

PhD Thesis

**Noncatalytic Supercritical Water
Gasification of Liquid Type Feedstocks for
Hydrogen Production: Investigation of
Reactor Performance**

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Clean Energy and Chemical Engineering

UNIVERSITY OF SCIENCE AND TECHNOLOGY

February 2012



Noncatalytic Supercritical Water Gasification of Liquid Type Feedstocks for Hydrogen Production: Investigation of Reactor Performance

Ratna Frida Susanti

**A Dissertation Submitted in Partial Fulfillment of
Requirements for the Degree of Doctor of Philosophy**

February 2012

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**UNIVERSITY OF SCIENCE AND TECHNOLOGY
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ACKNOWLEDGEMENTS

The past four years in KIST had given an extraordinary research experience and knowledge in this field. My loveliest memories will be the people who help me to survive during my time in Korea. I would like to express my sincere gratitude to:

God : He never leaves me in any situation. Strengthen me through difficult time I passed and cherish me with plenty of happiness.

Family : My husband, **Tatas**, who always understand my situation, encourage me to reach my dream with continuous support and love. My son, **Dehanson**, who gives me colorful life and happiness. "You are my life." My **parents** who support and bless me with beautiful prayer every day. My **grandmother** in memoriam who left me in February 14, 2011. "My biggest regret was not seeing you in your last time. I wish you could wait for us"

My advisors : **Dr. Kim Jaehoon** who guides, encourages and supports me continuously during my research life even before I was under his supervision. I am thankful for the opportunities to attend conferences and his concern to my personal life in Korea as foreigner with family. **Dr. Kim Jae-duck**, my former advisor, who support me consistently during my two years courses. "I wish for your healthy life"

Mr. Park Jang Min: who help me to be familiar with my equipment, stand by me for every problem with equipment, support me for every modification I wish. He is care not only for my experiment but also for my personal life in Korea. He is the most kindhearted person I know.

Thesis Exam Committee: **Prof. Ki Bong Lee, Dr. Jeong-Myeong Ha, Dr. Chang Soo Kim, Dr. Chang Won Yoon** who invest their time to review my thesis and give critical suggestions which help to improve my work.

Supercritical Fluid Laboratory Member: “They are my family”, to whom I shared my life for these four years. I would like to thanks to my mentor, **Dr. Bambang** who introduced this lab for the first time. He guided me for this research, acted as my second advisor and helped me to survive in Korea for the first time. **Agung** who kindly help me with life activity especially during my pregnancy time; **Edo** who share motivation and spirit during this final task; **Dimas** who is always very helpful in every computer problem, my little angel “**Endah**”, who always be my angel bodyguard and sister; my co-worker, **Laras**, who is patient and helpful; **Steffen**, to whom I always discuss and share about many things in research and the one who always advise me “to enjoy my life”; **Daewoo and Jaeyoung** for the consistent help for my daily life in Korea without enough Korean language capability, especially for becoming “삼촌” (uncle) for my baby and also **Young Jun, Seung Ah, Seok Ki** for their warm friendship.

My Indonesian friends in KIST and DEIGRATIA who share their friendship and love during my study here.

My colleagues at the Chemical Engineering Department of Parahyangan Catholic University, who constantly support my graduate study.

Thanks for your support.

Without all of you, I am nothing.

ABSTRACT*

Noncatalytic Supercritical Water Gasification of Liquid Type Feedstocks for Hydrogen Production: Investigation of Reactor Performance

Hydrogen is considered as the promising solution for both of energy issue due to fossil fuel depletion and environmental issue due to global warming. It because hydrogen can be produced from both of renewable and nonrenewable sources and only produce air as byproduct in the case of pure hydrogen fed to Polymer Electrolyte Membrane Fuel Cell (PEMFC). The production of hydrogen by the supercritical water gasification (SCWG), a high pressure steam reforming process conducted at above the critical point of water (374°C and 22.1 MPa), has several advantages compare to the conventional gasification due to the unique physical properties of supercritical water. The low dielectric constant of SCW (2-20) allows the homogenous phase reaction of organic feedstock (as carbon source), water and the gaseous product, eliminate the mass transfer limitation due to two phase reaction system; enable the reaction to be conducted at very short residence time. Compare to ambient water, it also has much lower viscosity, higher diffusivity and adjustable density depends on the temperature and pressure, beneficiary for conducting faster reaction.

I introduced the new reactor design, in this thesis named as “the 2nd generation Supercritical Water Gasification (SCWG),” having purpose to obtain the gas-liquid flow rate stability and improve the gaseous yield. This 2nd generation was the modification of the 1st generation SCWG, which has been utilized for gasification study by the previous researcher. The modification focus was in the reactor geometry. In the 1st generation SCWG, the reactor and condenser was in vertical position; allowing the feed to be fed from the top and liquid/gas flew out from the bottom. The modification done in the 2nd generation SCWG includes titling the reactor 75° from vertical position and adding the air-cooled tube. In this 2nd generation SCWG, feedstock fed from the bottom and liquid/gas flew out from the top. The apparatus performance was investigated for the noncatalytic gasification of isooctane, a model compound of gasoline. Under the similar operating condition, the 2nd generation of SCWG could improve the hydrogen yield almost 4 times higher. Further modification to the apparatus,

named as “the 3rd generation SCWG,” was done by changing the reactor material to enable the gasification experiment up to 800°C, 25 MPa and increasing the reactor volume up to 6 times larger to enable the observation at longer residence time. Again, isooctane was used as feedstock in order to compare with the previous results.

Our group is the first who investigates the isooctane gasification in supercritical water. In order to compare the results with the widely studied feedstock in SCWG, glucose was chosen as the second studied feedstock. Glucose is used as a biomass model compound as it is representative of the “building block” of cellulose, the major constituents of biomass. The low concentration studies of glucose gasification were done and the results then compared with that of done by other researchers under similar operating condition. At high temperature (>700°C), the yield of hydrogen was higher than that of observed by other researchers. The apparatus performance was also investigated using various feedstocks from hydrocarbon with one carbon number (C₁) to hydrocarbon with ten carbon number (C₁₀). Those feedstocks were methanol, ethanol, glycerol, glucose, isooctane and n-decane. They represent the straight, branch and aromatic hydrocarbon. Complete gasification of all feedstocks were observed under similar operating condition (25 MPa, 740°C; 10 wt%). Furthermore, the gasification of those feedstocks also studied at higher concentration of 20 wt% and low temperature of 650°C.

Finally the energy efficiency calculation was done to the system. The efficiencies of the experimental yields were compared to the equilibrium yields as well as the efficiencies of the system without heat recovery and with heat recovery. It can be concluded that the heat recovery could improve the efficiency largely. The other ways to improve efficiency are used the higher heating value of feedstocks and higher feedstock concentration.

* A thesis is submitted to committee of the University of Science and Technology in a partial fulfillment of the requirement for the degree of Doctor of Philosophy of Clean Energy and Chemical Engineering conferred in February 2012

Contents

ACKNOWLEDGEMENT	i
Abstract	iii
Table of Contents	v
List of Tables	xi
List of Figures	xiii
1. Introduction	1
1.1 Background.....	1
1.2 Research Objectives and Approach.....	5
1.3 Thesis Outline.....	6
2. Theory and Literature Review	8
2.1 Supercritical Water and its Properties.....	8
2.2 Supercritical Water Gasification (SCWG).....	17
2.2.1 Advantages of Supercritical Water Gasification.....	19
2.2.2 Disadvantages of Supercritical Water Gasification.....	20
2.3 Clasification of Supercritical Water Gasification (SCWG).....	22
2.3.1 Low-temperature SCWG (~500 °C).....	22

2.3.2 High-temperature SCWG (>500 °C).....	26
2.4 Chemical Reactions.....	27
2.4.1 Chemical Reactions.....	27
2.4.2 Estimation of Theoretical Maximum Hydrogen Gas Yield....	33
2.5 The Effect of Reaction Condition on SCWG	35
2.5.1 Temperature.....	35
2.5.2 Pressure.....	37
2.5.3 Feedstock Concentration.....	40
2.5.4 Residence Time.....	42
2.6 Current Status and Challenges.....	44
3. Experimental Method.....	49
3.1 Material.....	49
3.2 Supercritical Water Gasification (SCWG) Apparatus.....	50
3.2.1 Feed Preparation.....	51
3.2.2 Preheating System.....	53
3.2.3 Reactor System.....	54
3.3 Operating Procedure.....	58
3.4. Analytical Methods.....	59

3.4.1 Gas Product.....	59
3.4.2 Liquid Product.....	61
3.5. Calculation.....	62
3.5.1 Residence time.....	62
3.5.2 Yield.....	62
4. Noncatalytic Gasification of Isooctane in the 2nd Generation Supercritical Water Gasification System (SCWG).....	65
4.1 Introduction.....	65
4.2 Experimental.....	68
4.2.1 Material.....	69
4.2.2 Apparatus.....	69
4.2.3 Analytical methods.....	69
4.3 Result and Discussion.....	70
4.3.1 Effect of Temperature.....	70
4.3.2 Effect of Residence Time.....	75
4.3.3 Effect of Feed Concentration.....	79
4.3.4 Effect of Oxidant Concentration.....	82
4.3.5 New Reactor Design Concept.....	86

4.4 Conclusion.....	92
5. Noncatalytic Gasification of Isooctane in the 3rd Generation Supercritical Water Gasification (SCWG) System.....	93
5.1 Introduction.....	93
5.2 Experimental.....	95
5.3 Result and Discussion.....	96
5.3.1 Equilibrium Calculation.....	96
5.3.2 Effect of Residence Time.....	98
5.3.3 Effect of Feed Concentration.....	104
5.3.4 Effect of Oxidant.....	106
5.4 Comparison with other reforming methods.....	113
5.5 Conclusion.....	117
6. Investigation of Gasifier Performance for Gasification of Glucose as a Model of Biomass Compound in SCW.....	118
6.1 Introduction.....	118
6.2 Experimental.....	120
6.3 Result and Discussion.....	121
6.3.1 Reactions and Pathways.....	121

6.3.2 Investigation of Experimental Variable.....	123
6.3.2.1 Temperature.....	123
6.3.2.2 Residence Time.....	129
6.3.3 Feed concentration.....	132
6.3.4 Comparison with Other Result.....	136
6.4 Conclusion.....	141
7. Preliminary Study of Various Liquid Type Feedstock and Model Compounds for Hydrogen Production by Supercritical Water Gasification.....	142
7.1 Introduction.....	142
7.1.1 Methanol.....	142
7.1.2 Ethanol.....	144
7.1.3 Glucose.....	145
7.1.4 Glycerol.....	145
7.1.5 Fossil Fuel Model Compounds(Isooctane and n-decane).....	146
7.2 Experimental.....	147
7.3 Result and Discussion.....	148
7.3.1 Methanol.....	148

7.3.2 Ethanol, Glucose and Glycerol.....	153
7.3.3 Fossil Fuel Model Compound Gasification (isooctane and n-decane).....	162
7.4 Evaluation of Energy Efficiency.....	164
7.4.1 Evaluation of Energy Efficiency in the 3 rd Generation SCWG.....	166
7.4.2 External Energy.....	166
7.4.3 Heat Recovery.....	167
7.4.4 Mass Balance.....	167
7.4.5 Energy Used in Real System.....	170
7.5 Conclusion.....	174
8. Conclusion and recommendation for further research.....	175
8.1 Conclusion.....	175
8.2 Recommendation for Further Research.....	177
References.....	179

List of Tables

Table 2-1. Physicochemical properties of water in different states

Table 2-2. Theoretical maximum hydrogen gas yields of several feedstocks

Table 2-3. Theoretical maximum hydrogen gas yields of glucose in the presence
of oxidant

Table 3-1. The dimension of apparatus

Table 4-1. The typical composition of gasoline

Table 4-2. Supercritical water gasification comparison between the downdraft
and the updraft gasifier configuration.

Table 4-3. Comparison of supercritical water gasification results

Table 5-1. Comparison of hydrogen gas yield by noncatalytic supercritical water
gasification using hydrocarbon resources/model compounds

Table 5-2. Comparison of hydrogen gas yield by reforming of isooctane using
various methods.

Table 6-1. The comparison of experiment results under similar condition with
literature

Table 7-1. Gas composition of different feedstock under similar operating
condition

Table 7-2. The concentration effect of gasification of methanol, isooctane and n-decane at pressure of 25 MPa; temperature of ~740°C and residence time of 60 s

Table 7-3. Summary of SCWG experimental results and theoretical hydrogen yield using methanol (CH_3OH) as a feedstock

Table 7-4. Summary of SCWG experiments results and theoretical hydrogen yield using ethanol ($\text{C}_2\text{H}_5\text{OH}$) as a feedstock

Table 7-5. Summary of SCWG experiments results and theoretical hydrogen yield using glycerol ($\text{C}_3\text{H}_8\text{O}_3$) as a feedstock

Table 7-6. Summary of SCWG experiments results and theoretical hydrogen yield using glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) as a feedstock

Table 7-7. The mass balance of methanol, isooctane and n-decane gasification

Table 7-8. The electric power used for heating

Table 7-9. The energy efficiency calculation results

Table 7-10. The energy consumption summary

List of Figures

Figure 2-1. Selected properties of water as a function of temperature at 25 MPa

Figure 2-2. The reaction scheme of cellulose decomposition at 300°C

Figure 2-3. The reaction pathway of solid formation

Figure 2-4. The gaseous yield at equilibrium in terms of composition ratio as a function of temperature for SCWG of 1.8 wt% glucose at 25 MPa. The composition was calculated using Gibbs free energy minimization and Peng-Robinson equation of state.

Figure 2-5. Equilibrium gas yield as a function of pressure in the gasification of 10 wt% methanol at 700 °C

Figure 2-6. Equilibrium gas yield as a function of concentration in the gasification of biomass at 600 °C and 25 MPa

Figure 3-1. Schematic of 2nd and 3rd generation Supercritical water gasification apparatus.

Figure 4-1. Chemical structure of isooctane

Figure 4-2. Schematic of 1st generation SCWG

Figure 4-3. Effect of the reaction temperature on (a) total gas yield, total organic carbon (TOC) and carbon gasification efficiency (CE), (b) dry gas

composition, and (c) individual gas yield composition. The gasification was conducted at 25 MPa, a residence time of 6.9 s, and an isooctane concentration of 11.2 wt %.

Figure 4-4. Effect of the residence time on (a) total gas yield, total organic carbon (TOC) and carbon gasification efficiency (CE), (b) dry gas composition, and (c) individual gas yield composition. The gasification was conducted at 25 MPa, 632 °C and isooctane concentration of 15.25 wt %.

Figure 4-5. Effect of the isooctane concentration on (a) total gas yield, total organic carbon (TOC) and carbon gasification efficiency (CE), (b) dry gas composition, and (c) individual gas yield composition. The gasification was conducted at 25 MPa, 630 °C and a residence time of 18 s.

Figure 4-6. Effect of the oxidant concentration on (a) total gas yield, total organic carbon (TOC) and carbon gasification efficiency (CE), (b) dry gas composition, and (c) individual gas yield composition. The gasification was conducted at 25 MPa, 637 °C, a residence time of 18 s and an isooctane concentration of 9.9 wt%.

Figure 5-1. Calculated equilibrium gas yield (a) as a function of temperature at a fixed isooctane concentration of 6.2 wt% and (b) as a function of

concentration at a fixed temperature of 764°C. The pressure is 25 MPa

Figure 5-2. Calculated equilibrium (a) hydrogen gas yield, (b) carbon dioxide gas yield, and (c) methane gas yield as a function of ER at various temperatures, 25 MPa and an isooctane concentration of 6.2 wt%.

Figure 5-3. Effect of the residence time on (a) total gas yield, total organic carbon (TOC) and carbon gasification efficiency (CE), (b) individual gas yield composition, (c) dry gas composition and (d) pictures of liquid product samples. The gasification was conducted at 25 MPa, 763±2 °C and isooctane concentration of 6.3±0.3 wt%

Figure 5-4. Effect of the isooctane concentration on (a) total gas yield, total organic carbon (TOC) and carbon gasification efficiency (CE), (b) individual gas yield composition and (c) dry gas composition. The gasification was conducted at 25 MPa, 764±1 °C and a residence time of 106 s.

Figure 5-5. Effect of the oxidant concentration on (a) total gas yield, total organic carbon (TOC) and carbon gasification efficiency (CE), (b) individual gas yield composition and (c) dry gas composition. The gasification was conducted at 25 MPa, temperature of 764 ±1 °C, residence time of 105±1 s and isooctane concentration of 6.2±0.1 wt%.

Figure 6-1. Structures of D-Glucose

Figure 6-2. The decomposition of glucose to organic intermediate in SCW at 650°C

Figure 6-3. The equilibrium composition of gaseous product as a function of temperature at specific concentration at 25 MPa

Figure 6-4. The effect of temperature at pressure of 25 MPa, residence time of 60 s and concentration of 1.8 wt% (a) Gas Yield and TOC (b) Composition of gaseous product and CE

Figure 6-5. The effect of temperature to the liquid product compositions. Experiment conducted at pressure of 25 MPa, residence time of 60 s and concentration of 1.8 wt%.

Figure 6-6. The composition of liquid product at pressure of 25 MPa, temperature of 600°C, residence time of 30 s and concentration of 3.6 wt%: (1) acetic acid, (21) 5-Hydroxymethylfurfural, (22) 2-methyl-5-hydroxybenzofuran, (26) 1-(3-hydroxyphenyl)-ethanone, (30) 2-Naphthalenol, (33) 2-methyl-1,4-benzenediol, (35) 1,4-benzenediol (hydroquinone)

Figure 6-7. The effect of residence time at pressure of 25 MPa, temperature of 740 °C and concentration of 1.8 wt% (a) Gas Yield and TOC (b) Composition of gaseous product and CE

Figure 6-8. The effect of residence time to the liquid product compositions. Experiment conducted at pressure of 25 MPa, temperature of 740 °C and concentration of 1.8 wt%

Figure 6-9. The equilibrium composition of gaseous product as a function of concentration at temperature of 740°C at 25 MPa

Figure 6-10. The effect of concentration at pressure of 25 MPa, temperature of 740 °C and residence time of 60 s to the (a) Gas Yield and TOC
(b) Composition of gaseous product and CE

Figure 6-11. The comparison of the main chemical composition of reactor material

Figure 7-1. Chemical structures of feedstock

Figure 7-2. The diagram block of process (a) with heat recovery (b) without heat recovery



1. Introduction

1.1 Background

Due to its high energy density and environmental benignity, hydrogen is considered as a promising future energy source. Nevertheless, there are many barriers to the commercialization of hydrogen as the main energy source, such as competition with other mature technologies, price distortions, and requirements of new infrastructure. There is still a long way to go before the stable state of hydrogen can be established as a clean and renewable energy form. In this situation, some strategies have been formulated to reduce the dependence of fossil fuels and simultaneously create nature-friendly technologies. In the short-term, some strategies would be based on today's combustion engines and infrastructures.¹ The technologies developed are intended to utilize the current infrastructure for efficient hydrogen distributions as well as to use the available engines with marginal modifications. It includes the application of compact onboard reformer system to produce hydrogen from fossil fuel that can be used onboard automobiles.^{2,3} Long-term strategies would focus on the development of electric engines driven by fuel cells, along with the establishment of mature renewable technologies and stabilization of the economy. Hydrogen fuel cells require huge investments for developing new engines, producing hydrogen on a large scale, and constructing hydrogen distribution infrastructure.

Hydrogen is the most abundant element in the universe (up to 75% by

mass of all baryonic matter). However, hydrogen is not found in its free molecular form in a significant quantity. Most of the hydrogen is present in the compound form in water, hydrocarbons, and biomass. Therefore, biological, thermochemical, or electrochemical processes are required to free hydrogen from its compounds. Although biological routes are environment friendly and less energy-intensive than the other methods, BioH₂ is not ready to meet large-scale hydrogen production demands due to several limitations. Typically, the hydrogen production yield from the biological method is considerably lower than that from thermochemical or electrochemical hydrogen production method.⁴ Thus far, the reforming method is the most mature technology.⁵ Typically, the reforming method has considerably higher hydrogen production yields and more feedstocks flexibility. At present, the steam methane reforming (SMR), is the most economical and most widely used process in industries to produce hydrogen.^{4,6,7} Photochemical and thermochemical water splitting is a highly attractive hydrogen production alternative because it is renewable, and carbon dioxide is not emitted. However, the high temperature of thermochemical water splitting (up to 2500°C) causes material issue, high cost and low efficiency.⁵ While the photochemical methods are still limited for practical/large scale due to the needful of suitable photocatalyst and UV light which is account only for 3-4% of solar radiation energy.⁴ It is well-known that high purity hydrogen can be produced by the electrolysis of water. However, low energy efficiency, low yield, and limited production rate are major drawbacks.

The major reforming hydrogen production technologies include steam reforming (SR), partial oxidation (POX) and autothermal reforming (ATR). Although the steam reforming is the most common and well-established method, it is often considered to be unsuitable to develop a compact steam reformer system. Heterogeneous catalysts that are typically used in the steam reforming are often overheated and sintered during the reforming reaction, resulting from limited heat transfer through the reactor wall and low thermal conductivities within the catalyst bed ^{3,8}. In addition, the catalysts are often deactivated by the presence of sulfurous/carbonyl compounds in fuel and coke/tar formation as a typical byproduct of the gasification ². Autothermal reforming (ATR) also requires catalysts, thus unsuitable for the compact reformer system ^{2,5,9,10}. Partial oxidation can be conducted in the absence of catalyst at flame temperatures of 1300-1500 °C and in the presence of catalyst at lower temperature of >800 °C. However, the exothermic nature of the reforming reaction makes it difficult to control the temperature due to the coke formation. Thus, safety and thermal management become major barriers for the partial oxidation to be applied in practical, compact and portable gasification applications ⁵. In addition, the densities of the fluid phase are low due to the low working pressure of autothermal reforming (atmospheric) ¹¹⁻¹³, steam reforming (0.1-3.5 MPa) ¹⁴ and partial oxidation (atmospheric) ¹². As a result, large reactor volume is often required to perform gasification at the same fuel flow rate and the same residence time compared to a system with higher working pressure. Therefore, there are still considerable efforts underway to develop simpler, more compact, and more

efficient techniques that can produce hydrogen for ultimate onboard fuel cell applications.

Supercritical water gasification (SCWG) can be a potential alternative to produce hydrogen from fossil fuels using a compact reforming system. The highly dense, supercritical fluid phase allows to develop a compact reformer system¹⁴. In addition, much higher density of supercritical water than that of steam can result in higher thermal conductivity and specific heat. This is beneficial to carry out endothermic gasification reactions^{9,10}. Due to the single-phase reaction and low mass transfer resistance associated with beneficial physicochemical properties of supercritical water, the reforming reaction can be conducted in a very short residence time (typically less than 1 min)⁹. Thus large amounts of raw materials can be gasified using a compact supercritical water reactor. The dielectric constant of supercritical water is much lower and the number of hydrogen bonding is much smaller than those of the water at ambient condition or steam¹⁵. As a result, typical hydrocarbons can be completely soluble in supercritical water. Produced gases are also miscible in supercritical water condition¹⁵. Therefore, single-phase gasification reaction condition can be performed in supercritical water. This is in sharp contrast with the multi-phase reaction conditions associated with the conventional gasification techniques such as steam reforming and partial oxidation^{16,17}.

Over the last ten years, there has been considerable interest in the use of biomass as a renewable energy source. Many studies have demonstrated that supercritical water is an excellent reaction medium for producing hydrogen from

biomass and its model compounds ^{16, 18-21}. In the presence of homogeneous or heterogeneous catalysts, high hydrogen gas yields, up to the theoretical value, can be achieved. Hydrogen produced from biomass may be used in the future in renewable energy sources. For a seamless transition from a fossil fuel economy to a hydrogen economy, it may be necessary to explore hydrogen production from fossil oil sources. In spite of the advantages of SCWG, only a few studies have focused on hydrogen production from long-chain hydrocarbons (>C₆) using SCWG ²²⁻²⁴. It is more difficult to reform longer-chain hydrocarbons because many competing reactions take place, so, in some case, catalysts are needed to achieve high hydrogen gas yields ^{23, 24}. In such cases, the catalyst deactivation associated with the sulfur compounds present in fossils fuels ²⁵ and coke/tar formation ²⁶ can cause major problems. Development of a noncatalytic SCWG system that can generate high hydrogen gas yields is therefore highly desirable.

1.2 Research Objectives and Approach

The overall goal of this research is to investigate the noncatalytic reforming of various feedstocks, especially the long chain hydrocarbon in supercritical water. To achieve this goal, our research focused on the primary objectives briefly discussed below:

Objective 1: Design the new reactor geometry to achieve the gas-liquid flow rate stability at once improve the hydrogen gas yield. The previous work in our laboratory has been conducted in the vertical tubular reactor

Objective 2: Compare the performance of the gasifier with the previous gasifier (1st generation SCWG) system using the same experimental condition.

Objective 3: Increase the capacity of reactor up to ~6 times bigger to enable the observation at longer residence time and in the same time using different reactor material to enable the observation at higher temperature

Objective 4: Investigate the apparatus performance for the gasification of various liquid type feedstocks (hydrocarbon C₁-C₁₀)

Objective 5: Perform the overall energy efficiency calculation to the gasification system, by considering the heat recovery system.

1.3 Thesis Outline

This thesis is organized according to the following order. **Chapter 2** focuses on the theory and literature review of supercritical water including its advantages and limitation, the different focuses of supercritical water gasification process, chemical reaction, theoretical hydrogen yield and the current status of supercritical water gasification technology. **Chapter 3** describes the experimental details including the apparatus and specification, experimental procedures, analytical methods to analyze the gas-liquid product and the calculation methods to calculate the gas yield. **Chapter 4** explains the background of modification to the reactor geometry, aims and modification results. The performance of the 2nd generation of SCWG is examined with the isooctane gasification as did to the 1st generation SCWG. The effects of

temperature, concentration, residence time and oxidant are investigated. Lastly the results were then compared with the 1st generation SCWG. **Chapter 5** describes the modifications of the apparatus to address the limitation faced by the 2nd generation SCWG. The effect of residence time, concentration and oxidant are investigated at fixed temperature and pressure. In order to examine the reactor performance, it is necessary to compare the result with other work which gasify the same feedstock in supercritical water under similar experiment condition. So far, there is no isooctane reforming studies in supercritical water. The results are then compared with the other reforming methods (SR, ATR, POX) which reform the same feedstock (isooctane). **Chapter 6** addresses the limitation of previous chapter which could not compare the isooctane gasification result with the same reforming methods (SCWG) under similar experiment condition. In this chapter, glucose gasification was investigated as model compound of biomass. The gasification of glucose is widely studied in supercritical water. The effect of residence time, feed concentration and temperature was investigated. Lastly the various feedstocks studies from C₁-C₁₀ are done and the results are summarized in **chapter 7**. The energy efficiency calculation was done in the 3rd generation SCWG. The efficiency of the real experiment results is compared with the theoretical calculation as well as the efficiency with heat recovery and without heat recovery.