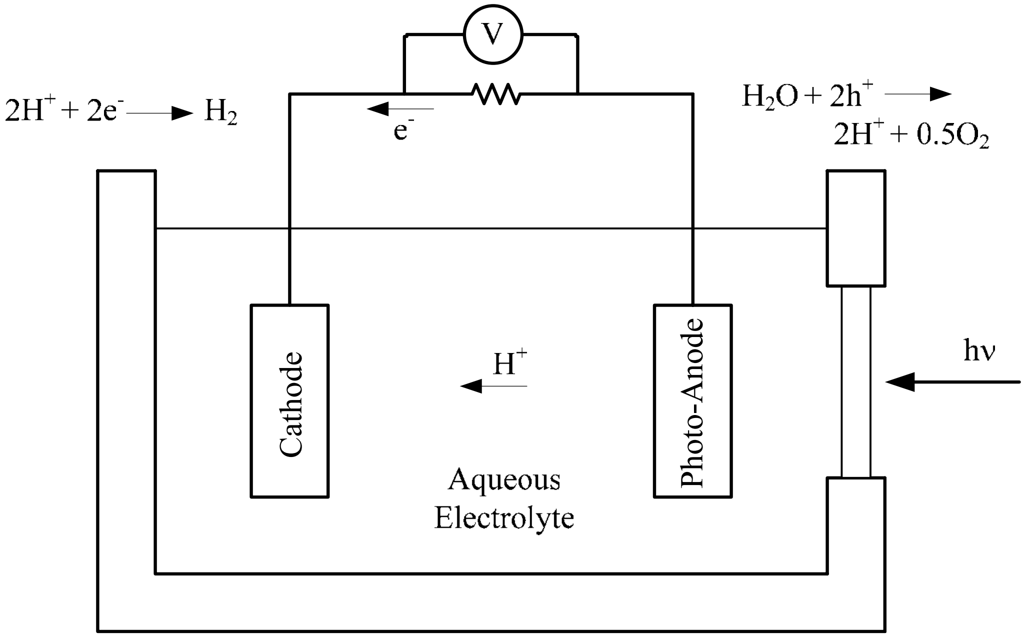

Figure 2.7: Principle of photoelectrochemical hydrogen production (adapted from Fujishima et al [37])

CHAPTER 3
BACKGROUND AND LITERATURE REVIEW

Introduction

Wood and other forms of biomass including energy crops and agricultural and forestry wastes are some of the main renewable energy sources available for hydrogen production. Biomass is considered the renewable energy source with the highest potential to contribute to the transportation energy needs of modern society for both the developed and developing economies around the world [41, 42]. Biomass can be converted to liquid and gaseous fuels via thermal, biological and physical processes.

In the thermal technique there are four methods suitable for the conversion of biomass: pyrolysis, gasification, liquefaction or direct combustion and primary products of these processes can be gas, liquid, solid char and/or heat depending on the conversion technology employed. Secondary higher value products may be produced by additional processing.

Pyrolysis

Pyrolysis is the thermal degradation (devolatization) of biomass in the absence of an oxidizing agent at temperatures in the range 200-500^{o}C. This leads to the formation of a mixture of liquids, gases and highly reactive carbonaceous char, the relative proportions of which depends on the heating rate. The products can be used in a variety of ways. The char can be upgraded to activated carbon, used in the metallurgical industry, as a domestic cooking fuel or for any suitable application. Pyrolysis gas can be used for power generation or heat, or synthesized to produce methanol. The tarry liquid (called bio-oil) can be upgraded to high grade hydrocarbon liquid fuels for combustion engines or used directly for power generation or heat.

Gasification

Gasification (also called pyrolysis by partial oxidation) is a conversion process in which the goal is to maximize the gaseous product yield. Relatively higher temperatures of 800-1100^{o}C are used compared to 200-500^{o}C in pyrolysis. The gaseous mixture produced contains H_2, CO, CO_2, CH_4, H_2O, and N_2 (if air is used as the gasifying medium) and various contaminants such as small char particles, small amounts of ash and tars. Air gasification produces a low heating value (LHV) gas (4-7 MJ/Nm^3). The fuel gas can be burned externally in a boiler for producing hot water or steam, in a gas turbine for electricity production or in an internal combustion engine. It can also be upgraded to methanol through synthesis. Before the fuel gas can be used in gas turbines or internal combustion engines, the contaminants (tar, char-particles, ash) have to be removed. The hot gas from the gas turbine can be used to produce steam to be utilized in a steam turbine in an Integrated Gasification Combustion Cycle (IGCC).

Combustion

Combustion is complete oxidation of the biomass feedstock. Combustion provides very hot gas that can be used to (1) heat a boiler and produce steam for process application (2) as a source of process or space heat (3) as the energy source for Rankine cycle or Stirling engines. Typically, temperatures of the order of 1200^{o}C are encountered in combustion.

Liquefaction

Liquefaction is a low temperature (250-300^{o}C), high pressure (100-200 bar) thermo-chemical conversion to convert biomass into liquid phase, usually in the presence of a catalyst. The main goal here is to maximize the liquid yield, and the product is a higher quality liquid (in terms of heating value) than the one produced in pyrolysis.

Of all the methods, biomass gasification has attracted the greatest interest as it offers higher efficiencies than combustion [42, 43]; other technologies (fast pyrolysis & liquefaction) are still at a relatively early stage of development [42]. Thermochemical biomass gasification has been identified as a possible method for producing renewable hydrogen [44]. Figure 3.1 shows a photograph of a pilot biomass gasification plant which uses peanut shells as feedstock for producing hydrogen.

Lab-Scale Production of Hydrogen from Biomass

A schematic of the experimental set-up used for producing hydrogen by gasification of biomass is shown in figure 3.2. Here biomass is fed continuously using a screw feeder to a fluidized-bed gasifier and steam is used as the gasifying medium. The gas coming out of the gasifier is passed through a metallic filter before being sent to a catalytic reactor.

The catalytic reactor reforms tars and higher hydrocarbon in the product gas to produce additional hydrogen. The gas is then cooled to condense and remove the steam and then passed through a filter to get rid of ash, dust and particulate matter. The clean, dry gas coming out of the filter is then sent to a gas-chromatograph for composition analysis. Any suitable biomass can be used as a feed to the gasifier. Biomass feeds can be agricultural wastes, energy crops, municipal solid wastes, woody and tree material and so forth. Table 3-1 gives the chemical composition, ultimate and proximate analysis and heating value of sawdust which is a typical biomass feedstock [44]. The C-H-O (Carbon-Hydrogen-Oxygen) composition for any biomass is approximately the same; feedstocks differ from each other in the amount of mineral matter (alkaline material) and moisture content. For comparison the chemical composition, ultimate and proximate analysis and heating value for a grade of coal (found in Belmont, Ohio) is also provided [16]. From the chemical composition it is seen that biomass feedstock has much less sulfur as compared to coal. This is another reason why a biomass feedstock is preferable over coal. However, oxygen content in biomass is higher than coal. Typically biomass consists of about 6% hydrogen by weight. The hydrogen yield of plain biomass gasification can be substantially improved if we use steam as a gasifying medium (this is explained in detail in the next chapter)

An Overview of Biomass Gasification for Hydrogen Production

Biomass gasification has been extensively studied over the last three decades in the United States and other countries around the world. Different research groups have investigated biomass gasification with different objectives like optimizing syngas production, maximizing the overall gas yield, hydrogen production, product gas cleaning for trouble-free downstream operation, effective waste utilization and so on. The objective of the present research is to study biomass gasification from the perspective of maximizing the hydrogen yield. A detailed literature review was conducted to know the state of the art. The following sub-areas were identified:

- Catalysis
- Pretreatment technologies
- Chemical kinetic studies
- Experimental studies on biomass gasification
- Thermodynamics of gasification
- Sorbent enhanced gasification

Catalysis

Biomass thermo-chemical gasification produces gases, liquids and solids. The product contains as major components H_2, CO, CO_2, CH_4, H_2O and N_2, smaller amounts of hydrocarbons, inorganics (H_2S, HCl, NH_3, alkali metals) and particulate matter. The organic impurities range from low molecular weight hydrocarbons such as methane to high molecular weight polynuclear aromatic hydrocarbons. The low molecular weight hydrocarbons can be used as fuel in gas turbine or engine applications, but are undesirable products in fuel cell applications and methanol synthesis. The high molecular weight hydrocarbons are collectively known as “tars”. Tars are undesirable in Integrated biomass Gasification Combined Cycle systems (IGCC) for a number of reasons. They can condense in exit pipes and on particulate filters leading to blockages and clogged filters. Tars also have varied impact on other downstream processes. They can clog fuel lines and injectors in internal combustion engines. The product gas from an atmospheric pressure gasification process needs to be compressed before it is combusted in a gas turbine and tars can condense in the compressor or in the transfer lines as the product gas cools. Biomass gasification product gas requires substantial conditioning including tar conversion or removal, before it is used in polymer electrolyte membrane (PEM) fuel cell systems that require essentially pure hydrogen.

There are a number of methods to separate or reform tars from the product gas like wet scrubbing, thermal cracking or catalytic cracking. Wet scrubbing involves cooling the gas in order to condense the tars. This technique does not eliminate tars but merely transfers the problem from gas phase to condensed phase. Thermal cracking is a hot gas conditioning option but it requires high temperatures (more than $1100^{o}C$) to achieve high conversion efficiencies. This process may also produce soot which is an unwanted impurity in the product gas stream. Catalytic steam reforming is an attractive hot gas conditioning method. Catalytic tar destruction has been studied for several decades and a number of reviews have been written in biomass gasification hot gas clean up [46-48]. Broadly three groups of catalyst materials have been used for biomass gasification systems: alkali metals, non-metallic oxides, and supported metallic oxides. Alkali metals enhance biomass gasification and are therefore considered primary catalysts and not tar reforming catalysts. Alkali salts are mixed directly with the biomass as it is fed into the gasifier. The non-metallic and supported metallic oxide catalysts are usually located in a separate fixed bed reactor, downstream from the gasifier, to reduce the tar content of the gasification product gas and are therefore referred to as secondary catalysts.

Non-Metallic Oxides

Calcined dolomites have been extensively investigated as biomass gasifier tar destruction catalysts. Dolomites are calcium-magnesium ore with the general formula $CaMg(CO_3)_2$. These naturally occurring catalysts are relatively inexpensive and disposable. So it is possible to use them as primary (in bed) catalysts as well as in secondary (downstream) reactors. Several research groups have conducted extensive studies on the tar conversion effectiveness of calcined dolomites and other non-metallic oxide catalysts. Simell and co-workers [49] performed a number of studies using model compounds to test the reforming effectiveness of dolomites. The catalysts were calcined at $900^{o}C$ and showed high toluene conversion efficiencies (>97%); however catalyst activity was almost completely lost when the CO_2 partial pressure was higher than equilibrium decomposition pressure of dolomite. Simell et al also reported decomposition of benzene when it was passed over Finnish dolomite at $900^{o}C$.

Aznar and co-workers [50] constructed a biomass gasification pilot plan to study catalytic product gas conditioning. The gasifying agents used were air, steam and a mixture of steam and oxygen, and pinewood was fed into the bottom of the bubbling bed. It was found that when 20g of calcined dolomite per kg of biomass was added, the tar content in product gas decreased by a factor of 4 to 6. They also observed that the hydrogen content of the product gas doubled and CO content reduced by a factor of two. Several other groups have also studied catalytic tar reforming with dolomites [51, 52]. All of these studies demonstrate that dolomite is a very effective tar reforming catalyst. High molecular weight hydrocarbons are efficiently removed at moderately high temperatures ($800^{o}C$) with steam and oxygen mixtures as the gasifying agent; however methane concentration is not greatly affected and benzene and naphthalene are often not completely reformed. A problem with dolomites which is reported by many investigators is a decrease in mechanical strength over time, which leads to catalytic attrition.

In summary, dolomites are inexpensive disposable chemicals that can be mixed with biomass and used as primary catalysts. They are mainly used for reforming many high molecular weight tar compounds. Dolomites however undergo attrition over a period of time and need to be replenished. Another problem with dolomites is the waste stream they generate once they undergo attrition.

Commercial Nickel Reforming Catalyst

A wide variety of Ni-based reforming catalysts are commercially available because of their application in the petrochemical industry for naphtha reforming and methane reforming to make syngas. Nickel based catalysts have also proven to be very effective for hot conditioning of biomass gasification product gases. They have high activity for tar destruction; methane in the gasification product gas is reformed, and they have some water gas shift activity to adjust the H_2/CO ratio of the product gas. The H_2 and CO contents of the product gas increase, while hydrocarbons and methane are eliminated or substantially reduced for catalyst operating above approximately 740^{o}C.

The groups that were active in studying calcined dolomite catalysts have conducted several studies involving nickel steam reforming catalysts too for hot gas conditioning. Aznar and coworkers [53] conducted several experiments with Ni-catalyst at temperatures between 750 and 850^{o}C and found initial tar conversion efficiency to be greater than 99%. An apparent kinetic model for tar reforming was determined for each catalyst tested based on a first order rate expression and the measured tar conversion as a function of time-on-stream. The kinetic studies gave an idea of the activation energy and pre-exponential factors obtained for the tar conversion reactions.

Simell and coworkers [54] have also investigated commercial Ni steam reforming catalyst for tar conversion using toluene as a model tar compound. They observed complete tar decomposition for catalyst operating at 900°C and 5 MPa. Kinoshita, Wang and Zhou [55] reported results from parametric studies on catalytic reforming of tars produced in a bench-scale gasification system. A commercial Ni-catalyst (UCG-90 B) was tested at various temperatures (650-800°C), space times (0.6-2.0s), and steam to biomass ratios (0-1.2) in a fluidized bed catalytic reactor. They reported achieving 97% tar conversion; product gas yield was higher in presence of the catalyst.

Several other groups (Bangala et al [56] & Wang et al [57]) have reported high effectiveness of Ni-catalyst (>90%) in tar reforming. However there are several factors which still limit the use of Ni-catalyst in commercial gasifiers which need to be addressed. Some of the main limitations include sulfur, chorine and alkali metals present in the gasification product gas which act as catalyst poisons. Coke formation on the catalyst surface can also be substantial when tar levels in the product gas are high. Coke can be removed by regenerating the catalyst; however repeated high temperature processing of nickel catalyst can lead to sintering, phase transformations and volatilization. To sum up, commercial nickel reforming catalysts have shown very high tar conversion potential (more than 90%). However these catalysts suffer from frequent de-activation due to poisoning by sulfur, by halides and by alkaline impurities.

Additional Catalyst Formulations

There are several limitations of Ni reforming catalysts used for tar conversion such as deactivation by coke formation, sulfur and chlorine poisoning and sintering. Addition of various promoters and support modifiers has been attempted by several groups to improve catalyst activity, lifetime, poison resistance, and resistance to coke formation. Rapagna et al [58] developed a catalyst with a Lanthanum additive (chemical formula $LaNi_{0.3}Fe_{0.7}O_3$) that was prepared by sol-gel process. The prepared catalyst displayed high CH_4 reforming activity at 500^oC resulting in 90% CH_4 conversion. Garcia et al [59] have prepared a number of Ni-based catalysts with different additives for optimal hydrogen production. They added Magnesium and Lanthanum as support modifiers, and Cobalt and Chromium were added to reduce coke formation. The Cobalt-promoted and Chromium-promoted Nickel catalyst on a $MgO\text{-}La_2O_3\text{-}\alpha\text{-}Al_2O_3$ support performed best in terms of yield and life time. Sutton and co-workers [60] studied the effect of different supports using Ni-catalyst. The research group impregnated Ni on various supports including Al_2O_3, ZrO_2, TiO_2, SiO_2 and a proprietary tar destruction support. High tar conversion was observed for all of the prepared catalysts.

Drawing a parallel from the auto-industry, Asadullah and co-workers [61, 62] have developed a novel series of catalysts using noble metals on oxide supports. These catalysts were prepared with Rhodium, Ruthenium, Platinum and Palladium and were tested on bench-scale fluidized-bed reactors using cellulose as a model biomass compound. The group found more than 80% tar conversion at temperatures as low as 550^oC. Different supports were used such as CeO_2, LiO_2, ZrO_2, Al_2O_3, MgO and SiO_2. It was found that Rh/CeO_2 gave 100% tar conversion at 550^oC. The group observed that although these catalysts give 100% tar conversion at relatively low temperatures (500 to 600^oC), they are not economically viable. This is mainly due to the high cost associated with the noble metal to the catalyst formulation.

Several catalysts have been investigated for tar reforming of biomass product gases. A critical gap identified for catalytic tar reforming technology in biomass gasification processes is the need for extended lifetime of promising commercial or novel catalysts. Catalytic hot gas conditioning will not become a commercial technology unless adequate catalyst lifetimes can be demonstrated, even for inexpensive, disposable catalysts like calcined dolomite. Frequent disposal of dolomite generates an additional waste stream and disposal of toxic spent Ni-catalysts becomes an environmental burden. Assessment of catalyst lifetimes will allow biomass gasification developers to actually evaluate the cost of operating a biomass gasification plant. The effect of catalyst poisons like sulfur, chlorine and alkali metals and continued catalyst regeneration can be critically evaluated with long term catalyst testing. Accurate catalyst cost and lifetime figures will provide important input for techno-economic analysis of developing gasification technologies.

Pretreatment Technologies

Experimental and theoretical studies on different types of biomass have showed that pretreatment increases the volatile (gas and liquid) yield of feed stocks. Pretreatment is carried out by washing the biomass with mild acid or alkali or by impregnating them with salts before actual gasification. It is hypothesized that during pretreatment the biomass undergoes de-ashing (removal of mineral matter) which leads to higher gas and hence hydrogen yields. Pretreatment for gasification or pyrolysis also increases the active surface area of biomass. In some cases (especially bio-oils) the heating value of pretreated biomass is higher than the original biomass feedstock.

Das and Ganesh [63] subjected sugarcane baggase to three different pretreatments (water leaching, mild HCl treatment and mild HF treatment) and found that the HF treatment reduces ash content of biomass to a negligible amount. The researchers also observed that the char produced in the process had a higher adsorption capacity as compared to untreated biomass. Raveendran and co-workers [64] impregnated a variety of biomass feed stocks with chloride (KCl, $ZnCl_2$) and carbonate (K_2CO_3 , $ZnCO_3$) salts and found that the gas yield increased substantially. The group later developed a correlation to predict the percentage change in gas yield when any biomass is subjected to potassium and zinc salt pretreatments. Conesa et al [65] subjected different almond shell samples to acidic and basic pretreatment followed by $CoCl_2$ (cobalt chloride) impregnation. The samples were then gasified and the gas composition was determined. The group found that the hydrogen yield of $CoCl_2$ treated almond shells was higher than plain almond shell. All the research groups have hypothesized that acid, alkaline or salt pretreatment alters the mineral matter content of raw biomass. This in turn affects the product yields since the mineral matter generally tends to have a catalytic effect during the gasification process. In general, biomass pretreatment is a technique of modifying the bio-chemical ingredients of feedstock and thereby controlling the gas and hence the hydrogen yield.

In a nutshell, biomass pretreatment is a simple and cost-effective way of influencing the product yield of any biomass gasification process. The process generally applies well to biomass with large mineral matter (Na, K, Ca, Mg, Fe, and P) content such as switch grass and rice husk.

Chemical Kinetic Studies

The development of thermo-chemical process for biomass conversion and proper equipment design requires a thorough knowledge and good understanding of several chemical and physical processes occuring in the thermal degradation process. Mathematical modeling and simulation of single representative biomass particle is a very useful tool for understanding the heat and mass transfer and chemical kinetic processes involved in biomass gasification or pyrolysis. When a solid biomass is heated following phenomena occur:

1) heat is transferred by radiation and/or convection to the particle surface and then by conduction to inside of the particle.
2) the temperature inside the particle increases causing
    a) evaporation of moisture present in the biomass particle
    b) pre-pyrolysis and pyrolysis reactions

c) mass transfer from surface of biomass particle due to formation and subsequent release of volatiles

This leads to the formation of pores in solid surface. During the process, the pores of the solid enlarge and this offers many reaction sites to the volatile and gaseous products. Chemical kinetic studies predict the transient temperature profile within the biomass particle as well as the yield of solid, liquid and gaseous products with time. This is done by mathematically modeling the combined effects of heat transfer and chemical reactions. The model is then verified with experimental results. On the experimental side, Thermal Gravimetric Analysis (TGA) of a single biomass particle gives the rate of mass loss versus time and temperature. This can be used to obtain the kinetic data (rate constant and activation energy) of biomass thermal degradation. The chemical kinetic data so obtained serves as a basis for detailed design of fixed and fluidized bed biomass reactors.

Several researchers have analyzed the chemical kinetics of biomass pyrolysis and gasification and have developed mathematical models for the same. Kung [66] developed a basic mathematical model for pyrolysis of wood slab. The model considers heat transfer due to conduction, internal heat convection and first order kinetics for the formation of volatiles and char. However no specific model is suggested to predict the concentration of the various intermediate components produced during the pyrolysis. Kansa et al [67] developed a more detailed mathematical model for the pyrolysis of wood. They incorporated internal force convection effects, their model used variable thermal and physical properties, a time-dependent surface radiant flux, a global Arrhenius pyrolysis reaction, and arbitrary boundary conditions. A comparison of their model with experimental data for maple wood showed good agreement at low surface heat fluxes, but agreement was poor for high fluxes. The authors concluded that for good agreement at high flux intensities, the effect of secondary pyrolysis reactions must be taken into account. The model developed by Kansa et al was more realistic than the basic model developed by Kung. Miyanami et al further improved the model developed by Kansa et al by incorporating the heat of reaction in the pyrolysis of solid particles based on the volume reaction model [68]. They carried out a transient analysis of the effects of the heat of reaction on the solid biomass conversion, fluid product concentration profile and temperature distribution in the solid biomass. The results of their model had better agreement with experimental results as compared to Kansa et al. Recently GrØnli [69] developed a mathematical model and conducted experiments to validate the pyrolysis of Scandinavian wood. He studied the pyrolysis of wood and developed a model that considered the effect of particle size on product composition. His work identified two categories of wood pyrolysis: small wood particle where internal thermal resistance is negligible and chemical kinetics is the controlling mechanism, and large particles where both chemical kinetics and heat transfer need to be considered. Gronli's work gave a better understanding of the factors that must be taken into account while modeling biomass pyrolysis of wood particles. More recently, Jalan and Srivastava [70] developed a model for the pyrolysis of a single wood particle. These researchers modeled the physical and chemical changes of a biomass particle as it undergoes pyrolysis. This was done by considering the primary and secondary reactions. An energy balance equation proposed by the authors took into account the non-isothermal reaction of the biomass particle. Numerical schemes were employed to solve the heat transfer equations and the equation involving chemical kinetics. The model predicted the temperature distribution within the pellet as a function of radial distance at different times as pyrolysis progressed. The authors found that their model compared well with the experimental data from literature.

In summary, chemical kinetic modeling studies of wood pyrolysis have been conducted by several researchers over the last three decades. These models provide better understanding of pyrolysis of solid biomass particles. Some of the models have been experimentally verified. The chemical data obtained (reaction rate, rate constant, order of reaction, and activation energy) serve as a valuable database for the design of biomass reactors.

Experimental Studies on Biomass Gasification

Experimental studies on biomass gasification have focused on various aspects like parametric analysis, catalytic tar cleaning, co-gasification of biomass with coal/plastic, hot gas cleaning, using multiple feed stocks, different gasifier reactor configurations and so on. In most cases the end objective was to maximize syngas production. Turn and co-workers [44] studied the effect of gasifier temperature, steam to biomass ratio (SBR), equivalence ratio (ER) (a measure of air supplied in biomass gasification) on gas yield (mainly H_2, CO, CO_2 and CH_4) in fluidized-bed gasification of sawdust. They found the highest hydrogen yield to occur at a gasifier temperature of 850°C and steam biomass ratio of about 1. The maximum hydrogen yield was found to be 0.128 g/kg dry ash-free biomass. Narvaez and co-workers [71] have analyzed the effects of temperature, equivalence ratio and the addition of dolomite in the air gasification of pine sawdust. The group found that maintaining an ER of 0.3, SBR of 2.2 and gasifier temperature greater than 800°C gave good quality (maximum heating value) gas with minimum tar content. Herguido and co-workers [72] used different feedstocks (pine saw dust, pine wood chips, cereal straw, and thistles) using steam as the gasification medium and studied the product yield (H_2, CO, CO_2, and CH_4 contents). The group found marked differences in product composition at low gasification temperature, but at temperatures exceeding 780°C, the gas composition was similar for all biomass feedstocks. Gil and co- workers [73] have studied the effect of different gasification media (air, steam, steam and oxygen mixture) on product gas composition. They observed that using steam in place of air gave a product gas with almost five times more hydrogen. Also the heating value of product gas in steam gasification (12.2–13.8 MJ/Nm^3) was higher than air gasification (3.7-8.4 MJ/Nm^3). Pinto and co-workers [74] have conducted experiments by co-gasifying biomass with plastic wastes and observed an increase in the hydrogen yield by about 17% when 40% (wt) of polyethylene was mixed with pinewood. One of the objectives of this research was effective utilization of plastic waste. It was found that when plain plastic was gasified it softened and stuck to the walls of the gasifier. Neither cooling nor palletizing of the waste plastic helped solve the problem. Mixing of biomass with plastic avoided the problem of plastic softening and effectively gasified all feedstock.

In a nutshell, many researchers have carried out experimental studies on biomass gasification. The studies have been varied e.g. simple parametric analysis, effect of gasifying media on product yield, effect of changing feedstock on product gas composition, co-gasification of biomass with plastic wastes, catalytic tar cleaning among others. The objective of the experimental studies in most cases was to maximize the syngas yield for power generation.

Thermodynamic Studies on Gasification

Biomass gasification produces a mixture of gases (mainly H_2, CO, CO_2 and CH_4), liquids (aromatic hydrocarbons or tars) and solids (char, ash). The process parameters (temperature, pressure, steam to biomass ratio, equivalence ratio, residence time, heating rate and so on) directly affect the product yield and composition. Biomass gasification also involves several reactions occurring in series and in parallel. Some of these reactions are as under:

Steam Gasification:

$$\mathrm{CH_{1.5}O_{0.7} + 0.7H_2O \rightarrow H_2 + CO + CO_2 + C_nH_m + tars + C(s)} \quad \Delta H_R = +119 \quad \mathrm{kJ/mol} \tag{3.1}$$

Oxidation:

$$C + 0.5O_2 \rightarrow CO \quad \Delta H_R = -111 \quad kJ/mol \tag{3.2}$$

$$CO + 0.5O_2 \rightarrow CO_2 \quad \Delta H_R = -254 \quad kJ/mol \tag{3.3}$$

Boudouard:

$$C + CO_2 \rightarrow 2CO \quad \Delta H_R = +172 \quad kJ/mol \tag{3.4}$$

Water-Gas:

$$C + H_2O \rightarrow CO + H_2 \quad \Delta H_R = +131.3 \ kJ/mol \tag{3.5}$$

$$C + 2H_2O \rightarrow CO_2 + 2H_2 \quad \Delta H_R > 0 \quad kJ/mol \tag{3.6}$$

Methanation:

$$C + 2H_2 \rightarrow CH_4 \quad \Delta H_R = -75 \quad kJ/mol \tag{3.7}$$

Water-Gas Shift:

$$CO + H_2O \rightarrow CO_2 + H_2 \quad \Delta H_R = -41 \quad kJ/mol \tag{3.8}$$

Steam Reforming:

$$CH_4 + H_2O \rightarrow CO + 3H_2 \quad \Delta H_R = +206 \quad kJ/mol \tag{3.9}$$

Some of the above reactions are exothermic and others are endothermic. Moreover the reactions occur in different reactors which operate at different temperatures. Most of the biomass gasification systems operate at atmospheric pressure and the gasifier operating temperature is in the range 800-850^{o}C. In many applications the product gas needs to be cooled to lower temperatures before being sent to downstream equipment. There is a potential for heat integration of the various reactors so that the net external heat input to the biomass gasification system is reduced. This increases the thermodynamic efficiency of the process. The hot gas coming out of the gasifier is at a sufficiently high temperature (700-800^{o}C) and can be used to produce steam for a Rankine cycle. The objective of the thermodynamic studies is to find the opportunities for heat integration and thereby improve the overall efficiency of the process.

In the past, focus on the thermodynamics of biomass gasification has been on areas not specifically addressing hydrogen production. Cairns et al calculated the gas-phase composition in equilibrium with carbon (graphite) for a CHO (Carbon/Hydrogen/Oxygen) system for different temperatures and O/H (atomic oxygen to hydrogen) ratios [75]. Schuster et al conducted a parametric modeling study of a biomass gasification system. A decentralized combined heat and power station using a dual fluidized bed steam gasifier was simulated. The group predicted net electricity to biomass efficiency of about 20% [76]. Kinoshita et al conducted equilibrium studies of biomass gasification with the objective of maximizing the methanol production. The theoretical methanol yields were determined and were compared with experimental results. They also determined the optimal process conditions for methanol production based on thermodynamic equilibrium [77]. Garcia et al also did an equilibrium study but this was for steam reforming of ethanol. They studied the effect of temperature, pressure and steam to ethanol feed ratio and determined the maximum hydrogen yield attainable at equilibrium [78]. Carapellucci [79] studied the thermodynamics and economics of biomass drying using waste heat from gas turbine exhaust and concluded that using gas turbine exhaust for biomass drying enhances the economic feasibility of biomass fired power plants. Lede et al [80] carried out a study on using solar energy for thermochemical conversion of biomass. The study highlights the technical and economic benefits and also lists the difficulties of using solar energy as a source of heat for gasification and pyrolysis of biomass. Zainal et al [81] also did an equilibrium modeling study to predict the performance of a downdraft gasifier for different biomass materials. The group investigated the effects of temperature and moisture content in biomass on the gas composition. Their equilibrium modeling results matched reasonably well with the experimental results. Alderucci et al [82] conducted a similar equilibrium analysis of biomass gasification where steam and CO_2 were the gasifying media. The product gas was assumed to be fed to a Solid Oxide Fuel Cell (SOFC); the efficiency of the fuel cell was then determined. The researchers found that CO_2 gasification gave better fuel cell efficiency as compared to steam gasification. Prins et al [83] studied the energetic and exergetic aspects of biomass gasification in the presence of steam and air. They found that the energy and exergy of product gas had sharp maxima at the point where all the carbon is consumed. They concluded that the choice of gasification medium should be governed mainly by the desired product gas composition. Crane et al [84] studied two alternatives to present day gasoline powered systems. They did this by comparing the exergy of emission of two alternate energy conversion technologies viz. methanol fuelled spark ignition engines and hydrogen fuelled fuel cells. The authors showed that the hydrogen powered fuel cell system was better than the methanol powered spark ignition engine from both energy and exergy perspectives.

Although some work has been reported on thermodynamics of biomass gasification no one has worked specifically on optimizing the process for hydrogen production. Hence the focus of the present research was to study the thermodynamics of gasification with the end objective of maximizing or improving the hydrogen yield.

Sorbent Enhanced Gasification

Biomass gasification consists of many reactions and processes. Steam biomass gasification is endothermic whereas partial oxidation of biomass is exothermic. One of the objectives of the present research is to identify suitable methods that can enhance the hydrogen yield and/or improve the process efficiency. The gasifier is an important reactor where the initial thermal breakdown of biomass takes place. If the heat duty of the gasifier can be reduced by combining reactions, it can make the process more efficient and the reactor can become compact. Detailed thermodynamic studies showed that conventional biomass gasification is limited by the equilibrium constraints and hence hydrogen yield cannot increase beyond a certain point. In order to produce more hydrogen one of the co-products of gasification (CO_2) must be removed. It was found in the studies that CO_2 formation limits the hydrogen yield due to equilibrium of the Water Gas Shift (WGS) reaction. In recent past, sorbents such as calcium oxide have been used to remove the CO_2 from the fossil fuel exhaust stream. When the CO_2 absorption reaction is coupled with the WGS reaction, the water gas shift proceeds to the right and thereby more hydrogen is produced.

Han and Harrison [85] studied the simultaneous water gas shift and carbon dioxide separation process for the production of hydrogen. They observed that removing CO_2 as it gets formed via the non-catalytic gas solid reaction between CaO and CO_2 provides the opportunity to combine reaction and separation into a single step. The resultant process for hydrogen production got simplified as there was no need of heat exchanger between catalyst beds as well as the absorption and stripping units for CO_2 removal. The authors studied the combined shift and carbonation reactions in a laboratory scale fixed-bed reactor using dolomite sorbent precursor. They studied the effects of temperature, pressure and space velocity on the conversion of CO in the WGS reaction. They observed that more than 99.5% of the carbon oxides got removed and the product gas was rich in hydrogen. Balasubramanian et al [86] conducted experimental studies on steam methane reforming in presence of a CO_2 sorbent. They added calcium oxide sorbent to a commercial steam methane reforming catalyst (nickel on alumina). The combined reforming, shift and CO_2 separation reactions were studied using a laboratory scale fixed bed reactor. The effects of temperature, steam to methane ratio, sorbent to catalyst ratio and feed gas flow rate were studied. The group found that hydrogen could be produced from methane in a single step without using a shift catalyst. The product gas was rich in hydrogen (more than 90%). A reduction in operating temperature by 150-200°C was also observed. Lin et al [87] have proposed a hydrogen production technique by reducing water (steam) using hydrocarbons. The CO_2 so produced was separated using a sorbent. The researchers named this technique as HyPr-RING (Hydrogen Production by Reaction Integrated Novel Gasification). They conducted an analysis of the HyPr-RING process and concluded that it has a potential to reduce the cost of hydrogen production as compared to conventional methods. The researchers further conducted a thermodynamic analysis of coal gasification in presence of CaO as per the HyPr-RING process [88]. A mass and energy balance was carried out and the temperature and pressure were varied over a wide range. The product gas composed of more than 90% hydrogen at a gasification temperature of 700°C and pressure of 3.0 MPa. This gave a gasification efficiency of 77%. Calcium oxide has also been used for plain CO_2 removal from the fossil fuel exhaust without any hydrogen co-production. Abanades et al studied the capture of CO_2 from combustion gases in a fluidized bed of CaO [89]. They conducted experiments to investigate the potential of CaO to capture CO_2 in a pilot-scale fluidized bed reactor. The researchers found that the CO_2 capture efficiency of CaO bed was very high. However the total capture capacity of the bed was found to decay with number of carbonation (CO_2 absorption) and de-carbonation (CO_2 desorption) cycles. Kyaw and Kubota studied the carbonation of CaO at various temperatures in the range 600 to 900°C at various CO_2 partial pressures [90]. The authors developed a kinetic rate model for the absorption of CO_2 by CaO. They observed that the CO_2 partial pressure is an important parameter that determines the conversion of CaO to $CaCO_3$. The authors also studied the reverse reaction (de-carbonation) and developed a kinetic model for the conversion of $CaCO_3$ to CaO [91]. Some other groups have studied the CO_2 absorption process and have identified sorbent enhanced reforming as a possible method to enhance the hydrogen yield and at the same time remove the product gas CO_2 during the gasification of any carbonaceous fuel [92].

The use of sorbents for simultaneous CO_2 removal and hydrogen enhancement is a relatively new concept which has become popular over the last few years [86, 87]. It has been proposed for coal gasification. A few research groups have applied the concept to steam methane reforming at laboratory scale. In principle, the concept of using sorbents can be applied to any carbonaceous fuel including biomass. So far no work has been done in applying the concept of sorbent enhanced gasification for biomass.

Scope of the Present Work

Biomass gasification is a potential technology that holds substantial promise for producing renewable hydrogen. In the previous sections we saw several areas of biomass gasification and pyrolysis that have been studied by different research groups around the world. Although hydrogen production by biomass gasification has been studied in the past, there are many areas that still need to be addressed in order to make the technology commercially feasible.

There are many barriers to the commercialization of biomass gasification for hydrogen production. One of them is the capital cost and efficiency of biomass gasification systems. The capital costs of biomass gasification/pyrolysis need to be reduced. This may be possible by combining some steps in the production process that can significantly reduce the capital cost. For example the two step shift and PSA separation process could be combined into a single step shift and integrated separation process or the gasification, reforming, shift and separation processes could be integrated into a single step. Improving the process efficiency and hydrogen yield of biomass gasification and pyrolysis is another area of concern. The efficiency is defined as the lower heating value of hydrogen divided by the sum of all the energy inputs into the process including the energy in the feedstock. There are many types of equipments which operate at different temperatures. A detailed thermodynamic analysis of the biomass gasification process is necessary. The thermodynamic analysis includes a study of the effect of the process parameters on hydrogen yield. The process variables temperature, pressure, steam to biomass ratio and equivalence ratio influence the hydrogen yield. The values of these parameters at which the hydrogen yield is maximum can be determined by a thermodynamic analysis. Biomass steam gasification is endothermic and heat energy needs to be supplied from external sources. Steam generation also requires energy. The product gas is later cooled before separating the hydrogen and this cooling process releases heat. Hence there are some processes that absorb heat and others that release heat. An energy analysis can potentially optimize the process by better heat integration of the various sub-systems. This will reduce the overall energy consumption and thereby improve the process efficiency. A thermodynamic study can also give a deeper understanding of the constraints that limit the hydrogen yield of conventional gasification. The equilibrium of the water gas shift reaction can be shifted towards higher hydrogen yield by separating one of the co-products (CO_2) from the exhaust stream. Sorbents such as calcium oxide have been used for removing the CO_2 from the exhaust of fossil fuels. If the CO_2 absorption reaction is combined with the water gas shift reaction, the equilibrium can be shifted in favor of hydrogen. Calcium oxide has been used as a sorbent in the steam reforming of methane for producing hydrogen at the laboratory scale. Hydrogen yields of more than 90% (volume) have been obtained. The concept has also been proposed for the steam gasification of coal. In principle, it can be applied to any carbonaceous fuel. Biomass is a renewable resource that contains substantial amount of carbon (about 45% mass) and hence is a good candidate for applying the concept of sorbent enhanced gasification. The present research investigates renewable hydrogen production from biomass using sorbents. Theoretical and experimental studies have been carried out with the end objective of increasing the hydrogen yield and the overall process efficiency.

Table 3-1: Feedstock composition

Parameter/Analysis type	Description	Sawdust	Coal
Ultimate Analysis (% dry basis)	C %	48.01	80.3
	H %	6.04	5.6
	O %	45.43	8
	N %	0.15	1.5
	S %	0.05	4.6
Proximate Analysis	VM %	71.04	38
	FC %	17.3	44
	Ash %	4.5	5
	Moisture %	7.5	13
Higher Heating value	MJ/kg	18.4	34.1

(sawdust data source [44], coal data source [16])

Figure 3.1: Biomass gasification pilot plant [Courtesy NREL]

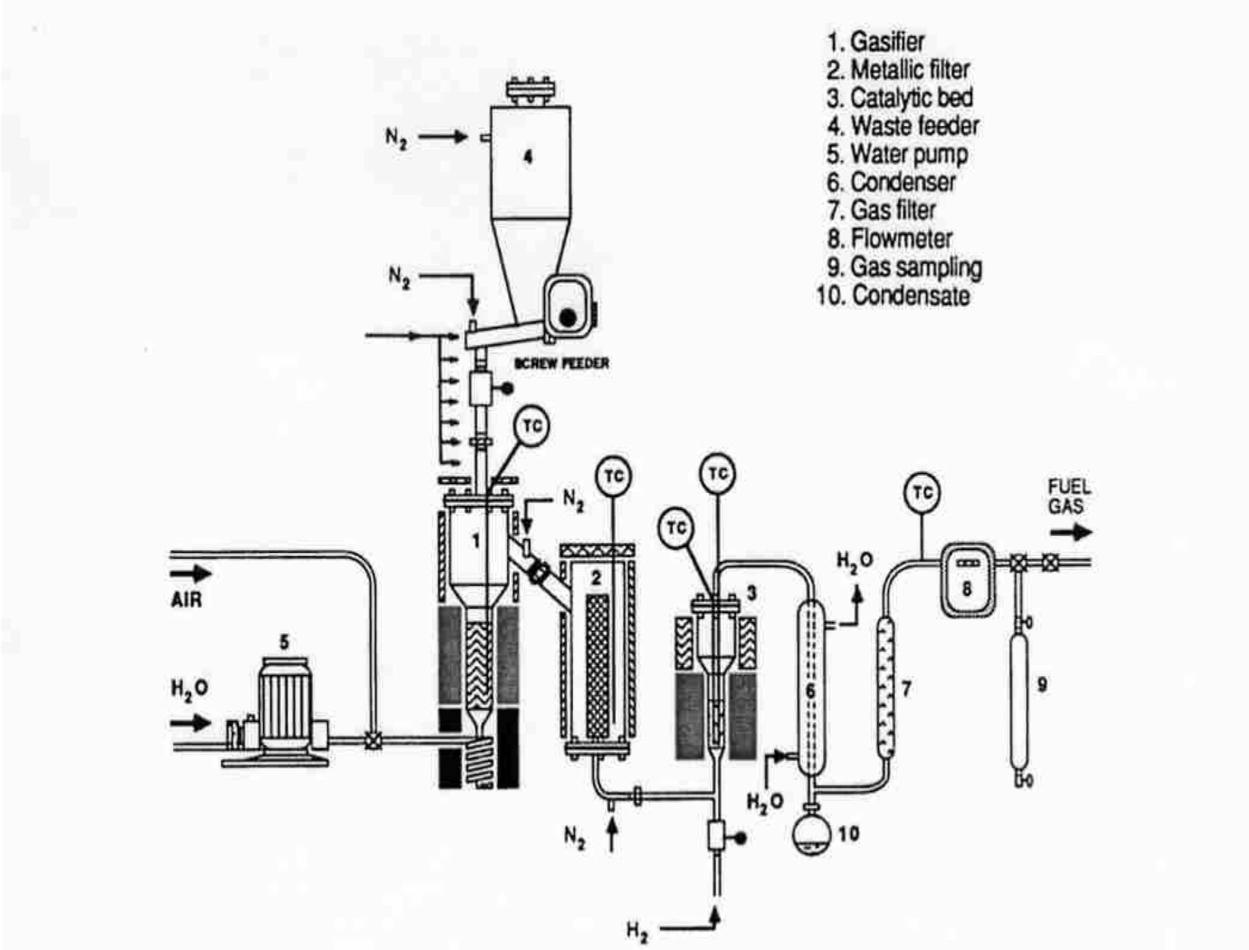

Figure 3.2: Schematic of biomass gasification set up for producing hydrogen (adapted from Olivares et al [45])

CHAPTER 4
THERMODYNAMIC ANALYSIS OF BIOMASS GASIFICATION

Introduction

A parametric analysis based on thermodynamics of biomass gasification was conducted. The gas yield depends on many process variables such as gasification temperature, pressure, the amounts of steam and/or air added to the gasifier. The objective of the study was to determine the operating conditions that would maximize the equilibrium hydrogen yield. An energy analysis was conducted to determine the thermodynamic efficiency of the gasification process with the end objective of maximizing the product gas hydrogen. The basic analysis lays the foundation for a novel gasification process that will be described in detail in the next chapter.

Fundamentals

The concept of chemical reaction equilibrium is based on the second law of thermodynamics for reacting systems. All spontaneous reactions occur in the direction of overall increase of entropy. When system composition reaches a point where the total entropy is maximum, it becomes "stuck" since any further change in composition would involve a decrease of entropy which cannot occur spontaneously. We know from thermodynamics that

$$s_{gen} = \Delta s_{sys} + \Delta s_{surr} \tag{4.1}$$

For any spontaneous reaction $s_{gen} \geq 0$. Since the environment is assumed to be at a constant temperature

$$\Delta s_{surr} = q / T \tag{4.2}$$

Hence for any spontaneous reaction,

$$\Delta s_{sys} + q_{surr} / T_{surr} \geq 0 \tag{4.3}$$

In differential form,

$$ds_{sys} + \delta q_{surr} / T_{surr} \geq 0 \tag{4.4}$$

The first law in differential form is given by:

$$\delta q - \delta w = du \tag{4.5}$$

For a reversible process, work term is Pdv. The second law in differential form as applied to a system can be written as

$$\delta q_{sys} \le T ds_{sys} \tag{4.6}$$

Substituting in the first law of equation (4.5) we have,

$$T ds_{sys} \ge du + \delta w$$

$$0 \ge du + P dv - T ds \tag{4.7}$$

We know from thermodynamics that Gibbs free energy is defined as,

$$g = u + Pv - Ts \tag{4.8}$$

Taking the derivative we get,

$$dg = du + P dv + v dP - T ds - s dT$$

For a constant pressure and temperature case, we have

$$dg = du + P dv - T ds \tag{4.9}$$

Combining equations (4.7) and (4.9) we see that for a spontaneous reaction at constant pressure and temperature,

$$0 \ge dg \tag{4.10}$$

This means that for a given temperature and pressure, a spontaneous chemical reaction will occur until the Gibbs free energy reaches a minimum point in composition space. Figure 4.1 shows the total Gibbs energy in relation to the reaction coordinate. Here 'ξ' is defined as the extent of reaction and characterizes the degree to which a reaction has taken place.

Gibbs energy is a function of temperature, pressure and composition (i.e. the moles of various components present e.g. H_2, CO, CO_2, CH_4 etc). This functionality can be represented as:

$$g = g(T, P, n_1, n_2, \ldots\ldots, n_{NS}) \tag{4.11}$$

Here n_i is the number of moles of species i. Taking total derivative of g gives

$$dg = \left(\frac{\partial g}{\partial T}\right)_{P,\,n} dT + \left(\frac{\partial g}{\partial P}\right)_{T,\,n} dP + \sum_{j=1}^{NS} \left(\frac{\partial g}{\partial n_j}\right)_{P,\,T,\,ni} dn_j \tag{4.12}$$

Since T & P are fixed for the point of minima, we have

$$\sum_{j=1}^{NS} \left(\frac{\partial g}{\partial n_j}\right)_{P,\,T,\,ni} dn_j = 0 \tag{4.13}$$

The number of moles of each species at equilibrium adjusts itself in such a way that the total Gibbs energy is minimized. The problem of determining the chemical composition at equilibrium now reduces to a minimization problem which needs to be solved keeping in mind the elemental (C, H, O, N) and mass constraints (i.e. mass of reactants = mass of products). Various texts [93] have carried out the mathematical treatment to cast the above problem as an optimization problem and solve it using a personal computer. Late Dr W. C. Reynolds of Stanford University developed an algorithm [94] to solve the above Gibbs energy minimization problem and it is now available as free software called Stanjan. The elemental composition of the various reactants at any specified temperature and pressure is supplied as input and Stanjan calculates the equilibrium yield of the product gases. In the next section various combinations of process parameters have been simulated to determine the most favorable conditions for hydrogen production.

Effect of Process Parameters on Equilibrium Hydrogen Yield

Biomass can be gasified using different gasifying media, the choice of which depends on the desired product gas composition and energy considerations. Commercial and research gasifiers generally use steam or air as the gasifying media [44, 55, 61, 71, 72, 95, 96]. Air gasification is an exothermic process, which produces a low heating-value gas (LHV 5-6

MJ/Nm^3) rich in CO and having small amounts of H_2 and higher hydrocarbons [71]. Steam gasification on the other hand is an endothermic process, which produces a medium heating-value gas (LHV 12-13 MJ/Nm^3) rich in H_2 and CO [72]. The process parameters including temperature, pressure, steam biomass ratio, equivalence ratio and residence time also influence the product-gas composition.

Effect of Temperature

The gasification temperature not only affects the product yield but also governs the process energy input. High gasification temperature (800-850°C) produces a gas mixture rich in H_2 and CO with small amounts of CH_4 and higher hydrocarbons. Figure 4.2 shows the equilibrium moles of various gases (H_2, CO, CO_2, CH_4) and solid carbon (C(s)) at 1 atm pressure, SBR (denoted by β, defined in section on 'Effect of Steam Biomass Ratio') of 1.0 and ER (defined in section on 'Effect of Equivalence Ratio') of 0. At low temperatures, solid carbon (C(s)) and CH_4 are present in the product gas. In actual gasifiers solid carbon is carried away to the catalytic bed and is deposited on the active catalyst sites thereby de-activating the catalyst. It is necessary to ensure that the product gas is free of any solid carbon. As temperature increases, both carbon and methane are reformed. At about 1000 K both are reduced to very small amounts (≤ 0.04 moles) and in the process get converted into CO and H_2. This explains the increase in hydrogen mole numbers. At about 1030 K, the H_2 yield reaches a maximum value of about 1.33 moles. At higher temperatures the H_2 yield starts reducing. This is attributed to the Water-Gas Shift (WGS) reaction:

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad \Delta H = -33.8 kJ/mol \qquad (4.14)$$

According to Le-Chatelier's principle, high temperature favors reactants in an exothermic reaction thus explaining the increase in CO and reduction in H_2 yield at higher temperature. For the present case a gasification temperature of about 1030 K gives the highest equilibrium hydrogen yield with negligible solid carbon in the product gas.

Effect of Pressure

Table 4-1 shows the effect of system pressure on equilibrium gas composition (gasification conditions T = 1100 K, $\beta = 1$, ER = 0). As pressure increases equilibrium H_2 and CO yields reduce. Simulations carried out to study the effect of reducing the pressure below 1 atm on equilibrium product yield showed that increase in H_2 yield is negligible (< 0.2%) even for pressures as low as 0.1 atm. Since high pressure reduces the H_2 yield, subsequent simulations were carried out at atmospheric pressure.

Effect of Steam Biomass ratio

SBR refers to moles of steam fed per mole of biomass. SBR, like temperature has a strong influence on both product gas composition and energy input. Figure 4.3 shows equilibrium yields (moles of gas) for process conditions T = 1000 K and ER = 0.

At low values of SBR, solid carbon and methane are formed. As more steam is supplied, both of these species are reformed to CO and H_2. For $\beta > 1$, C(s) and CH_4 moles reduce to very small values and H_2 and CO_2 yields increase monotonically; CO on the other hand reduces monotonically. This trend can be attributed to the Water-Gas Shift reaction; since system is being overfed with steam (for $\beta > 1$), H_2O mole numbers are increasing and as per Le-Chatelier's principle the equilibrium shifts in the forward direction. For $\beta > 1.5$, the hydrogen yield increases very slowly with most of the surplus steam going unreacted. This shows that operating at very high β (typically more than 2 for above conditions) may not be energy efficient, as additional H_2 produced may not justify the high cost of producing and supplying steam. In the next section, an energy analysis is done to find out the optimum β.

Effect of Equivalence Ratio

ER is a measure of the amount of external oxygen (or air) supplied to the gasifier. ER is obtained by dividing the actual oxygen (or air) to biomass molar ratio by the stoichiometric oxygen (or air) to biomass molar ratio. Oxygen (or air) is generally supplied as a gasifying and fluidizing medium. Using air in place of oxygen, though economical, has the negative effect of diluting the product gas due to the presence of nitrogen. Figure 4.4 shows the effect of ER on the equilibrium composition for the operating conditions of $T = 1100$ K and $\beta = 0$. As more oxygen (high ER) is supplied, it is observed that the H_2 and CO yields reduce and that of CO_2 increases. This is due to the oxidation of H_2 and CO to H_2O and CO_2. At low values of ER, small amounts of C(s) and CH_4 are formed in the gasifier, both of which get oxidized as more air is supplied.

Air gasification is an exothermic process and hence using air as a gasifying medium reduces the net energy consumption and improves the overall thermodynamic efficiency. However supplying more air dilutes the product gas thereby reducing the H_2 yield. The optimum ER would supply enough air for the biomass to be partially oxidized without significant dilution of the product gas.

Optimum Process Parameters

One of the objectives of the present analysis is to find the process conditions that are favorable for hydrogen production (very low or no solid carbon in the product gas, high H_2 yield and high efficiency). From Figure 4.4 it is clear that the maximum amount of hydrogen that can be produced at equilibrium in pure air gasification (no steam, $T = 1100$ K, and ER = 0.1) for the stated conditions is 0.7 moles. This value is smaller than the hydrogen that can be obtained at the same temperature with steam addition (about 1.3 moles of H_2 at $T = 1100$ K, $\beta = 1$, referring to Fig 4.2). The excess H_2 in the output stream is attributed to the WGS reaction, which cannot take place in pure air gasification due to the absence of steam, implying that for high H_2 yields one should go for steam gasification. Steam not only influences the water-gas shift but also reforms the hydrocarbons, solid char and tars and thereby produces more hydrogen. Steam gasification is an endothermic process; therefore using steam will be energy intensive [97]. Also most gasifiers use fluidized beds for better heat transfer. For energy efficiency and cost-effectiveness these beds use air (or oxygen) as a co-fluidizing medium with steam [44, 72, 96, 97]. From the above equilibrium analysis we see that as more steam is supplied the hydrogen yield increases. However, this additional hydrogen comes at the cost of extra energy that needs to be supplied in order to produce steam. The optimum β (steam/biomass ratio) is based on the balance of these two opposing factors. ER (equivalence ratio) affects both the gas composition and net energy input. From the earlier analysis we saw that the optimum ER, like optimum β depends on the balance between partial oxidation of biomass and dilution of the product gas. In the next section a first law analysis of the gasifier is carried out with the objective of determining the optimum operating conditions for hydrogen production.

Energy Analysis

A schematic of a biomass gasifier with a steam generator and an air pre-heater is shown in Figure 4.5. Wood designated by $CH_{1.5}O_{0.7}$ was the model biomass compound (chemical formula based on ultimate analysis [44]). The general reaction for combined steam and air gasification is written as:

$$\begin{aligned} CH_{1.5}O_{0.7} + \beta H_2O + \gamma(O_2 + 3.76N_2) \rightarrow n_{CH4}CH_4 + n_{CO}CO + n_{CO2}CO_2 + n_{H2}H_2 \\ + n_{H2O}H_2O + n_{N2}N_2 \end{aligned} \tag{4.15}$$

Here only the main components (H_2, CO, CO_2, CH_4) are considered. Yields of higher hydrocarbons (C_2H_2, C_2H_4, C_2H_6 and so on) were found to be negligible as compared to the main constituents and hence were not considered in the analysis. The gasification temperature was varied from 900 K to 1400 K (in steps of 100 K), steam to biomass molar ratio was varied from 0 to 5 (in steps of 1) and ER was varied in the range 0 to 0.4 (in steps of 0.1). These are the typical values of these variables encountered in most commercial and research gasifiers [44, 55, 61, 71, 72, 97, 98]. From equilibrium studies we know that increasing the pressure reduces the hydrogen yield, hence the pressure was maintained at 1 atm for all further analyses. A first law analysis of the gasifier was carried out across the control volume (dotted) as shown in fig 4.5.

An energy balance equation can be written as (assuming no heat losses and work = 0):

Energy in = Energy out (4.16)

$$\begin{aligned} H_{wood} + \beta H_{H_2O(v)} + \gamma(H_{O_2} + 3.76H_{N_2}) + Q_{EG} \rightarrow\ & n_{CH_4}H_{CH_4} + n_{CO}H_{CO} + n_{CO_2}H_{CO_2} \\ & + n_{H_2}H_{H_2} + n_{H_2O}H_{H_2O} + n_{N_2}H_{N_2} \end{aligned} \tag{4.17}$$

Here H is the enthalpy and Q_{EG} is the heat supplied to (or rejected by) the equilibrium gasifier. Enthalpy of each species is written in terms of enthalpy of formation and enthalpy change:

$$H = H^{o}_{f} + \Delta H \tag{4.18}$$

Q_{EG} is positive for an endothermic reaction (steam gasification) where heat is to be supplied from an external source. When Q_{EG} is negative heat is liberated and this generally happens during partial oxidation of biomass (air gasification). A zero value for Q_{EG} is an interesting case which represents adiabatic gasification. This would mean a self-sustaining process and can be used as a standard to compare actual gasifiers. We assume that the steam generator provides superheated steam at 700 K and the air-preheater heats the air from the ambient to 350 K before entering the gasifier. The efficiency of the process was then determined for a range of temperatures, SBRs and ERs. The efficiency was calculated as per the following definition given by USDOE [28]:

$$\eta = \frac{\text{LHV of hydrogen in product gas}}{\text{LHV of biomass + All other energies}} \tag{4.19}$$

$$\eta = \frac{n_{H2} * LHV_{H2}}{n_b * LHV_b + (Q_{EG} + Q_{steam} + Q_{air})} \tag{4.20}$$

$$Q_{steam} = n_{H2O} * \Delta H_{H2O} \tag{4.21}$$

$$Q_{air} = n_{O2} * \Delta H_{O2} + n_{N2} * \Delta H_{N2} \tag{4.22}$$

The moles of each species at equilibrium were calculated using Stanjan. The enthalpy of formation and enthalpy change for each species are taken from standard thermodynamic tables [99]. The values for all the heat duties (Q_{EG}, Q_{steam}, Q_{air}) were determined. The efficiency was then determined using the above equation for a range of temperatures, SBRs and ERs. Figures 4.6 – 4.9 show the efficiencies for the different combinations. For simplicity and clarity of graphs, the efficiency values for all the temperatures (900 to 1400 K), ERs (0.1 to 0.4 in steps of 0.1) and SBR values of 1, 2 and 5 have been shown.

Effect of Temperature on Thermodynamic Efficiency

As gasification temperature increases, biomass thermally disintegrates to produce more gases and volatiles. As temperature increases, the hydrocarbons in the presence of steam/air get reformed to produce H_2 and CO. Hence as hydrogen yield increases, the efficiency also increases. As gasification temperature further increases, more heat needs to be externally supplied to maintain the gasifier temperature. Also at higher temperatures (>1200 K) the hydrogen yield drops. Hence, the efficiency first increases to a maximum at around 1000 K (this is especially true for low ER values of 0.l or 0.2 and SBR of 1 as shown in Figs 4.6 and 4.7) and then decreases as the temperature is further increased upto about 1300-1400 K.

Effect of Steam Addition on Thermodynamic Efficiency

Figures 4.6 to 4.9 show the combined effect of adding steam and increasing the temperature for various equivalence ratios. As we have seen earlier, adding steam increases the hydrogen yield. However additional steam also demands additional energy. Therefore, there should be an optimum steam to biomass ratio which will justify the cost of extra steam. In this analysis, the steam biomass ratio was varied from 1 to 5. The plots for SBR values of 1, 2 and 5 are shown in the figures. At low SBR values (~1) the amount of hydrogen produced is relatively small. As SBR increases the efficiency increases due to higher H_2 yields. However at very high SBR values (>5) the efficiency drops due to large amounts of external heat needed to generate the steam. This trend was observed in all four graphs (Figs 4.6 – 4.9). In the analysis it was found that a SBR of 2.0 gives the highest efficiency among all the cases.

Effect of ER on Thermodynamic Efficiency

Gasification in presence of air or oxygen partially oxidizes the biomass and thereby releases energy. However, this also dilutes the product gas (especially if air is used) thereby lowering the heating value of product gas. At low ER values (~0.1) energy is released due to partial oxidation of biomass. Also the hydrogen yield is relatively high and so the efficiency is high. Typical efficiencies were of the order 50 to 55 % for SBR in the range 2 to 3 at gasification temperatures of 900 – 1000 K.

As ER increases the product gas starts getting diluted due to the presence of N_2. It was observed in the previous section that the H_2 yield drops beyond ER of 0.2. Hence, although the reaction is exothermic, a whole lot more biomass needs to be gasified in order to produce the same amount of hydrogen. At ER values ≥ 0.4 the efficiency starts dropping rapidly (typically $\eta \sim 44$ % for $\beta \sim 1$ or 2, $T = 1000$ K and $ER = 0.4$, referring to Fig. 4.9).

The optimum conditions for hydrogen production occur when we have high thermodynamic efficiency, with high hydrogen yields and little or no carbon formation. From the parametric analysis of the previous section and the energy analysis we see that this happens for T

~ 1000 K, SBR ~ 2, ER ~ 0.1 and atmospheric pressure. For the given biomass feedstock these conditions give a thermodynamic efficiency of 52%.

Comparison of Equilibrium Results with Experimental Data

Equilibrium studies are used to predict the maximum possible conversion in any chemical reacting system. By comparing experimental results with equilibrium calculations one can understand the relation between thermodynamics and chemical kinetics of the process. In general, it was observed that experimental results deviated considerably from the equilibrium calculations. Figure 4.10 compares equilibrium and experimental results where two parameters, the gasification temperature and residence time (τ), have been varied (experimental data obtained from [96]). Of the four sets of graphs, the first two are for temperature (700 and 800°C) and the last two are for residence times (0.4 and 1.4 s). In each set, the hatched bars are for theoretical (th) and the solid bar for experimental (ex) compositions (total of 8 bars for each T and each τ). For both temperatures, the H_2 and CO gas volumes are far from equilibrium, although the difference is less for higher temperature.

The theoretical CH_4 volume at equilibrium at 800°C (~ 0.01 %; not visible on graph) is much smaller than the experimental value. From the residence time graph, it is observed that for high residence times, the experimental values are closer to the equilibrium values. This is due to more time being available for reactions to take place and reach completion. Figure 4.11 shows how theoretical and experimental results compare for different β (1.9 and 6.5) and ER (0.09 and 0.37) (experimental data source [44]). The experimental H_2 yield is lower than the equilibrium yield for a β value of 1.9. Other gas mole fractions (CO, CO_2 and CH_4) too differ from the equilibrium values. For very high β, H_2 mole fraction comes close to the equilibrium value. For both low and high ERs the H_2 mole fraction is away from the equilibrium value. Both equilibrium and experimental results are more sensitive to T, τ and β than ER.

During biomass gasification many complex aromatic hydrocarbons called tars are released. These tars typically include benzene or multiple rings of benzene such as naphthalene, xylene or toluene and many complex higher hydrocarbon chains with several carbon atoms [55]. Equilibrium studies were done using benzene as a possible tar compound. The results however showed negligible benzene in the product stream (about ten orders of magnitude lower than other important products such as hydrogen and carbon monoxide). This is possibly due to the infinite time being available for the reactions to occur before equilibrium is reached. This was also verified from the actual experimental data where long residence time and high temperature drastically reduced the tars in product stream [72]. Since high residence times reduce the tar yield and equilibrium studies show product yield at very long times ($t \rightarrow \infty$), higher hydrocarbons and tars were not included in the equilibrium modeling studies.

Summary and Conclusion

A thermodynamic analysis of hydrogen production from biomass was done using equilibrium modeling. The effects of process parameters (temperature, pressure, SBR and ER) on hydrogen yield were studied. It was observed that combined steam and air gasification gave much higher H_2 yield than air gasification alone. Using air as a co-gasifying medium with steam helps reduce external energy input as the feedstock gets partially oxidized. The equilibrium hydrogen yield is found to initially increase with temperature to a maximum and then gradually reduce at higher temperatures. The hydrogen yield increases continuously with increase in SBR. Air gasification also produces hydrogen but the yield is lesser than steam gasification. The product gas in air gasification gets diluted due to the presence of nitrogen. Increasing the pressure was found to have a negative influence on the hydrogen yield and hence all subsequent simulations were carried out at 1 atm. The gasifier is the most critical component of any biomass gasification system. The gasifier was modeled as an equilibrium reactor and a first law analysis of the gasifier was carried out to determine the maximum thermodynamic efficiency at equilibrium. The optimum operating conditions were found to be T of 1000 K, SBR of 2. ER of 0.1 and P of 1 atm which gave an efficiency of 52%. The actual energy consumption would be higher due to equipment inefficiencies and heat losses from the gasifier, catalytic reactor and interconnecting tubing. Also in real gasifiers we will not reach equilibrium conditions and hence the product gas will contain less H_2 and CO and more CO_2. Nevertheless, the above figures give an idea of the theoretical maximum efficiency for the given conditions. A comparison of the theoretical equilibrium calculations with the experimental results shows considerable deviations between the two. Using longer residence times, higher temperatures and higher steam input the experimental results can come close to equilibrium predictions.

The basic studies gave an understanding of the thermodynamics of biomass gasification. In the next chapter a novel concept of combining different reactions and thereby getting an improvement in the hydrogen yield is discussed.

Table 4-1: Equilibrium gas moles at different gasification pressures

P (atm)	H_2	CO	CO_2	CH_4	Remark
0.1	1.303	0.746	0.253	1.61E-5	Low Press.
0.5	1.302	0.745	0.253	4.0E-4	System
1	1.301	0.744	0.254	1.59E-3	High Pressure
10	1.09	0.633	0.286	8.13E-2	System
25	0.897	0.491	0.326	1.82E-1	

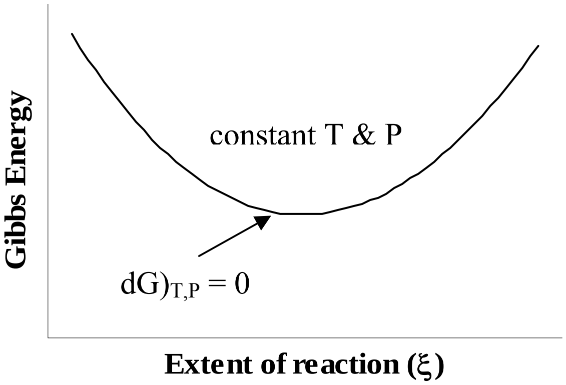

Figure 4.1: Variation of Gibbs energy with extent of reaction

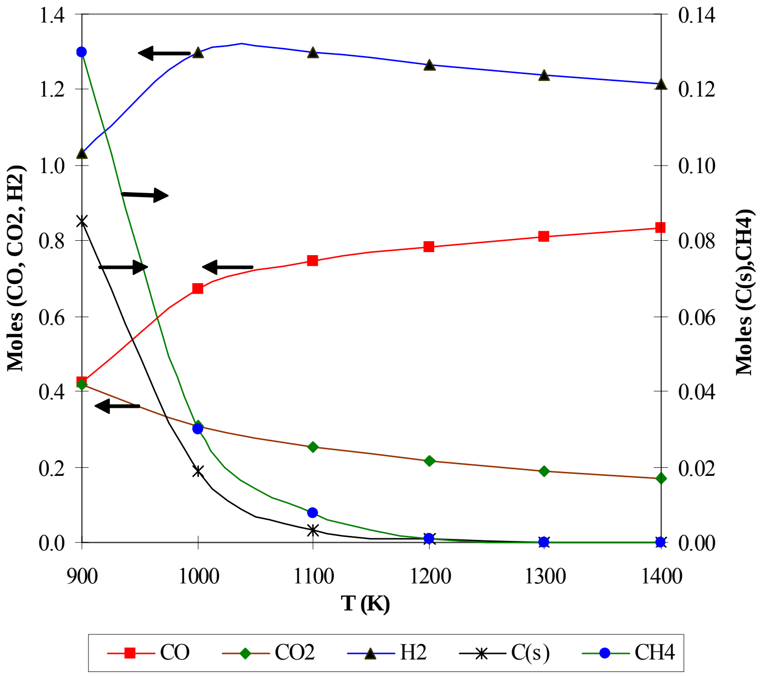

Figure 4.2: Effect of temperature for P = 1 atm, β = 1, ER = 0

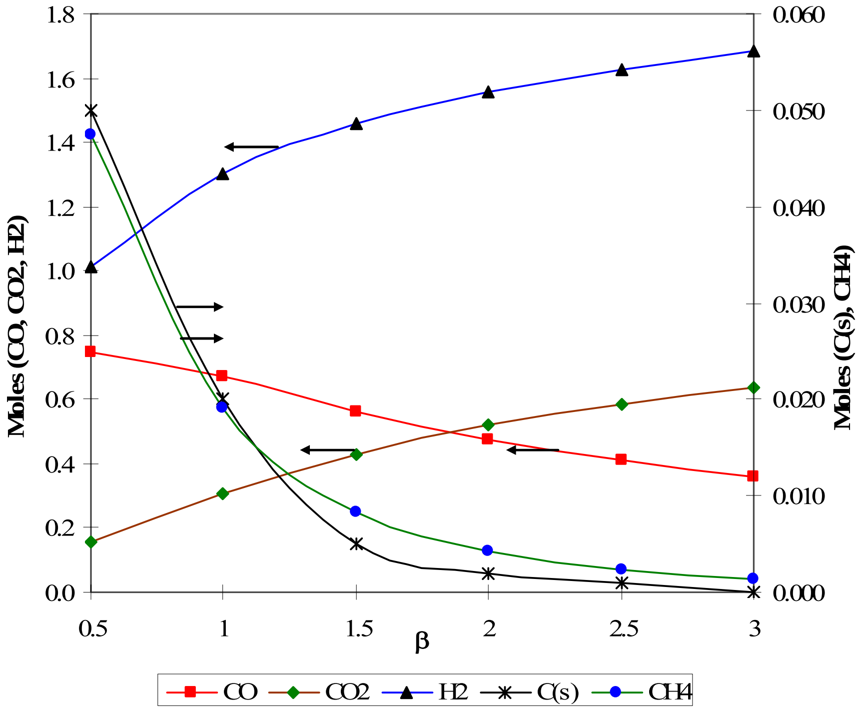

Figure 4.3: Effect of SBR on equilibrium composition

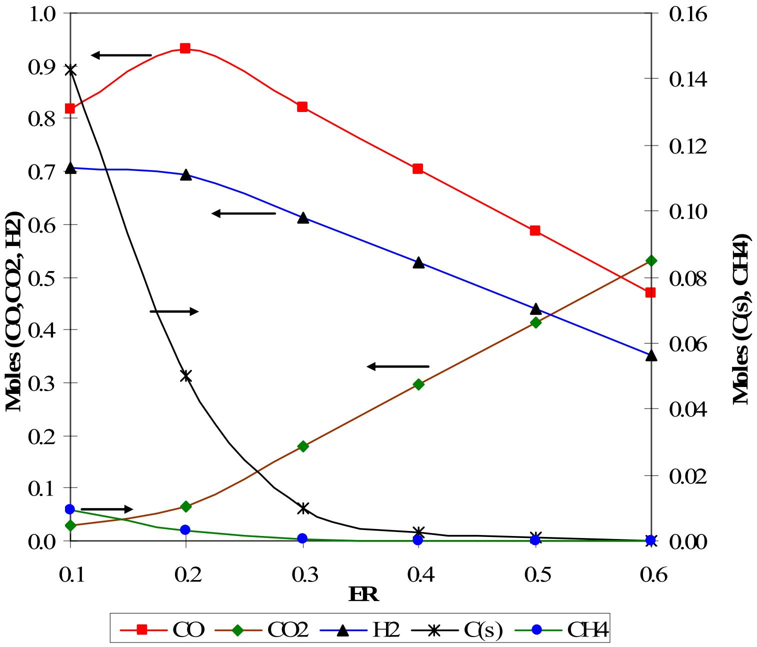

Figure 4.4: Effect of ER on Equilibrium composition

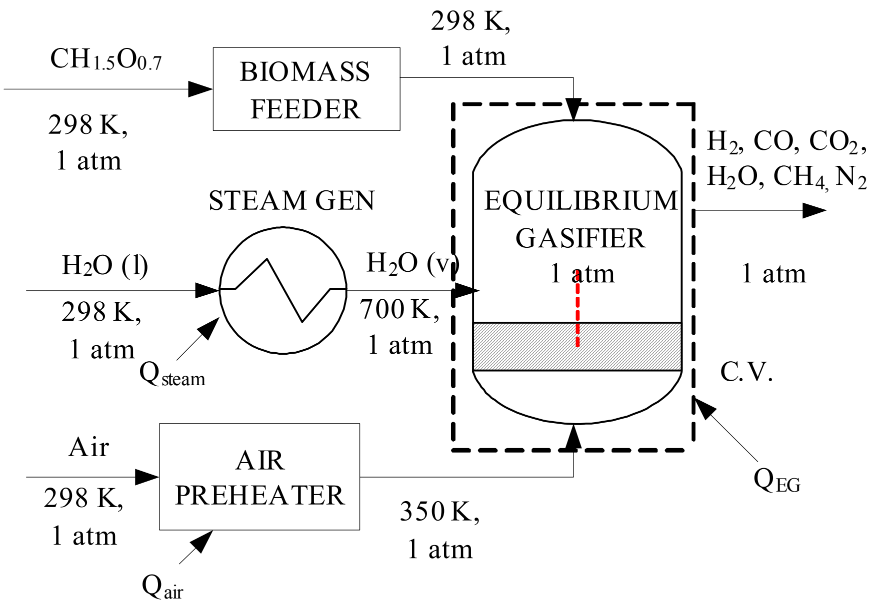

Figure 4.5 Schematic of biomass gasifier

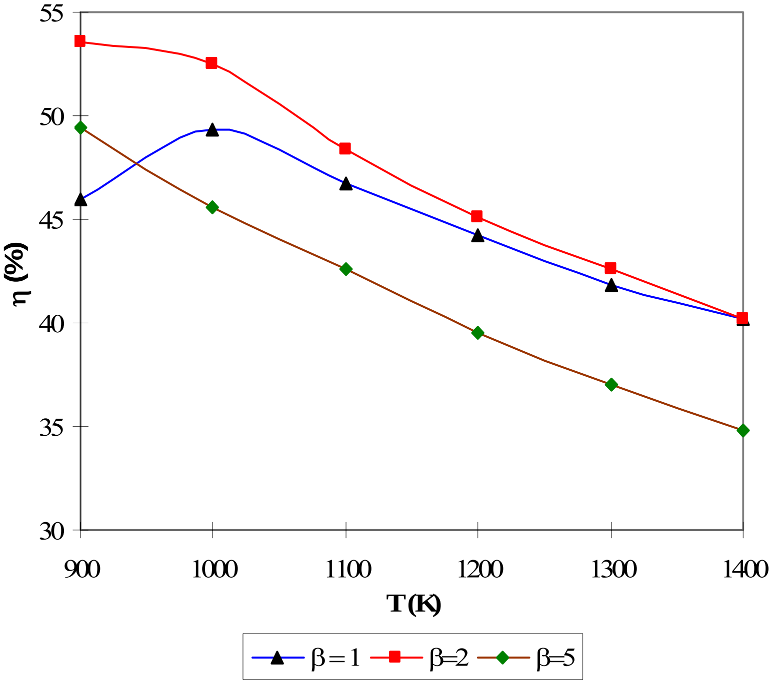

Figure 4.6: Efficiency Vs temperature for various β (ER = 0.1)

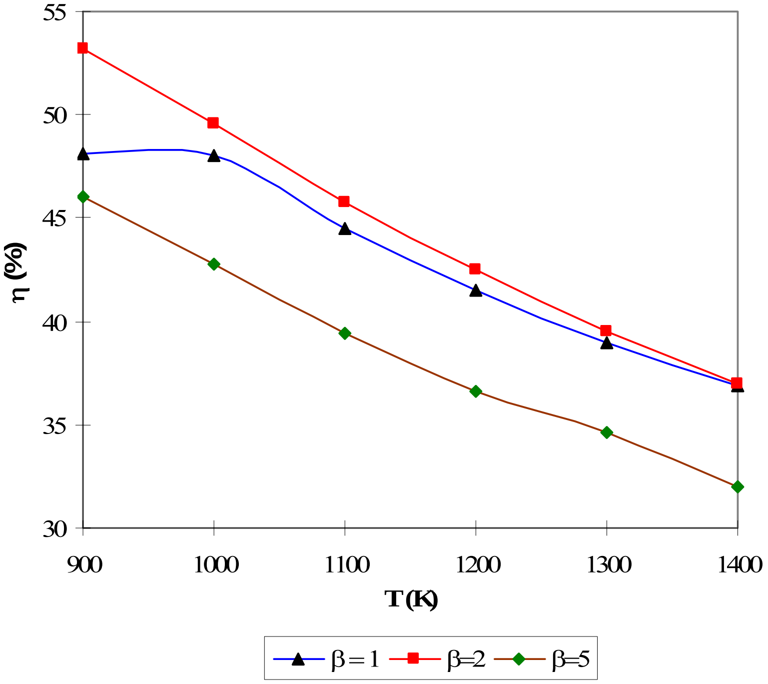

Figure 4.7: Efficiency Vs temperature for various β (ER = 0.2)

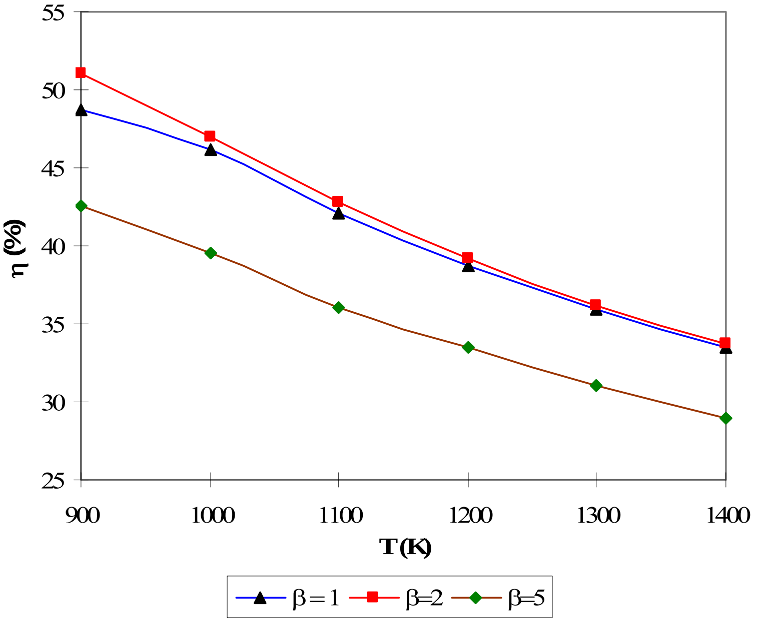

Figure 4.8: Efficiency Vs temperature for various β (ER = 0.3)

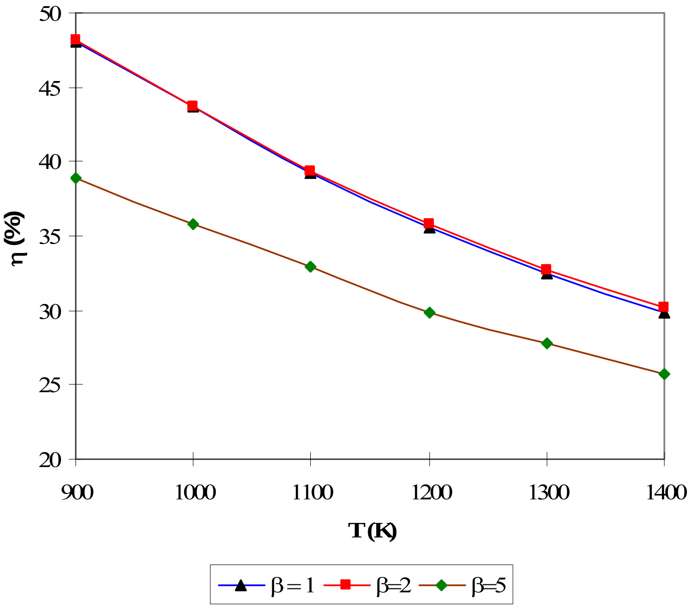

Figure 4.9: Efficiency Vs temperature for various β (ER = 0.4)

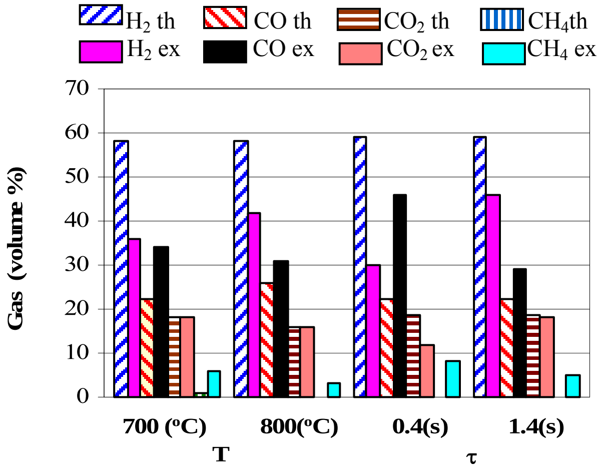

Figure 4.10: Comparison of equilibrium data with experimental data of Corella et al [96] for different temperatures and residence times

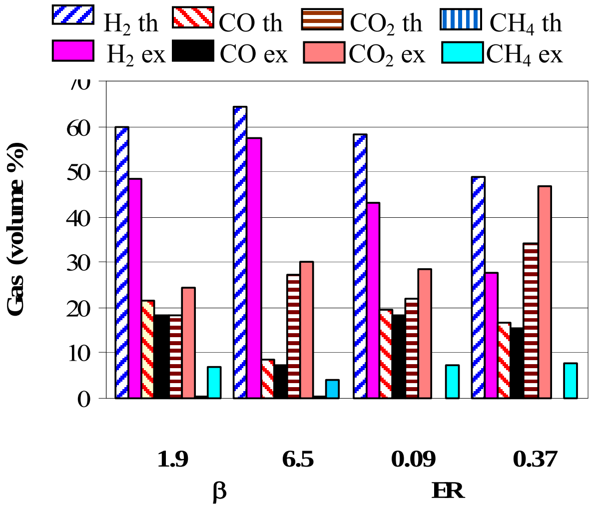

Figure 4.11: Comparison of equilibrium data with experimental data of Turn et al [44] for different β and ER

CHAPTER 5
ABSORPTION ENHANCED BIOMASS GASIFICATION

Introduction

Steam gasification of biomass produces a gas mixture rich in hydrogen and containing other gases such as CO, CO_2, CH_4 and small amounts of higher hydrocarbons. The maximum hydrogen that can be produced in conventional steam biomass gasification is limited by the thermodynamic equilibrium constraints at the specified gasifier temperature and pressure. The temperature option is limited by equilibrium product composition which does not favor hydrogen formation beyond 1100 K (this was observed in the previous chapter). At higher temperatures the biomass gets thermally dissociated, however, this does not translate into increased hydrogen yields; hence the temperature option is limited. The pressure option too is limited as higher gasification pressure (above one atmosphere) reduces the hydrogen yield and lower pressure does not offer any substantial increase in the hydrogen content. The steam to biomass ratio can be increased to give higher hydrogen yields, but this is at the cost of extra steam that needs to be supplied. As we increase the steam supply, the yield increases rapidly up to certain point but thereafter the increase is rather slow with most of the surplus steam going unreacted. Hence in order to increase the hydrogen yield we need to find new techniques which are simple, energy efficient and inexpensive. The products coming out of the biomass gasifier consist of other gases like CO, CO_2, and CH_4 which must be separated from H_2. Hence the problem of gas separation also needs to be addressed.

In recent years sorbents (such as calcium oxide) have been used for CO_2 removal from the exhaust of fossil fuel plants. The sorbent absorbs CO_2 and in the process releases heat which can be used for reforming the fuel. More recently, this technique was applied to the steam reforming of methane and a hydrogen rich, CO_2 free gas was obtained [86]. The product gas is expected to have more hydrogen with less contaminants. It can be used for any downstream application such as fuel cell or gas turbine with minimal cleaning. Hence there is a potential to reduce the number of equipment (and thereby reduce the capital costs) by using sorbents. In principle, the sorbent enhanced gasification process can be applied to any carbonaceous fuel such as coal, heavy oils, biomass, plastic or organic waste.

Concept of Absorption Enhanced Gasification

The concept of producing hydrogen by reforming hydrocarbons using sorbents dates back to as early as 1868 [100]. In 1967 Curran and co-workers [101] separated CO_2 at high temperature using calcined dolomite in the so-called "CO_2 Acceptor Gasification Process". More recently Harrison et al [86, 102, 103] have experimentally shown a novel method of improving hydrogen yield of conventional SMR and effectively separating CO_2. Lin et al [87, 88, 104] have used sorbents to develop an innovative HyPr-RING (Hydrogen Production by Reaction Interaction Novel Gasification) technique for producing hydrogen by gasification of coal. The underlying concept of absorbent enhanced gasification is shown in Figure 5.1.

There are two main reactors in the process. First is the gasifier/absorber. Here any carbonaceous fuel (in our case biomass) is supplied to the reactor to which steam is also being fed. The fuel reacts with steam to produce a gas mixture containing hydrogen, carbon monoxide, carbon dioxide and some hydrocarbons. The carbon monoxide reacts with steam to produce additional hydrogen as per the Water Gas Shift reaction.

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad \Delta H = -33.8 \text{ kJ/mol} \qquad (5.1)$$

The calcium oxide sorbent in the gasifier absorbs the carbon dioxide produced and gets converted to calcium carbonate

$$CaO + CO_2 \rightarrow CaCO_3 \qquad \Delta H = -168.2 \text{ kJ/mol} \qquad (5.2)$$

During the absorption process heat is released and this can be used for the endothermic steam gasification of biomass, thereby reducing the net external heat supply to the gasifier. The calcium carbonate is then regenerated by heating it in another reactor. The thermal energy for regeneration can be supplied either by burning external fuel or part of the biomass feedstock itself. The hydrogen produced may have small amounts of carbon monoxide, methane and tars. Hence, it is passed through a gas cleaning system so as to obtain a clean gas that is rich in H_2. Through simultaneous gasification and CO_2 absorption, the equilibrium of the homogenous water gas shift reaction is shifted toward H_2. For any general biomass fuel the reactions taking place in sorbent enhanced gasification (SEG) can be written as follows:

$$CH_xO_y + (1-y)H_2O \rightarrow CO + (0.5x + 1 - y)H_2 \qquad \Delta H_R > 0 \tag{5.3}$$

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad \Delta H_R < 0 \tag{5.4}$$

$$CaO + CO_2 \rightarrow CaCO_3 \qquad \Delta H_R < 0 \tag{5.5}$$

The overall reaction can be written as:

$$CH_xO_y + (2-y)H_2O + CaO \rightarrow CaCO_3 + (0.5x + 2 - y)H_2 \tag{5.6}$$

Equation (5.6) represents the idealized sum reaction for sorbent enhanced gasification. Here the formation of secondary products (methane, coke & tar) is neglected. Table 5-1 gives the values of the heats of reaction for different fuels with typical reaction temperatures.

Figure 5.2 shows a schematic of the Sorption Enhanced Gasification concept. The CO_2 absorption is an exothermic reaction and the biomass steam reforming reaction is endothermic and hence the overall reaction would consume less energy. The spent sorbent is regenerated in a subsequent process by supplying heat. For continuous gas production, solid fuel is gasified in presence of fresh sorbent at temperatures less than 700˚C. The carbonated bed material together with the biomass coke is removed and regenerated at 800-900˚C under air supply. Thus a hydrogen rich gas stream with small amounts of CO and CH_4 and a CO_2 rich exhaust gas stream are generated in two parallel process steps. In actual system two fluidized bed reactors with circulating absorbent bed material can be coupled as shown in the set-up of figure 5.2.

Application of SEG to Biomass Gasification

Sensitivity studies have been carried out in order to determine the effect of process variables on the equilibrium hydrogen yield. Ethanol was used as the model biomass compound. ASPEN PLUS (version 12.1) software was used to model the process flow. The choice of ethanol as a model compound was primarily due to convenience. The physical, thermodynamic and transport properties of ethanol are well-documented and are already built into ASPEN database, hence making it convenient to carry out simulations (the choice of this model compound does not endorse or imply producing hydrogen from ethanol; this is the subject of a separate study). The process variables studied were temperature, pressure, steam to biomass ratio and sorbent to biomass ratio. The general reaction for steam gasification of ethanol is given by:

$$C_2H_5OH + H_2O \rightarrow H_2 + CO + CO_2 + CH_4 + H_2O + \text{higher Hydrocarbons} \qquad (5.7)$$

Experimentally it has been found that higher hydrocarbons (two carbon atoms containing compounds such as ethylene or acetaldehyde) and solid carbon in the steam reforming of ethanol are negligible. Hence these were not considered in the simulations [105]. There are two cases considered here – base case (i.e. no sorbents) and sorbent enhanced gasification each of which is explained below.

Case I: Base case (no sorbent)

Ethanol and water are mixed in a mixer and sent to a heater where they are heated to the desired temperature. The product is then sent to the reformer which is modeled as a Gibbs reactor which is at the desired gasifier temperature and pressure. The products of reformer which are at thermodynamic equilibrium are then cooled before being sent to the water gas shift reactor where carbon monoxide reacts with steam to produce additional H_2 as per the following reaction.

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad \Delta H = -33.8 kJ/mol \qquad (5.8)$$

The flow sheet for base case is shown in Figure 5.3. The steam to biomass ratio (water to ethanol feed ratio) was varied between 3 and 8, the reformer temperature from 500 to 900°C (this is the temperature range for actual gasifiers) and the gasifier pressure from 100 kPa to 2500 kPa. The results of the sensitivity analysis are shown in figures 5.4 to 5.6. Figure 5.4 shows that the temperature has a significant effect on the equilibrium product yield. The ethanol and steam flow rates were fixed at 1 kmol/hr and 4 kmol/hr and the reformer was at atmospheric pressure. As the reaction temperature increases the hydrogen yields also increases until it reaches a maximum at 725°C and then decreases. The increase of hydrogen yield is due to the reaction of ethanol with steam. As the temperature increases, the hydrocarbons (methane) are reformed and converted to hydrogen. At high temperatures the Water-Gas Shift reaction occurs in the reverse direction and this reduces the hydrogen yield.

Figure 5.5 shows the effect of reformer pressure on product yield. It is observed that the pressure significantly impacts the equilibrium product yield. One can conclude from the figure that the highest hydrogen yield is obtained at atmospheric pressure and hence it is best to operate the reformer at one atmosphere. The effect of steam to ethanol ratio on product yield for a reformer temperature of 700°C is shown in Figure 5.6. The addition of steam increases the hydrogen yield while reducing the CH_4 and CO concentrations. Although high steam to ethanol ratio gives high hydrogen yields, it will be limited by the cost of the system.

Case II: Ethanol gasification in the presence of CaO sorbent (sorbent placed in the reformer)

Figure 5.7 shows the flowsheet of sorbent enhanced biomass gasification. Adding CaO to the steam reforming of ethanol can be considered with the following reaction

$$CaO(s) + CO_2(g) \rightarrow CaCO_3(s) \qquad \Delta H = -168\ kJ/mol \qquad (5.9)$$

The removal of CO_2 from the gaseous phase will displace the equilibrium of the gas mixture to a higher hydrogen yield and a lower CO concentration. The products are the same as in the base case plus CaO and $CaCO_3$. The flow sheet of the simulation is shown in Fig. 5.7. Again ethanol and water are mixed together and are sent to the heater (HEATER1) at 700°C. The mixture enters the Gibbs reactor (REFORMER) which in this case includes solid CaO. The reformer output is sent to the separator (SEP) for separation of gases from solids. The gases including H_2, CO, CO_2, CH_4 and steam are cooled to 300°C in the heat recovery heat exchanger (HT-RECOV) and enter the Water-Gas Shift (WGS) reactor. The solids are sent to the regeneration reactor (REGENERA) in which $CaCO_3$ decomposes to CO_2 and CaO at 850°C.

The effect of temperature on the product molar flow rates is shown in figure 5.8. At temperatures lower than 750°C the hydrogen production is greatly enhanced by the separation of CO_2. Above this temperature the molar flows are similar to the previous case. The maximum hydrogen is produced at 650°C (which is almost 100°C lesser than the base case). It is also observed that the maximum hydrogen produced in the sorbent enhanced gasification case (5.24 mol/mol of ethanol) is almost 12% more than the corresponding figure for the base case (4.68 mol/mol of ethanol). The amount of carbon oxides (CO and CO_2) produced is less than the base case due to absorption by CaO. It is observed that the sorbent absorption is effective up to 800°C, thereafter, the hydrogen yield drops and is similar to the base case. This is probably due to the reverse reaction (calcination) of $CaCO_3$ which is favored at those temperatures. When CO_2 is no longer absorbed, the hydrogen yield starts dropping.

The effect of pressure on the product molar flow rates is shown in figure 5.9. Similar to the base case, operating the reactor at high pressures is not desirable due to the decrease in hydrogen yield.

The steam to ethanol ratio was changed from 3 to 8. This ratio greatly enhances the steam reforming of ethanol in the presence of CaO. Figure 5.10 shows the results of varying this ratio at a reformer temperature of 700^{o}C and atmospheric pressure. The results are similar to the previous case with hydrogen yield being consistently higher than the base case (by about 10%).

Finally, the effect of adding sorbent on the product yield is shown in figure 5.11. CaO/ethanol ratio of zero corresponds to the base case (no sorbent). As the amount of CaO is increased, it absorbs the carbon dioxide and gets converted to $CaCO_3$. The carbon dioxide goes on getting absorbed as it is produced until only a small amount (corresponding to equilibrium) remains. Hence after a certain CaO/ethanol ratio the $CaCO_3$ reaches saturation. The amount of hydrogen too goes on increasing as the CO_2 is getting absorbed. Beyond a certain point the increase in hydrogen is not significant. Also the surplus unused CaO shows up in the product stream. Adding excess CaO is energy inefficient as it simply gets heated and cooled and does not help in the CO_2 removal. Hence, it is essential to add only the necessary amount of CaO as needed for removing the CO_2 from the product gas. For the given conditions adding sorbent more than a CaO/ethanol ratio of 4 does not give any substantial improvement in the hydrogen yield.

Energy Analysis

A simple energy analysis has been carried out to study the effect of sorbent addition on hydrogen yield of ethanol steam reforming. In order to have a common basis for comparison, the process conditions for both cases were kept the same and are given below:

Ethanol flow rate : 1 kmol/hr
Steam flow rate : 4 kmol/hr
Reformer pressure : 1 atm
Reformer temperature : 700^{o}C
WGS reactor temperature : 300^{o}C
Regenerator Temperature : 850^{o}C
CaO flow rate : 3 kmol/hr

The enthalpy of various streams was calculated. The first law of thermodynamics was applied to each of the reactors and heat exchangers and the heat-duty was then calculated. The heat duty of the different reactors and the product gas distribution for the two cases considered is given in Table 5-2.

The thermodynamic efficiency is then calculated as per the following definition:

$$\eta = \frac{\text{Energy Output}}{\text{Energy Supplied}} \tag{5.10}$$

$$\eta = \frac{\text{Lower Heating Value of Product gas}}{\text{LHV of biomass + Total heat supplied}} \tag{5.11}$$

Here the total heat supplied includes

1) heat input to the heater (or vaporizer) that is used to produce steam and ethanol,
2) heat input to the reformer
3) heat input to the regenerator (applicable to the sorbent case only)

The Lower heating value of product gas is calculated as follows:

$$\text{LHV of gas} = n_{H_2} * LHV_{H_2} + n_{CO} * LHV_{CO} + n_{CH_4} * LHV_{CH_4} \qquad (5.12)$$

Table 5-3 gives the values of the output and input energy and the thermodynamics efficiency for the two cases. A simple thermodynamic analysis shows that the efficiency of the sorbent enhanced gasification is higher than conventional gasification.

In actual biomass gasification systems there will be many reactors and heat transfer equipment. The heater (Figure 5.3) may be fired by any fuel (biomass or natural gas) and the flue gases coming out can be used for making steam or hot water. The heat rejected by the cooler and the WGS reactor (Figures 5.3 and 5.7) could act as a low temperature heat source and may be used to heat the incoming biomass feed. The regenerator may be fired by any fuel (natural gas or biomass). In this case the flue gases could act as a high temperature heat source (since the regenerator operates at high temperature) and could be used to produce superheated steam for the gasifier or reformer. The calcium oxide cooling reactor (CaO-cool, Figure 5.7) can also be used to heat some other fluid stream within the system. An actual biomass gasification system therefore will have many sources of waste heat that can be used internally.

In light of the heat integration possibilities identified above, the overall system efficiency will be different from the efficiency values obtained above. The objective of the present study was to introduce the concept of sorbent enhanced biomass gasification and hence a simple energy analysis was conducted. In order to get more realistic data an optimization of the complete system taking into account all the available waste heat sources and thermal integration needs to be conducted.

Conclusion

Sorbent Enhanced Gasification (SEG) is a novel technology for producing a hydrogen rich gas from carbonaceous fuels like biomass. The concept has been used for CO_2 removal from fossil fuel exhaust. We have applied this concept to enhance the hydrogen yield of conventional biomass gasification. The potential advantages of SEG are:

- higher hydrogen yields
- lower operating temperature as compared to conventional gasification
- lower heat requirements of the reformer/gasifier due to in-situ heat supply (hence a smaller gasifier will be required; this also means a reduction in capital cost)
- it is a novel technique for producing a hydrogen rich and CO_2 free gas; the product gas will need minimal cleaning and hence many downstream equipments such as Water Gas Shift reactor and PSA (Pressure Swing Adsorption) unit used conventionally may not be required in the sorbent case. Hence there is a possibility of significantly reducing the capital cost of hydrogen production from biomass
- a pure CO_2 stream is produced and CO_2 can be either used for suitable applications or sequestered for appropriate disposal

In the next chapter experimental studies conducted to validate the concept of sorbent enhanced biomass gasification are discussed.

Table 5-1 Reactions in SEG for some typical fuels

Fuel	Type of Reaction	Reactions	T(^{o}C)	ΔH (kJ/mol)
Methane CH_4 (x = 4, y = 0)	Reforming	$CH_4 + H_2O \rightarrow CO + 3H_2$	650	+224.6
	Shift	$CO + H_2O \rightarrow CO_2 + H_2$	650	-36.7
	Absorption	$CaO + CO_2 \rightarrow CaCO_3$	650	-171
	Overall	$CH_4 + 2H_2O + CaO \rightarrow CaCO_3 + 4H_2$	650	+16.9
	Regeneration	$CaO + CO_2 \rightarrow CaCO_3$	850	+168
Wood $CH_{1.5}O_{0.7}$ (x = 1.5, y = 0.7)	Reforming	$CH_{1.5}O_{0.7} + 0.3H_2O \rightarrow CO + 1.05H_2$	700	+98.1
	Shift	$CO + H_2O \rightarrow CO_2 + H_2$	700	-35.5
	Absorption	$CaO + CO_2 \rightarrow CaCO_3$	700	-169.5
	Overall	$CH_{1.5}O_{0.7} + 1.3H_2O + CaO \rightarrow CaCO_3 + 2.05H_2$	700	-106.9
	Regeneration	$CaO + CO_2 \rightarrow CaCO_3$	850	+168

Table 5-2: Comparison of energy consumption in biomass gasification with and without sorbent

	Case I (Base case)	Case II (SEG)
Output (kmol/hr)		
H_2	4.79	5.69
CO	0.097	0.089
CO_2	1.53	0.762
CH_4	0.001	0.053
H_2O	1.84	1.195
Heat Duty (kW)		
HEATER1	+108.6	+108.6
REFORMER	+65.9	+38
COOLER 1/ HT-RECOV	-33.9	-27.9
WGS	-15.8	-6.7
REGENERATOR	NA	+61.2
CO_2-COOL	NA	-12.4
CAO-COOL	NA	-34.9

Table 5-3: Thermodynamic efficiency and energies

	Case I (Base case)	Case II (SEG)
LHV of product gas (kJ/hr)	1176.3×10^3	1435.9×10^3
LHV of biomass (kJ/hr)	1242×10^3	1242×10^3
Total heat supplied (kJ/hr)	628.1×10^3	748.2×10^3
Efficiency as given by 5.11	62.9 %	72.1 %

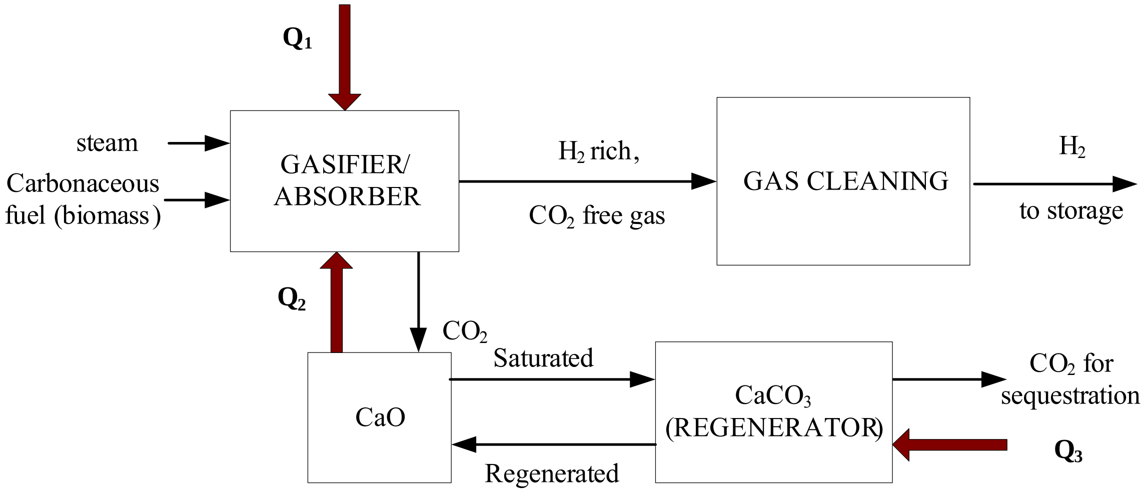

Figure 5.1: Concept of absorption enhanced gasification

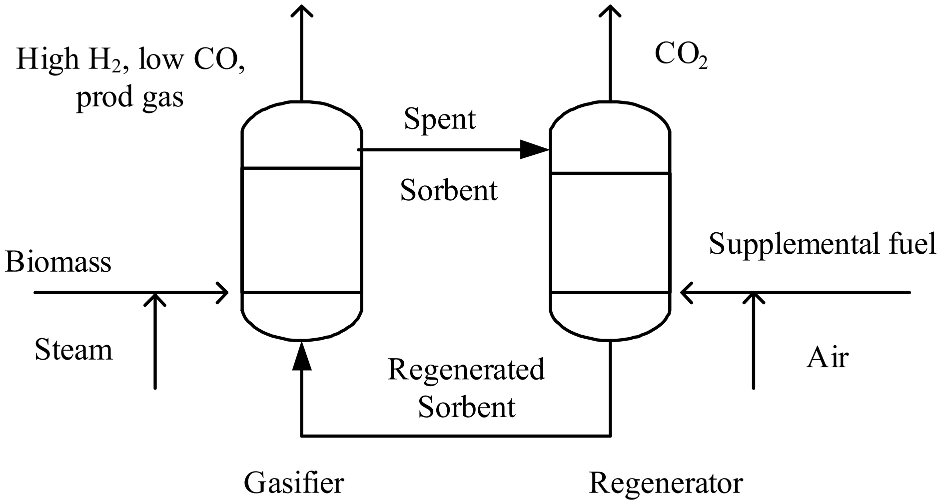

Figure 5.2: Schematic of SEG (concept)

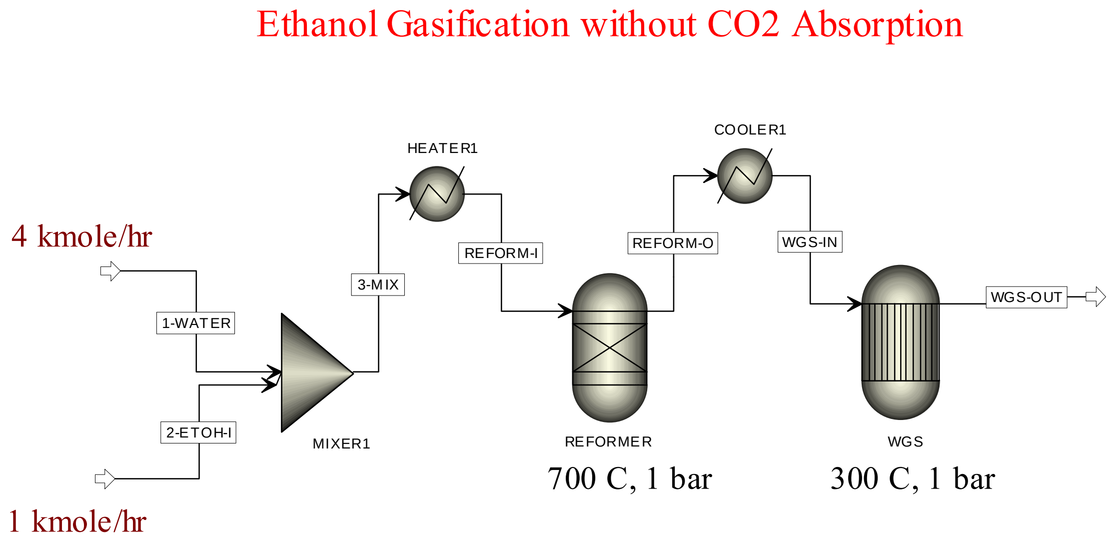

Figure 5.3: Flow sheet for conventional biomass gasification

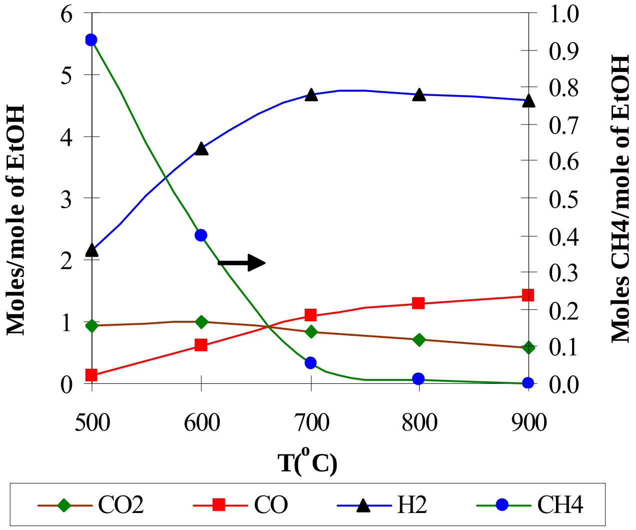

Figure 5.4: Effect of reformer temperature on product yield

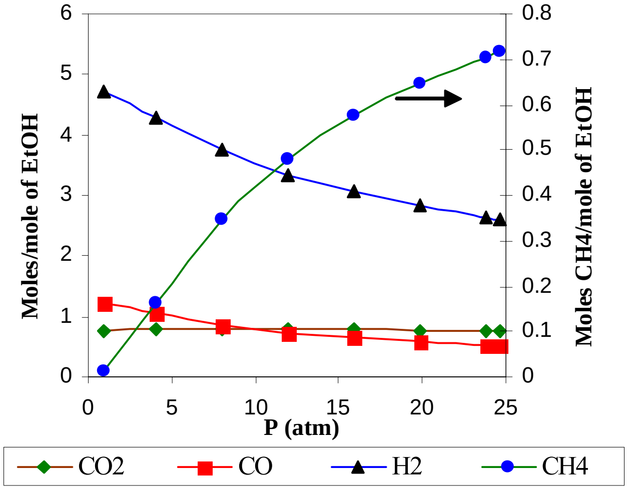

Figure 5.5: Effect of reformer pressure on product yield

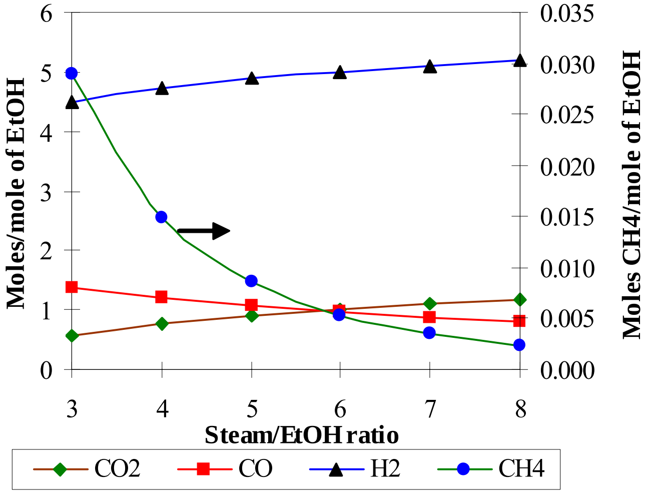

Figure 5.6: Effect of steam ethanol ratio on product yield at 700°C

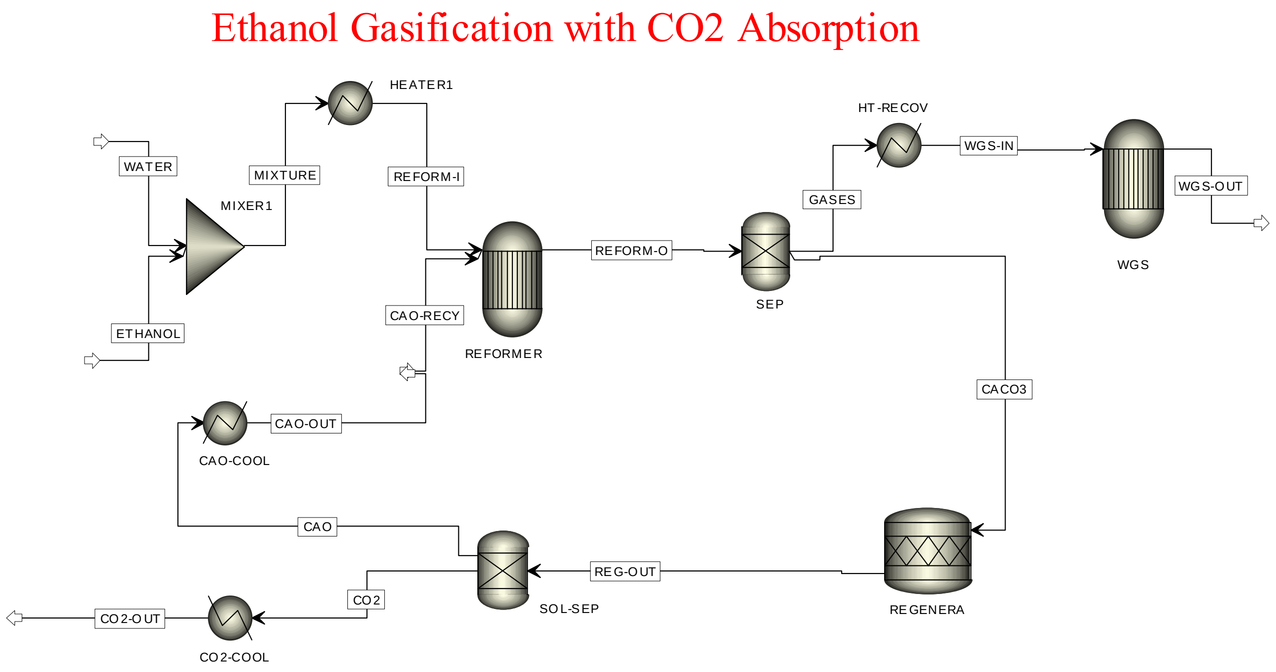

Figure 5.7: Flow sheet for ethanol gasification with CaO sorbent

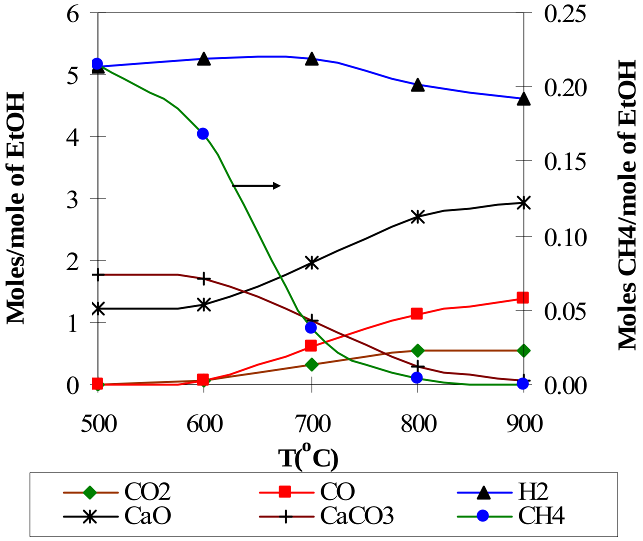

Figure 5.8: Effect of temperature on product yield for sorbent enhanced reforming

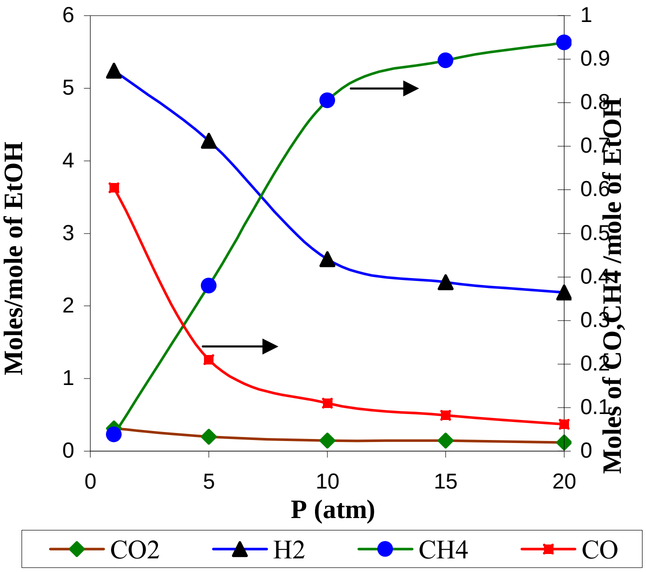

Figure 5.9: Effect of pressure on the product yield for sorbent enhanced reforming

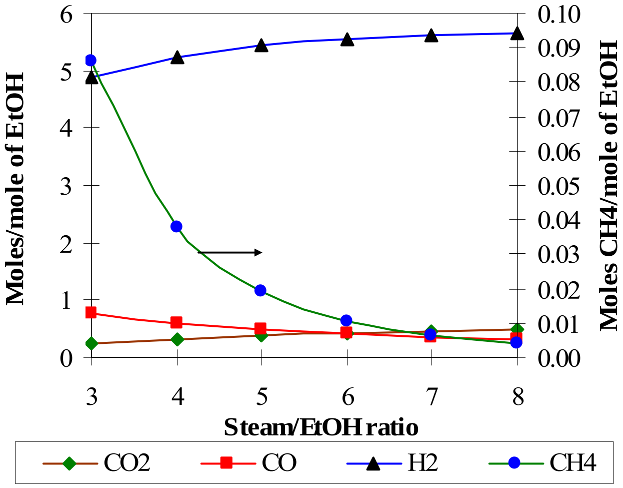

Figure 5.10: Effect of steam/ethanol ratio on product yield for sorbent enhanced reforming

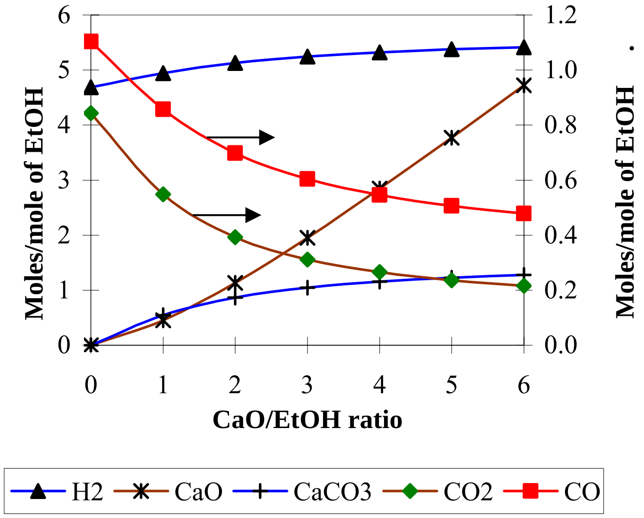

Figure 5.11: Effect of CaO/ethanol ratio on the product yield

CHAPTER 6
EXPERIMENTAL STUDIES ON BIOMASS GASIFICATION

Objective

The overall objective of experimental study was to understand the effect of adding calcium oxide sorbent on the hydrogen yield during the steam gasification of biomass. Specific objectives were to:

1) experimentally determine the total gas yield, hydrogen yield and yields of other important constituents (carbon monoxide, carbon dioxide and methane) by gasifying plain biomass (Southern pine bark) in the presence of steam
2) to determine possible increase in hydrogen yield and overall gas yield by adding calcium oxide sorbent during biomass gasification.
3) determine the carbon conversion efficiency (fraction of carbon in biomass that is converted into carbon containing gases) of biomass gasification with and without sorbents

The effects of the following variables were studied:

a) Temperature
b) Presence of sorbent

Output variables studied were:

a) Gas composition
b) Total gas yield (ml/g of biomass gasified)
c) Yields of hydrogen, carbon monoxide, carbon dioxide and methane (in ml/g biomass)
d) Carbon conversion efficiency

Experimental Facility

Test Set-up

Figure 6.1 shows a sketch of the test set-up for biomass gasification. It consists of the following components:

a) gasifier (primary reactor)

b) secondary reactor

c) steam generator

d) gas cooling system (heat exchanger)

e) heaters, insulation and tubing/fittings

f) instrumentation

g) gas analysis facility (GC)

Gasifier (Primary reactor)

This is a fixed-bed batch type reactor made of ¾” SS316 tubing. The gasifier can hold about 6 gm of biomass feedstock. Southern pine bark in the form of pellets (2 to 5 mm in size) is introduced from the top and is supported approximately at the center of the gasifier by quartz wool packing. A radiant ceramic heater placed concentrically around the gasifier heats the biomass bed. A K-type thermocouple is used to measure the temperature of the bed.

Secondary reactor

This reactor is identical in construction to the primary reactor except that it is used to hold the calcium oxide sorbent. Quartz wool packing is used as a support and a K-type thermocouple is used to measure the temperature of the sorbent bed. A radiant ceramic heater placed concentrically around the reactor tube heats this reactor.

Steam generator

This consists of a ¼” SS 316 tubing and is divided into two parts. The first part is a straight portion of the tube around which a rope heater is wound helically which acts as a boiler. The boiler generates superheated steam at about 150°C and 1 atm. Thereafter the steam enters another ¼” tube which is bent in the form of a helical coil. The helical coiled tube is placed concentrically inside a radiant ceramic heater. The helical coil acts as a superheater and generates superheated steam at a temperature of 500°C and 1 atm. To enhance the heat transfer coefficient on the steam side, a steel wire (0.02” thick) in the form of a spring was inserted inside the ¼” helical coil.

Gas cooling system (heat exchanger)

The steam and gas mixture coming out of the catalytic reactor is cooled by a concentric tube heat exchanger. Ethylene glycol solution flows through the outer tube while steam and gas mixture flows through the inner tube. The ethylene glycol solution is later cooled by a refrigerant circulating in a liquid bath (Polyscience make). The cooled gas is then passed through a vacuum trap, kept in an ice bath, to collect any moisture left uncondensed. The gas is then sent to a gas chromatograph (GC) for online analysis before collecting it in a sample bag.

Heaters, insulation and tubing/fittings

The ratings of the various heaters used in the set-up and their maximum achievable temperatures are as given in Table 6-1. Swagelok fittings (SS316) were used to connect the reactors, steam generator and the intermediate tubing. All the tubing material used was of SS310 or SS316. Silica alumina insulation (Thermal Ceramics Inc make) was wrapped around the intermediate tubing and fittings to minimize the heat losses.

Instrumentation

a) Temperature measurement: K-type thermocouples were used to measure the temperatures of

1) steam at boiler exit
2) steam at superheater exit
3) gasifier bed
4) secondary reactor bed
5) boiler tube surface
6) superheater tube surface

The four heaters were controlled by four TICs (Temperature Indicators and Controllers, Omega make, model CN9000A). The controllers were set within 1% range.

b) Pressure measurement: The pressure of the gas was measured by a Bourdon gauge after it came out of the gasifier but before it entered the secondary reactor. The measurement was done to ensure that there is no pressure build up while gas is flowing over the packed sorbent bed.

c) Flow measurement: The gas flow rate was measured using a Soap Bubble Film Flowmeter.

Gas Analysis Facility

The biomass-generated gas coming out of the test set-up was analyzed on-line by passing it through the sampling loop of a Gas Chromatograph The GC (SRI make) has two columns (Molecular Sieve and Hayesep-D) and is equipped with a Thermal Conductivity Detector. The Molecular Sieve column separates hydrogen, Ar, O_2, N_2, CH_4 and CO whereas the Hayesep D column separates CO_2 and higher hydrocarbons (C_1-C_6). Helium was used as the carrier gas for all the components. A desktop computer installed with PeakSimple software (version 3.29) was used as a chromatography analysis station and storage device.

GC Calibration

The GC was calibrated for four important gases, which are found in the highest proportion (H_2, CO, CO_2 and CH_4). Argon gas was used as the internal standard. Gas standards of each of the four calibration gases were purchased in the form of lecture bottles. Different concentrations of the calibration gas and the internal standard were accurately injected into the GC using mass flow controllers.

Following was the calibration procedure:

1) The calibration standard (eg H_2) and Argon were passed through two different mass flow controllers kept in parallel such that a total of 100 ml/min was supplied to the GC (Figure 6.4)
2) Different concentrations (from 0% to 100 % H_2 in steps of 20% with the balance being Ar) of gases were passed through the sampling loop and chromatograms were obtained for each case. The concentrations covered the expected range of the gas.
3) The area counts of the calibration standard and Argon were noted and graphs of area count versus concentration were plotted. The graphs were then curve fitted; figures 6.5 to 6.8 show the calibration curves for the four gases.

Test Methodology

In all the experiments 'Southern pine bark' was used as the model biomass compound. The biomass is popularly used as mulch and is spread around trees to prevent erosion and to enrich the soil. It was bought from a local store. Typically five grams of pine bark in the form of pellets (2-5 mm in size) were used for each test run. The pellets were made by breaking the "as received" pine bark and grinding it. Figure 6.9 shows the biomass "as received" and figure 6.10 shows the pelletized form. The feedstock composition was determined by proximate and ultimate analyses and is given in Table 6-2.

The biomass and sorbent were accurately weighed in an electronic balance (Denver instruments make, least count: 0.0001 g) and then fed into the gasifier and secondary reactor respectively with quartz wool packing that acted as a support. Silver goop (a high temperature heat resistant paste) was used on all fittings and tubes in order to prevent the seizure at high temperature. Water was supplied to the gasifier by means of a peristaltic pump (Cole Parmer). A fixed water flow rate was maintained for each experiment. This was based on practical considerations and these included: maintaining a uniform flow of steam around the biomass bed and maintaining reasonable steam temperature. High flow rate would blow the biomass bed and low flow rate could not generate sufficiently high temperature as the flow was laminar. Based on these considerations a water flow rate of 5 g/min was maintained for each experiment. The operation sequence while starting the test was as follows:

1) the GC carrier gas (Helium) cylinder was opened and the GC was switched ON
2) the condenser was turned ON and the coolant temperature was set at 15^{o}C
3) the rope heater, superheater and heater for catalytic reactor were then turned ON
4) after the three heaters had reached the set-point, the pump was turned ON
5) finally the gasifier heater was turned ON

The stopping sequence was as follows:

1) all heaters were first turned OFF
2) pump was turned OFF
3) condenser was turned OFF after all the steam had condensed
4) the GC was turned OFF and the Helium gas cylinder was closed

Test Results and Analysis

Effect of Temperature

The pine bark was steam gasified at different temperatures from 500 to 700°C. No sorbent was used in this case. The baseline data of total gas yield and yields of hydrogen, CO, CO_2 and methane were obtained. Table 6-3 and Figure 6.11 show the effect of temperature on the products of biomass gasification. It was found that the total gas yield increased monotonically with the temperature (Table 6-3). This was expected, as higher temperatures favor conversion of higher hydrocarbons and tars into gas. The hydrogen yield was also found to increase steadily with the increase in temperature.

The total gas yield of 1111 ml/g of biomass at 700°C compared well with the results of other groups. Turn et al obtained a total gas yield of about 1000 ml/g while gasifying sawdust in presence of steam and air at 750°C [44]. Herguido et al obtained a gas yield of approximately 1050 ml/g while steam gasifying straw at 700°C [72]. Walawender et al steam gasified cellulose at various temperatures in the range 600 to 800°C and they found a total gas yield of about 1250 ml/g at 680°C [106].

The carbon conversion efficiency is defined as the ratio of moles of carbon in the product gas per mole of carbon in the biomass.

$$X = \left(\frac{M_{pro}}{M_{wood}} \right) \text{ x } 100$$

Where,

M_{pro}: total moles of carbon in the product gas (CO, CO_2, CH_4)

M_{wood}: moles of carbon in the biomass

Carbon conversion efficiency, in a way represents the effectiveness of the gasification process in converting the solid biomass into gas. It was found that the carbon conversion efficiency increased from a mere 23% at 500°C to approximately 40% at 700°C. Walawender et al had obtained a carbon conversion efficiency of 32% at 600°C [106]. The carbon conversion efficiency increases with temperature as the tars and higher hydrocarbons get converted into gas. The hydrogen in the product gas also increases with temperature. This trend was also observed by other research groups [97, 107, 108]. Hoveland et al conducted experiments by gasifying cellulose in the presence of steam and found that the hydrogen yield continuously increased from 250 ml/g at 600°C to 600 ml/g at 750°C [108]. The CO_2 yield was also found to be high and this was attributed to the presence of steam, which oxidizes all the hydrocarbons and tars.

For hydrocarbons such as methane:

$$CH_4 + 2H_2O \longrightarrow CO_2 + 4H_2 \tag{6.1}$$

Higher hydrocarbons also get oxidized in presence of steam:

$$C_nH_m + 2nH_2O \longrightarrow nCO_2 + (2n + m/2)H_2 \tag{6.2}$$

In addition to the above reactions, steam also converts char into additional hydrogen and carbon dioxide as per the water gas reaction:

$$C + 2H_2O \longrightarrow CO_2 + 2H_2 \tag{6.3}$$

Also there is the water-gas shift reaction, which converts the CO into CO_2 and produces H_2 in the presence of steam

$$CO + H_2O \longrightarrow CO_2 + H_2 \tag{6.4}$$

Equilibrium calculations were done to understand how closely actual results meet thermodynamic results. The equilibrium yields of important gases were determined. The actual yields were different from the equilibrium yields; however the difference between the two reduced with increasing temperature (as we had observed in Chapter 4). The theoretical equilibrium hydrogen (and CO_2) yield is high because all the hydrocarbons and tars are broken down and converted into these gases (as per reactions 6.1 to 6.4) as there is no limitation on time for reactions to occur. In actual gasification however, the reactions do not reach completion and hence the actual H_2 and CO_2 yields are lower than predicted by equilibrium.

The methane and carbon monoxide molecules get converted into H_2 and CO_2 in the presence of steam and hence their equilibrium yields are lower than actual. Higher temperatures favor hydrocarbon (methane) conversion into additional H_2 and CO_2 and hence at 700^{o}C the equilibrium methane is reduced to zero.

Effect of Sorbent

Experiments were carried out by gasifying the biomass in the presence of calcium oxide sorbent. Table 6-6 summarizes the effect of sorbent addition on gas yields at different temperatures. The biomass was placed in the gasifier reactor and calcium oxide was placed in the secondary reactor. Calcium oxide sorbent was in the form of powder (particle size 0.045 mm). The sorbent in the powder form offers substantial surface area for the reactions to occur and it is hypothesized that the gas yield will be high.

Figures 6.12 to 6.14 show the individual gas yields at different gasification temperatures. In all the experiments the CaO sorbent to biomass molar ratio was maintained at 1. The temperature was varied in the same range as the base case (500-700^{o}C). In general, it was observed that the total gas yield was higher than the base case. The carbon conversion efficiency (Table 6-7) was also found to be higher than the base case. The high gas yield is attributed to the cracking of tars and complex hydrocarbons in the presence of calcium oxide sorbent which provided active surface area for steam reforming reactions to occur. The breakdown of hydrocarbon molecules releases the hydrogen atoms, which would otherwise be locked with the carbon atoms. This was verified by the quality of tar-laden water that was obtained from two tests conducted at 600°C. From the figure 6.15 it was observed that the tar-laden sample of plain biomass gasification (dark colored) had far more particulates and suspended matter as compared to the sorbent enhanced gasification. The tar laden water for the sorbent enhanced case was found to be relatively clear and free of particulate matter.

The sorbent was found to be very effective at temperatures in the range 500-600°C. At 500°C the hydrogen yield was found to increase substantially from 320 ml/g for the base case to 719 ml/g for the sorbent enhanced case. At higher temperature, (700°C) the total gas and hydrogen yields were found to approach the base case. This might be due to the fact that the carbonation reaction (CO_2 absorption) reaction becomes less dominant at temperatures above 700°C.

The CO_2 in the product gas is absorbed by the calcium oxide sorbent. The calcium oxide sorbent gets converted into calcium carbonate. The degree of conversion depends on the thermodynamic conditions such as pressure, temperature and partial pressure of CO_2 in the gas mixture and on chemical kinetic parameters such as surface area and pore volume of sorbent.

Conclusion

1) Biomass steam gasification in the presence of calcium oxide gives substantially higher gas yield as compared to plain biomass gasification. In the experiments conducted it was observed that the total gas yield at 500°C increased from 550 ml/g to 1360 ml/g.
2) The hydrogen yield at 500°C also increased substantially while using sorbent from 320 ml/g (base case) to 719 ml/g (sorbent case). This is attributed to the catalytic action of calcium oxide sorbent in whose presence the tars and complex hydrocarbons, which normally remain uncracked got reformed by reacting with steam to yield more hydrogen.

3) The carbon conversion efficiency (fraction of carbon in biomass converted into carbon containing gases – a measure of effectiveness of gasification) also improved considerably while using sorbent (from a mere 23% to more than 63% at 500°C).

4) The high gas and hydrogen yield trend is observed until the gasification temperature of 700°C after which the sorbent case gave almost similar yield as the base case. This is attributed to the carbonation reaction (CO_2 absorption) which becomes less dominant at temperatures above 700°C.

5) The hydrogen yield at 500°C using sorbent (719 ml/g) is comparable to the hydrogen yield at 700°C for plain biomass gasification (712 ml/g). Hence there is a potential to reduce the gasifier operating temperature by 150-200°C. This was proved on a lab scale gasifier. In practice even if it is possible to operate the commercial gasifier at 100°C lower than conventional and get the same amount of hydrogen it will result in substantial savings in the heat input to the gasifier.

6) The product gas, while using sorbent, is rich in hydrogen, free of CO_2 and is relatively clean of any particulates and tars. If we can set the operating conditions such that we get an almost pure hydrogen gas stream with very little contaminants, it may be possible to eliminate all or most of the gas cleaning equipment used downstream of the gasifier in conventional biomass gasification systems such as High Temperature Water Gas Shift (HT-WGS), Low Temperature Water Gas Shift (LT-WGS) and Pressure Swing Adsorption (PSA) unit. With no WGS reactors there is no need of any catalyst and hence there will be savings in running cost. In place of these three reactors there will be a single reactor used for regenerating the used sorbent. Hence, there is a potential to reduce the capital cost of biomass gasification plants for hydrogen production.

Table 6-1 Heater ratings

Heater type	Rating	Rated temperature
Gasifier heater	1400 W, 220V	982°C
Catalytic reactor heater	870 W, 110V	982°C
Heater for Superheater	1700 W, 110V	982°C
Boiler	500 W, 110V	482°C

Table 6-2: Ultimate and proximate analyses

Ultimate analysis		Proximate analysis	
C	51.13 %	Fixed Carbon	26.94 %
H	6.10 %	Volatiles	63.21 %
N	0.14 %	Moisture	9.22 %
S	0.04 %	Ash	0.63 %
O	41.96 %		

Table 6-3: Effect of temperature on the products of biomass gasification

T	500°C	600°C	700°C
Biomass (g)	5.0010	5.0300	5.0400
Steam flow (g/min)	5.0000	5.0000	5.0000
Volume of gas (ml)	2750	4400	5600
Total gas Yield (ml/g biomass)	549.9	874.8	1111.1
H_2 (ml/g)	320.3	573.0	712.2
CH_4 (ml/g)	34.1	28.0	15.6
CO (ml/g)	66.4	79.1	90
CO_2 (ml/g)	108.8	181.5	288.9

Table 6-4: Carbon conversion efficiency (no sorbent)

T	500^{o}C	600^{o}C	700^{o}C
C conversion	22.9 %	30.3 %	40.3 %

Table 6-5: Equilibrium yields of biomass gasification products

T	500^{o}C	600^{o}C	700^{o}C
H_2 (ml/g)	1250	1325	1400
CH_4 (ml/g)	0.01	0.003	0
CO (ml/g)	11.9	17.4	27.9
CO_2 (ml/g)	910	1025	1200

Table 6-6: Effect of temperature on gas composition in the presence of sorbent

T	500°C	600°C	700°C
Biomass(g)	5.000	5.0067	5.0176
Steam flow (g/min)	5.0000	5.0000	5.0000
Sorbent (g)	11.200	11.210	11.207
Volume of gas (ml)	6800	7100	6200
Total gas Yield (ml/g biomass)	1360.0	1418.1	1235.7
H_2 (ml/g)	719.4	852.3	773.5
CH_4 (ml/g)	66.6	38.3	43.2
CO (ml/g)	106.1	78	53.1
CO_2 (ml/g)	432.5	384.3	316.3

Table 6-7: Carbon conversion efficiency (sorbent enhanced gasification)

T	500°C	600°C	700°C
C conversion	63.5%	56%	49%

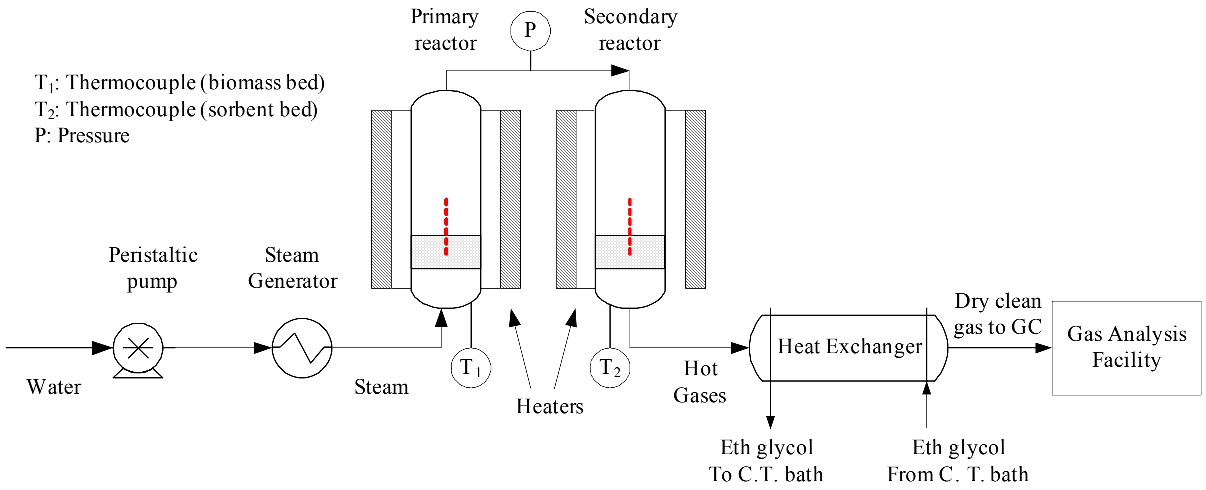

Figure 6.1: Biomass gasification test set-up

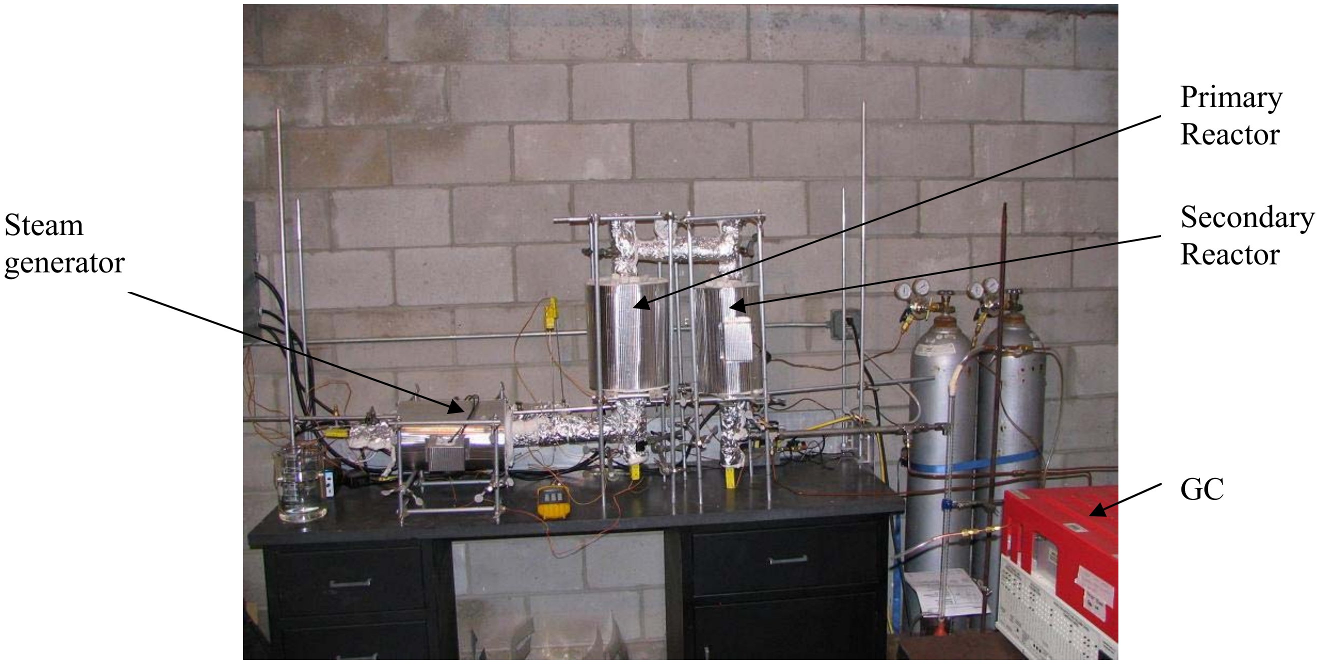

Figure 6.2: Photograph of the test set-up


Figure 6.3: Gas chromatograph (SRI 8610C)

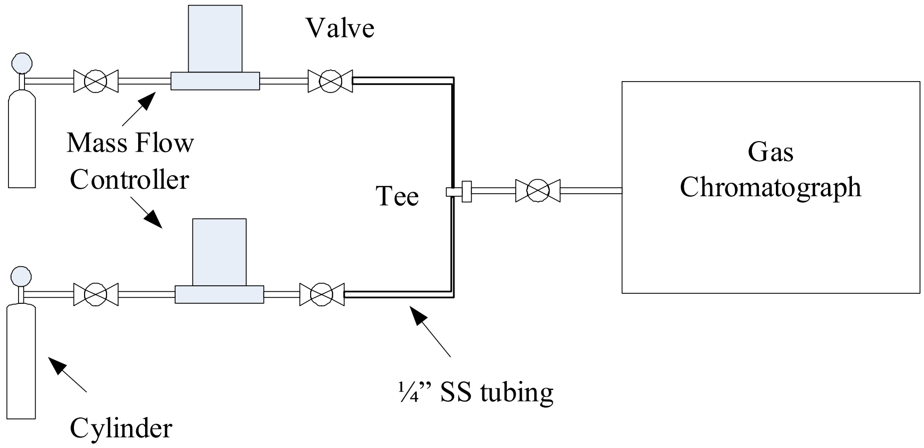

Figure 6.4: Set-up for GC calibration

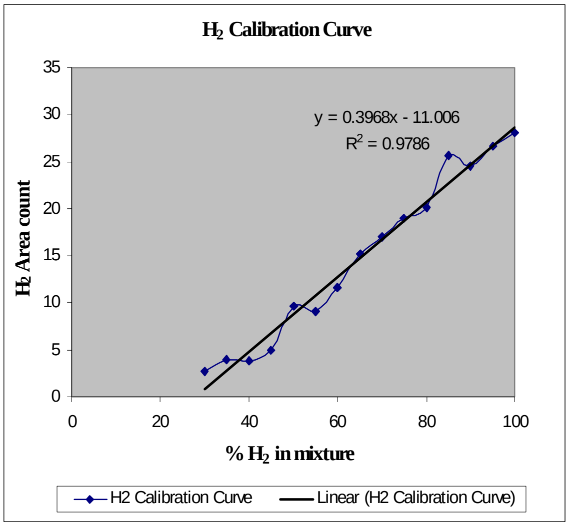

Figure 6.5: Hydrogen calibration curve

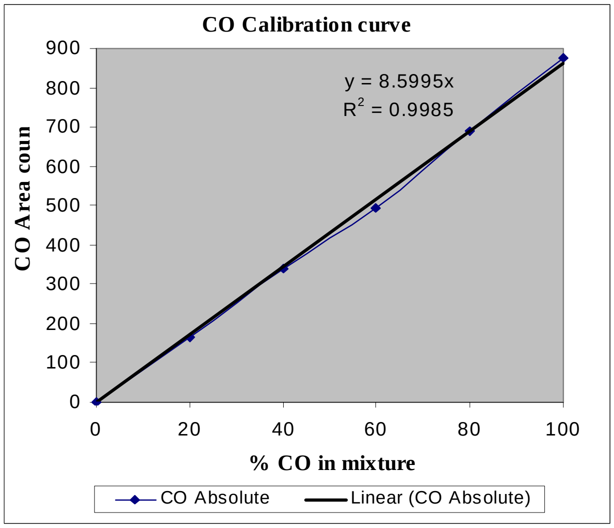

Figure 6.6: CO calibration curve

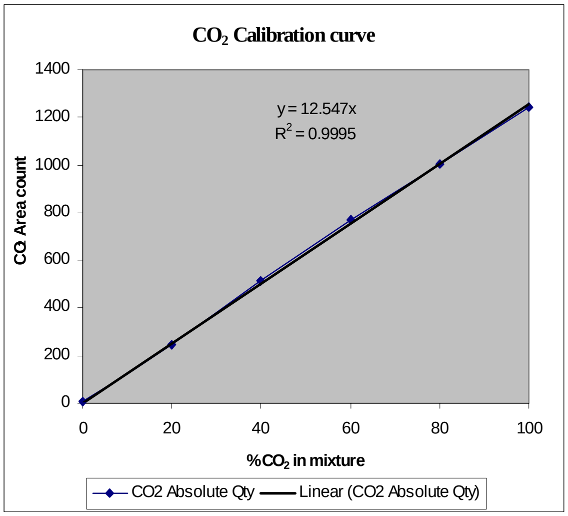

Figure 6.7: CO_2 calibration curve

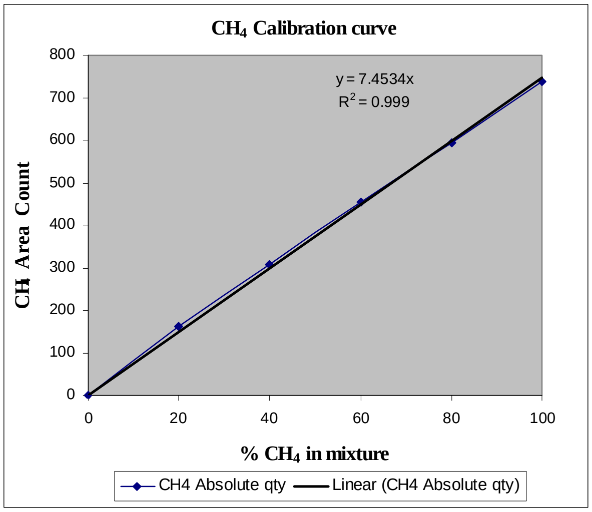

Figure 6.8: CH_4 calibration curve

Figure 6.9: Southern pine bark “as received”

Figure 6.10: Pelletized pine bark

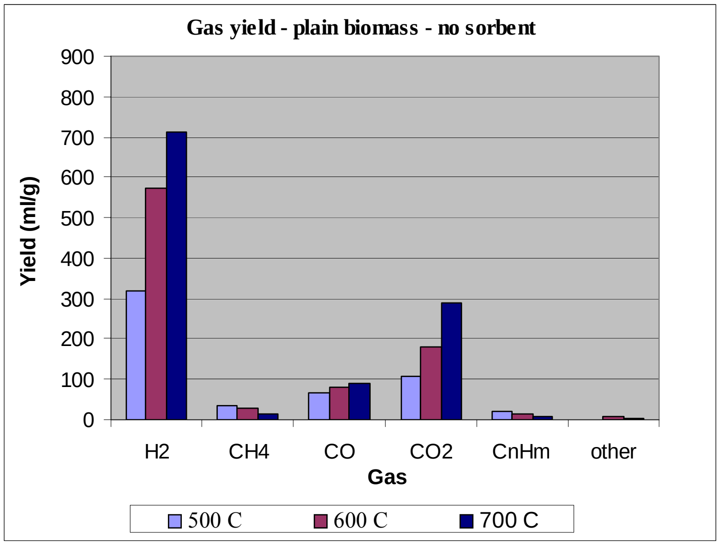

Figure 6.11: Effect of temperature on gas yields (no sorbent)

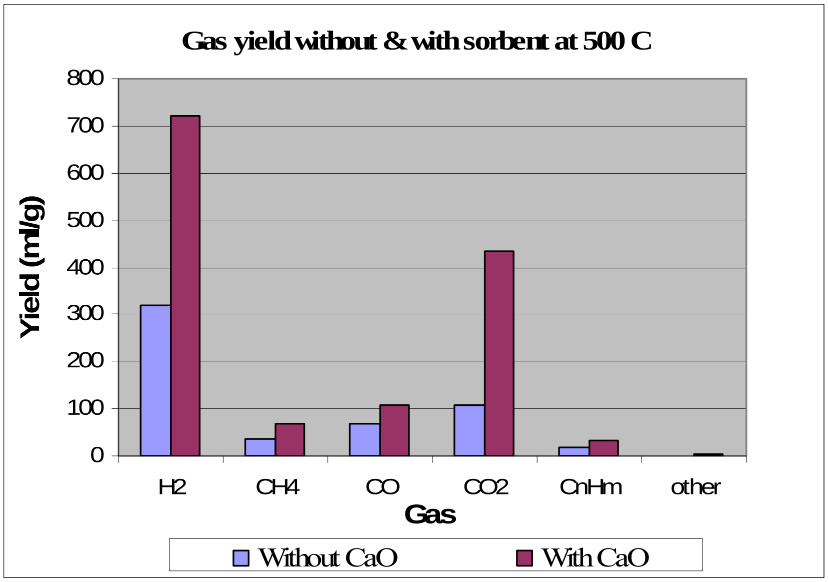

Figure 6.12: Effect of sorbent addition at 500^{o}C

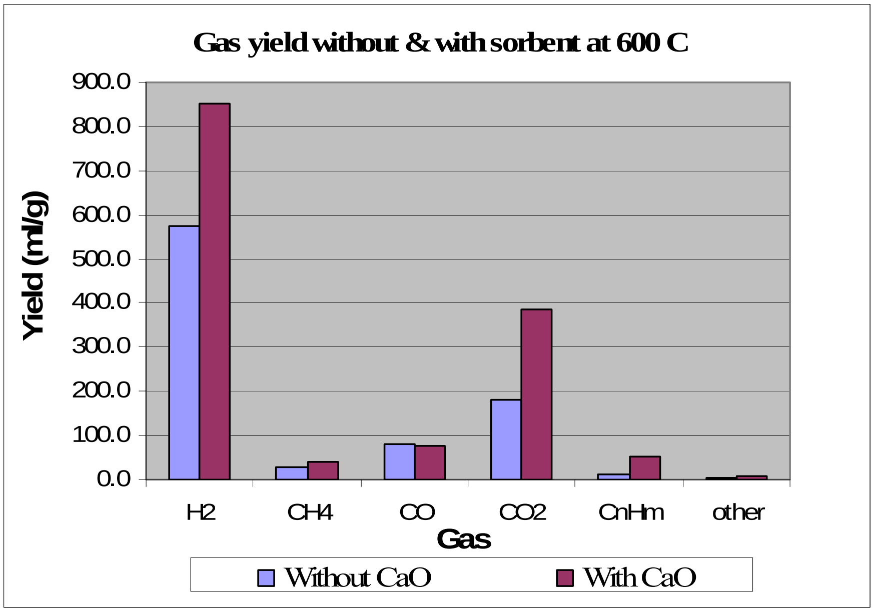

Figure 6.13: Effect of sorbent addition at 600°C

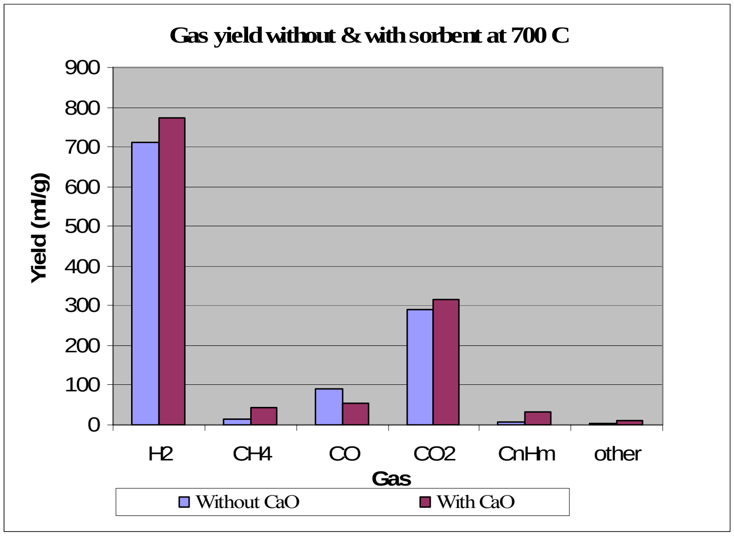

Figure 6.14: Effect of sorbent addition at 700°C

Figure 6.15: Tar laden condensate samples of plain biomass gasification (left) and sorbent enhanced gasification

CHAPTER 7
REGENERATION OF SPENT SORBENT

Introduction

In the previous chapter the concept of sorbent enhanced biomass gasification was proved experimentally. We saw that the calcium oxide absorbs CO_2 in the product gas and thereby shifts the reactions in favor of hydrogen. After some time the calcium oxide gets saturated and is converted to calcium carbonate. For successful application of the technology the carbonate must be fully converted back to its original oxide form and must be reusable over many cycles. The process of converting the used sorbent (calcium carbonate) back to its oxide form is called regeneration. In recent past, regeneration has been studied for CO_2 (and in some cases for SO_2 removal) in the gasification and combustion of carbonaceous fuels [86, 88, 89, 109]. In order for the sorbent enhanced biomass gasification for hydrogen production to be technically feasible and commercially viable, the sorbent must be easily regenerated and must be usable over several alternate calcination carbonation cycles [110, 111].

The Reversible Calcination Carbonation Process

The process of converting calcium carbonate to calcium oxide is well-known in the cement manufacturing industry as calcination. The calcination reaction is endothermic and typically occurs at 850^{o}C.

$$CaCO_3 \rightarrow CaO + CO_2 \qquad \Delta H = +178 \text{ kJ/mol} \qquad (7.1)$$

The reverse reaction is called carbonation and is favored at lower temperatures (typically 600 – 700^{o}C)

$$CaO + CO_2 \rightarrow CaCO_3 \qquad \Delta H = -178 \text{ kJ/mol} \qquad (7.2)$$

Figure 7.1 shows the characteristics of the reversible calcination-carbonation reaction. From figure 7.1 it is observed that the calcination reaction is favored at high temperatures and low pressures (below and to the right of the equilibrium curve) whereas carbonation reaction is favored at low temperatures and high pressures (region above and to the left of the equilibrium curve). This shows that calcination can be accomplished at a lower temperature by reducing the CO_2 partial pressure. This can be achieved either by creating vacuum or adding another gas stream (such as steam or nitrogen) into the reaction vessel.

The calcination reaction has served as the basis of production of lime from limestone. Lime and cement manufacturing are energy intensive processes that occur at temperatures in the range 1200-1300 K [112]. The carbonation reaction although has no commercial implication, has still been studied by a number of researchers interested in the kinetics of gas solid reactions. Dedmen and Owen [113] studied the reaction of CO_2 with calcined limestone over the temperature range of 100 to 600^oC. They reported that the reaction occurred in two stages: a rapid initial stage where most of the CO_2 was absorbed. This was followed by a much slower diffusion-controlled stage where CO_2 molecules diffused through the carbonate layer. Similar behavior was observed in the independent works carried out by Barker [114] and Bhatia and Perlmutter [115].

The heat required for the endothermic calcination reaction can be supplied in different ways. The most economical way would be to combust a conventional fuel such as natural gas or coal and the energy released by the exothermic process can be supplied to the endothermic calcination reaction. Alternately part of the biomass feedstock can also be combusted. If there is a waste heat stream available (such gas turbines or a solid oxide fuel cell exhaust) it can also be used. Another alternative would be to use concentrated solar energy. Figure 7.2 shows a schematic of a biomass gasification system with calcination of used sorbent. The set-up consists of two main reactors: gasifier reactor and calciner. Biomass is steam gasified in the gasifier reactor which has a fixed bed (or for large units a fluidized bed) of calcium oxide sorbent. The CO_2 absorption process releases heat which can be used in-situ for the endothermic steam gasification of biomass. A hydrogen rich, CO_2 free product gas with very little tars is produced. This hydrogen rich gas is cleaned of any particulate matter or residual tars and later sent to a gas turbine or fuel cell. The sorbent after some time gets saturated. It is regenerated by heating in the calciner. The CO_2 released can be collected for safe storage and disposal. Some ways of supplying heat to the calciner and their implications are discussed below:

Combusting a Carbonaceous Fuel

The calciner or regenerator can be supplied heat energy by combusting any carbonaceous fuel. A stoichiometric mixture of fuel and oxygen can be directly supplied to the calciner and the CO_2 so produced can be collected along with the CO_2 that is being desorbed by the carbonate. The CO_2 produced from the two sources can be sequestered, compressed and stored for appropriate disposal. Alternately, natural gas can be supplied to the calciner along with air. The gas mixture coming out of the calciner will consists of CO_2 and N_2 (By using air in place of oxygen also has the advantage that CO_2 partial pressure will be less, due to presence of inert nitrogen and that way the calcination can be carried out at a lower temperature).

The gas mixture can then be supplied with additional natural gas (or methane) and water (or steam) to produce ammonium bicarbonate which is popularly used as a fertilizer. The following reaction shows how CO_2 can be converted into a useful byproduct:

$$3CH_4 + 4N_2 + 14H_2O + 5CO_2 \rightarrow 8NH_4HCO_3 \qquad \Delta H = 5.44 \text{ kJ/mol} \qquad (7.3)$$

Ammonium bicarbonate is solid at room temperature and is popularly used as a fertilizer in the agro and farming industries. Here five molecules of CO_2 are consumed and are converted into solid form. Lee et al [116] conducted a technical and economic study at Oak Ridge National Laboratory to integrate CO_2 sequestration from fossil fuel plants with co-production of ammonium bicarbonate. As per their study they found the fertilizer co-production to be important from economic point of view. The authors did some preliminary calculations and concluded that the methane supplied for CO_2 removal justifies the economic benefits obtained by producing fertilizers like ammonium bicarbonate. The authors have suggested further detailed investigation into the technical and economic aspects of this concept. Alternately, instead of using methane, part of the hydrogen produced in the process can also be used with the CO_2 and N_2 to produce ammonium bicarbonate as per the following reaction:

$$2CO_2 + N_2 + 3H_2 + 2H_2O \rightarrow 2NH_4HCO_3 \qquad \Delta H = -86.18 \text{ kJ/mol} \tag{7.4}$$

Fiaschi et al [117] have developed a novel system for the capture of CO_2 produced from fossil sources and convert them later into useful fertilizers. Heat can also be supplied by combusting part of the solid biomass feedstock with very little or no penalty on the carbon-dioxide emissions.

Using Concentrated Solar Energy

Solar energy can also be used to drive the endothermic calcination reaction. The advantages of using solar energy are three fold

- no discharge of pollutants
- gaseous product stream is not contaminated (with combustion products)
- a one time investment with no running cost

Zedtwitz et al [118] have proposed the use of solar energy for the thermal gasification of coal. The authors envisaged a solar concentrating plant (consisting of a solar tower or solar tower reflector system) to direct the sunlight onto a reactor located on the ground. The concentrating system was capable of achieving heat flux intensities of about 5000 kW/m^2. Such radiation fluxes can attain temperatures up to 1500 K which is more than the typical calcination temperature of 1100-1200 K. Haueter et al [31] have developed a solar chemical reactor for the thermal decomposition of zinc oxide which will be used for thermochemical hydrogen production by water splitting. The prototype reactor was of 10 kW capacity and could generate solar radiation heat flux of 3500 kW/m^2 and temperatures up to 2000 K. For successful application of the solar technology it has to be economically viable. Similar reactors can be built for calcination of used sorbents in biomass plants. The economics of using solar reactor technology has to be carefully studied. Some government subsidies and incentives like tax credits for totally CO_2 free hydrogen production can make the concept of using solar energy for regeneration with hydrogen production from biomass economically feasible. An important feature of using concentrated solar energy for sorbent regeneration is that the process becomes fully renewable. On the other hand, if CO_2 is sequestered it will be a process with negative carbon potential i.e. carbon dioxide although was absorbed during photosynthesis, it was not released into the environment.

Waste Heat from Gas Turbine Exhaust or from SOFC

Gas turbine exhaust stream can also be used for supplying heat to the endothermic calcination process. The gas turbine can be fired from the hydrogen rich product gas. The exhaust stream coming out of the gas turbine can first be used for heating the calciner at 850-900^{o}C and thereafter can also be used for producing steam to run a steam turbine at 500-600^{o}C. Alternately, the product gas from the biomass gasification system can be used directly to run a solid oxide fuel cell. The exhaust of the SOFC can then be used to heat the calciner at 850-900^{o}C and thereafter once again be used for generating steam in a Heat Recovery Steam Generator (HRSG) to run a steam turbine at 500-600°C.

Kinetics of the Reversible Calcination Carbonation Reactions

The reversible non-catalytic gas solid reaction between CaO(s) and CO_2(g) has been studied by many researchers. Silaban and Harrison [109] conducted multi-cycle tests by calcining $CaCO_3$ at 750 – 900°C at pressures of 1-15 atm in the presence of N_2. The reverse carbonation reaction was carried out in the same pressure range but at a slightly lower temperature (550-750°C). The researchers characterized the samples by determining the surface area and pore volume. They observed that the surface area and pore volume of the "as-received" and carbonated samples ($CaCO_3$) were quite small as compared to those of calcium oxide. At the end of first carbonation it was found that almost 30% of the calcium oxide sorbent had not reacted. The surface characterization suggested that pore closure might have prevented CO_2 gas molecules from reaching the unreacted calcium oxide core. In the second calcination the surface area reduced even further. The authors hypothesized that sintering might have taken place at high temperature. At the end of the second carbonation the authors found that more than 40% of the original calcium oxide sorbent remained unreacted due to sintering and pore closure. The authors observed that carbonation of plain CaO occurs in two steps: rapid initial step where most of the calcium oxide is converted to calcium carbonate. This is followed by a much slower diffusion controlled step where CO_2 molecules diffuse through the carbonate layer. The authors concluded that pore plugging leads to incomplete carbonation and sintering inhibits effective regeneration.

To overcome the problem of pore closure, Gupta and Fan [119] studied the pore size distribution of calcium carbonate precursors from four different sources. The authors hypothesized that incomplete conversion of calcium oxide to carbonate can be attributed to the micro pores which are susceptible to pore blockage and plugging. They suggested synthesizing a new calcium oxide sorbent from a carbonate precursor which has large sized pores which they called meso pores. Accordingly they synthesized sorbents from pre-cursors in the mesoporous range. Multi cycle tests conducted on mesoporous sorbents showed remarkable improvement (conversion of CaO to $CaCO_3$ increased by about 35% above conventional). This was attributed to the high porosity and pore volume which was big enough for the $CaCO_3$ product layer not to plug the pores. Kuramoto et al [120] also conducted multi cycle tests and found sintering to occur during the high temperature calcination process. Sintering causes reduction in the surface area and ultimately leads to incomplete regeneration. To counter this problem, the authors hydrated (added water) the samples before carbonating them. The researchers hypothesized that the water or steam molecules would fill the pore volume and thereby reduce sintering; tests were carried out at atmospheric and high pressures. It was observed that the hydrated sorbent samples had higher conversion (>85%) as compared to the regular sorbent. However, these are only preliminary results, further detailed investigation is necessary.

Sorbents other than Calcium oxide

Many research groups that used pure calcium oxide sorbent observed sintering and pore closure to occur during the reversible calcination carbonation reactions. When these groups conducted multi cycle tests they also found the conversion to decrease and hypothesized that sintering and pore closure ultimately lead to incomplete regeneration. One way of addressing this problem is to use a stabilizing material which does not take part in the carbonation process. Compounds such as MgO are inert at high temperature and do not participate in the CO_2 absorption/desorption process. They can serve as excellent stabilizing materials. Hence the sorbent can maintain its porosity over several cycles. Bandi et al [121] tested dolomite (50%Mgo, 50%CaO) and huntite (75% MgO, 25% CaO) in a Thermal Gravimetric Analyzer

(TGA). The carbonation was carried out at 830°C and calcination was carried out at 500°C. The researchers measured the absorption capacity over several cycles and found that dolomite suffered loss in absorption capacity of about 30% after 15 cycles. The performance of dolomite was found to be much better than pure calcite. They attributed this to the structural stabilizing effect of MgO which prevented the pores from closing. Huntite too was found to maintain high levels of CO_2 absorption capacity (>85%) even after 45 cycles. Kato et al [122] tested many silicates and among them found Lithium orthosilicate (Li_2SiO_4) to maintain high level of CO_2 absorption capacity

$$Li_2SiO_4 + CO_2 \rightarrow Li_2CO_3 + SiO_2 \qquad (7.5)$$

This sorbent was originally developed at Toshiba (Japan) in 2001 and the research group is presently investigating the long term stability of the sorbent. The researchers believe Li_2SiO_4 to be a promising material for CO_2 absorption.

In recent times, sodium based sorbents have been tested in the laboratory for CO_2 absorption from fossil fuel plants. The advantage of sodium based sorbents is the low operating temperature (CO_2 capture can take place at temperatures as low as 60-70°C and regeneration takes place at 120-200°C). Liang et al [123] conducted multi-cycle tests using sodium carbonate sorbent. The group found that as much as 90% of the CO_2 could be captured at appropriate reaction conditions. Based on the sorbent durability and energy consumption during regeneration, the researchers found the concept of sodium based sorbent for CO_2 removal to be better than the amine-scrubbing process for CO_2 removal which is presently followed.

The choice of appropriate sorbent depends on many factors such as calcination and carbonation temperatures, energy consumed, sorbent durability over multiple cycles, sorbent availability and the capital and maintenance costs. The choice of the correct sorbent will affect the economic viability of the process.

Summary

The calcination reaction has been studied in the past for the production of lime from limestone. More recently, the reversible calcination-carbonation reaction has received renewed interest from the scientific community due to the possibility of CO_2 removal from fossil fuel exhaust. Although many research groups have been actively working for the past several years, till date no single sorbent has been found that can be effectively regenerated and re-used over many cycles. The main concerns that need to be addressed are sintering and pore closure. Sintering occurs at high temperatures and reduces the surface area of sorbent; pore pluggage blocks the CO_2 molecules from reaching the core and hence lot of CaO remains unreacted (as much as 40%). Many efforts are being pursued to address these problems. Some of them include modifying the surface morphology to reduce plugging, hydration of sorbent and adding stabilizing materials like magnesium compounds or silicates to the sorbent. However, no one method can ensure effective regeneration. A further detailed study of the chemical kinetics and surface characterization is needed to understand the mechanism of regeneration and address the concerns.

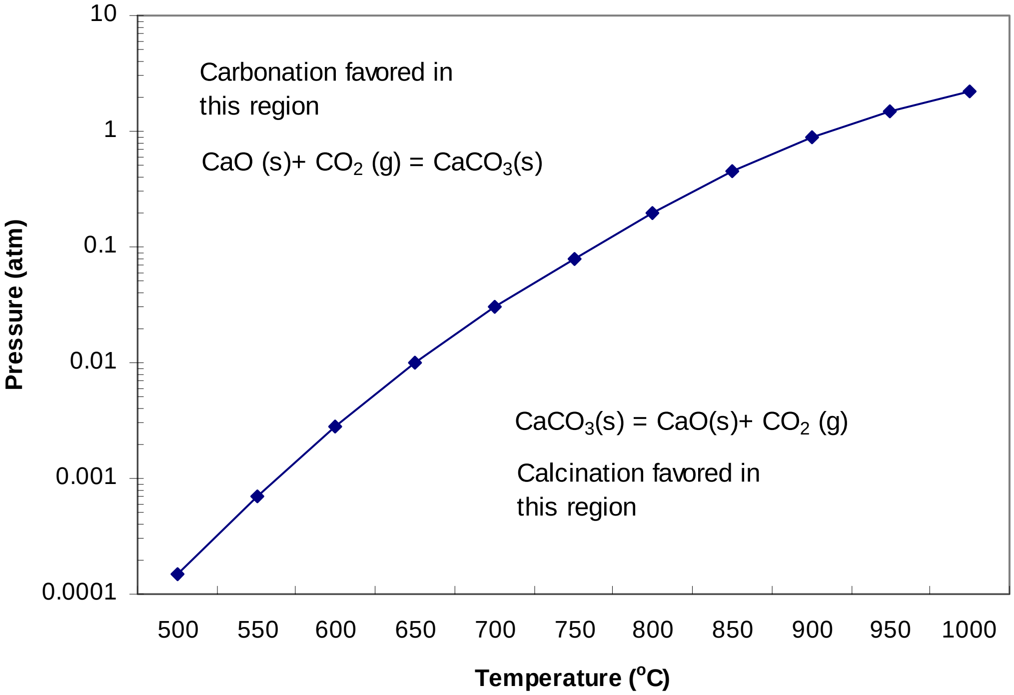

Figure 7.1: Equilibrium CO_2 pressure as a function of temperature (adapted from Silaban et al [109])

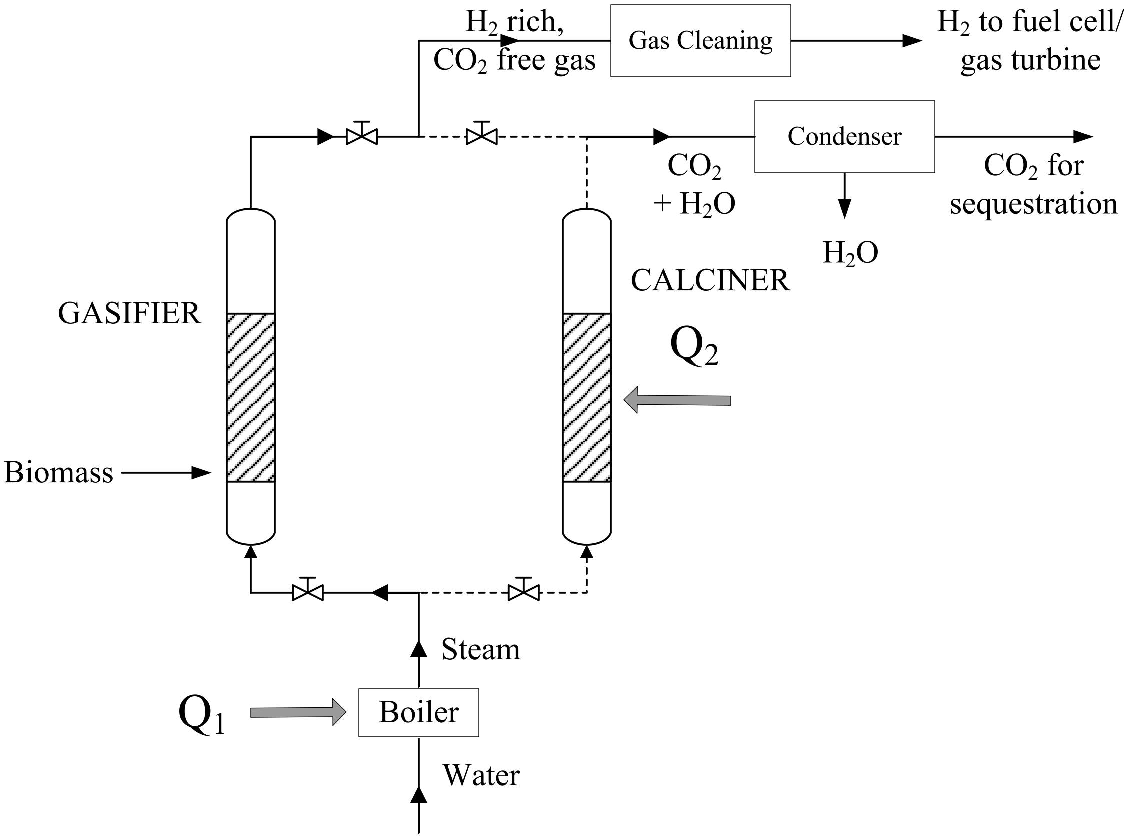

Figure 7.2: Biomass gasification with calcination of used sorbent

CHAPTER 8
SUMMARY, CONCLUSION AND RECOMMENDATIONS

Summary

The concept of sorbent enhanced gasification has been applied to biomass for producing hydrogen. First a thermodynamic analysis was carried out and later simulations were done to study the effect of adding sorbents on hydrogen yield. Later on experiments were conducted to verify the concept of using sorbents and finally regeneration of spent sorbent was studied.

The basic thermodynamic analysis of biomass gasification was carried out to determine the equilibrium hydrogen yield. The following conclusions were drawn from the thermodynamic studies:

1) The highest hydrogen yield was observed at gasification temperatures of around 1000 – 1100 K; steam gasification gave higher hydrogen yields than air gasification. This was due to the reformation of tars, char and higher hydrocarbons. Using air as a co-gasifying medium partially oxidizes the biomass and hence reduces the net energy consumption; however, it dilutes the product gas. The highest hydrogen yield was found when the gasifier was operated at atmospheric pressure.
2) The highest obtainable hydrogen yield was limited by thermodynamic equilibrium. To get more hydrogen, the equilibrium constraints must be removed. This is possible by constantly removing one of the co-products of gasification (CO_2) thereby driving the reactions in favor of hydrogen.

The basic studies laid the foundation of the concept of using sorbents for gasifying biomass. The concept was theoretically investigated by carrying out simulations in ASPEN process simulator. Calcium oxide was used as the model sorbent and ethanol was the model biomass compound. The effects of important process variables such as temperature, pressure, steam to biomass ratio and sorbent to biomass ratio on hydrogen yield were studied. The output variables included gas yields (H_2, CO, CO_2 and CH_4), reformer heat duty and thermodynamic efficiency. Based on the simulations the following conclusions were drawn:

3) The hydrogen yield while using the sorbent increased by 19% in comparison to conventional biomass gasification

4) The CO_2 content of the product gas was reduced by almost 50% due to absorption by CaO

5) The reformer heat duty was reduced by almost 42% due to in-situ heat transfer

6) The gasifier operating temperature was lowered by about 100-150^{o}C in the presence of the sorbent; in other words the same hydrogen yield was obtained by running the gasifier at about 100 – 150^{o}C lower than the conventional gasification temperature

7) Sorbent enhanced gasification is a novel technique for producing a hydrogen rich and CO_2 free gas; the product gas will need minimal cleaning and hence many downstream equipment such as Water Gas Shift reactor and PSA (Pressure Swing Adsorption) unit used conventionally may not be needed in the sorbent case. Hence there is a possibility of significantly reducing the capital cost of hydrogen production from biomass

8) A pure CO_2 stream is produced which can be either used for suitable applications or sequestered for appropriate disposal

Based on the encouraging results from the simulations, experimental studies on sorbent enhanced biomass gasification were carried out using Southern pine bark and calcium oxide. The temperature of the gasifier was varied from 500 to 700^{o}C. The yield of individual gases and the total yield were determined. Based on these studies, following conclusions can be drawn:

9) The hydrogen yield at 500^{o}C increased substantially from 320 ml/g without the sorbent to 719 ml/g while using sorbent.

10) The hydrogen yield at 500^{o}C with sorbents was more than the hydrogen yield at 700^{o}C for plain gasification. Hence there is a possibility of reducing the operating temperature of the gasifier (this confirmed the observation made in the simulation).

11) CO_2 absorption is an exothermic reaction while biomass steam gasification is endothermic. The two reactions can be coupled together so that there is in-situ energy transfer. Therefore the external heat duty of the gasifier can be significantly reduced. Hence a smaller and more compact gasifier can be used in place of the conventional. This would reduce the capital cost of the gasifier which is a significant part of the overall cost of biomass plant.

12) The overall gas yield increased from 550 ml/g to 1360 ml/g at 500^{o}C. It was also observed that the tars in the product gas were less when the sorbent was used. Based on these observations it was concluded that the sorbent had a catalytic effect in reforming the tars to additional gas.

13) The carbon conversion efficiency (which in a way quantifies the effectiveness of gasification) improved considerably from 23% to 63% at 500^{o}C while using the sorbent.

14) The high overall gas and hydrogen yields were observed until a gasification temperature of 700^{o}C after which the sorbent case gave almost the same yield as the case without the sorbent. This is due to the fact that the carbonation reaction (CO_2 absorption) is effective in the temperature range 500 - 700^{o}C. Beyond this temperature CO_2 is no longer absorbed (this was also observed in theoretical simulations).

15) The product gas while using the sorbent is rich in hydrogen, is CO_2 free and is relatively clean of any particulates and tars. If we can set the operating conditions such that we get almost pure hydrogen gas with very little contaminants, it may be possible to eliminate all or most of the downstream equipment used in conventional biomass gasification systems

such as High Temperature Water Gas Shift reactor (HT-WGS), Low Temperature Water Gas Shift (LT-WGS) reactor and Pressure Swing Adsorption (PSA) unit. With no WGS reactors there is no need of any catalyst and hence there will be savings in the running cost. In place of these reactors there will be a single reactor used for regenerating the sorbent. Hence there is a potential to reduce the capital cost of biomass gasification plants for hydrogen production.

Conclusions

1) Conventional biomass gasification is constrained by equilibrium of water gas shift reaction. This constraint can be removed by using a CO_2 sorbent such as calcium oxide.
2) The hydrogen yield is enhanced as the water gas shift reaction goes to completion in the absence of CO_2; CO and CO_2 in the product gas reduce drastically
3) In-situ heat transfer reduces the reformer (gasifier) duty thereby making it compact
4) Product gas is rich in hydrogen with small amounts of impurities and can be sent to the downstream equipment with minimum gas conditioning
5) Less gas cleaning and conditioning equipment implies reduced capital cost and hence there is a potential to become cost competitive to conventional gasification

Recommendations for Further Work

Sorbent enhanced biomass gasification is a novel technique for producing renewable hydrogen. The concept has been proved theoretically and experimentally with remarkable improvement in hydrogen yield. For successful application of this technology the sorbent must be regenerated for further use. Many research groups are currently investigating the multi-cycle performance of calcium oxide sorbent. Sintering and pore pluggage have been identified as the key problems. Further work must focus on addressing these problems. Some techniques include modification of sorbent surface to create mesopores so as to create enough surface area to prevent plugging. Other research groups are developing alternate sorbents by adding stabilizing materials such as MgO and silicates which resist pore closure and sintering at high temperature.

Sorbent regeneration by itself is an area of intense research and deep study involving different sub-areas like chemical kinetics, surface chemistry, thermodynamics, catalysis and material characterization. Future research must concentrate on and integrate these sub-areas with the end objective of developing a sorbent that can be effectively used over multiple calcination-carbonation cycles without any attrition or loss of capacity.

APPENDIX
LIST OF PUBLICATIONS

Journals

- **Mahishi MR**, Sadrameli SM, Vijayaraghavan S, Goswami DY. A novel approach to enhance the hydrogen yield of biomass gasification using CO_2 sorbent, *Accepted for publication by the ASME Journal of Engineering for Gas Turbines and Power*.

- **Mahishi MR**, Goswami DY. An experimental study of hydrogen production by gasification of biomass in the presence of a CO_2 sorbent, *Accepted for publication by the International Journal of Hydrogen Energy, Elsevier publications*.

- **Mahishi MR**, Goswami DY. Thermodynamic optimization of biomass gasifier for hydrogen production *under review with International Journal of Hydrogen Energy*, Elsevier publications.

Conference Proceedings

- **Mahishi MR**, Vijayaraghavan S, Deshpande DA, Goswami DY. A thermodynamic analysis of hydrogen production by gasification of biomass. *Proceedings of the 2005ISES Solar World Congress, August 6-12, 2005, Orlando, FL.*

- **Mahishi MR**, Sadrameli MS, Vijayaraghavan S, Goswami DY. Hydrogen production from ethanol: A thermodynamic analysis of a novel sorbent enhanced gasification process. *American Society of Mechanical Engineers, Advanced Energy Systems (publication) AES vol 45, pp 455-463, 2005.*

REFERENCES

[1] Kazim A, Veziroglu TN. Utilization of solar-hydrogen energy in the UAE to maintain its share in the world energy market for the 21st century. Renewable Energy 2001; 24: 259-274.

[2] Abdallah MAH, Asfour SS, Veziroglu TN. Solar hydrogen system for Egypt. International Journal of Hydrogen Energy 1999; 24(6): 505-517.

[3] Jefferson M. Sustainable energy development: performance and prospects. Renewable Energy 2006; 31(5): 571-582.

[4] Fuelcells.org. Benefits of Fuel Cells in Transportation. Internet resource found at http://www.fuelcells.org/basics/benefits_transp.html, last accessed November 2006

[5] Spath PL, Mann MK. Life cycle assessment of hydrogen production via natural gas steam reforming. In: National Renewable Energy Laboratory, Golden, CO, NREL/TP-570-27637, 2001.

[6] Barnett TO, Adam JC, Lettenmaier DP. Potential impacts of a warming climate on water availability in snow-dominated regions. Nature 2005; 438: 303-309.

[7] Laura C. IEA World Energy Outlook 2004; Implications for energy and CO_2 emissions (accessed from www.iea.org) last accessed November 2006.

[8] International Energy Outlook 2006 report. June 2006. Energy Information Administration Office of Integrated Analysis and Forecasting: US Department of Energy, Washington DC (www.eia.doe.gov/oiaf/ieo/index.html) last accessed Novermber 2006.

[9] Quantifying Energy: BP Statistical review of World Energy. June 2006. An annual report prepared by the British Petroleum oil company (www.bp.com) last accessed November 2006.

[10] Pena MA, Gomez JP, Fierro JLG. New catalytic routes for syngas and hydrogen production. Applied Catalysis A: General 1996; 144: 7-57.

[11] Prins R, De Beer VHJ, Somorjai GA. Structure and function of the catalyst and the promoter in Co-Mo hydrodesulphurization catalysts. Catalysis Reviews – Science and Engineering 1993; 35(1):1- 41.

[12] Hindermann JP, Hutchings GJ, Kiennemann A. Mechanistic aspects of the formation of hydrocarbons and alcohols from CO hydrogenation. Catalysis Reviews – Science and Engineering 1993; 35(1): 1-127.

[13] Nielsen A. Ammonia synthesis: Exploratory and applied research. Catalysis Reviews 1980; 23 (1 & 2): 17-51.

[14] Chang CD. Methanol-to-gasoline process: Reaction mechanism. ACS Symposium Series 1988; 368: 596-614.

[15] Dupian X, Krul RA, Schaverien CJ, Makkee M, Moulijn JA. Production of clean transportation fuels and lower olefins from Fischer Tropsch synthesis waxes fluid catalytic cracking conditions: The potential of highly paraffinic feedstocks for FCC. Applied Catalysis B: Environmental 2006; 63(3-4): 277-295.

[16] Culp AW. Principles of Energy Conversion. Second edition. Tata McGraw Hill Edition 2000.

[17] US Department of Energy site (http://www.energy.gov/energysources/hydrogen.htm), last accessed November 2006

[18] Veziroglu TN, Barbir F. Hydrogen: The wonder fuel. International Journal of Hydrogen Energy 1992; 17(6): 391-404.

[19] Dincer I. Technical, environmental and exergetic aspects of hydrogen energy systems. International Journal of Hydrogen Energy 2002; 27: 265-285.

[20] The Hydrogen Economy: Opportunities, Costs, Barriers and R&D Needs (2004). National Academy of Engineers and National Research Council, The National Academies Press, Washington DC (www.nap.edu).

[21] Sherif S, Veziroglu TN, Barbir F. Hydrogen Energy Systems. In: Wiley Encyclopedia of Electrical and Electronics Engineering. 9, JG Webster(Ed), John Wiley and Sons, NY, 1999.

[22] Ogden JM. Review of small stationary reformers for hydrogen production. Report to the International Energy Agency, 2001.

[23] Padro, C.E.G. and Putsche, V., Survey of the Economics of Hydrogen Technologies, National Renewable Energy Laboratory, September 1999, NREL/TP-570-27079.

[24] Babu SP. Biomass gasification for hydrogen production – process description and research needs. Gas Technology Institute, 1700 S Mount Prospect Road, des Plaines, IL 60018-1804, USA.

[25] Aeschlimann M. Electrolyzers for producing hydrogen. Brown Boveri Rev. 1975; 62(10-11): 501-508.

[26] Konopka AJ, Gregory DP. Hydrogen Production by Electrolysis: Present and Future. Institute of Gas Technology, Chicago, Illinois 60616, IECEC 1975 Record.

[27] Ivy J. Summary of Electrolytic Hydrogen Production: Milestone Completion Report. September 2004, NREL/MP-560-35948.

[28] US Department of Energy, Office of Energy Efficiency and Renewable Energy, Hydrogen, Fuel Cells and Infrastructure Technologies Program (HFCIT), Multiyear Research Development and Demonstration Plan: Planned Program Activities for 2003-2010, 1-34 (available online at http://www.eere.energy.gov/hydrogenandfuelcells/mypp/pdfs/production.pdf)

[29] Funk JE. Thermochemical hydrogen production: Past and present. International Journal of Hydrogen Energy 2001; 26(3): 185-190.

[30] Steinfeld A. Solar thermochemical production of hydrogen – a review. Solar Energy 2005; 78: 603-615.

[31] Haueter P, Moeller S, Palumbo R, Steinfeld A. The production of zinc by thermal dissociation of zinc oxide – solar chemical reactor design. Solar Energy 1999; 67(1-3): 161-167.

[32] Kameyama H, Yoshida K. Br-Ca-Fe water decomposition cycles for hydrogen production. In: Proceedings of the 2nd World Hydrogen Energy Conference, 829-850, 1978.

[33] Weidenkaff A, Reller A, Wokaun A, Steinfeld A. Thermogravimetric analysis of the ZnO/Zn water splitting cycle. Thermochimica Acta 2000; 359: 69-75.

[34] Aochi A, Tadokoro T, Yoshida K, Kameyama H, Nobue M, Yamaguchi T. Economic and technical evaluation of UT-3 thermochemical hydrogen production for an industrial scale plant. International Journal of Hydrogen Energy 1989; 14(7): 421-429.

[35] Matsuoka M, Kitano M, Takeuchi M, Anpo M, Thomas JM. Photocatalytic water splitting on visible light- responsive TiO_2 thin films prepared by a RF magnetron sputtering deposition method. Topics in Catalysis 2005; 35(3-4): 305-310.

[36] Oudenhoven J, Scheijen F, Wolffs M. Fundamentals of Photocatalytic Water Splitting by Visible Llight: A Review of Literature by Technical University of Eindhoven, Netherlands, 1-22, 2004.

[37] Fujishima A, Honda K. Electrochemical photolysis of water at a semiconductor electrode. Nature 1972; 238(5358); 37-38.

[38] Avachat US, Jahagirdar AH, Dhere NG. Multiple bandgap combination of thin film photovoltaic cells and a photoanode for efficient hydrogen and oxygen generation by water splitting. Solar Energy Materials and Solar Cells 2006; 90(15): 2464-2470.

[39] Hawkes FR, Dinsdale R, Hawkes DL, Hussy I. Sustainable fermentative hydrogen production: Challenges for process optimization. International Journal of Hydrogen Energy 2002; 27:1339-1347.

[40] Benemann JR. Feasibility analysis of photo-biological hydrogen production. International Journal of Hydrogen Energy 1997; 22: 979-987.

[41] International Energy Agency, World Energy Outlook 2000, IEA, Paris, 2000.

[42] Bridgwater AV. Renewable fuels and chemicals by thermal processing of biomass. Chemical Engineering Journal 2003; 91: 87-102.

[43] European Commission, Communication from the commission: Energy for the future: Renewable energy sources – white paper for a community strategy and action plan com(97) 599, Final of 26.11.97, Brussels, 1997.

[44] Turn SQ, Kinoshita C, Zhang Z, Ishimura D, Zhou J. An experimental investigation of hydrogen production from biomass gasification. International Journal of Hydrogen Energy 1998; 23(8): 641-648.

[45] Olivares A, Aznar MP, Caballero MA, Gil J, Frances E, Corella J. Biomass gasification: Produced gas upgrading by In-bed use of dolomite. Industrial & Engineering Chemistry Research 1997; 36(12): 5220-5226.

[46] Devi L, Ptasinski KJ, Janssen JJG.et al. A review of the primary measures for tar elimination in biomass gasification process. Biomass and Bioenergy 2003:;24: 125-140.

[47] Dayton D. A review of the literature on catalytic biomass tar destruction, Milestone Completion report. NREL Report: NREL/TP-510-32815, December 2002.

[48] Sutton D, Kelleher B, Ross JRH. Review of literature on catalysts for biomass gasification. Fuel Processing Technology 2001; 73: 155-173.

[49] Simmel PA, Leppälahti JK, Kurkela EA. Tar decomposing activity of carbonate rocks under high CO_2 partial pressures. Fuel 1995; 74(6): 938-945.

[50] Aznar MP, Frances E. Testing of downstream catalysts for tar destruction with a guard bed in a fluidized bed biomass gasifier at pilot scale. VTT Symposium; 164: 263-268, 1996.

[51] Taralas G, Vassilatos V, Krister S, Jesus D. Thermal and Catalytic Cracking of n-heptane in presence of calcium oxide, magnesium oxide and calcined dolomites. Canadian Journal of Chemical Engineering 1991; 69(6): 1413-1419.

[52] Vassilatos V, Taralas G, Sjostrom K, Bjornbom E. Catalytic cracking of tar in biomass pyrolysis gas in the presence of calcined dolomites. Canadian Journal of Chemical Engineering 1992; 70: 1008-1013.

[53] Aznar MP, Caballero MA, Gil J, Martin JA, Corella J. Commercial steam reforming catalyst to improve biomass gasification with steam-oxygen mixtures: Part 2

Catalytic tar removal, Industrial & Engineering Chemistry Research 1998; 37(7): 2668-2680.

[54] Simell P. Catalytic hot gas cleaning of gasification gas. VTT Publications, 330, 1-68.

[55] Kinoshita CM, Wang Y, Zhou J. Effect of reformer condition on catalytic reforming of biomass gasification tars. Industrial & Engineering Chemistry Research 1995; 34(9): 2949-2954.

[56] Bangala DN, et al. Steam reforming of naphthalene on Ni-Cr/Al_2O_3 catalysts doped with MgO, TiO_2 and La_2O_3. AIChE Journal 1998; 44: 927-936.

[57] Wang D, Chornet E. Catalytic steam reforming of biomass-derived oxygenates: acetic acid and hydroxyacetaldehyde. Applied Catalysis A: General 1996; 143: 245-270.

[58] Rapagna S, Jand N, Foscolo PU. Catalytic gasification of biomass to produce hydrogen rich gas, International Journal of Hydrogen Energy 1998; 23(7): 551-557.

[59] Garcia L, French R, Czernik S, Chornet E. Catalytic steam reforming of bio-oils for the production of hydrogen: effect of catalyst composition. Applied Catalysis A: General 2000; 201: 225-239.

[60] Sutton D, Kelleher B, Doyle A, Ross JRH. Investigation of nickel-supported catalysts for the upgrading of brown peat derived gasification products. Bioresource Technology 2001; 80: 111-116.

[61] Asadullah M, Fujimoto K, Tomishige K. Catalytic performance of Rh/CeO_2 in the gasification of cellulose to synthesis gas at low temperature. Industrial & Engineering Chemistry Research 2001; 40: 5894-5900.

[62] Asadullah M, Tomishige K, Fujimoto K. A novel catalytic process for cellulose gasification to synthesis gas. Catalysis Communications 2001; 2(2): 63-68.

[63] Das P and Ganesh A. Influence of pretreatment of biomass on pyrolysis products, Indian Institute of Technology, Bombay, Powai, Mumbai 400 076, India (Internet Resource: http://bioproducts-bioenergy.gov/pdfs/bcota/abstracts/3/z246.pdf)

[64] Raveendran K, Ganesh A, Khilar KC. Influence of mineral matter as biomass pyrolysis characteristics. Fuel 1995 ; 74(12): 1812-1822.

[65] Conesa J, Marcilla A, Cabarello JA. Evolution of gases from the pyrolysis of modified almond shells: Effect of impregnation with $CoCl_2$. Journal of Analytical and Applied Pyrolysis 1997; 43: 59-69.

[66] Kung HC. A mathematical model of wood pyrolysis. Combustion and Flame 1972; 18: 185-195.

[67] Kansa EJ, Perlee HE, Chaiken RF. Mathematical modeling of wood pyrolysis including internal forced convection. Combustion and Flame 1977; 29: 311-324.

[68] Miyanami K, Fan LS, Walawender WP. Mathematical model for pyrolysis of a solid particle - effects of the heat of reaction. Canadian Journal of Chemical Engineering 1977; 55(3): 317 – 325.

[69] GrØnli MG. A theoretical and experimental study of the thermal degradation of biomass. DØktØr IngeniØr thesis submitted to the Norwegian University of Science and Technology, 1996.

[70] Jalan RK, Srivastava VK. Studies on pyrolysis of a single biomass cylindrical pellet – kinetic and heat transfer effects. Energy Conversion and Management 1999; 40: 467-494.

[71] Narvaez I, Orio A, Aznar MP, Corella J. Biomass Gasification with air in an atmospheric bubbling fluidized bed: effect of six operating variables on the quality of the product raw gases, Industrial & Engineering Chemistry Research 1996; 35: 2110-2120.

[72] Herguido J, Corella J, Gonzalez-Saiz J. Steam gasification of lignocellulosic residues in a fluidized bed at a small pilot scale: effect of the type of feedstock. Industrial & Engineering Chemistry Research 1992; 31: 1274-1282.

[73] Gil J, Corella J, Aznar MP, Caballero MP. Biomass gasification in atmospheric and bubbling fluidized bed: Effect of the type of gasifying agent on the product distribution. Biomass and Bioenergy 1999; 17: 389-403.

[74] Pinto F, Franco C, André RN, Miranda M, Gulyurtlu I, Cabrita I. Co-gasification study of biomass mixed with plastic wastes. Fuel 2002; 81: 291-297.

[75] Cairns EJ, Tevebaugh AD. CHO gas phase composition in equilibrium with carbon and carbon deposition boundaries at one atmosphere. Journal of Chemical & Engineering Data 1964: 9(3): 453-462.

[76] Schuster G, Löffler G, Weigl K, Hofbauer H. Biomass steam gasification – an extensive parametric modeling study. Bioresource Technology 2001; 77: 71-79.

[77] Kinoshita CM, Wang Y, Takahashi PK. Chemical equilibrium computations for gasification of biomass to produce methanol. Energy Sources 1991; 13: 361-368.

[78] Garcia EY, Laborde MA. Hydrogen production by the steam reforming of ethanol: Thermodynamic analysis. International Journal of Hydrogen Energy 1991; 16(5): 307 – 312.

[79] Carapellucci R. Power generation using dedicated woody crops: Thermodynamics and economics of integrated plants. Renewable Energy 2002; 27: 143-159.

[80] Lede J. Solar thermochemical conversion of biomass. Solar Energy 1999; 65: 3-13.

[81] Zainal ZA, Ali R, Lean CH, Seetharamu KN. Prediction of performance of a downdraft gasifier using equilibrium modeling for different biomass materials. Energy Conversion & Management 2001; 42: 1499-1515.

[82] Alderucci V, Antonucci PL, Maggio G, Giordano M, Antonucci V. Thermodynamic analysis of SOFC fuelled by biomass-derived gas. International Journal of Hydrogen Energy 1994; 19(4): 369-376.

[83] Prins MJ, Ptasinski KJ, Janssen FJJG. Thermodynamics of gas-char reactions: first and second law analysis. Chemical Engineering Science 2003; 58: 1003-1011.

[84] Crane P, Scott DS, Rosen MA. Comparison of exergy of emissions of from two energy conversion technologies considering the potential for environmental impact. International Journal of Hydrogen Energy 1992; 17(5): 345-350.

[85] Han C, Harrison DP. Simultaneous shift reaction and carbon-dioxide separation for the direct production of hydrogen. Chemical Engineering Science 1994; vol. 49, No. 24 B: 5875-5883.

[86] Balasubramanian B, Ortiz AL, Harrison DP. Hydrogen from methane in a single-step process. Chemical Engineering Science 1999; 54: 3543-3552.

[87] Lin S, Harada M, Suzuki Y, Hatano H. Hydrogen production from coal by separating carbon dioxide during gasification. Fuel 2002; 81: 2079-2085.

[88] Lin SY, Suzuki Y, Hatano H, Harada M. Developing an innovative method HyPr-RING to produce hydrogen from hydrocarbons. Energy Conversion and Management 2002; 43: 1283-1290.

[89] Abanades JC, Anthony EJ, Lu DY, Salvador C, Alvarez D. Capture of CO_2 from combustion gases in a fluidized bed of CaO. Environmental and Energy Engineering AIChE Journal, 2004; 50(7): 1614-1622.

[90] Kyaw K, Kubota M, Watanabe F, Matsuda H, Hasatani M. Study of carbonation of CaO for high temperature thermal energy storage. Journal of Chemical Engineering of Japan 1998; 31(2): 281-284.

[91] Kubota M, Kyaw K, Watanabe F, Matsuda H, Hasatani M. Study of decarbonation of $CaCO_3$ for high temperature thermal energy storage. Journal of Chemical Engineering of Japan 2000; Vol 33 No. 5: 797-800.

[92] Lee DK, Baek IH, Yoon WL. Modeling and simulation for the methane steam reforming enhanced by in-situ CO_2 removal utilizing the CaO carbonation for hydrogen production. Chemical Engineering Science 2004; 59: 931-942.

[93] Van Ness HC, Smith JM, Abbott MM. Introduction to Chemical Engineering Thermodynamics (sixth edition). Crawfordsville, IN: McGraw Hill, 2001.

[94] Reynolds WC. Stanjan interactive computer programs for Chemkin equilibrium analysis. Stanford University Report, 1981.

[95] Asadullah M, Ito S, Kunimori K, Yamada M, Tomishige K. Biomass Gasification to hydrogen and syngas at low temperature: Novel catalytic system using fluidized bed reactor. Journal of Catalysis 2002; 208: 255-259.

[96] Corella J, Aznar MP, Delgado J, Aldea E. Steam Gasification of Cellulosic waste in a fluidized bed with downstream vessels. Industrial Engineering & Chemistry Research 1991; 30: 2252-2262.

[97] Franco C, Pinto F, Gulyurtlu I, Cabrita I. The study of reaction influencing biomass steam gasification process. Fuel 2003; 82: 835-842.

[98] Minkova V, Marinov SP, Zanzi R, Björnbom E, Budinova T, Stefanova M, Lakov L. Thermochemical treatment of biomass in a flow of steam or in a mixture of steam and CO_2. Fuel Processing Technology 2000; 62: 45-52.

[99] Barin I. Thermochemical Data for Pure Substances (Vol 1, Third Ed). Weinheim, New York, 1995.

[100] Tessie Du Motay M, Marechal M. Bull Soc Chi 1868; 9: 334.

[101] Curran GP, Fink CE, Gorin E. CO_2 acceptor gasification process: Studies of acceptor properties. In: Advances in Chemistry, Fuel Gasification, American Chemical Society, Washington, 69; 141-165: 1967.

[102] Ortiz AL, Harrison DP. Hydrogen production using sorption-enhanced reaction. Industrial & Engineering Chemistry Research 2001; 40 (23): 5102-5109.

[103] Harrison DP, Peng Z. Low-carbon monoxide hydrogen by sorption-enhanced reaction. International Journal of Chemical Reaction Engineering 2003; 1: Article A37.

[104] Lin S, Harada M, Suzuki Y, Hatano H. Process analysis for hydrogen production by reaction integrated novel gasification (HyPr-RING). Energy Conversion and Management 2005; 46: 869-880.

[105] Cavallaro S, Freni S. Ethanol steam reforming in a molten carbonate fuel cell: A preliminary kinetic investigation. International Journal of Hydrogen Energy 1996; 21(6): 465-469.

[106] Walawender WP, Hoveland DA, Fan LT. Steam gasification of pure cellulose 1: Uniform temperature profile. Industrial & Engineering Chemistry Process Design and Development 1985; 24: 813-817.

[107] Wang Y, Kinoshita CM. Experimental analysis of biomass gasification with steam and oxygen. Solar energy 1992; 49(3): 153-158.

[108] Hoveland DA, Walawender WP, Fan LT. Steam gasification of pure cellulose 2: Elevated freeboard temperature. Industrial & Engineering Chemistry Process Design and Development 1985; 24: 818-821.

[109] Silaban A, Harrison DP. High temperature capture of carbon-dioxide: Characteristics of the reversible reaction between CaO(s) and CO_2(g). Chemical Engineering Communication 1995; 137: 177-190.

[110] Abanades JC, Rubin ES, Anthony EJ. Sorbent cost and performance in CO_2 capture systems. Industrial and Engineering Chemistry Research 2004; 43: 3462-3466.

[111] Han C, Harrison DP. Multicycle performance of a single-step process for H_2 production. Separation Science and Technology 1997; 32(1-4): 681-697.

[112] Boynton RS. In: Chemistry and Technology of Lime and Limestone. Wiley, New York, 1980.

[113] Dedman AJ, Owen AJ. Calcium cyanide synthesis Part 4 – The reaction of $CaO + CO_2 \rightarrow CaCO_3$. Transactions of the Faraday Society 1962; 58: 2027-2035.

[114] Barker R. The reversibility of the reaction $CaCO_3 \rightarrow CaO + CO_2$. Journal of Applied Chemistry and Biotechnology 1973; 23: 733-742.

[115] Bhatia SK and Perlmutter DD. Effect of the production layer on the kinetics of the CO_2-lime reaction. AIChE Journal 1983; 29: 79-86.

[116] Lee JW, Li R. Integration of fossil energy systems with CO_2 sequestration through NH_4HCO_3 production. Energy Conversion and Management 2003; 44: 1535-1546.

[117] Fiaschi D, Manfrida G, Massini M, Pellegrini G. Some innovative readily applicable proposals for chemical separation and sequestration of CO_2 emissions from power plants. Proceedings of the 7th Biennial Conference on Engineering Systems Design and Analysis 2004; 1: 161-167.

[118] Zedtwitz Pv, Steinfeld A. The solar thermal gasification of coal-energy conversion efficiency and CO_2 mitigation potential. Energy 2003; 28: 441-456.

[119] Gupta H and Fan LS. Carbonation-Calcination cycle using high reactivity calcium oxide for carbon-dioxide separation from flue gas. Industrial and Engineering Chemistry Research 2002; 41: 4035-4042.

[120] Kuramoto K, Fujimoto S, Morita A, Shibano S, Suzuki Y, Hatano H, Shi-Ying L, Harada M, Takarada T. Repetitive carbonation calcination reactions of Ca-based sorbents for efficient CO_2 sorption at elevated temperatures and pressures. Industrial and Engineering Chemistry Research 2003; 42: 975-981.

[121] Bandi A, Specht M, Sichler P, Nicoloso N. In-situ gas conditioning in fuel reforming for hydrogen generation. In: Proceedings of the Fifth International Symposium on Gas Cleaning at High Temperature, Morgantown, WV, 2002.

[122] Kato M, Nakagawa K. New series of lithium containing complex oxides. Lithium silicates for application as a high temperature CO_2 absorbent. Journal of the Ceramic Society of Japan 2001; 109(1275), 911-914.

[123] Liang Y, Harrison DP, Gupta RP, Green DA, McMichael WJ. Carbon dioxide capture using dry sodium based sorbents. Energy and Fuels 2004; 18: 569-575.

BIOGRAPHICAL SKETCH

Madhukar was born and raised in Bombay, India. He completed his bachelor's degree in Mechanical engineering from the University of Bombay in Summer 1996 and later completed his master's degree in Mechanical engineering (with specialization in Thermal science and Fluid dynamics) from the Indian Institute of Technology, Bombay, in Spring 1999. He worked for a well-known automotive company in India (Tata Auto Comp Systems Limited) as a Design Engineer for three years where he was in charge of thermal design of automotive cooling systems for cars, trucks and commercial vehicles. Madhukar joined the MAE Department at UF in Spring 2003 and was admitted to the direct PhD program. Upon graduation he plans to pursue research either in industry or academia in the areas of thermal design, energy conversion and fuel cells.