Energy Research and Development Division

FINAL PROJECT REPORT

Production of Substituted Natural Gas from the Wet Organic Waste by Utilizing PDU-scale Steam Hydrogasification Process

Prepared for: California Energy Commission

Prepared by: University of California Riverside (CE-CERT)

OCTOBER 2012

CEC-500-2013-104

PREPARED BY:

Primary Author(s):
Chan Seung Park
Joseph M. Norbeck
Wei He
Yoothana Thanmongkhon

University of California, Riverside
CE-CERT
1084 Columbia Avenue
Riverside, CA 92507
951-781-5791
951-781-5790 (fax)
www.ucr.edu

Contract Number: 500-11-004

Prepared for:

California Energy Commission

Rhetta deMesa
Contract Manager

Linda Spiegel
Office Manager
Energy Generation Research Office

Laurie ten Hope
Deputy Director
ENERGY RESEARCH AND DEVELOPMENT DIVISION

Rob Oglesby
Executive Director

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ACKNOWLEDGEMENTS

We acknowledge funding from the California Energy Commission under Contract Number 500-11-004.

PREFACE

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Production of Substituted Natural Gas from the Wet Organic Waste by utilizing PDU-scale Steam Hydrogasification Process is the final report for the project (contract number 500-11-004, conducted by University of California, Riverside. The information from this project contributes to Energy Research and Development Division's Transportation Research Program.

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ABSTRACT

Renewable natural gas has been identified by the California Energy Commission as an important alternative fuel that can contribute to achieving a number of goals set by California related to conventional fuel replacement and emissions reduction in the transportation sector.

The steam hydrogasification reactor developed for this project can produce various forms of energy products from carbonaceous resources in a cost-effective and efficient manner. The objectives of this project were to demonstrate this technology using comingled biosolids and biomass as the feedstock in a bench-scale process demonstration unit and to provide a preliminary modeling evaluation and design for a five tons per day pilot-scale facility.

The process demonstration unit was designed, fabricated and operated in the gasification laboratory at the University of California at Riverside. A water gas shift reactor was integrated with the process demonstration unit to maximize substituted natural gas production. Substituted natural gas production was successfully demonstrated in the process demonstration unit and the proposed technical objectives were achieved during the demonstration.

A preliminary design for a pilot plant was completed. Preliminary process economic analyses were completed for a 3,500 bone dry tonnes per day substituted natural gas plant using biosolids and green waste as feedstock. It was estimated that the substituted natural gas production cost was $4.39 per million British thermal units with an internal rate of return of 16.68 percent under the assumed economic and process parameters. This technology has the potential to enable renewable natural gas production in a commercially viable manner that can contribute toward achieving California's conventional fuel replacement and emissions reduction goals.

Keywords: California Energy Commission, Public Interest Energy Reserach, Renewable Natural Gas, Steam Hydrogasification, Water Gas Shift, Process Demonstration Unit

Please use the following citation for this report:

Park, Chan Seung; Norbeck, Joseph M.; He, Wei; Thanmongkhon Yoothana (University pf California, Riverside). 2012. ***Production of Substituted Natural Gas from the Wet Organic Waste by utilizing PDU-scale Steam Hydrogasification Process.*** California Energy Commission. Publication number: CEC-**500-2013-104.**

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EXECUTIVE SUMMARY

Introduction

Renewable natural gas (RNG) has been identified by the California Energy Commission (CEC) as an important alternative fuel that can contribute to achieving a number of goals set by California related to conventional fuel replacement and emissions reduction in the transportation sector. Specific targets have been identified in policy measures including but not limited to SB 1250 (Perata, Energy: Cost-Effective Energy Efficiency Programs: Renewable Energy Resources, Chapter 512, Statutes of 2006), AB 1007 (Pavley, Alternative Fuels Bill, Chapter 371, Statutes of 2005), the Bioenergy Action Plan, and the Low Carbon Fuels Standard (LCFS).

Renewable natural gas can be produced from carbonaceous and renewable feedstocks through a number of technologies including anaerobic digestion, landfill waste decomposition, gasification and pyrolysis. RNG is often produced from waste matter through anaerobic digestion and feedstock decomposition. These methods are often inefficient and the product gas quality is very inferior to natural gas produced from fossil sources. Thermochemical pathways such as gasification and pyrolysis offer high conversion efficiencies while generating a superior quality product gas. However, conventional thermochemical processes such as partial oxidation are not suitable for RNG production due to the high capital and operating costs associated with the technologies. Compared to fossil fuel production projects, RNG production is by nature limited to small- to medium-scale projects due to the limited concentration of feedstocks at a single location or by the gas production capability of landfills. Projects that use conventional thermochemical process for RNG production lack economic viability due to the high costs.

The steam hydrogasification reactor (SHR) developed at the University of California at Riverside (UCR) can produce various forms of energy products from carbonaceous resources in a cost-effective and efficient manner. This technology can handle wet feedstock without drying, does not require expensive oxygen plants, and operates at relatively lower temperatures compared to conventional gasification processes. Each of these properties offers an advantage compared to other thermochemical gasification processes and demonstrations have shown that SHR is the most efficient and economic process compared to other existing technologies.

Project Purpose

The objectives of this project were to demonstrate SHR technology using comingled biosolids and biomass as the feedstock in a bench-scale process demonstration unit (PDU) and to provide a preliminary modeling evaluation and design for a five tons per day pilot-scale facility.

Project Results

The PDU was designed, fabricated and operated in the gasification laboratory at UCR. A water gas shift (WGS) reactor was integrated with the PDU to maximize substituted natural gas (SNG) production. SNG production was demonstrated in the PDU and the proposed technical objectives were achieved during the demonstration.

A preliminary design for a five tons per day pilot plant was completed. Preliminary process economic analyses were completed for a 3,500 bone dry tonnes (BDT) per day SNG plant using biosolids and green waste as feedstock. It was estimated that the SNG production cost was $4.39 per million British thermal units (MMBtu) with an internal rate of return (IRR) of 16.68 percent under the assumed economic and process parameters. Feedstock costs and feedstock delivery costs were not taken into consideration and the economic results should be considered highly uncertain at this time. Nevertheless, this initial economic analysis provided considerable confidence for moving forward with the pilot plant design and evaluation.

Project Benefits

This technology has the potential to enable RNG production in a commercially viable manner to contribute to achieving California's conventional fuel replacement and emission reduction goals.

CHAPTER 1: Introduction

California must produce nearly 2.4 billion gasoline gallon equivalents per year of alternative transportation fuels by 2017 in order to meet the petroleum reduction objectives set under the Moderate Case scenario of the State Alternative Fuels Plan – AB 1007. Currently, California imports more than 95 percent of the biofuels used in-state. Ramping up in-state biofuel production without competing with existing cropland will be difficult unless other non-crop biomass resources can be used. A recent California biomass availability assessment found that California generates approximately 83 million dry tons of biomass waste per year creating various unresolved waste disposal issues for agricultural and forest biomass residue streams, and large volumes of biosolids resulting from wastewater treatment facilities. Studies show that 32.1 million dry tons of biomass from agricultural residues are available every year for fuel production when sustainability and harvesting efficiency factors are considered. Further research and development is required to establish commercially-viable waste-to-energy conversion technologies that can simultaneously contribute supplies of renewable transportation fuels and transform waste materials into renewable transportation fuels.

Wet organic waste such as biosolids, food wastes and green/vegetation waste are important sources of renewable carbon that are under- utilized in the production of biofuels. Currently, most of these wastes are landfilled. The fraction of these wastes generated in California has increased from 23 percent (2004) to 26 percent (2008) and is expected to increase more so in the future. These types of wastes tend to have more environmental issues associated with proper disposal compared to other types of the waste. Typically, these waste streams do not lend themselves as feedstock for large capacity commercial facilities because the quantities needed are seldom available within a reasonable transportation distance. Technologies used to process these waste streams must be commercially viable in smaller scales and also be able to accommodate the diverse nature of local feedstocks including ones with high moisture content.

RNG has the potential to make a significant contribution as a transportation fuel and help the State of California achieve stated fossil fuel replacement and emissions reduction goals in the transportation sector. However, conventional thermochemical processes such as partial oxidation are not suitable for RNG production due to the high capital and operating costs associated with the technologies.

This final report presents the results associated with the development of a promising new waste-to-energy technology known as the Steam Hydrogasification Reaction (SHR) process to produce RNG. SHR process has been demonstrated successfully for the production of clean syngas at the Process Demonstration Unit (PDU) scale with support from the Public Interest Energy Research (PIER) program of the California Energy Commission (CEC).

The PDU was designed, fabricated and operated in the gasification laboratory at UCR for the project. A Water Gas Shift (WGS) reactor was integrated to the PDU to maximize the SNG

production. SNG production was successfully demonstrated in the PDU and the proposed technical objectives were achieved during the demonstration.

CHAPTER 2:
Project Deliverables

2.1 Goals of agreement

The goals of the research project are to:

- Demonstrate and validate the feedstock pretreatment system to produce a pumpable slurry from the comingled biomass/ biosolids, food waste and green waste that will be used in the SHR process, achieving a feedstock supply rate of 0.1 ton per day (10 pounds per hour) for 24 hours of continuous operation. (Task 2)

- Demonstrate and validate the production of SNG with SHR integrated with WGS process from the pretreated feedstock mentioned above. The throughput will be 0.1 ton per day (10 pounds per hour) of feedstock. (Task 3)

- Complete the basic engineering design for a 5 tons/day scale pilot plant using key information obtained through the PDU demonstration including the comparative life cycle energy production cost between different technologies to producing SNG from wet organic wastes. (Task 4)

- Complete the feasibility study of algae feedstock for SHR process and new zeolite encapsulated Fischer-Tropsch (FT) catalyst for synthetic gasoline production. (Task 5)

2.2 Technical Performance Objectives

The objectives of the project are to:

- Validate the performance and product quality of the feed pretreatment process of the PDU under the optimum conditions. (Task 2)

  The target specifications for the product composition are:

  a) Rheological Properties
     - Solid loading of the slurry > 30%
     - Viscosity < 1 centi P

  b) Material Loss
     - CO_2: < 10 Vol%
     - C_1-C_6: < 500 ppmv

- Validate the production and quality of SNG from the SHR-WGS integrated process of the PDU under the optimum operating conditions. (Task 3)

  The target specifications for the producer gas composition are:

a) Producer Gas Yield and Energy Content
   - MMBtu/hr of SNG from 1 ton per day of raw food waste.

b) Producer Gas Composition - dry basis (pre clean-up), H_2-free basis
   - CO: 5-20 Vol%
   - CH_4: 60-80 Vol%
   - CO_2: < 25 Vol%
   - Tars: < 3 mg/m3
   - Sulfur: < 150 ppmv
   - NH_3: < 0.05 Vol%

- Develop the basic engineering design of the 5 tons per day pilot plant to be sited at the wastewater treatment facility in Riverside, California or at another city site if determined later during the project phase of the program. This basic engineering design of the pilot plant will allow both technical and economic feasibility analysis of a commercial scale process. The design of the pilot plant shall contain the following deliverables. (Task 4)

  - Block Flow Diagram
  - Process & Utility Flow Diagrams
  - Heat & Mass Balances
  - Plant Layouts & Equipment Arrangement Plan
  - Equipment, Vessel Specification / List -Long Lead Item List
  - Estimated Project Cost

- Complete the comparison life cycle energy production cost between different technologies to producing SNG from wet organic wastes. The result shall contain the following deliverables.

  - Process Higher Heating Value (HHV) efficiency
  - Process Flow Diagram with Mass Balance
  - Production cost as $/ MMBtu

- Complete the feasibility study of algae feedstock for SHR process. The feasibility study shall contain the following deliverables. (Task 5)

  - Laboratory scale test result of algae SHR tests including carbon balance and product analysis.
  - Preliminary estimation of process economics for algae to biofuel pathway.

- Complete the feasibility study of new zeolite encapsulated FT catalyst for synthetic gasoline production. The feasibility study shall contain the following deliverables. (Task 5)

- Laboratory scale test result including analysis of synthetic gasoline produced.
- Preliminary estimation of process economics for synthetic gasoline production.

2.3 Deliverables of Technical Tasks

Table 2-1 identifies sections in the report where the performance and outcomes of project deliverables relating to the technical tasks of the contract are described in further detail.

Table 2-1: Project deliverables and related section in the report

Task #	Deliverables	Section in this Report
2	• Pretreatment Process Test Plan • Optimum Process Conditions Report • Pretreatment Process Test Report	Section 3.2 Section 3.3 Section 3.4
3	• PDU Demonstration Test Plan • WGS Detailed Design Flow sheet • Process Mass and Energy Balance Report • Process Performance Results Report	Section 4.2 Section 4.3 Section 4.4 Section 4.5
4	• Pilot Plant Design Report • Block Flow Diagram • Process & Utility Flow Diagrams • Life Cycle Comparison Report	Section 5.1 Section 5.2 Section 5.3 Section 5.4
5	• Algae Feedstock Study Results Report • Gasoline Production Study Results Report	Section 6.1 Section 6.2

CHAPTER 3:
Feedstock Preparation

3.1 Process Description

Previous research reveals that the feeding of biomass feedstock, such as wood wastes and biosolids, into a pressurized reactor poses technical challenges. Conventional methods of feeding materials into a pressurized gasifier, such as screw feed and locker hoper, are unreliable and operationally expensive. To handle and transport biomass feedstocks in a cost and energy efficient manner, a pumpable slurry of biomass feedstocks with high energy and carbon content is much more favorable. Additionally, the high moisture content in biomass also favors a wet feeding method. Biomass slurries are not formed by simply mixing the wood wastes and biosolids. There are two reasons for this: 1) the low energy and carbon content in wood wastes and biosolids, and 2) the hygroscopic and hydrophilic nature of wood wastes. In order to prepare pumpable wood wastes and biosolids slurries with high energy and carbon content, a pre-processing step has to be implemented. This has been achieved by using a Hydrothermal Pretreatment (HTP) process developed by our research group.

The HTP system assembly, shown in Figure 3-1, will be operated in the stirred batch configuration. The hydrothermal reactor with temperature and pressure transducer, controller, 3 zone electric heater, serpentine cooling coil, and coolant recycling system were designed by our research team and fabricated by Parr Instrument Company. The system controller box, magnetic stirrer with electric motor and the pneumatic lift support frame were designed and fabricated by Parr Instrument Company.

The hydrothermal reactor is made of 316-stainless steel. This material was chosen because of its high nickel and molybdenum concentration and the resultant corrosive resistance to sulfuric, phosphoric, and acetic acids. Preliminary test results from a mini batch HTP reactor showed slight acidity of the slurry products (pH of 3 to 4), which is mainly due to acetic acid produced from the wood wastes and biosolids. The hydrothermal reactor has a volumetric capacity of 5 gallons. A magnetic stirrer which is powered by an electric motor is implemented to rotate the agitator inside. The reactor is heated by a 3 zone electric heater jacket, as shown in Figure 3-1. A serpentine cooling coil with a coolant circulating system is implemented to transfer heat out of the hydrothermal reactor, as shown in Figure 3-2. The hydrothermal reactor assembly was installed in the College of Engineering – Center for Environmental Research Technology (CE-CERT) gasification laboratory with calibration gas, coolant supply and power cord installation. A computer assisted control system with remote control software, provided by Parr Instruments, was connected to the hydrothermal slave box controller. Further details of the HTP system description can be found in the previous project report submitted to PIER[1].

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[1] ***Development of Steam Hydrogasification Process Demonstration Unit-5 lb/hr PDU Design Report.*** Submitted to PIER, Feb. 2012 PIER contract number: **500-09-008**.

Figure 3-1: Hydrothermal Reactor Design

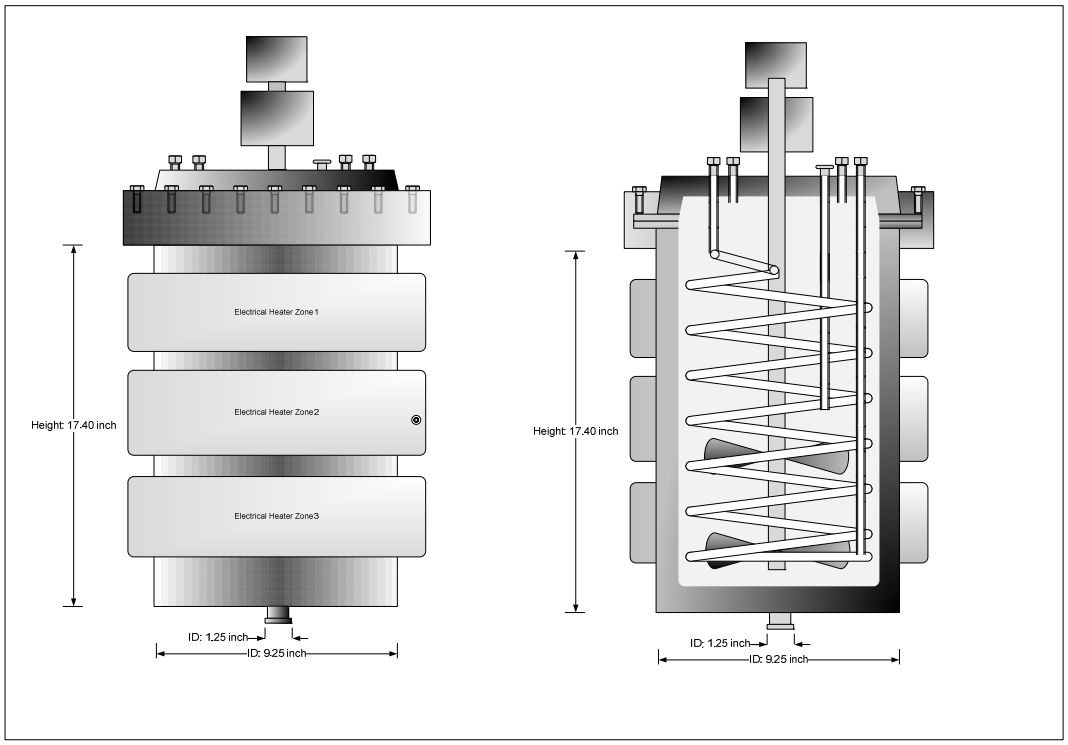
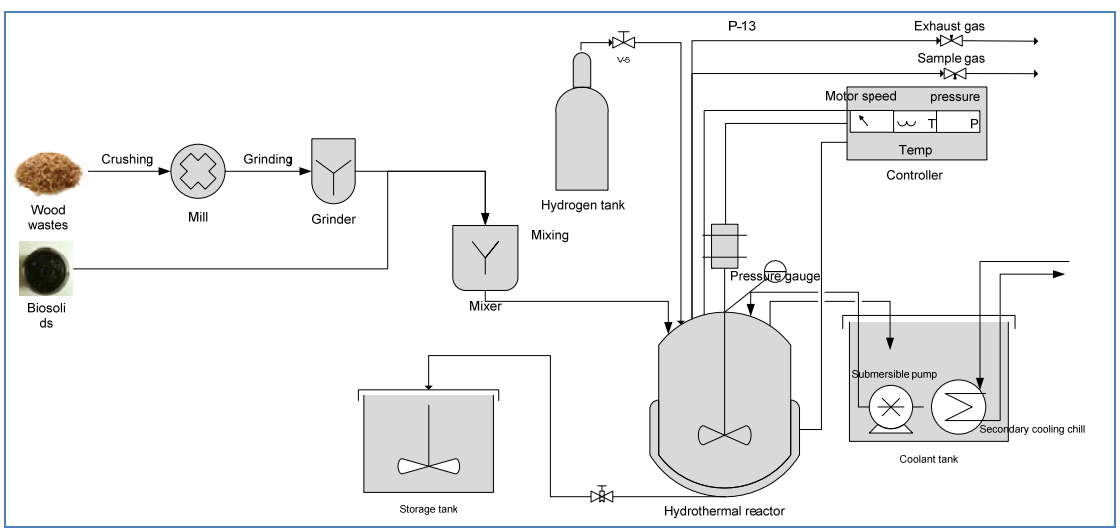


Figure 3-2: Flow sheet of CE-CERT Hydrothermal Pretreatment (HTP)



3.2 Pretreatment Process Test Plan

3.2.1 Preparation of Biomass Wastes and Biosolids

Biomass feedstock is prepared from pine wood sawdust. The pine wood is initially crushed in a laboratory mill (Thomas–Willey model 4, Arthur H. Thomas Company) to reduce its particle

size. Then the crushed wood particles are pulverized in a grinder (Braun KSM-2W). The pulverized particles are then sieved into three particle size ranges: 75μm-90μm, 150μm-180μm and 355μm-425μm. The particles with certain particle size range are then dried in a vacuum oven at 70C for 3 hours for vaporization of the inherent moisture. Dissolved Air Floatation Thickener (DAFT: discharged from the Wastewater Treatment Plant, Riverside, CA) is used as a representative of biosolids. It is expected that the chemical compositions of biosolids vary among treatment plants and, to a limited extent, within the same plant over time. Proximate and ultimate analyses are carried for the pine wood and two biosolids samples collected in spring and summer season from Riverside wastewater treatment plant as shown in Table 3-1. It is observed that the seasonal change of the chemical composition of biosolids is insignificant. The biosolids sample #1 is used to represent biosolids in this task.

Table 3-1: Results of Proximate and Ultimate Analysis on Pine wood and Biosolids

Analysis	Compound	Pine wood	Biosolids Sample #1 [a]	Biosolids Sample #2 [b]
		Weight %		
Proximate Analysis	Moisture, M	5.65	94.8	95.2
	Volatile Matter, VM	81.52	3.65	3.45
	Fixed Carbon, FC	12.58	0.44	0.36
	Ash	0.26	1.11	0.99
	Higher Heating Value, HHV (Btu/lb)	8093	N/A	N/A
Ultimate (Dry Basis) Analysis	C	47.56	40.80	40.93
	H	6.31	6.22	6.69
	O [c]	45.81	23.12	23.02
	N	0.05	7.47	7.66
	S	0.01	1.04	1.07

Biosolids sample collected in a) Jul. 2008, b) in Feb. 2009 from Riverside WWT plant, c) by difference

3.2.2 HTP of Comingled Wood Wastes and Biosolids

A batch type reaction vessel made of Inconel is used as a hydrothermal reactor in the HTP process. The reactor is heated by an electrical heater. The heating rate is measured to be 20°C/min. The initial headspace gas in the reactor is hydrogen. Then the reactor is heated up to a desired temperature and is kept at that temperature for 30 minutes. After the HTP, the reactor is convectively cooled down by forcing compressed air. A cooling rate of 42.5°C/min is achieved by using the experimental setup. When the temperature in the reactor reaches room temperature, exhaust gas is collected in a Tedler bag and slurry is collected and sealed in glass jars. The pressure in the reactor reaches 1420psi when temperature approached 240°C, due to the increase of the partial pressure of water by the vaporization in the reactor headspace.

A series of experiments are performed to investigate the impact of experimental conditions on the carbon redistribution in the resultant products, such as gas, liquid and solid fractions. The impact of initial mass ratio of biomass to biosolids on the carbon redistribution is tested. In such tests, the prepared wood particles in the particle size of 150μm-180μm are mixed with biosolids to a weight ratio of 1:3, 1:2 and 1:1.5, and then are hydrothermally treated at a temperature of 240°C. The initial carbon to water ratio in such comingled mixtures were 1:5, 1:3.5 and 1:2 respectively. The impact of initial wood particle sizes on the carbon redistribution is also analyzed. In such tests, the prepared wood particles with particle sizes of 75μm-90μm, 355μm-425μm and 1.18mm-1.4mm were mixed with biosolids to a weight ratio of 1:1.5, and then are hydrothermally treated at a temperature of 240°C. Moreover, the comingled wood wastes and biosolids mixture with an initial wood particle size of 150μm-180μm, and an initial wood wastes to biosolids weight ratio of 1:1.5 is hydrothermally pretreated under temperatures of 180˚C, 210˚C and 240˚C to investigate the impact of pretreatment temperature on the carbon redistribution in the resultant products after HTP.

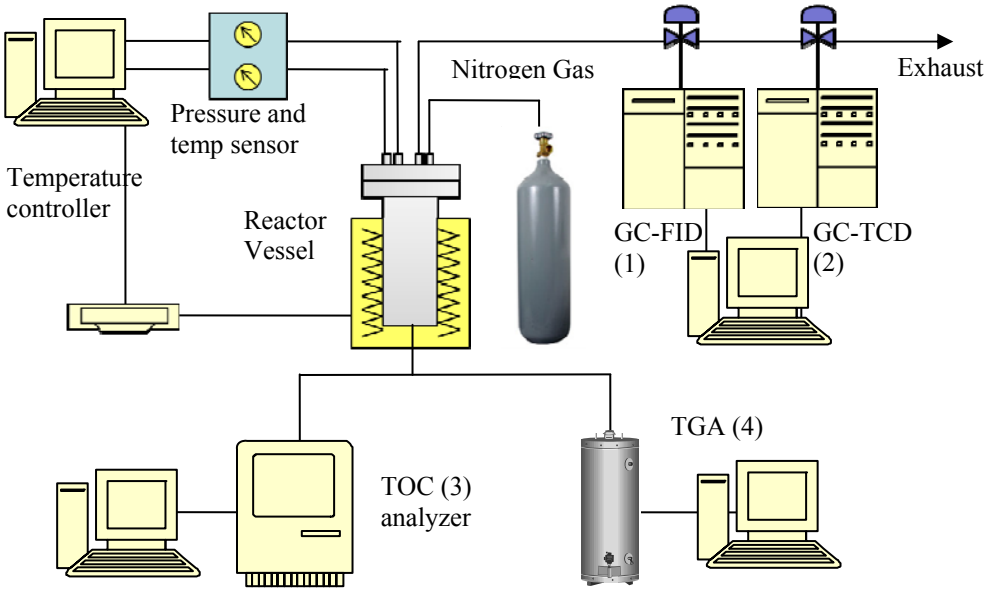
3.3 Optimum Process Conditions Report

3.3.1 Experimental

Gaseous product after the HTP was sampled in a Tedler bag and analyzed of its carbon composition and concentration by a Hewlett Packard 5890 series II Gas Chromatography (GC) equipped with Flame Ionization Detector (FID, 1) and Thermal Conductivity Detector (TCD, 2). The hydrocarbon (C_xH_y) and carbon oxide (CO and CO_2) concentrations in the gas phase were obtained, respectively. Resultant slurries after HTP were separated of their liquid and solid fraction by using a vacuum filtration. The liquid fraction was then tested of its organic and inorganic carbon concentrations by using a Shimadzu TOC-5050 Total Organic Carbon (TOC, 3) analyzer. The solid fraction was dried and analyzed by Thermogravimetric Analyzer (TGA, 4) to determine the volatile compound, fixed carbon and ash compositions. The block diagram of the experimental setup implemented in this study is shown in Figure 3-3.

Figure 3-3: Experimental Setup of Lab Scale HTP with Products Analysis System

(Numbers in the parenthesis denote the corresponding captions in the text.)



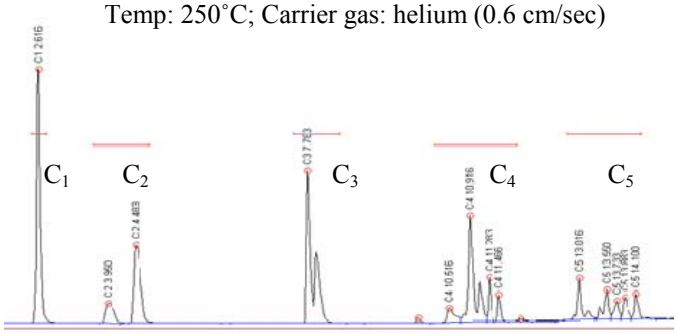
3.3.2 Carbon in the gas phase after HTP

Hydrocarbons with a carbon number less than six were detected in the gas phase after HTP. It is believed that hydrocarbons with a carbon number over six condensed in liquid phase when the reactor was cooled down to room temperature. Carbon oxides were also detected in the gas phase. Figure 3-4 shows gas analysis results of a typical HTP process. The process conditions for this HTP for biosolids to biomass ratio of 3:1 were at a temperature of 240°C with the biomass particle size of 150μm-180μm. Explicit intervals between groups of peaks were observed in the GC-FID results, as shown in Figure 3-4(b). Since C_xH_y was detected sequentially by its carbon numbers, carbon species were then categorized into groups based on their carbon numbers. And carbon concentration in the gas phase was then calculated by its carbon numbers timed with the concentrations of carbon species.

Figure 3-4: Typical a) GC-TCD and b) GC-FID analysis results of gas phase after HTP

(a) Column: ALLTECH 8100/2, Oven temp: 30 ˚C for 10 min; Inj./Det. Temp: 260˚C; Carrier gas: helium (0.3 cm/sec)

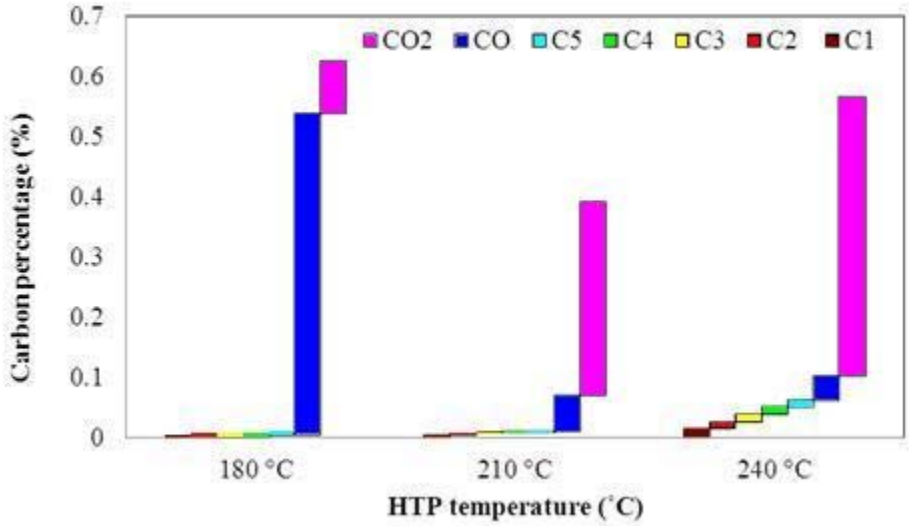
(b) Column: RT-QPLOT (cat.# 19718), Oven temp: 50 ˚C (2min) to 220 ˚C @ 15 ˚C /min; Inj./Det. Temp: 250˚C; Carrier gas: helium (0.6 cm/sec)



The effect of pretreatment temperature on the carbon compositions in the gas phase after HTP was evaluated and results are shown in Figure 3-5. Carbon percentage was used to exhibit how much carbon presented in each carbon species, and it was defined in the equation below:

$$Carbon\ Percentage = \frac{Carbon\ mole\ in\ Each\ Species}{Total\ Carbon\ mole\ in\ the\ feedstocks} \times 100\%$$

Figure 3-5: Effect of temperature on carbon percentages in the gas phase after HTP



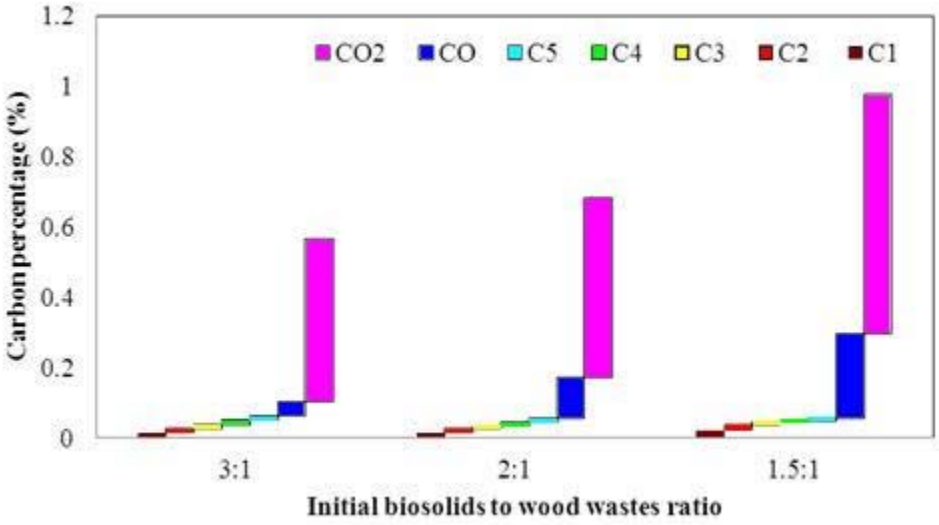
A noticeable increase of C_xH_y concentrations was observed when pretreatment temperature reached 240°C. But the total carbon percentage presented in the gas phase in the form of C_xH_y was less than 0.07 percent. Major carbon species in the gas after HTP was CO when pretreatment was performed at 180°C. As pretreatment temperature increased, CO concentration decreased while CO_2 concentration increased and became a major product. The total carbon percentage in the gas phase was less than 0.7 percent after the HTP. It is believed that low temperature catalytic Water Gas Shift (WGS) reaction occurred when temperature exceeded 210°C, through a reaction shown below [16], which led to the conversion of CO to CO_2.

$$CO + H_2O \leftrightarrow CO_2 + H_2$$

Additional analysis of H_2 concentration in the product gas after HTP showed a production of H_2, which also supported the assumptions made above.

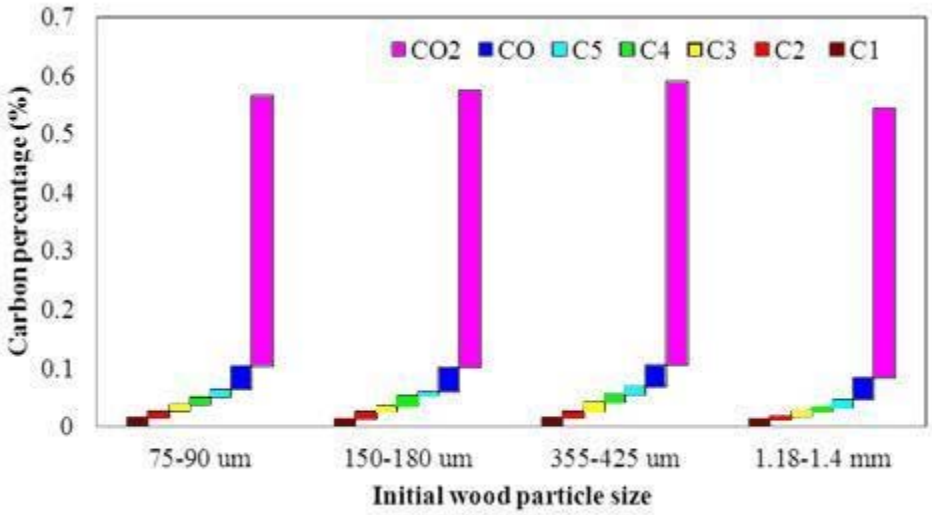
Carbon percentage in the gas phase was also evaluated on varying the initial biosolids to wood wastes mass ratios. These experiments were carried out with an initial wood particle size of 150μm-180μm, and the pretreatment temperature was set at 240°C. The results are shown in Figure 3-6. It was observed that with an increase of wood wastes to biosolids ratios in the feedstocks, more CO and CO_2 were produced, and C_xH_y concentrations in the gas phase had insignificant change. It was believed that with an increase of wood wastes in the feedstocks, more carbon was available for chemical conversions as was shown in Table 3-1. Figure 3-6 also showed that with an initial biosolids to wood wastes ratio of 1.5:1, less than 1.2 percent of carbon was present in the gas phase.

Figure 3-6: Effect of initial biosolids to wood wastes ratios on carbon percentages in the gas phase after HTP



The effect of initial wood particle size on carbon percentages in the gas phase after HTP was also evaluated. Effect of initial wood particle size on the carbon percentages in the gas phase after HTP, was shown in Figure 3-7.

Figure 3-7: Effect of initial wood particle sizes on carbon percentages in the gas phase after HTP

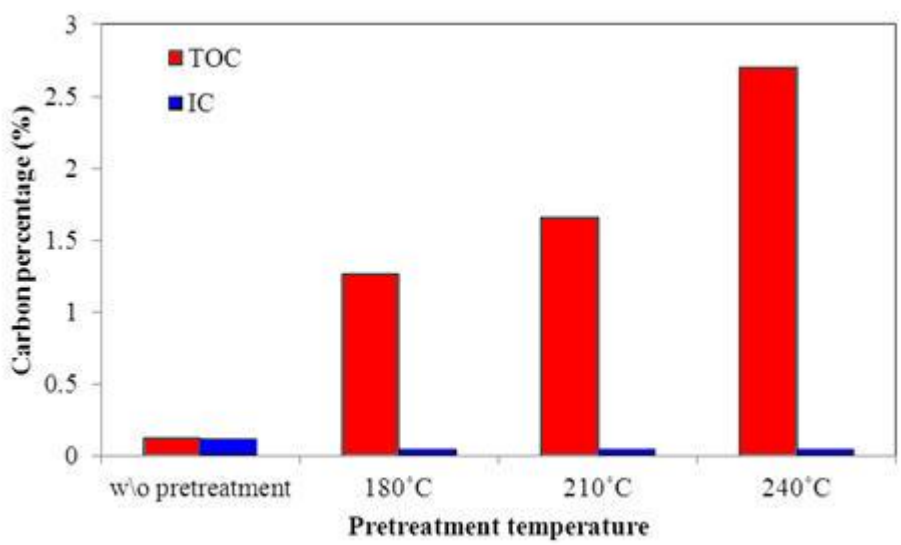


3.3.3 Carbon in the liquid phase after HTP

Liquid in pretreated slurries included two parts: free bulk liquid and inherent moisture. Liquid in the bulk phase was defined as the liquid that could be separated from slurries by mechanic force, such as vacuum filtration. Inherent moisture was the liquid that was trapped in the microstructure of solids, and it could be measured by TGA. In this study, it was assumed that carbon compositions were identical in the two liquid forms. The organic and inorganic carbon fractions in the free bulk liquid were measured by using TOC analyzer. And carbon percentage in the liquid phase included carbon in both liquid forms.

The effect of temperature on carbon percentages in the liquid phase after HTP was evaluated. The results are shown in Figure 3-8. It was observed that less than 0.2 percent of carbon exhibited in liquid before HTP, which was the carbon dissolved in biosolids. Inorganic carbon in the liquid phase was consumed when HTP was applied. It was also observed that with an increase of pretreatment temperature, more carbon exhibited in liquid phase. Over 95 percent of carbon presented in the liquid phase was in the form of organic carbon. And the total carbon percentage presented in the liquid phase after HTP was less than 3 percent of the total carbon initial loaded in the feedstocks.

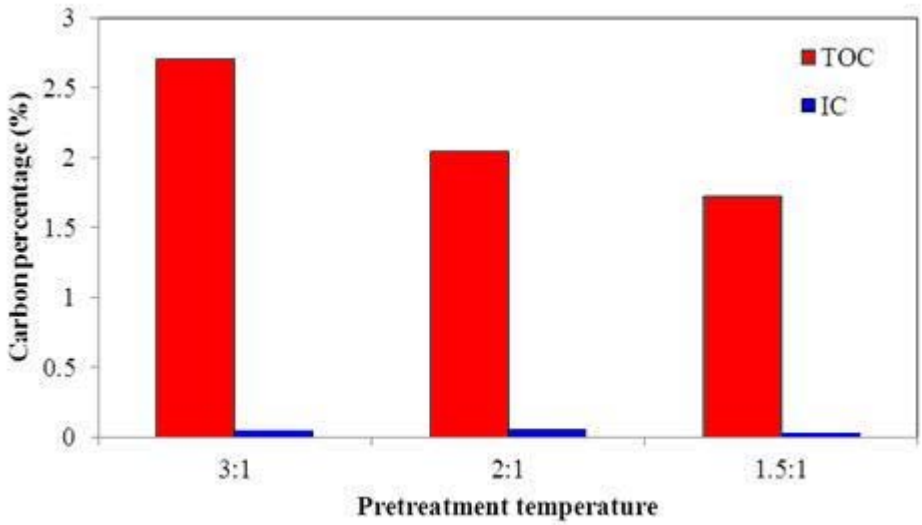
Figure 3-8: Effect of temperature on carbon percentages in the liquid phase after HTP



The effect of initial biosolids to wood wastes ratios on carbon percentage in the liquid phase after HTP was also evaluated. Results are shown in Figure 3-9. Even though higher organic and inorganic carbon concentrations were detected in the liquid phase with a higher initial wood wastes loading as more carbon was initially loaded, the carbon percentage in the liquid phase decreased with an increase of initial wood wastes to biosolids ratio.

The effect of initial wood particle size on carbon percentages on the liquid phase after HTP was also evaluated. It was found the initial wood particle size has insignificant effect on the carbon percentages in the liquid phase after HTP.

Figure 3-9: Effect of initial biosolids to wood wastes ratios on carbon percentages in the liquid phase after HTP



3.4 Pretreatment Process Test Report

3.4.1 HTP Process Performance for the comingled wood wastes and biosolids

Conversion efficiency through the carbon redistribution in the gas, liquid and solid phase was calculated. The results are shown in Table 3-2. It can be concluded that over 96 percent of carbon in the original feedstock was conserved in the solid phase after HTP process. The most of carbon fractions were conserved in the solid phase.

Table 3-2: Carbon redistribution in gas, liquid and solid phase after HTP of comingled wood wastes and biosolids

	Initial biosolids to wood wastes ratio					
	3:1				2:1	1.5:1
	Pretreatment temperature					
	w\o pretreatment	180˚C	210˚C	240˚C		
Carbon percentage in gas (%)	0	0.62	0.39	0.56	0.68	0.98
Carbon percentage in liquid (%)	0.24	1.31	1.70	2.74	2.10	1.76
Carbon percentage in solid (%)	99.76	98.07	97.91	96.7	97.22	97.26
Total (%)	100	100	100	100	100	100

Hydrothermal Pretreatment was performed on producing a pumpable comingled wood wastes and biosolids slurry. Carbon redistribution in the gas, liquid and solid phase after the HTP was evaluated. Results showed that pretreatment temperature had a major effect on carbon redistribution. With increased pretreatment temperature, more CO_2 was produced and less CO was produced in the gas phase. Loss of carbon content in the products was less than 1.0 percent of original carbon loading. Analysis of liquid product showed that over 95 percent of carbon presents in liquid phase was organic carbon. And overall carbon distributed in liquid phase was lower than 2.8 percent of initial carbon loading. Analysis of solid phase showed around 20 percent increase of fixed carbon by HTP. And carbon recovery in solid phase after HTP was over 96 percent. The HTP process produced the slurry form of biomass and biosolids for the application to gasification by increasing the physical properties favorably. And these results meet the target properties defined in the technical objectives of the project. (Section 2.2, page 13)

CHAPTER 4:
PDU Scale Demonstration of SNG Production

4.1 Process Description

4.1.1 Introduction

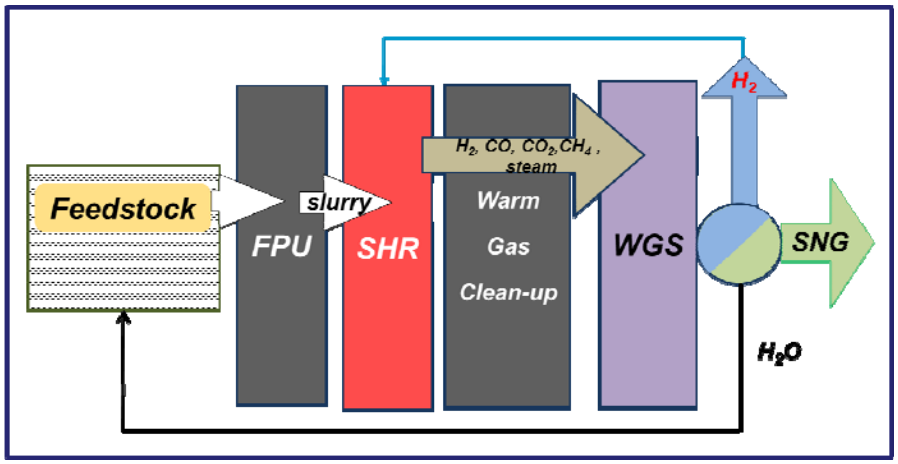
SHR is the hydrogasification reaction carried out in the presence of steam. It has been reported that the presence of steam enhances the rate of methane formation compared to conventional dry hydrogasification. The hydrogen necessary for the SHR is generated internally and is recycled back to the SHR reactor. So there is no need for an external hydrogen supply. The SHR step produces a methane rich gas with a high concentration of steam. The SHR step is followed by the Water Gas Shift (WGS) step to produce Substitute Natural Gas (SNG). It is important to note that the WGS step requires high temperature steam as a feedstock. Thus, there is no need to remove the steam from the SHR product gas stream. Figure 4-1 shows the block flow diagram of the overall process with Feedstock Pretreatment Process (FPU) which was detailed in the chapter 3 of the report.

The major benefit of the process can be summarized as follows:

- The utilization of water in the feedstock is one of the most unique features of the process. Feedstocks with high moisture content such as food waste, biosolids or biomass can be easily utilized without the feedstock drying procedure that is required with other dry feed technologies.
- The process does not require external gasifying reactant such as oxygen or steam. This will dramatically not only simplify the process but also reduce the capital cost of the process.

The overall net process efficiency as shown in the Figure 4-1 is estimated as 62 percent (for SNG). The net process efficiency is defined as the ratio between the Higher Heating Value (HHV) of the product gas and HHV of the feedstock.

Figure 4-1: Block Flow Diagram of SHR-WGS process system to produce the SNG



4.2 PDU Demonstration Test Plan

4.2.1 Overview of Test Plan

- Producer gas, contained H_2, CH_4, CO and CO_2, generated by a SHR using biosolids comingled with woody biomass as feedstock was simulated by Aspen plus software.

- A laboratory scale of continuous WGS reactor system was set up to optimize the process condition. Critical condition was to achieve the production of sufficient hydrogen for the recycle as a feed for the SHR process.

- Parameters obtained from the above results were used to design the PDU scale WGS reactor, which is connected to PDU scale SHR. Demonstration of SNG production SHR-WGS system will be followed.

- The data from the PDU demonstration is utilized for the pilot scale process design, life cycle process analysis and process economics analysis.

4.2.2 Design of SHR reactor

The project team chose the fluidized bed reactor in a bubbling-slugging-fluidizing regime as the reactor for the PDU scale SHR process. In addition to their long history of being used as chemical process reactors and high heat transport rates, bubbling beds are also well-known for their reliability when used with biomass gasification. Residence time of the reactor is expected to be over 10 seconds. Longer residence time is favored because of slower gasification rate compared to partial oxidation reaction.

There are four parts in the reactor system: a fluidized bed reactor where the main chemical reaction occurs, a distributor that controls the gas inlet, a cyclone to collect sands that are taken out of the reactor by gas flow and a gas chamber.

Nominal reactor temperature of 750°C and pressure of 400 Pisa in the atmosphere of hydrogen and steam were chosen for the design basis. Silica sand provided by U.S Silica Company was used as inertia material in the fluidized bed. Other important physical properties are listed in Table 4-1 and Table 4-2. Sand is assumed to be uniformly spherical.

Table 4-1: Physical properties of silica sand in fluidized reactor

Diameter (μm)	Density (g/cm^3)
150	2.65

Table 4-2: Physical properties of hydrogen gas flow in fluidized reactor

Temperature (°C)	Pressure (atm)	Density (g/cm^3)	Viscosity (N-s/m^3)
750	10.2	2.43E-4	1.90E-5

Symbols used in fluidized bed calculation is summarized below

U_{mf}	minimum fluidization velocity
U_{ms}	minimum slugging velocity
U_t	terminal fluidization velocity
U	fluidization velocity
Re	Reynolds number
Ar	Archimedes number
d_p	solid particle diameter
D	reactor inner diameter
D_B	fluidization bubble diameter
ρ_g	gas density
ρ_s	solid density
μ	gas viscosity
H_L	critical slugging bed height
H_{mf}	minimum fluidization bed height
H_0	minimum bed height
H_{max}	maximum bed height under fluidization velocity U
TDH	Transport disengagement height
R_s	ideal bed height

Reactor Dimension

The reactor is 14 feet in height with an outer diameter of 10.0 cm and an inner diameter of 9.40cm. Calculation of fluidized bed height and gas velocity as well as some other important parameters is listed as follows:

Minimum fluidization velocity (U_{mf})

U_{mf} is the minimum gas velocity that can support the particles in the reactor. Reynolds number and Archimedes number are involved in the calculation of U_{mf} (Wen and Yu).

$$Re_{mf} = [(33.7)^2 + 0.0400Ar]^{1/2} - 33.7 \qquad (3\text{-}1)$$

$$Ar = \frac{d_p^3 \cdot \rho_g \cdot (\rho_s - \rho_g) \cdot g}{\mu^2} \qquad (3\text{-}2)$$

$$Re_{mf} = \frac{U_{mf} \cdot \rho_f \cdot d_p}{\mu_g} \qquad (3\text{-}3)$$

Thus we can obtain the value of U_{mf} through Eq. (3-3). Here U_{mf} = 0.019m/s.

Minimum slugging velocity (U_{ms})

U_{ms} is the minimum superficial gas velocity for a slugging bed. As the size of bubbles grows, the wall of the reactor is playing greater roles on fluidization. Transition from a bubbling bed to a slugging bed begins when the bubble diameter reaches the reactor diameter. We use Ums as the upper limit for fluidization velocity in our design. According to Baeyens and Geldart, if the bed height is lower than the critical bed height $H_L=1.3D^{0.175}$ (3-4) where bubble coalescence is complete,

$$U_{ms}=U_{mf}+0.07\sqrt{gD}+0.16(H_L-H_{mf})^2 \qquad (3\text{-}5)$$

If the bed height exceeds H_L then

$$U_{ms}=U_{mf}+0.07\cdot\sqrt{gD} \qquad (3\text{-}6)$$

U_{ms} is the gas velocity at the transition to a slugging bed, which is the desired fluidization gas flow rate. Since longer residence time is preferred, we use Eq. (3-6) of the deeper bed model. Thus U_{ms} = 0.086m/s.

Terminal velocity (U_t)

Terminal velocity is the maximum superficial gas velocity and it is also based on physical properties of sand and gas in the reactor (Souza - Santos). U_t is an important reference in fluidized bed design.

$$U_t = d_p \cdot \left[\frac{4\cdot(\rho_s-\rho_f)^2\cdot g^2}{225\cdot\rho_f\mu}\right]^{1/3} \quad (3\text{-}7)$$

U_t = 2.06m/s.

Transport disengagement height (TDH)

TDH is the vessel height required for disengaging larger particles from further upward movement.

TDH = $9.55Ar^{-0.56}Re^{0.75}$ (unit: m) (3-8)

Ideal height = Rs ≧(bed height+TDH)×1.2 [2] (3-9)

TDH = 0.08m. If ideal height is assumed to be 4.27m (total height of the reactor), H≦3.48m.

Maximum slugging bed height

According to Davidson and Harrison,

$$\frac{0.711(gD_s)^{\frac{1}{2}}}{U-U_0} = \frac{H_0}{H-H_0} \quad (3\text{-}10)$$

This could be rearranged into

$$\frac{H_{max}}{H_0} = 1 + \frac{U-U_0}{0.35\sqrt{gD}} \quad (3\text{-}11)$$

This is the ratio of maximum slugging bed height and origin bed height. Assuming that H_{max}=4.27m at $U=U_{ms}$, H_{max}/H_0=1.20, H_0 = 3.56m. But according to Eq. (3-9), bed height should be less than 3.48m. So we choose 3.48m as the final bed height design.

Summary

Table 4-3 summarizes the final results of the SHR design parameter used in this task.

Table 4-3: Fluidized bed reactor design summary

Reactor inner diameter (cm)	Reactor total height (m)	Sand size (micron)	Bed height (m)	Bed pressure (atm)	Temperature (°C)	Gas velocity (m/s)
9.40	4.27	150	3.48	10.2	750	0.019-0.086

4.2.3 Mockup test

Mock up test set up

The mock up test is to examine the fluidization performance and the viability of the PDU design. A 12-feet-high transparent plastic cylinder with the same inner and outer diameters as the real PDU is used as the reactor. The test is controlled under atmospheric pressure and room temperature, using the same 150 micron silica sand as fluidization solids and air as flow gas. A U-tube manometer with water is connected to the top of the reactor to measure the pressure drop during the fluidization.

Using the same formula (Eq. (3-1)-(3-6)), another series of gas flow rate based on the operation condition is obtained and tested. Bed height in the test is set to 1.83m (6 feet, half of the total height), which is higher than the critical height H_L (0.860m). Summary of the test set up is listed in table 4-4.

Table 4-4: Fluidized bed mock up test operation condition

Reactor inner diameter (cm)	Reactor total height (m)	Sand size (micron)	Bed height (m)	Bed pressure (atm)	Temperature (°C)	Gas velocity (m/s)
9.40	3.35	150	0.860	1	25	0.0863

Mock up test result

The sand begins to bubble very quickly. This is in accordance to the small U_{mf} value which can be deducted from Eq. (3-1)-(3-3) in Section 3.4 of this report. At the gas flow rate reaches 0.086m/s, the diameter of sand bubble approaches the cylinder diameter and the bubbles begin to burst. A bubbling-slugging bed is formed. Since the bed height reached the critical height, sand slugging is always in a stable axial plug flow state. The maximum bed height also fits the H_{max}/H_0 ratio obtained from Eq. (3-11), which is 1.20. A pressure drop of 127.4 Pa is observed during the fluidization.

The result of the mock test shows that the bed performance predicted at the bubbling-slugging transition gas velocity based on previous calculation is reliable. As U_{mf} and U_{ms} is mostly related to physical properties of sand and reactor size only, the test result can prove that the design of a fluidized bed reactor with the same size under high temperature and pressure is also viable.

4.2.4 PDU (SHR) Detailed Design

From the basic engineering data collected from section 4.1 & 4.2, research team started the detailed engineering. Final outcome of the detailed design drawing, part list and photo were presented in Table 4-5, Figure 4-2 and 4-3.

Figure 4-2: PDU Scale SHR process diagram

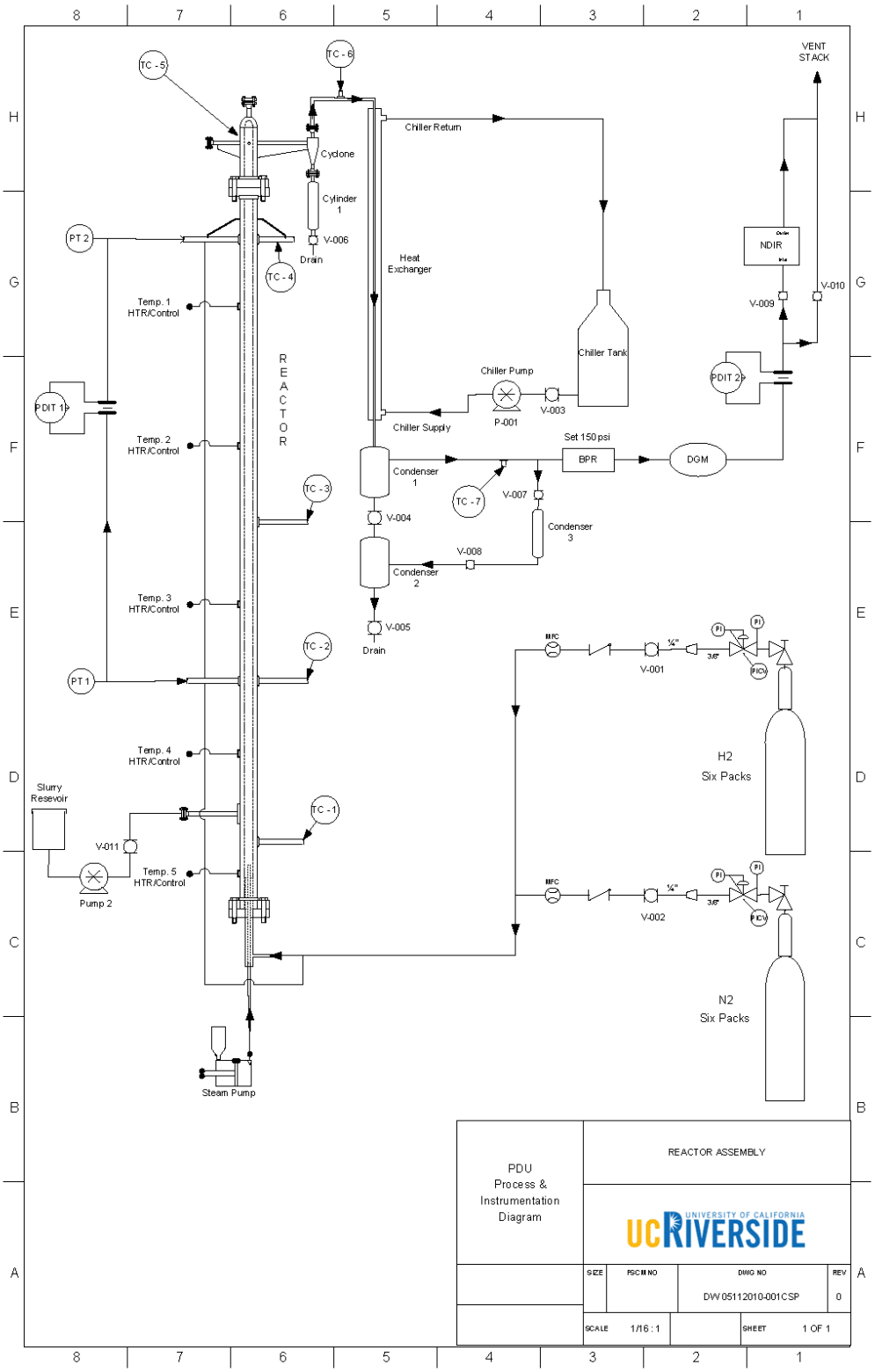


Table 4-5: Part list and description of the PDU of SHR system

Item	Part No.	Description
1	TC-1	Thermal couple used to measure temperature at the bottom of the reactor
2	TC-2	Thermal couple used to measure temperature in the middle of the reactor
3	TC-3	Thermal couple used to measure temperature in the middle of the reactor
4	TC-4	Thermal couple used to measure temperature in the middle of the reactor
5	TC-5	Thermal couple used to measure temperature at the top of the reactor
6	TC-6	Thermal couple used to measure temperature before heat exchanger
7	TC-7	Thermal couple used to measure temperature after the heat exchanger
8	V-001	Valve used to isolate Hydrogen supply
9	V-002	Valve used to isolate Nitrogen supply
10	V-003	Valve used to isolate Chiller tank
11	V-004	Valve use to isolate condenser 2
12	V-005	Valve used to drain condenser 2
13	V-006	Valve used to drain cylinder 1
14	V-007	Valve used to isolate condenser 3
15	V-008	Valve use to isolate condenser 2
16	V-009	Valve used to isolate NDIR
17	V-010	Valve used to close vent
18	V-011	valve used to isolate Pump 2
19	PT-1	Pressure transducer used to measure pressure at the bottom of the reactor
20	PT-2	Pressure transducer used to measure pressure at the top of the reactor
21	PDIT-1	Pressure differential used to measure pressure difference between the top of bottom of the reactor
22	PDIT-2	Pressure differential used to measure the volume flow rate of gases as the gases pass through a venturi tube
23	BPR	Back Pressure Regulator used to keep reactor at desired pressure
24	NDIR	Non Dispersive Infrared Sensor used to measure the percentage of CH_4, CO, CO_2
25	DGM	Dry Gas Meter used to measure flow rate
26	Condenser 1	Condenser used to collect water
27	Condenser 2	Condenser used to collect water
28	Condenser 3	Condenser used to collect water
29	Cyclone	Cyclone used to separate solid particles from the gases
30	Cylinder 1	Collect all the solid particles from the cyclone

31	Chiller Tank	Water tank used to hold the water that will be pump through heat exchanger
32	Heat Exchanger	Heat Exchanger used to cool down gases and also convert steam back to water
33	HTR/control	Thermal couple/heater controller used to control the temperature of the heaters
34	Steam Pump	Pump used to pump steam back into the reactor
35	Pump 2	Pump used to pump the feedstock
36	Reactor	14 ft. reactor, 3.5" ID made from Inconel pipe

Figure 4-3: Photo of SHR PDU system

4.3 WGS Detailed Design Flowsheet

4.3.1 Designing WGS Reactor

Selection of catalyst for the experiment

From the literature review of the catalyst performance and availability from the catalyst supplier, High Temperature Shift (HTS) catalysts from SUD-CHEMIE Catalyst Group are selected. The commercial name of the catalyst is "HTS ShiftMax®120" and well-known for the combination of high activity and extremely good physical robustness. The composition and physical characteristics of the catalyst is presented in Table 4-6.

Table 4-6: Normal composition of ShiftMax®120

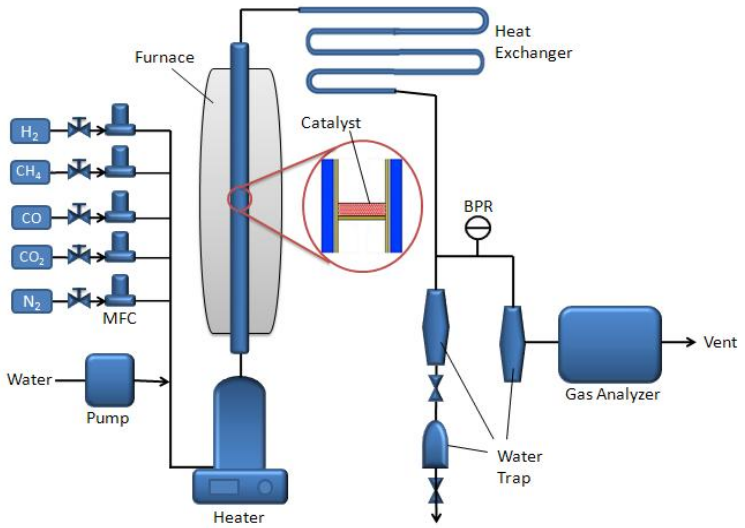
Composition	Content (wt.%)
Fe_2O_3	80
Cr_2O_3	8.5
CuO	2
Shape	Tablets
Size (mm)	6x6

The typical operational pressure of the catalyst is at the pressure between atmospheric and 600 psig (42kg/cm^2). Nominal operating temperatures at the inlet of the reactor ranges from start to run value of as low as 316°C up to 382°C as it becomes deactivated. Since the WGS reaction generates heat, a temperature rise was observed through the bed of catalyst.

Design of WGS by laboratory continuous WGS reactor study

A laboratory scale continuous WGS reactor was developed for the optimum design of WGS part of PDU. Figure 4-4 shows a schematic diagram of the reactor. Photo of the reactor is also shown in Figure 4-5. The unit has multiple mass flow controller units in order to simulate the composition of the producer gas from the SHR. The system is comprised of a reactor tube which is a ½ inch diameter of stainless steel pipe, a heating unit, a cooling unit, three water traps, a mass flow meter and a gas outlet that allows product gases to be collected by tedlar gas sampling bag. The composition of the product gas is determined by a Residual Gas Analyzer (RGA). A mixture gas together with the steam was fed into the system.

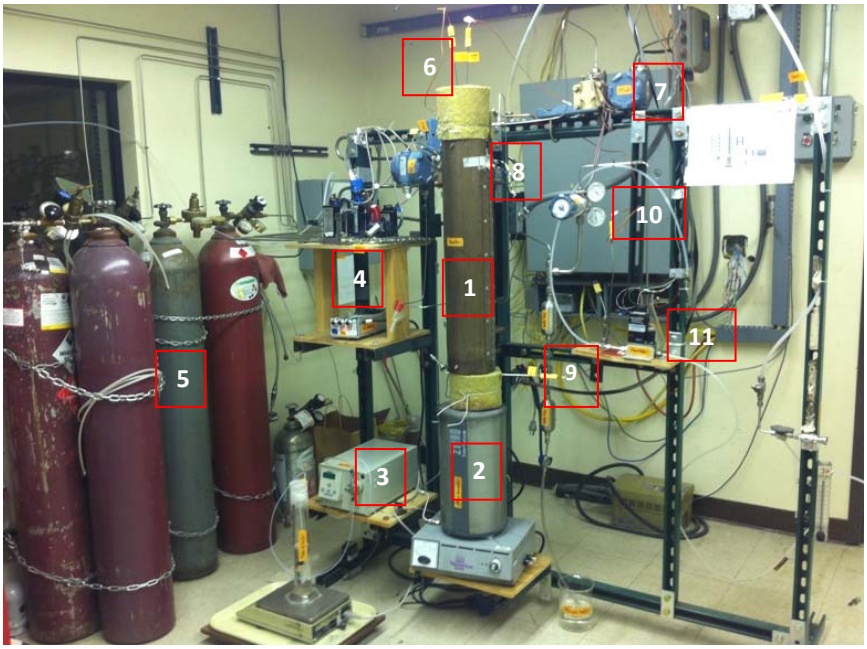
Figure 4-4: Schematic diagram of micro-WGS reaction system



Equipment Description

1. Fixed bed reactor is made from stainless steel tube 1/2 inch diameter and 30 inch long with a furnace to control temperature of the reactor.
2. Steam generator is made from stainless steel tube 1/8 inch shaped as a coil installed in the electrical heater used to control the temperature of steam and mixture gas before fed into the reactor.
3. High pressure water pump with the maximum capacity of 10 ml/min has been coupled with the steam generator to produce the steam.
4. Mass flow controllers (MFCs) with a control panel are used for manipulating the mass flow rate and composition of the input gas.
5. Industrial grade of H_2, CH_4, CO and CO_2 gas cylinders are used as the producer gas generated from the steam hydrogasification process.
6. Thermocouple for measuring and controlling the reaction temperature.
7. Pressure transducers are used for investigating the pressure drop across the packed bed of the reactor.
8. Double pipe heat exchanger, composed of 1/4 inch tube as inner pipe and 1/2 inch tube as outer pipe, is used for cooling the product gases to condense the water after the reaction.
9. A series of water traps is used to separate the condensate water and product gas.
10. Back pressure regulator is used for controlling the reaction pressure.
11. Mass flow meter is used for measuring the total flow rate of the product gas.
12. Gas residue analyzer (RGA) is used for analyzing the composition of the final product.

Figure 4-5: Experimental setup of the water gas shift reaction system



4.3.2 Experimental Procedure

- Verify the performance of WGS reaction system
  - The conventional WGS reaction using CO and steam as feed is used to verify the performance of the continuous laboratory of WGS reaction system.
  - 5.0 g of HTS catalyst with particle size about 75-150 μm is prepared by grinding and sieving.
- WGS reaction system applied on the SNG production using producer gas from SHR
  - An artificial producer gas (H_2, CH_4, CO, CO_2 and steam) from SHR is preheated to 180°C. The fraction of methane in the producer gas, assumed as an inert gas in the shift reactor, is varied by the water/feed mass ratio. The conversion of CO to H_2 was determined at varying space velocity per unit mass of catalyst.
  - Composition of SHR producer gas was generated by Aspen Plus. Input condition of SHR was; 1.5:1 of mass ratio for the biosolids to biomass, 1:1 molar ratio of H_2 to C. The dry feed gas composition is comprised of H_2, CH_4, CO and CO_2 underneath the atmospheric condition shown as table 4-7.

Table 4-7: Composition of an artificial producer gas from SHR

Gas composition from SHR	sccm (gas)	mL/min (liq.)
H_2	163	-
CO	28	-
CO_2	63	-
CH_4	90	-
H_2O	-	0.4
Total	344	-

- CO conversion is calculated by this equation.

  CO conversion = 1 – (mole of CO at WGS exit / initial mole of CO)

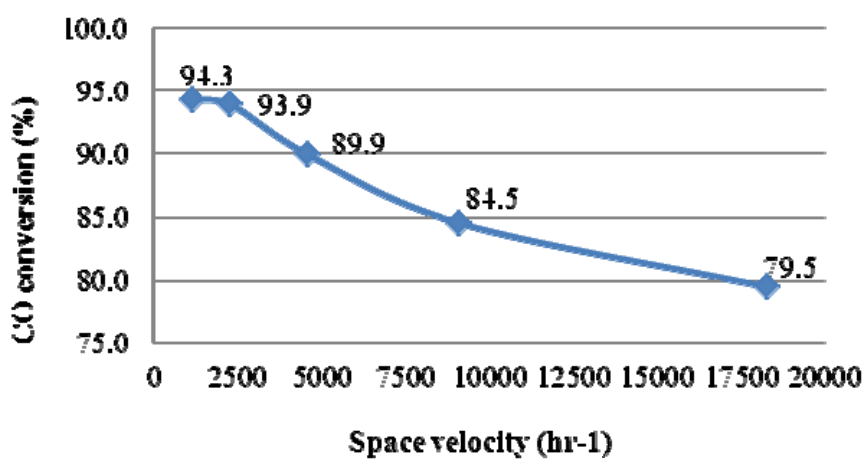
  A H_2/C mole ratio of 1.0 and H_2O/feedstock mass ratio of 1.5 has been determined based on the results with biosolids and green waste as feedstock

4.3.3 Result and Design Flowsheet

Results of the conventional WGS reaction

Operation of WGS with the conventional input condition was performed to verify the functionality of the WGS system. The experimental condition was controlled at 350°C with several space velocities of pure Carbon Monoxide feed. These results are shown in Figure 4-6. CO conversion was achieved in 85-90 percent using the space velocity between 4500-9000 hr^{-1} of wet gases, which met the catalyst performance provide the vendor. Therefore this setup can be implemented with the SHR for further study to produce SNG.

Figure 4-6: CO Conversion at different space velocity of the conventional WGS reaction at 350°C



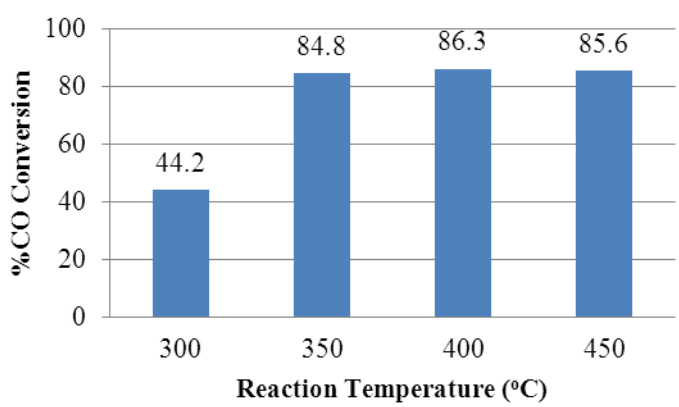
The mixture gas with steam which simulated the producer gas of the SHR process using woody biomass comingled with biosolids as feedstock was fed into the system to investigate the shift reaction following the conceptual idea of the SNG production. The reaction was successfully able to convert CO to H_2 with approximately 85 percent conversion using 1-1.3 mm. particle size of HTS catalyst, as shown in Table 4-8, at the condition of 350°C with the space velocity of 5500-6000 hr^{-1} on a wet gas basis. Pressure drop across the bed was slightly developed in the reactor.

Table 4-8: Proper conditions of WGS reaction for SHR producer gas

Amount of catalyst (g)	10	10	20
Particle size	1-2mm	75-150μm	1-1.3mm
Temperature (°C)	350	350	350
Space velocity (hr^{-1})	5900	6300	5700
CO conversion (%)	65	75	85
Pressure drop (psi)	1-2	25-30	1-2

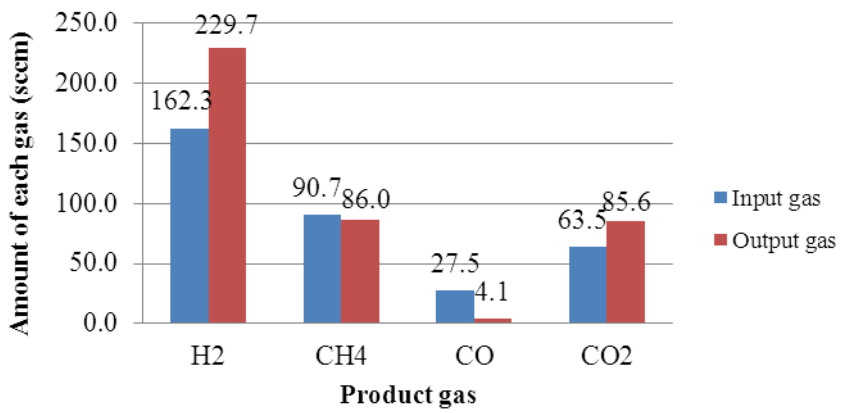
In order to optimize the operating condition, the variation of reaction temperature was studied under atmospheric conditions. Figure 4-7 shows that about 85 percent of CO in feed has been reacted in the condition of 350°C and higher. It is the optimal condition of the WGS reaction using for configured with the SHR in order to initiate the SNG production process. Moreover, the amount of produced H_2 was sufficient to be recycled as a feed for SHR after purification.

Figure 4-7: CO Conversion of WGS reaction for SHR producer gas at different temperature



In Figure 4-8, the amount of each product gas, as dry basis, is compared between input and output to investigate the possibility and reliability of the WGS reaction. The overall output gas increases about 15 percent and H_2 is 30 percent increased. However, CH_4, based on the experimental result, is slightly decreased about 5 percent during the shift reaction. Finally, all data we got from the laboratory scale of WGS reaction system will be summarized and used to design a new reactor for the SNG demonstration unit.

Figure 4-8: Comparison of the gas distribution between input and output of the WGS at 350°C



Design for a PDU scale WGS reactor

The main reactor is made from stainless steel tube (SUS 316) 25.4 mm of outer diameter and 167 cm long enclosed by an electric heater (capacity : 1.9 kW). Four thermocouples are placed on the surface of reactor. The catalyst (HTS ShiftMax®120) is located in the reactor tube and the height of catalyst bed was 110 cm. The catalyst is supported by a section of metal type wool of 38 cm long. Total mass of the catalyst loaded is 300 gram. The schematic diagram of the reactor system is shown in Figure 4-9. Figure 4-10 is a photo showing the entire PDU system of SHR process integrated with the WGS reactor.

Optimum temperature for the WGS reaction was 350°C from the laboratory reactor test. The heating system consists of four parts of inconel tube heaters of 25.4mm i.d and 380 mm length. An incolony heater rated at 550W and 120V is coiled in the gypsum block. In order to keep the isothermal condition, the reactor is insulated by Kaowool ceramic wool. Reactor pressure is controlled by a back pressure regulator from atmospheric pressure to 150 psi. The product gases from the reactor are passed to water cooled heat exchanger, which is consisted of a stainless steel tube enclosed by water jacket, three thermocouples which indicate the coolant inlet-outlet temperature and exit temperature of condenser and water flow meter which controls the flow of coolant. The condensed liquid from condenser is collected by a water/gas separator.

The product gas was sampled at several different places via sampling valves. The Residual Gas Analyzer (RGA, QMS 300 series, Stanford research systems) was used for the continuous monitoring of the product gas and sends the analyzed data to the Labview program in the computer.

Figure 4-9: Schematic diagram of the WGS reactor system

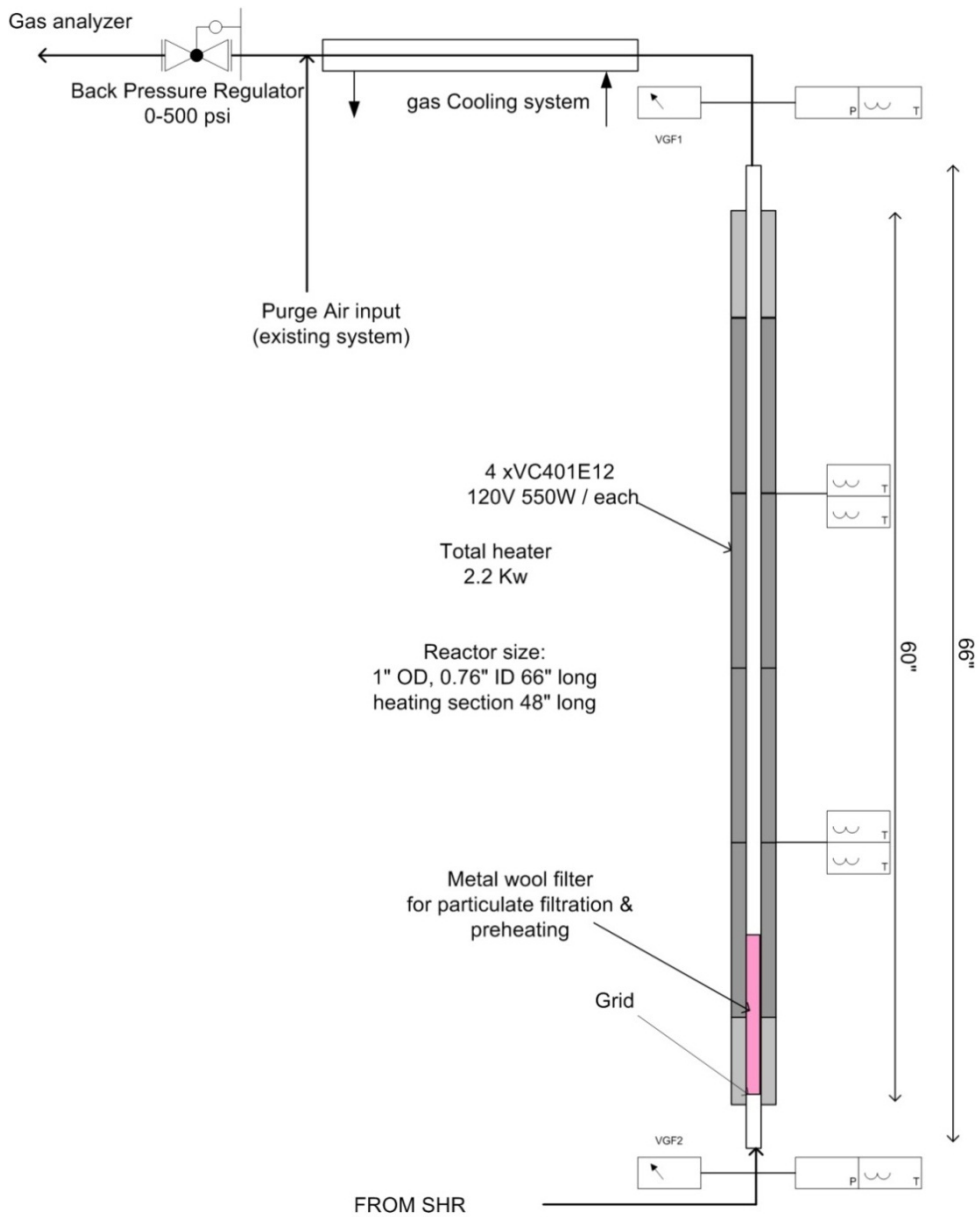
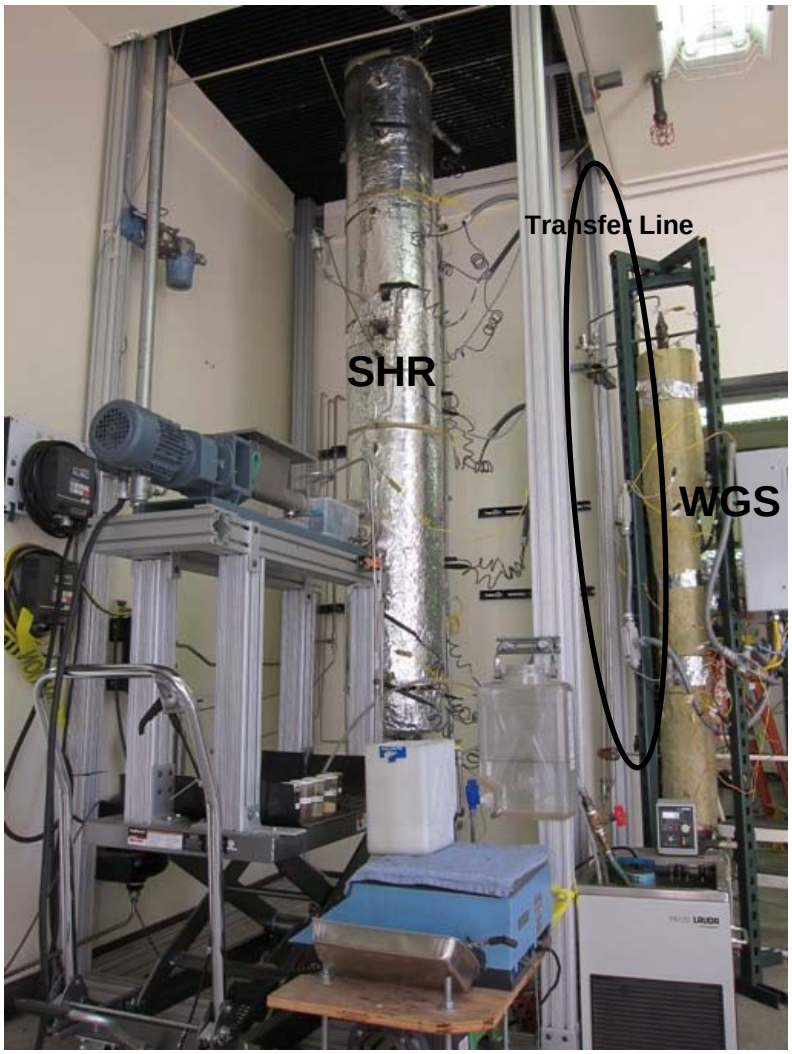


Figure 4-10: Photo of WGS reaction systems interfaced to SHR through heated transfer line



4.4 Process Mass and Energy Balance Report

4.4.1 SHR simulation

All of the gaseous and liquid components used in the SHR simulation were described as distinct molecular species using Aspen's own component properties database. Thermodynamics for the gasification and downstream unit operations are estimated by Peng–Robinson equation (PR) for high temperature, high pressure phase hydrocarbon behavior. The biosolids, biomass and ash components were modeled as non-conventional components using proximate and ultimate date to calculate the chemical and physical property.

The enthalpy model for the nonconventional components is HCOALGEN and the density model is DCOALIGT. The HCOALGEN model includes a number of empirical correlations for

heat of combustion, heat of formation and heat capacity. All other values used were retrieved from the Aspen plus database. The whole simulation is controlled using FORTRAN routines (calculator blocks) and design specifications. Material, energy, and carbon balances were given for each process unit and no detailed chemical kinetic models were considered in the simulation.

The SHR is simulated using decomposition and gasification units. These units are based on built-in Aspen reactor blocks and calculate the equilibrium composition in the reactor under the given conditions by means of Gibbs free energy minimization. The decomposition block converts the non-conventional feedstock into its basic elements, such as C (solid), H_2, O_2 and N_2, on the basis of yield information using the RYIELD block and the gasification block calculates the equilibrium product gas composition using the RGIBBS block.

Table 4-9: Feedstock composition in PDU test

	Compound	Biosolids	Pine wood
Proximate	**Volatile Matter**	60.25	82.54
	Fixed Carbon	10.00	17.17
	Ash	29.75	0.29
Ultimate	**C**	29.57	49.25
	H	5.39	5.99
	O	20.83	44.36
	N	5.79	0.06
	S	1.56	0.05

The fraction of leftover char is assumed as a function of gasification temperature only in the report. The char ratio is defined as the fraction of leftover char among the overall carbon in the feedstock. Based on the previous lab scale gasification test, the char ratio is set to be 35.2 percent, 17.9 percent and 9.2 percent with gasification temperature at 650°C, 750°C and 850°C, respectively.

The initial solid load in the slurry is 40 percent based on previous HTP test results. The total amount of H_2 injected in the system is defined as a function of total amount of carbon in the feedstock and the H_2/C molar ratio is set to be 1.0 all through the test. The carbon conversion efficiency is defined as fraction of the carbon in fuel gas (CO, CH_4 and C_{2+}) with expression given below.

$$\text{Chemical Conversion Efficiency} = (C_{feedstock} - C_{CO_2} - C_{char})/C_{feedstock}$$

The mass and heat balance of the PDU operated under different temperature is given in Table 4-10 based on the simulation results.

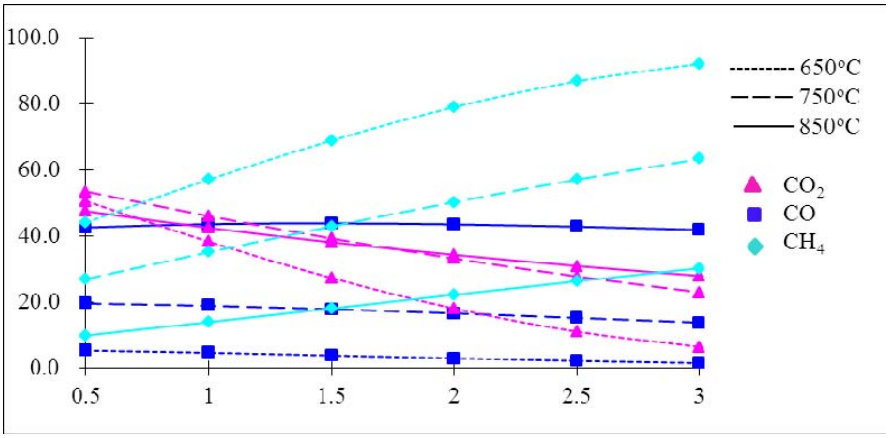
Table 4-10: PDU mass and energy balance from simulation

PDU performance						
Operation temperature (^oC)	650		750		850	
Operation pressure (psi)	150		150		150	
Slurry feed rate (lb/hr)	5.0		5.0		5.0	
Slurry solid load	40%		40%		40%	
H_2/C molar ratio	1.0		1.0		1.0	
Char ratio (%)	35.2		17.9		9.2	
Outlet gas	lb/hour	Vol%	lb/hr	Vol%	lb/hr	Vol%
H_2	0.14	22.8%	0.22	34.3%	0.31	44.0%
CO	0.07	0.8%	0.34	3.8%	0.87	8.8%
CO_2	0.86	6.6%	1.31	9.2%	1.33	8.6%
CH_4	0.47	9.8%	0.36	7.0%	0.16	2.8%
H_2O	3.17	59.4%	2.62	45.2%	2.26	35.4%
NH_3	0.02	0.5%	0.02	0.5%	0.02	0.4%
H_2S (PPM)	637		584		531	
Chemical conversion efficiency (%)	40.0		44.3		52.2	
Minimum heat requirement (kw)	2.0		2.5		3.1	

SHR operation temperature and H_2/C ratio impact

H_2/C molar ratio ranges from 0.5-3.0 with 0.5 interval is used to investigate the H_2 impact on gas composition at different gasification temperature. The analysis is performed under the assumption that all the carbon in the product gases was present in the form of CO, CO_2 or CH_4. The mole percentages presented here are calculated using these three species only. Other components present in the product gas such as H_2O and H_2 are not included in the product mole percentage calculations. Hence, the mole percentages presented have been normalized to 100 % based on the three carbon containing species, CO, CO_2 and CH_4, shown in Figure 4-11.

Figure 4-11: Molar fraction of CH_4, CO and CO_2 at different gasification temperature



It can be observed that the concentration of CH_4 decreases with increasing gasification temperature whereas the concentration of CO and CO_2 increases. This can be expected since the hydrogenation of carbon which is the primary CH_4 generation reaction is mildly exothermic. The steam carbon reaction ($2C+3H_2O \rightarrow 3H_2+CO+CO_2$) is endothermic. On the other hand, with H_2/C increasing, the concentration of CH_4 increases while the concentration of CO and CO_2 decreases. This trend can be simply explained as the high concentration of H_2 shifts the chemical equilibrium to its favorable side within the system that promotes the hydrogenation of carbon and restrains the formation of CO and CO_2.

According to the simulation results, either increasing the H_2/C molar ratio or decreasing the gasification temperature can promote the CH_4 production in the SHR theoretically. In terms of H_2/C molar ratio, it must be ensure that the H_2 can sustain internal system cycle which also means no outside H_2 source is needed. Detail H_2 sustainability will be discussed in the pilot plant simulation section. For the gasification temperature effect, it is far more complicated in the really world than the simulation. Low temperature leads more leftover char and significant amount of tar will be generated that could block the pipeline and make the gas cleanup system more complex. Meanwhile, the low temperature also requires long residence time and adds the equipment cost, especially in large scale plant. After all, more research regarding optimum gasification temperature from biosolids and biomass comingling feedstock will be further investigated based on PDU test results.

4.4.2 SHR-WGS simulation

The clean product gas from SHR then enters the WGS. The WGS was simulated using a built-in equilibrium block. The product gas from the WGS is then sent through a separator where the excess H_2 is removed for recycle to the SHR.

Figure 4-12: Methane concentrations in SHR product gas at 200 psi operating pressure

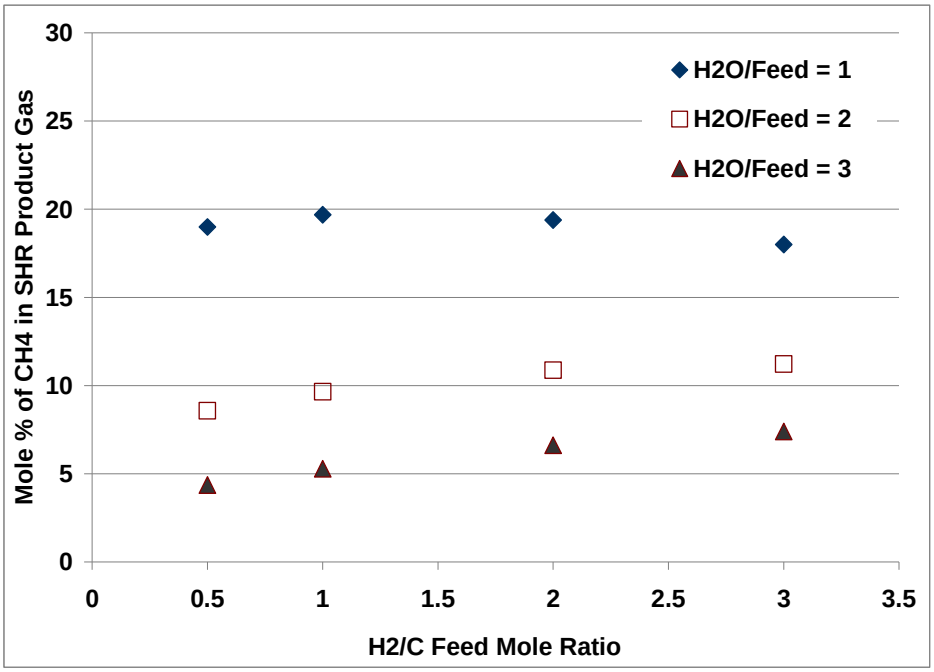


Figure 4-13: Methane concentrations in SHR product gas at 400 psi operating pressure

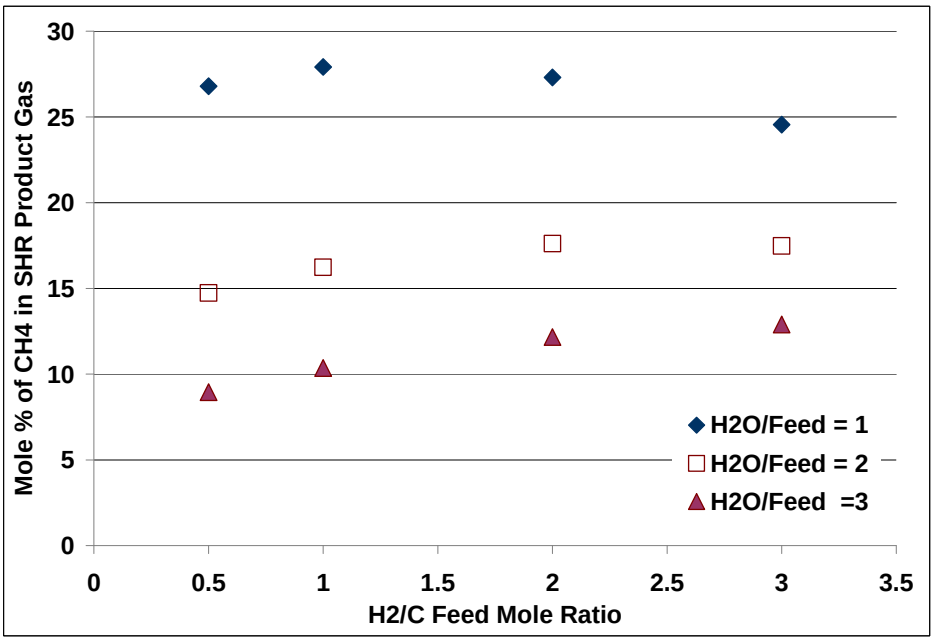
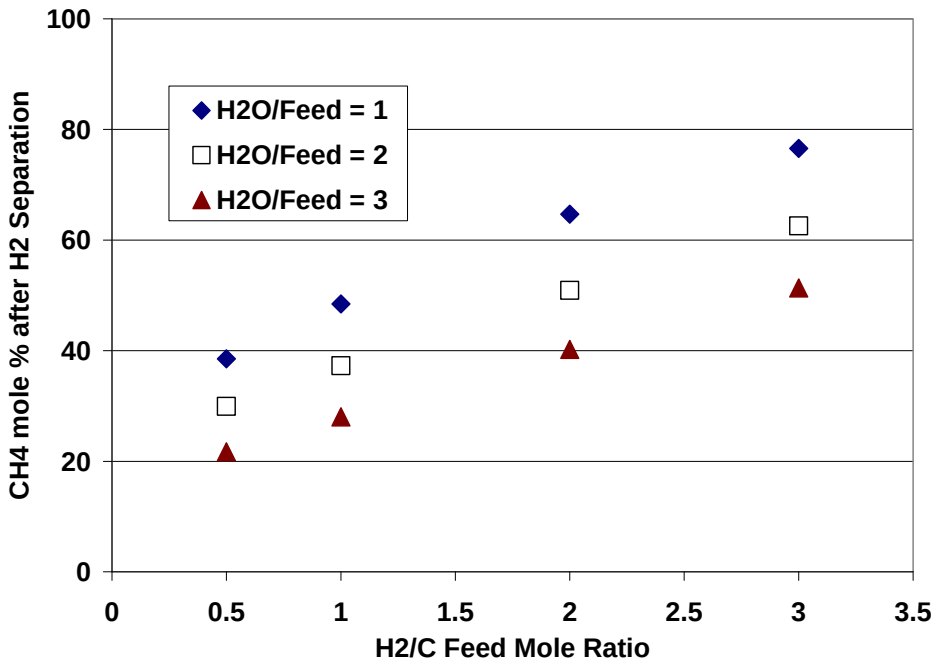


Figure 4-12 and 4-13 show the mole % of methane in the SHR product gas for varying H_2/C and H_2O/Feed ratios at 200 and 400 psi operating pressures respectively. The operating temperature was set at 850°C for both cases. The concentrations were calculated on a dry basis. It can be seen

that the methane concentration varies over a wide range for different feed ratios. It is important to identify the optimal feed composition based on the desired product gas composition and also the overall efficiency of the process. From the results, it can also be seen that the methane concentration increases with increasing pressures.

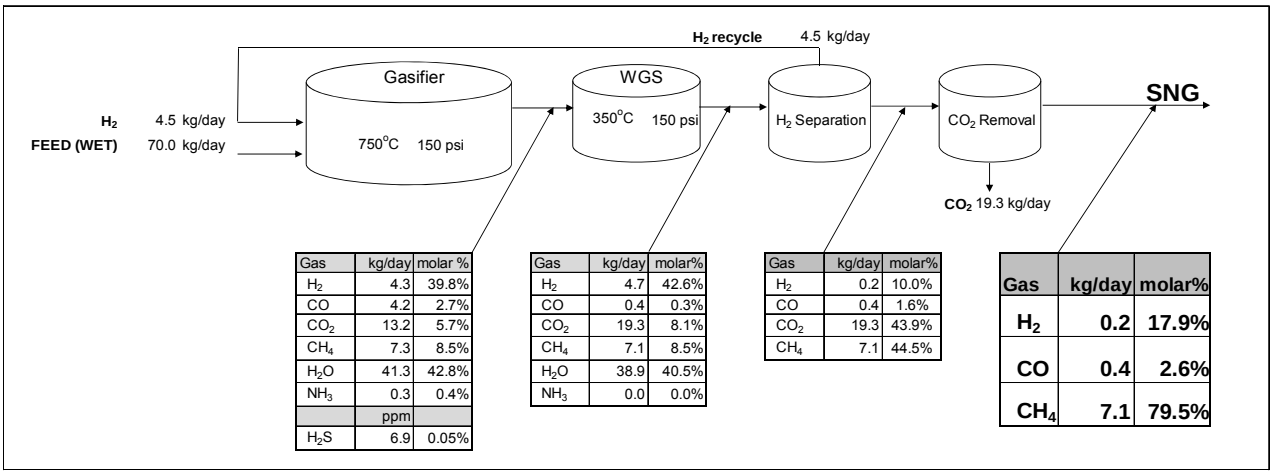
Figure 4-14 shows the molar concentration of methane in the final product gas. This concentration is calculated after the separation of H_2 for recycling back to the SHR. The pressure was set at 400 psi for both the SHR and the Shift Reactor. The operating temperature of the SHR was set at 850°C and the Shift Reactor at 350°C. It can be seen that the final product gas contains significant quantities of methane (up to 85 percent). The methane concentration of the product gas can be further improved by means of methanation.

Figure 4-14: Methane concentrations in the shift reactor product gas after H_2 separation



Pre-calculation of the PDU test was simulated before actual operation. Figure 4-15 shows the production of the overall process using biosolids comingled with pine wood as feedstock to produce the SNG at 70 kg/day of wet feed. The reaction temperature is set at 750°C for SHR and 150°C for WGS reactor and pressure is 150 psi. Carbon conversion was prossibly achieved 64 percent and it could be estimated 45 percent of CH_4 content in the process producer gases and 91 percent(mass) or 80 percent (mole) of CH_4 content with final separation of CO_2.

Figure 4-15: Mass balance of process simulation for the PDU system



Gas	kg/day	molar %
H_2	4.3	39.8%
CO	4.2	2.7%
CO_2	13.2	5.7%
CH_4	7.3	8.5%
H_2O	41.3	42.8%
NH_3	0.3	0.4%
	ppm	
H_2S	6.9	0.05%

Gas	kg/day	molar%
H_2	4.7	42.6%
CO	0.4	0.3%
CO_2	19.3	8.1%
CH_4	7.1	8.5%
H_2O	38.9	40.5%
NH_3	0.0	0.0%

Gas	kg/day	molar%
H_2	0.2	10.0%
CO	0.4	1.6%
CO_2	19.3	43.9%
CH_4	7.1	44.5%

Gas	kg/day	molar%
H_2	0.2	17.9%
CO	0.4	2.6%
CH_4	7.1	79.5%

4.5 Process Performance Result Report

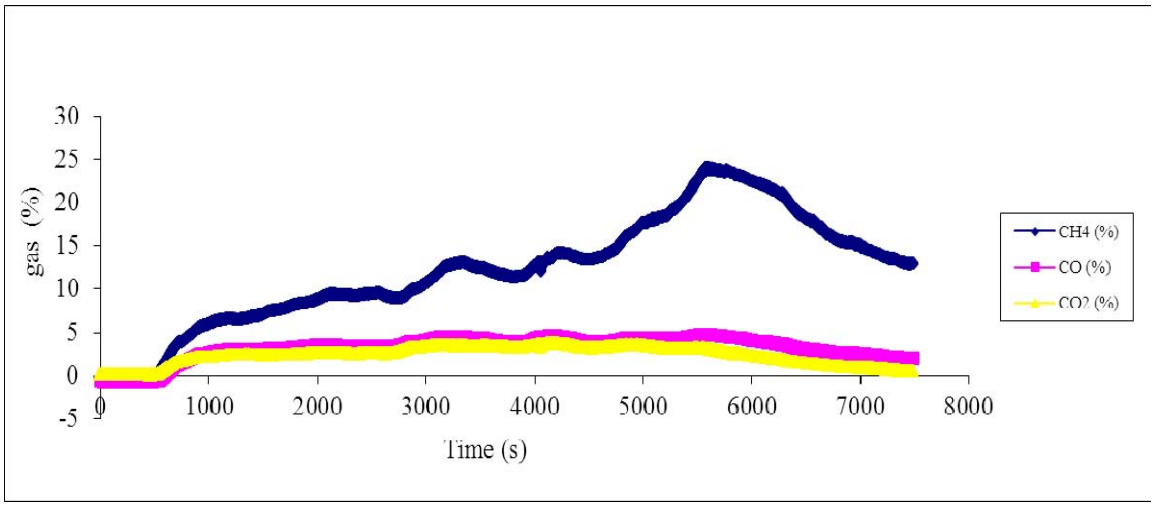
This section describes the PDU process operation result. The description of PDU system was detailed in section 4.3. The feedstock tested were biosolids comingled with woody biomass and processed food waste. The carbon contents of the feedstock were 48.37 percent and 56.67 percent respectively. The PDU was initially started with SHR process alone. Once SHR process reaches steady state, WGS part of the process started to convert the producer gas of SHR process. The operating conditions were set at 750°C and 150 psi for SHR and 350°C with the same pressure for WGS reactor.

4.5.1 PDU operation result – SHR alone

Biosolids comingled with pine wood

The temperature of the reactor was gradually increased to 750°C to avoid the thermal shock. Nitrogen was used for the fluidizing gas and purge gas during this stage, and the pressure of the reactor was maintained at 150 psi. The slurry feedstock prepared by the HTR process (Section 3) was fed into the reactor using progressive cavity pump when the reactor temperature reaches steady state. Then, nitrogen gas was switched to hydrogen gas to keep pressurizing and fluidizing the sand. The hot producer gas was cooled down thru heat exchanger. The condensate was separated via steam traps. The flow of product gas was measured by a venturi meter and analyzed by Non Dispersive Infra-Red (NDIR) spectrometer. As shown in the Figure 4-16, CH_4 increased from 0 to 23-25 percent within about 90 minute from the startup. CO and CO_2 were approximately 4-5 percent and 2.5-3 percent respectively.

Figure 4-16: Real time of producer gas generated from SHR using biosolids comingled with pine wood as feedstock



Food waste

The analysis of food waste is presented in Table 4-11 and the food waste was collected from the cafeteria of UCR campus. The food waste was preprocessed thru the food waste pretreatment process developed by Food Recycle Science (FRS)[2]. The machine was provided from FRS with additional modification for the SHR process. This was the part of the in-kind contribution from FRS to this project.

Table 4-11: Composition of food waste

Proximate	**Volatile Matter**	67.20
	Fixed Carbon	24.32
	Ash	8.48
Ultimate	**C**	56.67
	H	6.93
	O	23.14
	N	3.68
	S	1.10

The pre-processed food waste feedstock was used to produce the producer gas at the same operating conditions. Figure 4-17 shows process record with the percentage of each gas produced. CH_4, CO and CO_2 were generated approximately 14 percent, 2.3 percent and 3.4

[2] FRS ecorect machine ET-100, http://www.foodrecycle.com for further details.

percent, respectively. Producer gas generated from the SHR for both feedstock's are summarized in Table 4-12

Figure 4-17: Real time of producer gas generated from SHR using food waste as feedstock

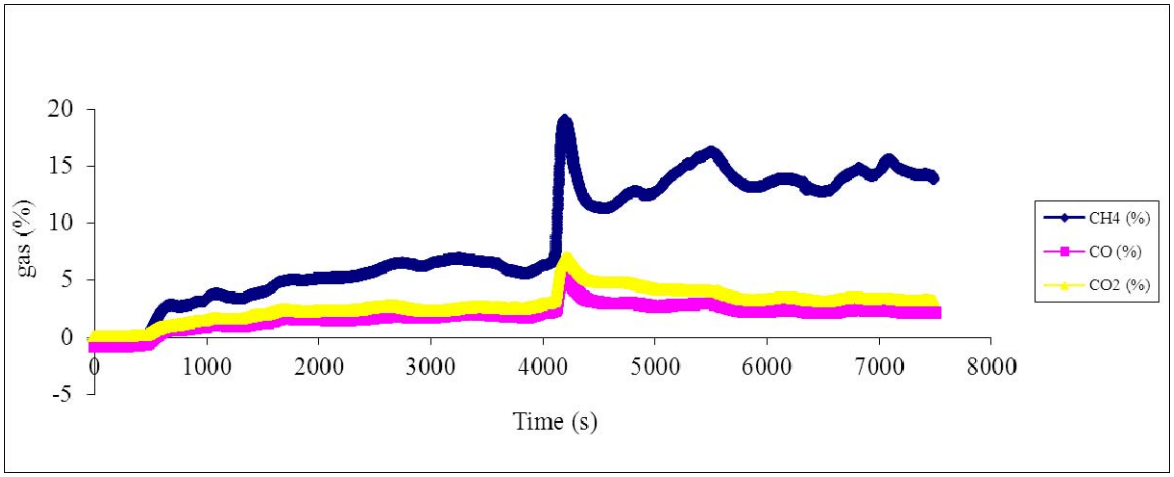


Table 4-12: Experimental results from SHR only operation using the different feedstock

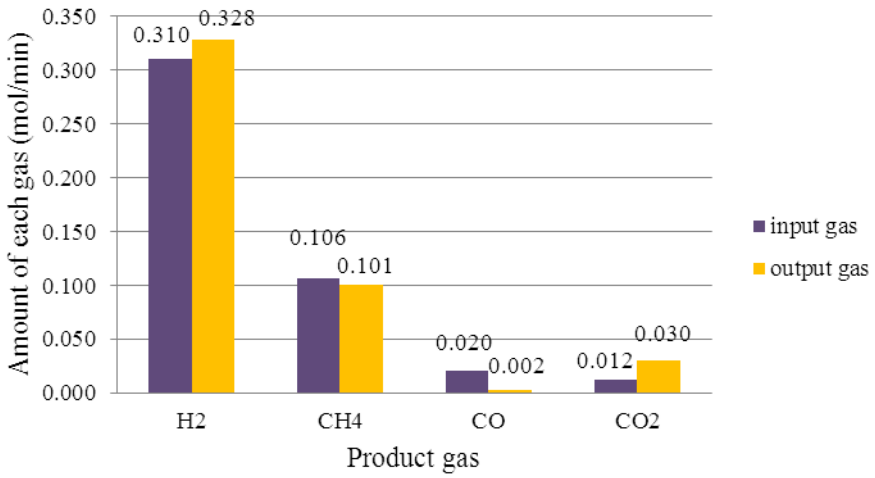
Conditions and Results	Biosolids comingled with pine wood	Food waste
Slurry feed rate (g/min)	48.63	48.63
Percentage of Carbon (%)	48.37	56.67
Rate of Carbon input (mole/min)	0.47	0.46
Moisture content (%)	76	80
Total flow rate of product gas (Liter/min)	10.05	20.26
Total flow rate of product gas (mole/min)	0.448	0.904
H_2 (mole/min)	0.310	0.726
CH_4 (mole/min)	0.106	0.126
CO (mole/min)	0.020	0.021
CO_2 (mole/min)	0.012	0.031

4.5.2 PDU operation result of SHR integrated with WGS reactor

Biosolids comingled with pine wood

Figure 4-18 shows the composition of producer gas for SHR and SHR-WGS process. The pressure was set at 150 psi for both the SHR and WGS. The operating temperature of the SHR was set at 750°C and the Shift Reactor at 350°C. The amount of H_2 is sufficient for recycling back to the SHR gasifier. After separation process, it can be seen that molar concentration of the final product gas is approximately contained 84 percent (mole) of CH_4, 2 percent (mole) of CO and 14 percent (mole) of H_2.

Figure 4-18: Comparison of the gas distribution between input and output of the WGS at 350°C



Food waste

The operating conditions were set at 750°C and 350°C for SHR and WGS reactor, respectively. The final product generated from food waste approximately consisted of 76 percent of CH_4, 5 percent of CO and 19 percent of H_2, after separation process. Also the amount of H_2 was sufficient for recycling back to the SHR.

Table 4-13 shows the summary of the performance of the PDU test run. The overall performance is almost similar with the simulation results, especially CH_4 content in the product gas. However, the content of CO_2 is lower than CO_2 calculated from the simulation result. The overall results of the SNG production can be achieved at 75-85 percent (mole) of CH4 content in the product gas using biosolids comingled with woody biomass or food waste following the objectives.

Table 4-13: Summarizes measured performance of PDU in final state (mole % or vol%)

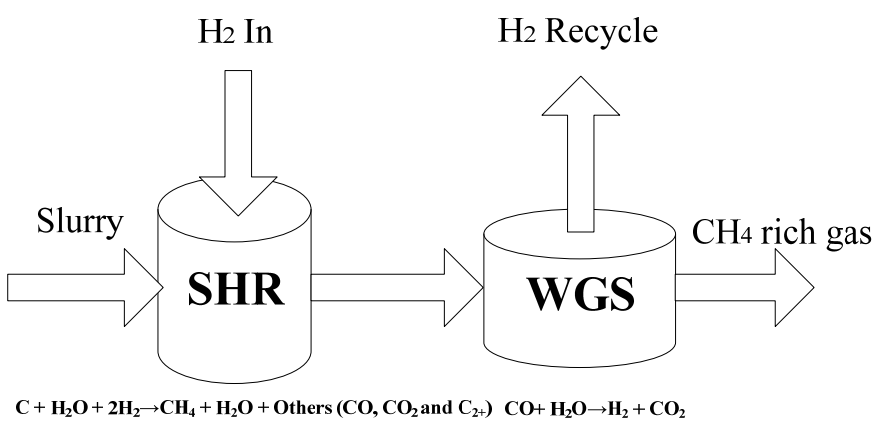
	SHR only	**SHR + WGS**	Target (Task 3)
Product gas yield	1.5 m3 (~1.5kg, wet)/ kg feed	**1.5 m3 (~1.5kg, wet)/ kg feed**	>1200 kg / ton of feed
Energy Content	14 MJ / kg feed	**15 MJ / kg feed**	>12 GJ/ ton of feed
H_2	55 Vol%	**2 Vol%**	5 Vol%
CO	10 Vol%	**14 Vol%**	5-20 Vol%
CH_4	30 Vol%	**84 Vol%**	60-80 5 Vol%
CO_2	5 Vol%	**25 Vol% (Before Separation)**	< 25 Vol%
Sulfur, Tar, NH3	n/a	**n/a**	< 0.01 ppm

CHAPTER 5:
Basic Engineering Design for the 5 TPD Pilot Plant

5.1 Pilot Plant Design Report

A 5 ton per day steam hydrogasification pilot plant is designed and simulated with downstream Water Gas Shift (WGS) unit that converts CO into H_2 and CO_2 at the presence of steam. The WGS unit is simulated using Aspen equilibrium blocks and calculate the chemical equilibrium inside the reactor at the given temperature and pressure. CO conversion higher than 85 percent can be achieved based on the simulation results. The whole process schematic flow diagram is given in Figure 5-1.

Figure 5-1: Schematic of SHR with WGS

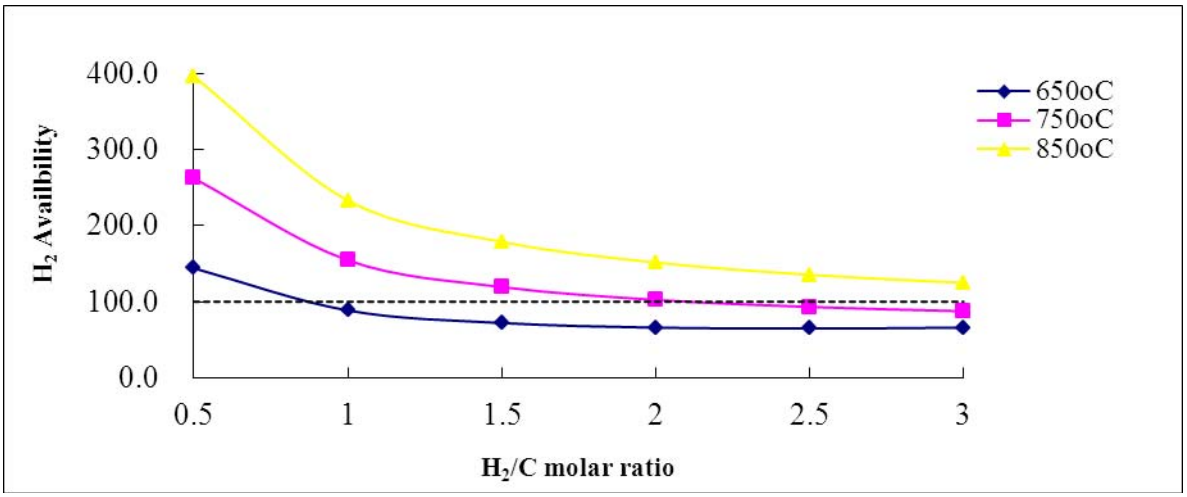


System H_2 availability is discussed in detailed in this section with definition given below.

$$H_2 \text{ availability} = \frac{H_2 \text{ Recycle}}{H_2 \text{ In}} \times 100$$

In order to sustain an internal H_2 cycle between SHR inlet and WGS outlet, the H_2 availability must be higher than 100. H_2 availability at pilot scale gasifier operated at 650°C, 750°C and 850°C is given in Figure 5-2 with initial H_2/C molar ratio ranges from 0.5-3.0.

Figure 5-2: H_2 availability with gasification temperature at 650°C, 750°C and 850°C



Based on the simulation results, any point below the dash line is considered as unfavorable and cannot make the system self-sustainable. The maximum H_2/C molar ratio that meets the system H_2 internal cycle at different gasification temperature is given in Table 5-1.

Table 5-1: Maximum H_2/C molar at different gasification temperature

Temperature (°C)	650	750	850
Max H_2/C molar ratio	0.8	2.0	5.0

5.2 Block Flow Diagram

Mass and energy balance of pilot plant with maximum H_2/C molar ratio at 650°C, 750°C and 850°C is given in Figure 5-5, Figure 5-6 and Figure 5-7, respectively. The heat requirement in gasifier, gas cooling system, WGS unit and steam condensing is calculated in the unit of kW. It should be noticed that the number in minus represents heat is imported into the system while vice versa.

As shown in these figures, 750°C of process temperature with 2 to 1 ratio of hydrogen to carbon mole input ratio shows the maximum product yield (41.3 percent of carbon conversion to SNG, 519 Kg per day). In this process condition, 93 percent of CH_4 concentration can be achieved. (Dry bases, after separation of CO_2 and H_2)

Figure 5-3: Mass and heat balance of pilot plant with gasification temperature at 650°C

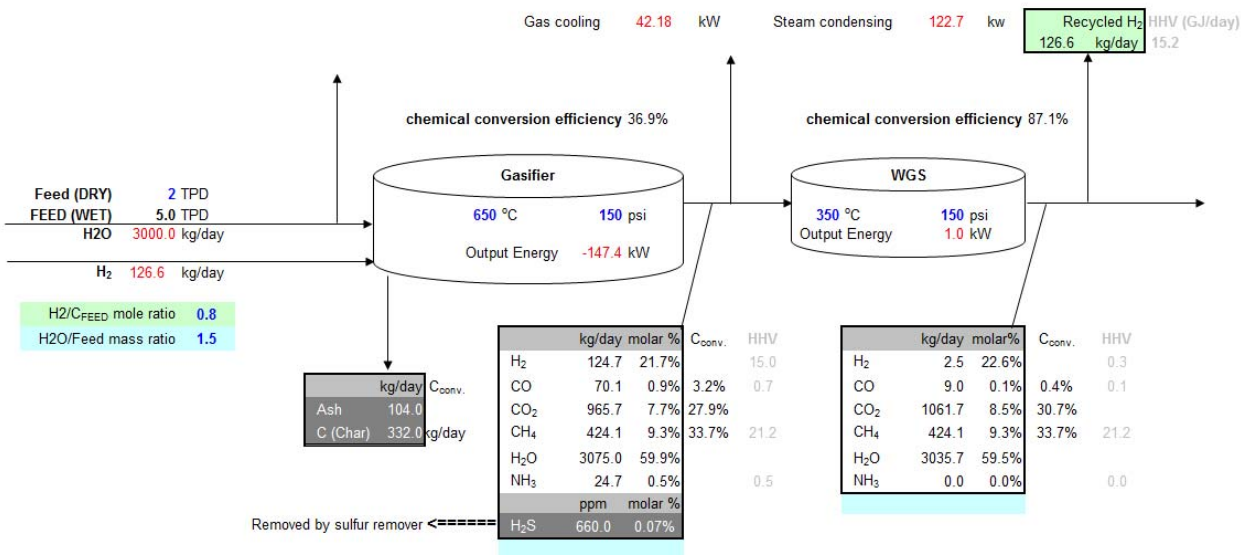


Figure 5-4: Mass and heat balance of pilot plant with gasification temperature at 750°C

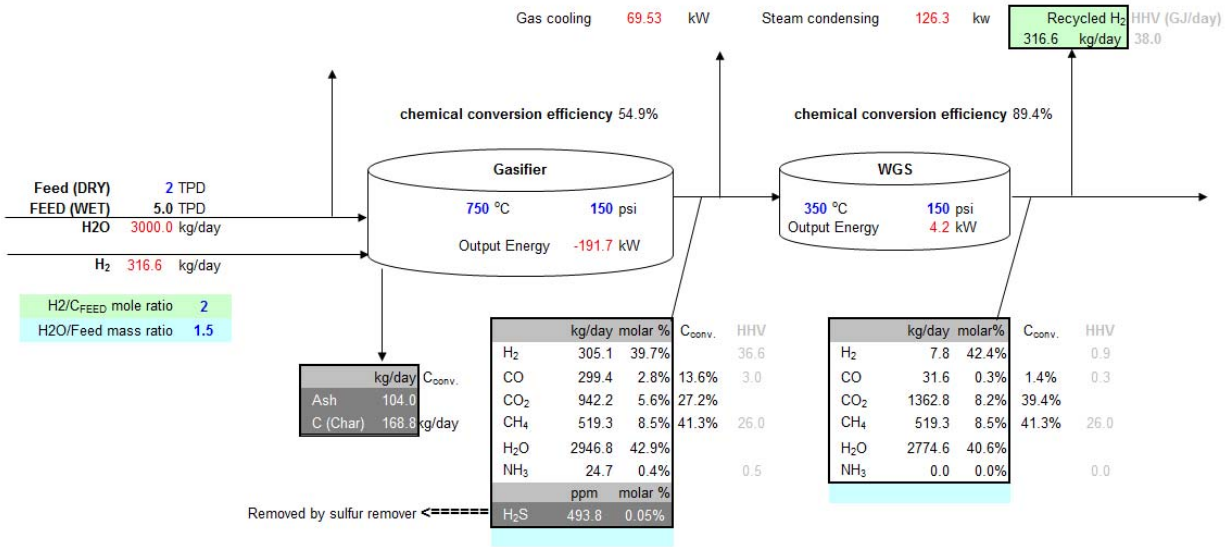
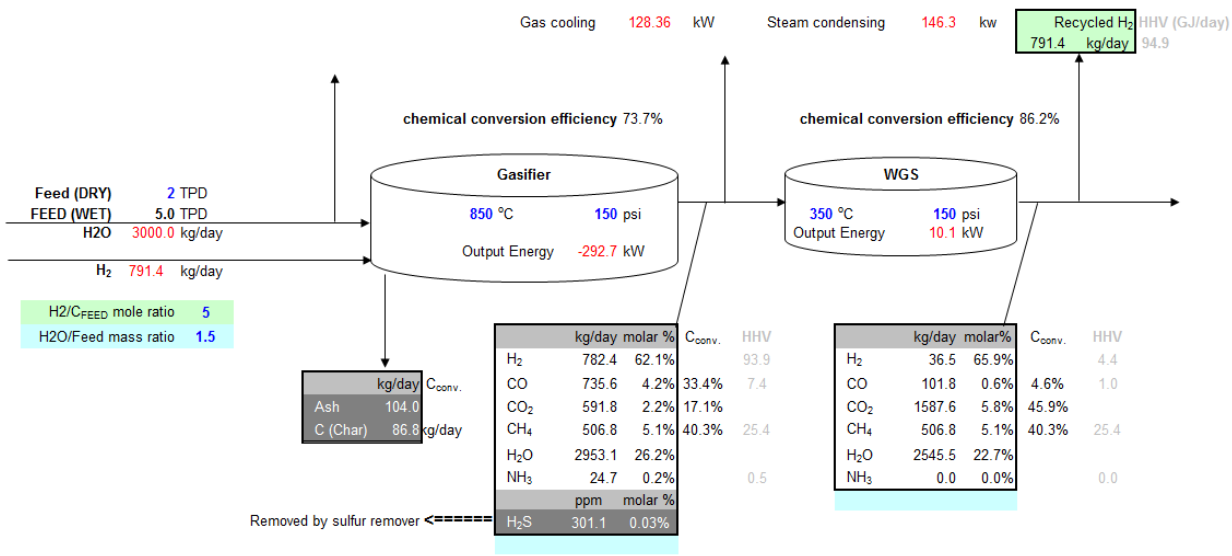


Figure 5-5: Mass and heat balance of pilot plant with gasification temperature at 850°C



5.3 Process & Utility Flow Diagram

A commercial scale of 5 TPD plant using steam hydrogasification configured with a WGS reactor is studied in this report. The whole design consists of 5 major steps: Feedstock preparation, SHR, Gas cleanup system, WGS reactor, H_2 separation and CO_2 removal. The technologies described in the design included a warm gas clean up system, WGS reaction, and CO_2 removal and these technologies are considered to be commercially established.

The gasification temperature and pressure was set at 750°C and 150 psi, respectively. The carbon conversion was approximately set at 80 percent in SHR with char 18 percent remained in the residue. The optimum H_2O/feed ratios were determined as 1.5 based on previous simulation work in order to maximize gas yield as well as process heat recovery. The H_2/C ratio should be as high as possible to promote CH_4 formation, however, it must be guaranteed sufficient H_2 is left for system internal cycle in SHR. The operation area and design description are shown in Figure 5-6.

5.3.1 Pretreatment Section

Biosolids and green waste are used as feedstock. The feedstock is mixed in a certain ratio in order to be pumpable slurry as mentioned before. Desired water content ranges from 50-55 percent in the feedstock can be achieved in order to meet the gasification requirement. A hydrothermal pretreatment step is employed due to the hygroscopic and hydrophilic property of feedstock in slurry formation. A batch type pretreatment reactor is operated at 230°C and 400

psi for 30 minutes. Stable and homogeneous slurry can be obtained after the hydrothermal pretreatment and is directly pumped into the SHR reactor. Two reactors in parallel are used in the pretreatment process to keep the slurry feed constant and continuous.

5.3.2 Gasification Section

Feedstock is injected via slurry injectors into a bed of sand operated at 150 psi which uses recycled H_2 flow for fluidization. The additional energy source for the SHR is recirculated sand heated by char combustion with pressurized air in an external fluidized bed regenerator. It is recognized that the heat requirements of the gasification could not be met just with char combustion and would require additional fuel if less char is produced in SHR.

The sand in the SHR reactor is mildly fluidized and the gas bubbles leaving the fluidized bed enter a large expanded section of the vessel where larger char particles can be disengaged from the gas. This also allows the gas to have a long residence time to promote cracking of tars and higher hydrocarbons. Fine char/ash produced in the moderate-temperature SHR reactor flows with the gas to initial stage of a two stage internally supported cyclone, where disengaged solids falls into a standpipe back into the fluidized bed. Ash particles escaping the SHR and regenerator cyclones are cooled and collected by hot gas filters, depressurized, and conveyed to ash bins for storage and eventual removal for onsite storage or disposal.

5.3.3 Warm Gas Cleanup Section

The steam in the SHR producer gas needs to be cooled down to 350ºC in the downstream WGS reactor after contaminants removal. It is not wise to clean the gas by cooling down the steam below the boiling point which leads a heavy heat penalty. Based on this reason, RTI warm gas cleanup technology is employed in this study in order to improve the system thermal efficiency that consists of a number of parts. Initially the gas contacts a bed containing HCl adsorbents. The second step is a compact Transport Desulfurization Reactor (TDR) system that utilizes a regenerable ZnO sorbent for sulfur removal and conversion into SO_2. The SO_2 is converted into elemental sulfur via a reaction with hydrogen. A third step is the use of a regenerable sorbent for fixed-bed ammonia/HCN conversion. Finally, trace elements (Hg, As, and Se) can be removed at temperatures above 250°C.

5.3.4 WGS Reactor

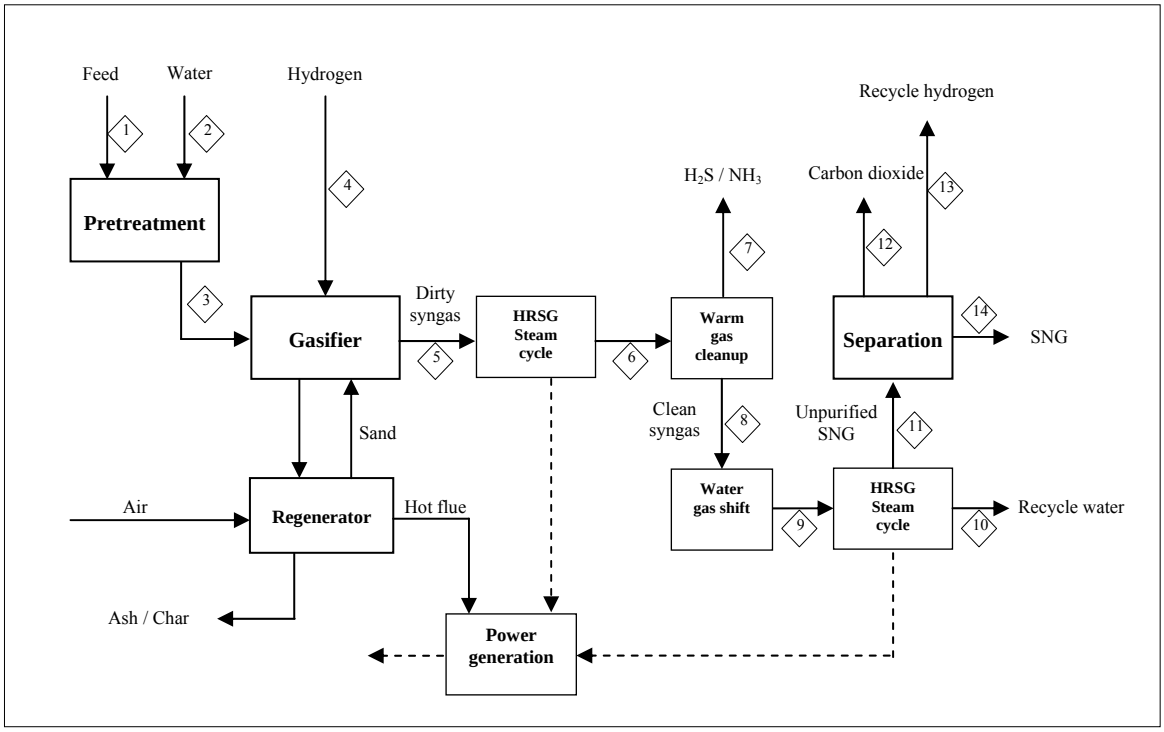
The WGS reactor is controlled at 350°C as the same operating pressure. CO is reacted with the internal steam in the fixed bed reactor filled with a commercial Iron-based catalyst. 85-90 percent of conversion would be expected to achieve a sufficient amount of H_2 to recycle after the separation step. CH_4 generated in the gasification step is approximately 15-20 percent content of dry product gas. The amount of CH_4 is almost unchanged during the shift reaction.

5.3.5 Separation Section

After leaving the WGS unit, the product gas flows into a series of heat exchangers, Heat Recovery and Steam Generation (HRSG), and cool the gas down to 30°C to condense the remaining H_2O before entry into the CO_2 removal process utilizes methyldiethanolamine

(MDEA) as solvent and CO_2 is removed by counter-current contact with MEDA solution in adsorption tower. The Pressure Swing Adsorption (PSA) unit is utilized for H_2 separation to provide the necessary enriched hydrogen stream for recycle to the SHR.

Figure 5-6: Overall process flow diagram with individual stream process temperature, pressure and mass flow rate in the accompanying table



Steam	1	2	3	4	5	6	7
T (°C)	25	25	150	25	750	350	350
P (psi)	14.7	14.7	150	14.7	150	150	150
M (TPD)	2	3	5	0.32	5.03	5.03	0.025
Steam	8	9	10	11	12	13	14
T (°C)	350	350	30	30	30	30	30
P (psi)	150	150	14.7	150	150	150	150
M (TPD)	5.01	5.01	2.77	2.24	1.36	0.32	0.56

Finally, the overall carbon conversion of this SNG process is approximately 60 percent with the content of CH_4 higher than 90 percent and the process efficiency is expected 70-75 percent based on the heating value.

5.4 Life Cycle Comparison Report

5.4.1 Production Cost Estimation

Capital cost estimation required for the life cycle cost is mainly based on economic analysis made by National Energy Technology Laboratory (NETL) within Department of Energy (DOE). NETL has reviewed the SHR process through a Cooperative Research And Development Agreement (CRADA) by validating the equilibrium model, process flow sheet for FT (Fischer Tropsch) liquids production and power generation with integrated gasification combined cycle (IGCC) using SHR technology and bituminous coal as feedstock (4000 TPD) in 2008. Although the feedstock used in this case is biosolids and green waste instead of coal, the same number was used in assessment the cost of the facilities, utilities and chemicals.

The major assumptions used in the economic model were:
Plant Size: 3500 BDT/day
Capital cost: 625.2 Million USD
Feedstock: Biosolid and green waste generated within Southern California
Two year construction & start up
Cost for feedstock: $0/ton
Total Labor Costs per year: 1 percent of the capital cost
Maintenance Cost per year: 2 percent of capital cost
Operating Cost per year (chemicals, royalties): 2 percent of capital cost
Loan interest rate: 3 percent
Inflation rate: 3 percent
SNG selling price: $6/MMBtu
Other costs such as feedstock gathering, delivering, loading/unloading, and storing are not taken into consideration in this case.

The result shows the production cost of the SNG in a 3500 BDT/day plant using green waste and biosolids as feedstock is $4.39/MMBtu with IRR of 16.68 percent.

It should be noted that the feedstock cost and other costs such as feedstock delivery costs are not included in the analysis which could be predominate factors that influence the production cost and IRR.

5.4.2 Comparison to the other processes

Table 5-2 shows a comparison of different processes for producing the SNG. SHR process shows less capital requirement and relatively faster rate of SNG production in comparision to other competing processes. For the application of smaller sized, distributed feedstock such as biosolids or biomass, SHR process definitely shows benefit in its process economics.

Table 5-2: Comparison of the SNG producing processes

	Anaerobic Digestion	Hydrogasification	Methanation of Syngas	Steam Hydrogasification
Limitation in the Feedstock?	Yes (cannot process Lignin)	No	No	No
Can process Wet feedstock	Yes	No	No	Yes
Minimum Process size for economics	~ 10 TPD	Large	Large	~100 TPD
Reaction Rate	10-25 day	~ 1 min.	~ 10 sec	~ 30 sec
Producer Gas Pressure	Atmospheric Pressure	High Pressure	High Pressure	High Pressure
Waste water treatment facility requirement	High	Low	Low	Very Low (Can produce clean water byproduct)
Capital cost	Low	High	High	Low
Production cost $/MMBtu	-	N/A	N/A	~5

A comparison of the life cycle production cost with other competing process is provided in Table 5-3.

Table 5-3: Production cost of the different SNG producing processes

	Anaerobic Digestion	Indirect Gasification/ Methanation	POX Gasification/ Methanation	POX Gasification/ Methanation
Production Cost ($/MMBtu)	$ 7.56	$7.05	$11.2	$8.42
Feed	Diary Waste	Biomass	Biomass	Illinois Coal
Capacity	807,000ft^3/day	1000MWth		1000TPD
Reference	Linkoping[3]	[4]	[5]	[6]

[3] Krich, K., Augenstein, D., etc. ***Biomethane from Dairy Waste: A Sourcebook for the Production and Use of Renewable Natural Gas in California***. Western United Dairymen. 2005.

[4] Zwart, R.W.R., Boerrigter H., etc. ***Production of Synthetic Natural Gas (SNG) from Biomass: Development and operation of an integrated bio-SNG system***. Energy Research Center of the Netherlands. 2006.

[5] Chandel, M., Williams. E. ***Synthetic Natural Gas (SNG): Technology, Environmental Implications, and Economics***. Duke University. 2009.

[6] Bartone, L.M., White, J. ***Industrial Size Gasification for Syngas, Substitute Natural Gas and Power Production***. National Energy Technology Laboratory (NETL). 2007.

CHAPTER 6:
Feasibility Studies for (1) Algae Feedstock (2) Gasoline Production

6.1 Algae Feedstock Study Plan & Result

6.1.1 Background and Research Plan

Microalgae are currently being promoted as a next generation biofuel feedstock. Compared with terrestrial plants, microalgae have a high oil content and growth rate. Mass microalgae cultivation can be performed on unexploited lands using saline water in arid regions, thus avoiding competition for limited arable lands. In addition, nutrients from microalgae cultivation can be obtained from wastewater, particularly nitrogen and phosphorus. Microalgae can typically be used to capture CO2 emissions from stationary sources, including power plants and other industrial emitters for mitigating greenhouse gas (GHG) emissions related impacts of fossil fuel[7,8].

Algae biomass can be converted to fuel in several ways. Normally, the production pathways for microalgae-based biofuels consist of cultivation, harvesting/dewatering, extraction and conversion. Microalgae can be cultivated in open ponds and photobioreactors (PBRs). Open ponds are much cheaper than PBRs. However, closed PBRs have a better control of cultivation conditions such as mass transfer and contamination than open ponds[9]. Harvesting consists of biomass recovery which removes wet biomass from cultivation systems and is often combined with dewatering or drying process. Drying requires heat to remove high moisture content from algae biomass. Lipid extraction can be achieved by mechanical expulsion or solvent extraction. One should consider the energy consumption, cost and environmental toxicity with drying and lipid extraction[10].
Lipid-based fuels are produced by transesterification or catalytic treatment (cracking, hydrotreating, and deoxygenation) of lipid extracted from microalgae. The remaining biomass is considered for conversion of biogas in order to generate power and heat.

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[7]Amin, S., ***Review on biofuel oil and gas production processes from microalgae***. Energy Conversion and Management 2009, 50, (7), 1834-1840.

[8] Clarens, A. F.; Resurreccion, E. P.; White, M. A.; Colosi, L. M., ***Environmental life Cycle Comparison of Algae to Other Bioenergy Feedstocks***. Environmental Science & Technology 2010, 44 (5), 1813-1819.

[9] Ghirardi, M. L.; Jorquera, O.; Kiperstok, A.; Sales, E. A.; Embirucu, M., ***Comparative energy life-cycle analyses of microalgae biomass production in open ponds and photobioreactors***. Bioresource Technology 2010, 101, (4), 1406-1413.

[10] Ferrell, J.; Sarisky-Reed, V. ***National Algal Biofuels Technology Roadmap; U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, Biomass Program***. 2010.

Steam Hydrogasification Reaction (SHR) is the thermo-chemical conversion of biomass that requires feedstocks with high moisture content like microalgae. SHR can convert the biomass to combustible gas along with steam and hydrogen. The commercial gasification uses oxygen or air as the gasifying agent and small oxygen production plants are extremely expensive. Therefore, the removal of the oxygen requirement by utilizing self-generating hydrogen increases the process efficiency and economics. Thus, SHR process is an attractive option for conversion of biomass, biosolids and microalgae into fuels.

This study investigates the feasibility of using algae for the SHR process feedstock thru process modeling adjusted from the experimental result with the laboratory scale SHR reactor. The results will be present in the form of the capital and production costs of a microalgae-to-liquid production plant utilizing 2000 dry ton per day of microalgae. The goal is to produce sustainable liquid transportation fuels with electricity as a co-product within the next 5-8 years.

The core parts of the process include the Steam Hydrogasification Reactor (SHR), a Steam Methane Reformer (SMR) and a Fisher Tropsch Reactor (FTR). All are demonstrated technologies. Enhanced conversion of carbon into methane in a high steam environment with hydrogen can be achieved in the SHR without the need of catalysts or the use of oxygen from an air separation unit. This process uses the entire mass of the algae and wet algae with high moisture content can be used as feedstock directly.

6.1.2 Algae Feedstock Study Results:

Laboratory Scale SHR of Algae Feedstock

Microalgae (Chlorella vulgaris) were used in the experiment. The microalgae were dried in the vacuum oven at 105°C to get rid of inherent moisture. The composition of the microalgae sample is shown in Table 6-1.

Table 6-1: Proximate and ultimate analysis of microalgae sample

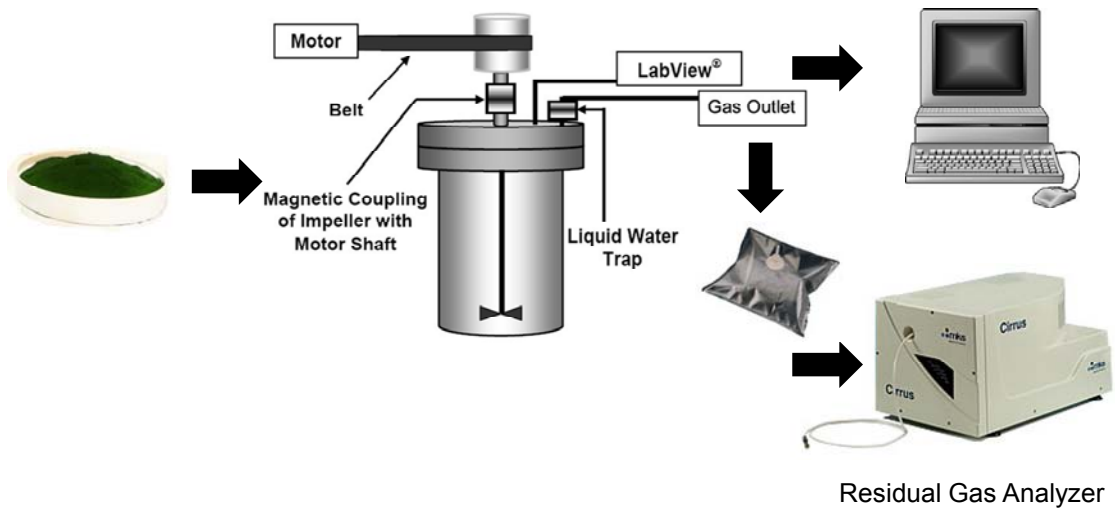
Proximate Analysis (wt% on wet basis)	
Moisture content	6.11
Ash content	5.87
Fixed carbon	21.80
Volatile matter	70.22
Ultimate Analysis (wt% on dry basis)	
C	47.84
H	6.29
N	8.12
S	0.568
O (by different)	31.31

The reactor was specifically designed to enable continuous stirring under high temperature and pressure. The reactor tube was made of inconel® alloy, has a volume of 260 ml. and has a maximum operating pressure and temperature of 800°C at temperature 500 psi. The reactor

setup is comprised of a heating system, a batch reactor, a water trap, and a gas outlet that allows product gases to be collected by tedlar gas sampling bag.

A schematic diagram of the stirred batch reactor used for SHR is shown in Figure 6-1. A 0.5 g of microalgae was used for all of experiments. The steam/microalgae ratio was calculated on a mass basis and the hydrogen/carbon ratio was calculated on a mole basis in experiment. The H_2O/microalgae mass ratio of 2.0 has been chosen. The reaction condition was set at hydrogen/carbon molar ratio of 1.0 at temperature 750°C and pressure 400 psi.

Figure 6-1: Schematic diagram of the stirred batch reactor for SHR of microalgae



After the test, the product gas was collected by Tedlar bag and analyzed by the Residual Gas Analyzer (RGA). RGA can identify and analyze gaseous components based on the quadruple mass spectrometer. RGA is used to identify and analyze gaseous components to provide the composition of gas containing H_2, CH_4, CO and CO_2 from the reactor. The carbon conversion is defined as the amount of carbon in the feedstock that is converted into gaseous products:

$$\text{Carbon conversion (\%)} = \left(\sum N_{c,i} / N_{c,\,feed} \right) \times 100$$

$N_{c,i}$ = Number of moles of carbon in product gas (i), mol

$N_{c,\,feed}$ = Number of moles of carbon in feed, mol

Results are shown in Figure 6-2. The 65 percent carbon conversion around the 750°C was achieved. Unconverted carbon, which is mainly a form of char, will be used for the heat source for SHR process in the subsequent process simulation study. Producer gas from the SHR was combined to SMR to produce the syngas. The H_2/CO ratio of the syngas required to be 2.1 for the FT reactor to generate synthetic fuels. The excess hydrogen is used to recycle back to SHR.

The hydrogen recycle is defined as the amount of hydrogen that can be provided by the SMR to SHR as a feed.

The H_2O to mass ratio and the H_2/Carbon mole ratio of the algae feedstock for SHR are also important parameters that can control the product gas composition and also considerably influence the process efficiency. The carbon dioxide portion of the producer gas can be separated and captured for a carbon source of growing microalgae.

Figure 6-2: Products distribution and total carbon conversion from the gasification of microalgae sample at various temperatures

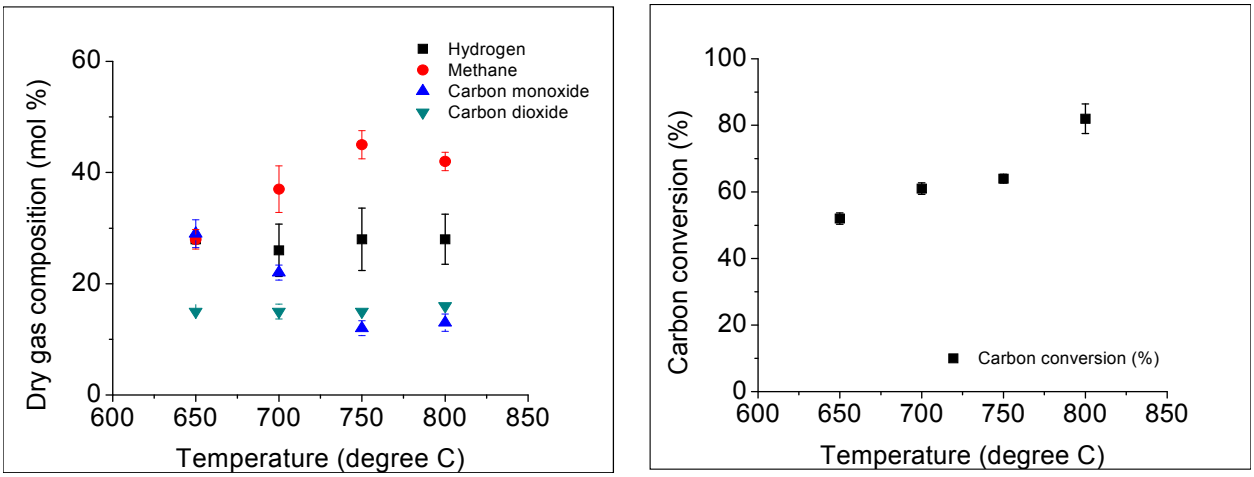
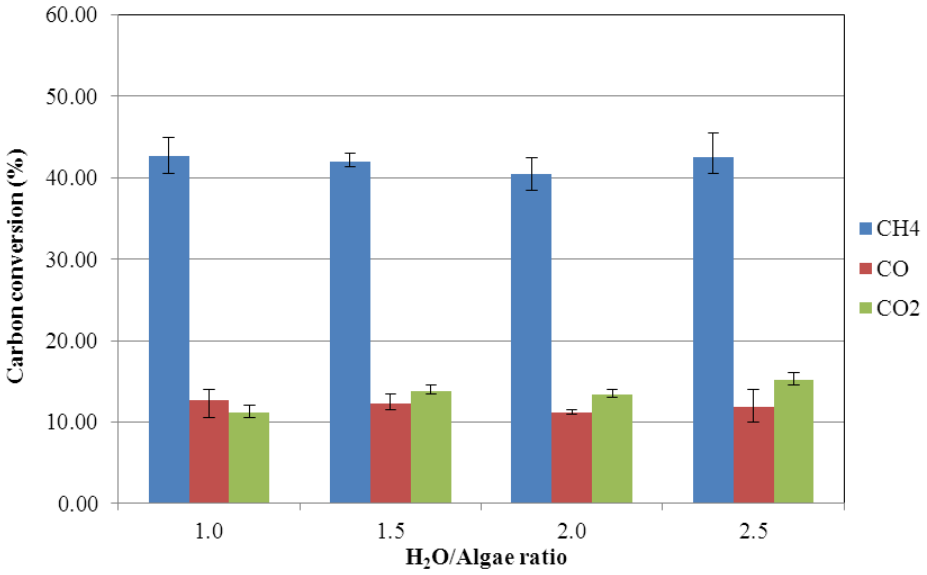


Figure 6-3: Conversion of CH_4, CO and CO_2 in SHR product gas



The results that varied H_2O/algae mass ratio from 1.0 to 2.5 are shown in Figure 6-3. It was observed that the fraction of methane and carbon dioxide trivially decreased and fraction of

carbon dioxide increased slightly with increase in H_2O/algae ratio of feed. The increment in H_2O/algae ratio may cause the reforming reaction, which results in methane decreased. Also under the condition the water gas shift reaction becomes favored, which caused an increase in carbon dioxide and decrease in carbon monoxide.

Process Modeling

The process was modeled and capital costs estimated. A discounted cash flow rate of return analysis was performed to determine the fuel production cost. The analysis shows that the nth plant is expected to require $500-600 million capital investment. The fuel production costs have a very large uncertainty associated with the cost and yield of microalgae production and/or harvesting. Estimates for the production cost of algae found in the literature range from a low of $50/dry ton to over $1000/dry ton. In addition, a pioneer plant is expected to be more costly to build and operate than an nth plant since algae-to-liquid based on gasification has not yet been commercialized. Pioneer plant analysis found that fuel production cost increases by 50-80 percent and capital investment costs are almost double. Nevertheless, the proposed thermochemical pathway, using the entire mass of algae without separation of the oils, appears to be a viable and potentially cost competitive pathway to renewable fungible fuels.

Figure 6-4: Flow Diagram of 2000 TPD Algae to Fuel Plant

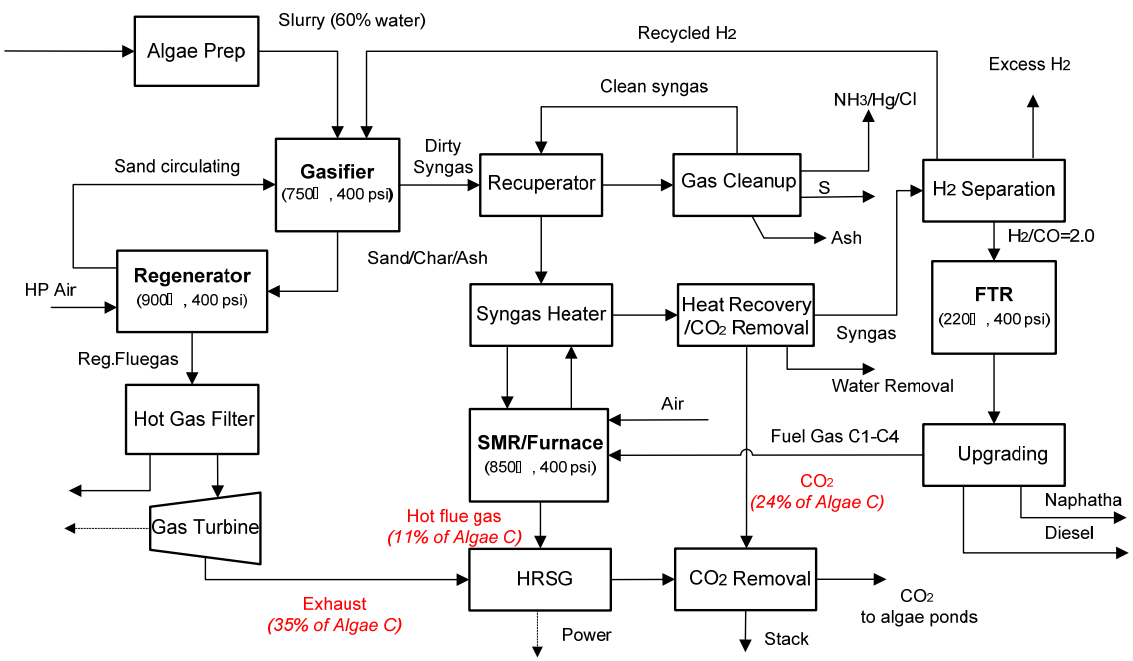


Figure 6-4 shows block flow diagram of 2000TPD commercial plant from the ASPEN process simulation adjusted by laboratory experimental data. The plant will convert algae into diesel

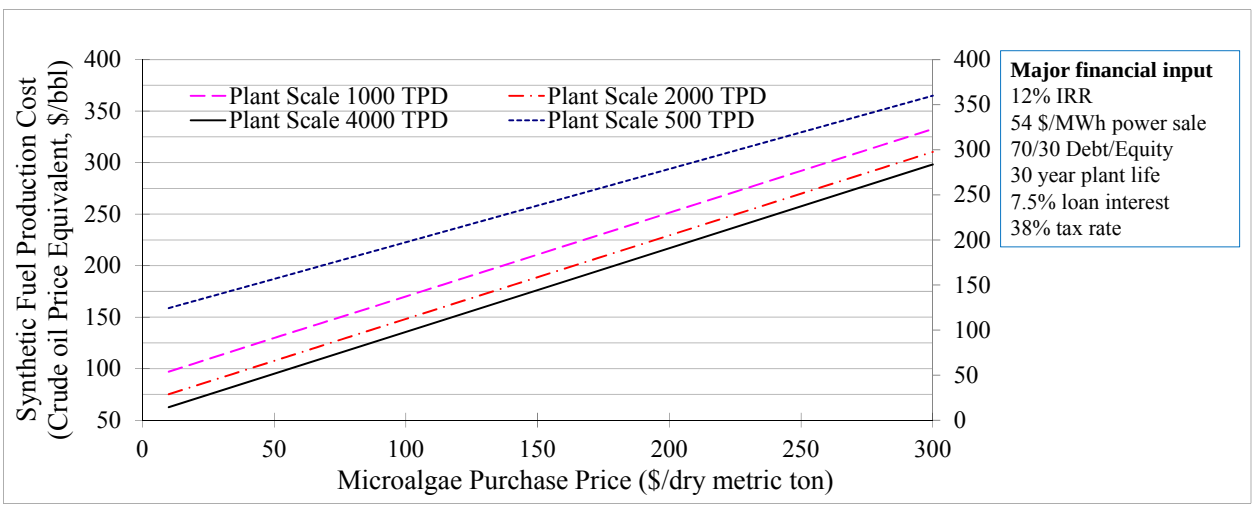
fuel. The major process blocks are SHR, SMR and FTR. Hot gas cleanup process and HRSG plant for the sulfur recovery and CO_2 removal was also included. Major result from the plant is summarized in the Table 6-2 below.

Table 6-2: Plant performance Result

Plant performance (Aspen Plus simulation results)	
Total microalgae input (Dry, ton/day)	1800
Total energy input (Mw_{th}, HHV)	508.5
Net plant power (Mw)	30.9
Liquids production (BBL/day)	2216
FT liquid fuels (Mw, HHV)	157.1
Specific liquids production rate (BBL/dry metric ton microalgae)	1.2
Fuel efficiency (% , HHV)	30.9
Fuel + electricity efficiency (%, HHV)	37.0
CO_2 recovery (ton/day)	2113

Figure 6-5 shows the production cost dependency on the plant scale and microalgae feed price.

Figure 6-5: Microalgae feedstock price and plant scale as a function of production cost



6.2 Gasoline Production Study Plan & Result

6.2.1 Background and Research Plan

Syngas can be converted to high-quality sulfur-free liquid fuels through Fischer-Tropsch (FT) synthesis. However, the product from FT synthesis has a wide range, and further steps such as hydrocracking and isomerization are required to improve fuel selectivity and quality. These steps are usually catalyzed by zeolite catalyst, because of its acidity and shape selectivity. In recent years, researches have been done on combining conventional FT catalysts with zeolite or

other acidic support to produce more iso-paraffin, and narrow product distribution, which is close to synthetic gasoline.

Firstly, the combination was a physical mixture of zeolite with conventional FT catalyst[11]. Martínez et al[12]. prepared a hybrid catalyst by physically mixing KFeCo FT catalyst with ZSM-5 catalyst at 1:1 mass ratio. It is found that product distribution is shifted towards gasoline-range iso-paraffin and aromatics. In addition, another combination of FT catalyst with zeolite support was also investigated[13]. Espinosa et al[14]. synthesized a bifunctional catalyst by impregnating Co in Beta zeolite. FT synthesis experiment with this catalyst showed significant increase of iso-paraffin selectivity. However, the selectivity of C13-C17 range is about 20 wt%, which means that this catalyst cannot effectively break down heavy components. Recently, FT catalyst with zeolite shell has been developed. The zeolite shell can effectively remove all heavy components larger than its channel size, thus gasoline range product selectivity is significantly improved. Yang et al.[15] synthesized a zeolite-shell catalyst, which has a zeolite shell around conventional FT catalyst. This core-shell structure has a very high selectivity towards gasoline-range iso-paraffin. However, the zeolite shell cause different diffusion rate of H_2 and CO, which results in a high selectivity of methane. Methane selectivity was reduced by using H-β/Co/Al2O3 core-shell catalyst, while maintaining high iso-paraffin selectivity. Similarly, Huang et al.[16] prepared CoZr/H-ZSM-5 hybrid catalysts through hydrothermal synthesis method. The combination of Fischer-Tropsch catalyst and acidic zeolites can improve gasoline-range hydrocarbon selectivity and iso-paraffin selectivity. Street et al.[17] studied gasoline-range aromatics production from syngas. Mo/HZSM-5 catalyst had been synthesized, and Fischer-Tropsch synthesis was conducted with CO_2 containing syngas mixture. The product liquid is mostly gasoline-range aromatics. However, organic phase selectivity of the synthesis is only 0.8 percent. Chevron is also actively involved in F-T gasoline research. They have developed a zeolite-support Co

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[11] Martnez, A., et al., ***Catalytic behavior of hybrid Co/SiO2-(medium-pore) zeolite catalysts during the one-stage conversion of syngas to gasoline***. Applied Catalysis A: General, 2008. 346(1): p. 117-125.

[12] Martnez, A. and C. Lopez, ***The influence of ZSM-5 zeolite composition and crystal size on the in situ conversion of Fischer Tropsch products over hybrid catalysts***. Applied Catalysis A: General, 2005. 294(2): p. 251-259.

[13] Bessell, S., ***Investigation of bifunctional zeolite supported cobalt Fischer-Tropsch catalysts***. Applied Catalysis A: General, 1995. 126(2): p. 235-244.

[14] Espinosa, G., et al., ***Catalytic behavior of Co/(Nano [beta]-Zeolite) bifunctional catalysts for Fischer-Tropsch reactions***. Catalysis Today, 2011.

[15] Yang, G., et al., ***Preparation, characterization and reaction performance of H-ZSM-5/cobalt/silica capsule catalysts with different sizes for direct synthesis of isoparaffins***. Applied Catalysis A: General, 2007. 329: p. 99-105.

[16] Huang, X., et al., ***CoZr/H-ZSM-5 hybrid catalysts for synthesis of gasoline-range isoparaffins from syngas***. Applied Catalysis A: General, 2011.

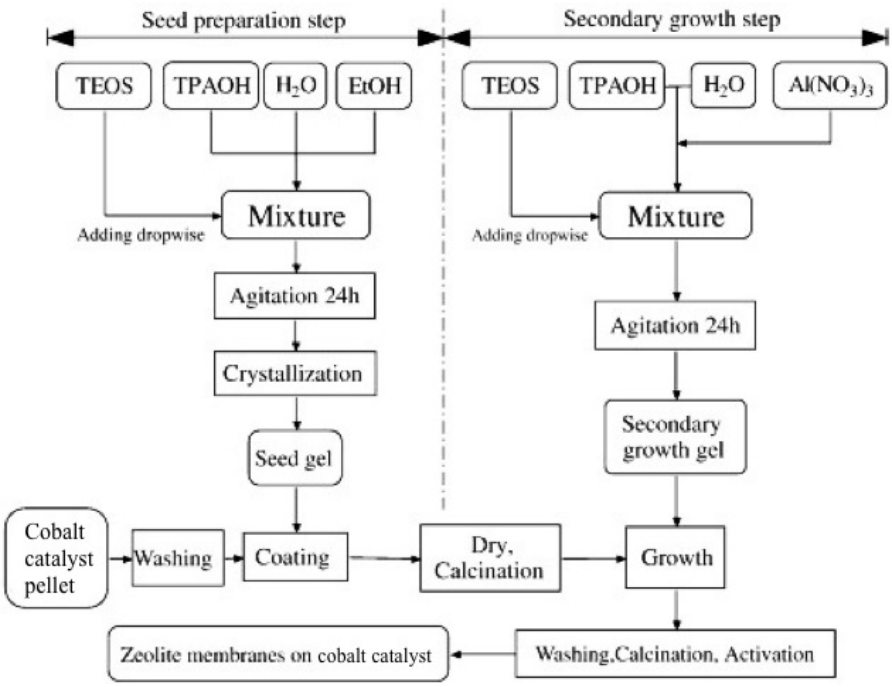
[17] Street, J., et al., ***Gasoline-range hydrocarbon production using biomass derived synthesis gas over Mo/H+ZSM-5***. Fuel, 2012.

hybrid F-T catalyst, which impregnate Co in ZSM-12 zeolite[18]. This catalyst is basically same with previous studies, except that they use different kind of zeolite support.

6.2.2 Gasoline Production Results

FT catalyst with a zeolite shell around the conventional FT catalyst is synthesized. The nominal combination of the conventional FT catalyst is 20 wt. percent Co and 1 wt. percent Ru supported on alumina pellets with particle size of 1.0 mm (Sasol 610110).

Figure 6-6: Schematic diagram of the zeolite shell synthesis by secondary growth method

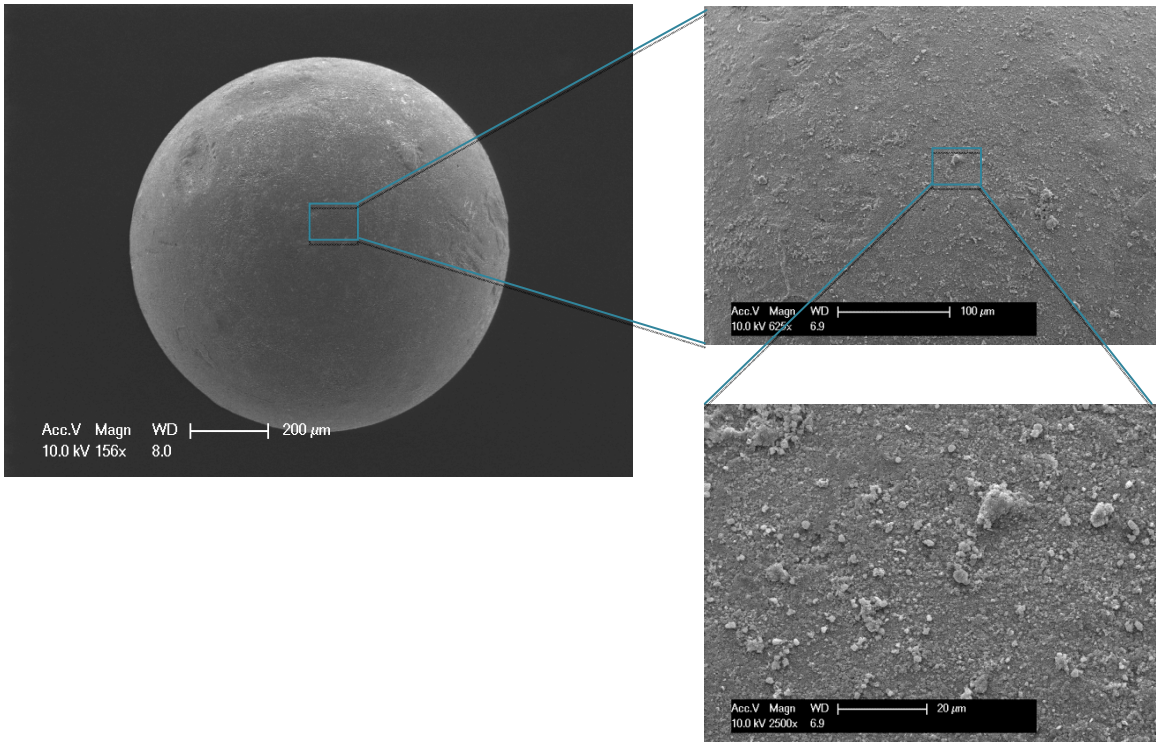


In this work, ZSM-5 membrane is synthesized by secondary growth method, which has been recognized to be superior to conventional zeolite synthesis. The schematic illustration of the membrane synthesis process is shown in Figure 6-6. First, the conventional FT catalyst pellets were cleaned with 2M KOH solution. Then the pellets were neutralized by concentrated HCl and distilled water. Afterwards, the catalyst pellets were immersed in the silicalite-1 seed sol with ultrasound treatment for 2 min, then dried and calcined in air at 450 °C for 3 hours. The second growth solution was also prepared by dissolving $Al(NO_3)_3$ in tetrapropylammonium hydroxide (TPAOH) and distilled water, followed by dropwise addition of tetraethyl orthosilicate (TEOS). The adsorption ratio of the solution is 250. Then 0.1g of the seeded catalysts were immersed in 25mL of the secondary growth solution, and put in autoclave at 185

[18] Kibby, ***Zeolite supported cobalt hybrid fischer-tropsch catalyst.*** 2011.

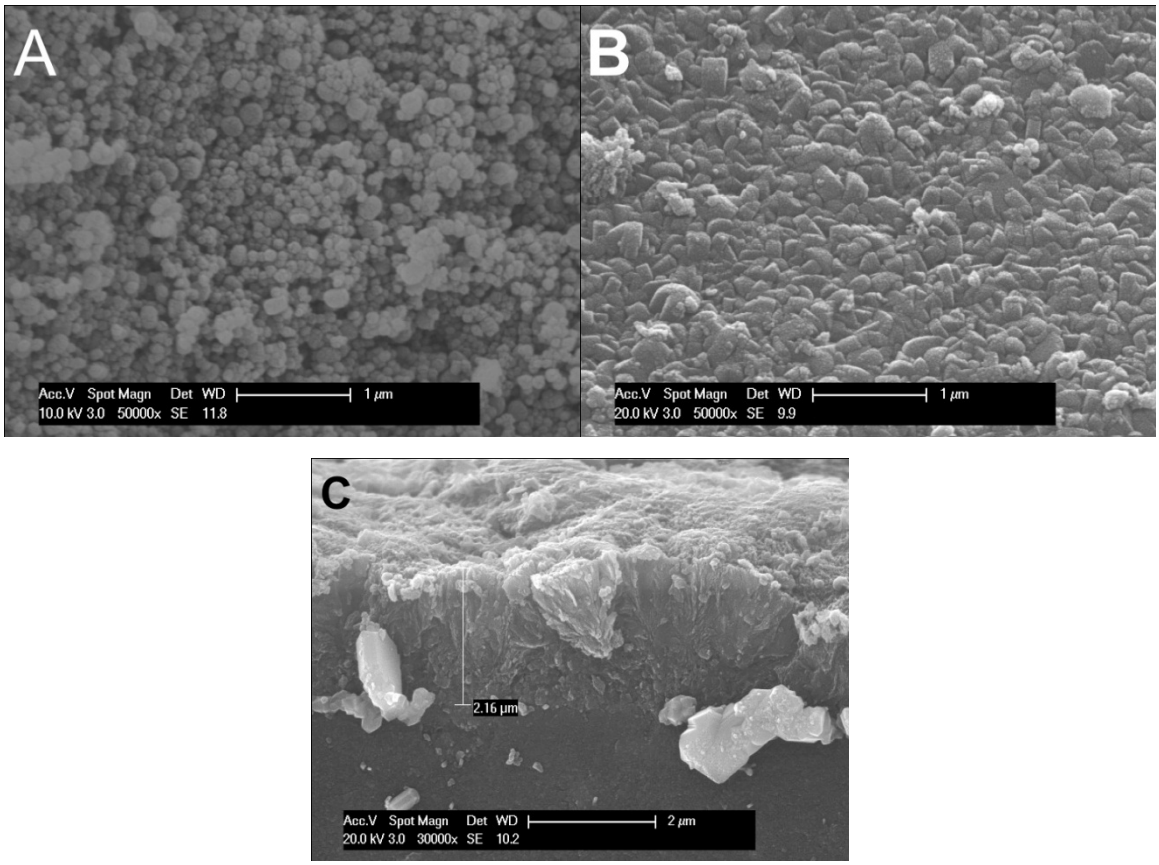
°C for 48 hours. After the synthesis, the ZSM-5 coated catalysts were calcined at 450°C for 2 hours, in order to remove the template from the zeolite pores.

Figure 6-7: SEM images of the catalyst surface



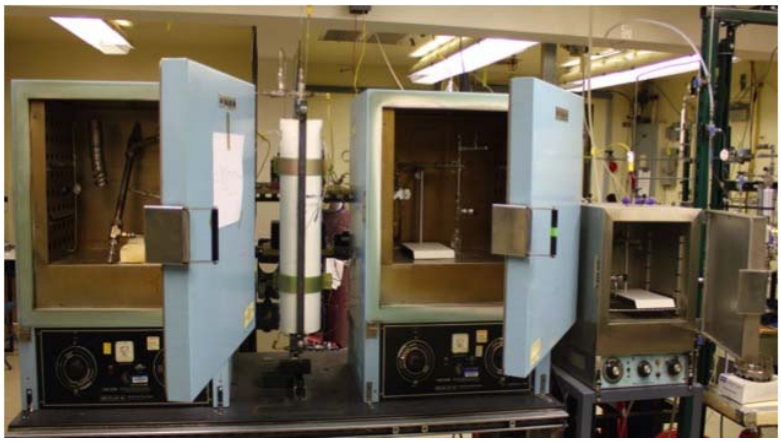
Scanning electron microscope (SEM) images of the zeolite-coated FT catalyst pellets are shown in Figure 6-7. As observed from the SEM images, the pellets have perfect zeolite coating, with no crack. The surface and cross-sectional SEM images of the catalyst pellets are also obtained, as shown in Figure 6-8. Figure 6-8A shows the surface of the catalyst pellets after the coating of silicalite-1 seeds. It can be seen that catalyst surface is covered by silicalite-1 seeds, which provide growth positions and can help with full coverage of ZSM-5 shell in second growth step. And we did observe a good coverage of ZSM-5 shell with no crack on most of the catalyst pellets after second-step synthesis (Figure 6-8B). In Figure 6-8C, a ZSM-5 coating on Co FT catalysts is clearly observed. The thickness of the coating is about 2.16μm. A thinner coating of the zeolite shell is beneficial to heat transfer, and has less influence on mass transfer resistance.

Figure 6-8: Surface and cross-sectional SEM images of the ZSM-5 coated Co catalyst. The surface image after seed coating: A; the surface SEM image after second step coating: B; the cross-sectional SEM image: C



Fischer-Tropsch synthesis (FTS) experiments have been conducted. Photo of the experimental setup is shown at Figure 6-9. Two kinds of catalysts are used in the experiments. One is conventional Co-Al_2O_3 FT catalyst; the other one is zeolite-shell/Co-Al_2O_3 catalyst. The experiment condition was 220°C, 180 psi, space velocity 2 NL/g-cat./hr., H_2/CO ratio 2.2. After each experiment, the liquid sample was analyzed.

Figure 6-9: Photo of Laboratory Scale Modified FTS Reactor for the Gasoline Production



The product obtained from the FTS reactor is shown at Figure 6-10. The gas chromatograph (GC) chromatograms are shown in Figure 6-11. It can be observed from the figure that the carbon number distribution of the conventional FTS liquid can range from C_6 to C_{25}. However, for the FTS with novel zeolite-shell catalyst, this distribution was significantly limited to C_6~C_{15}. It is because long-chain hydrocarbons were trapped by the zeolite shell, and were not able to penetrate until they were cracked to short-chain hydrocarbons. Note that most of these products are in gasoline range (C_5~C_{12}). In addition, conventional FTS mainly generated straight chain paraffin; while FTS with zeolite-shell catalyst produced more olefin and iso-paraffin. Note that olefin and iso-paraffin have higher octane value than straight-chain paraffin. To sum up, compared with conventional FTS, liquid products generated with novel zeolite-shell catalyst have higher gasoline range selectivity. Product octane value is also enhanced by the zeolite-shell catalyst.

Figure 6-10: Synthetic Gasoline Produced in the Lab

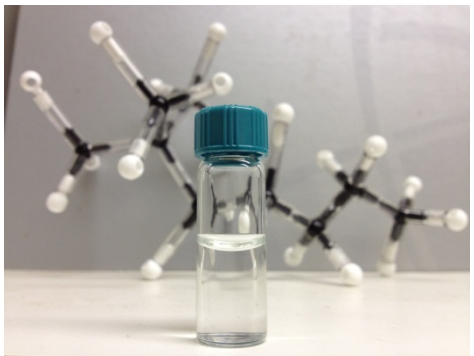
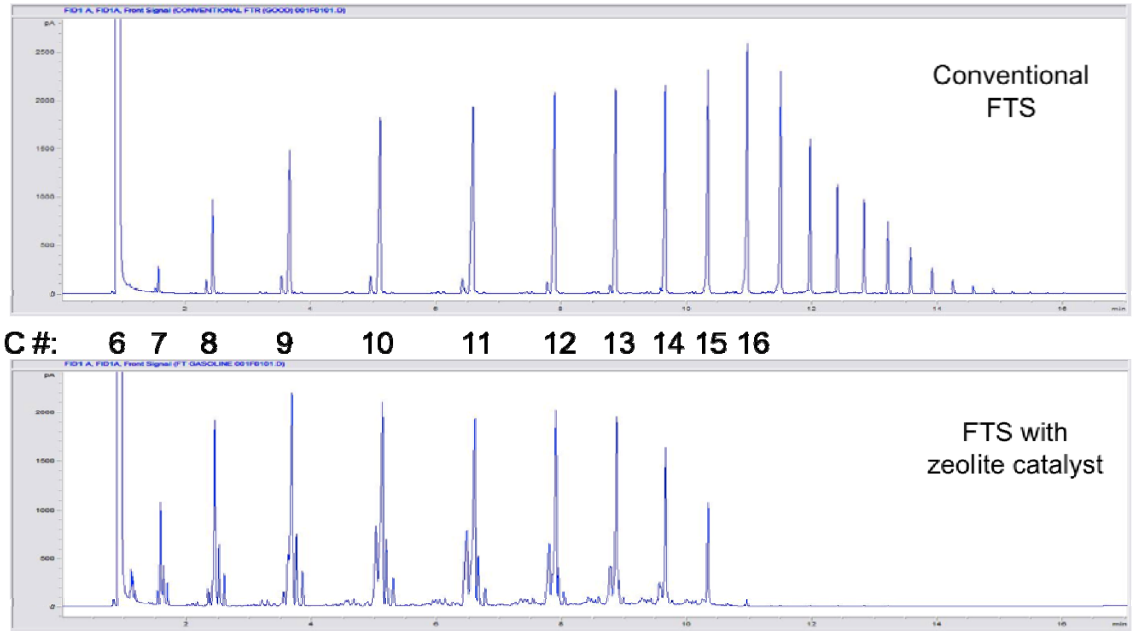
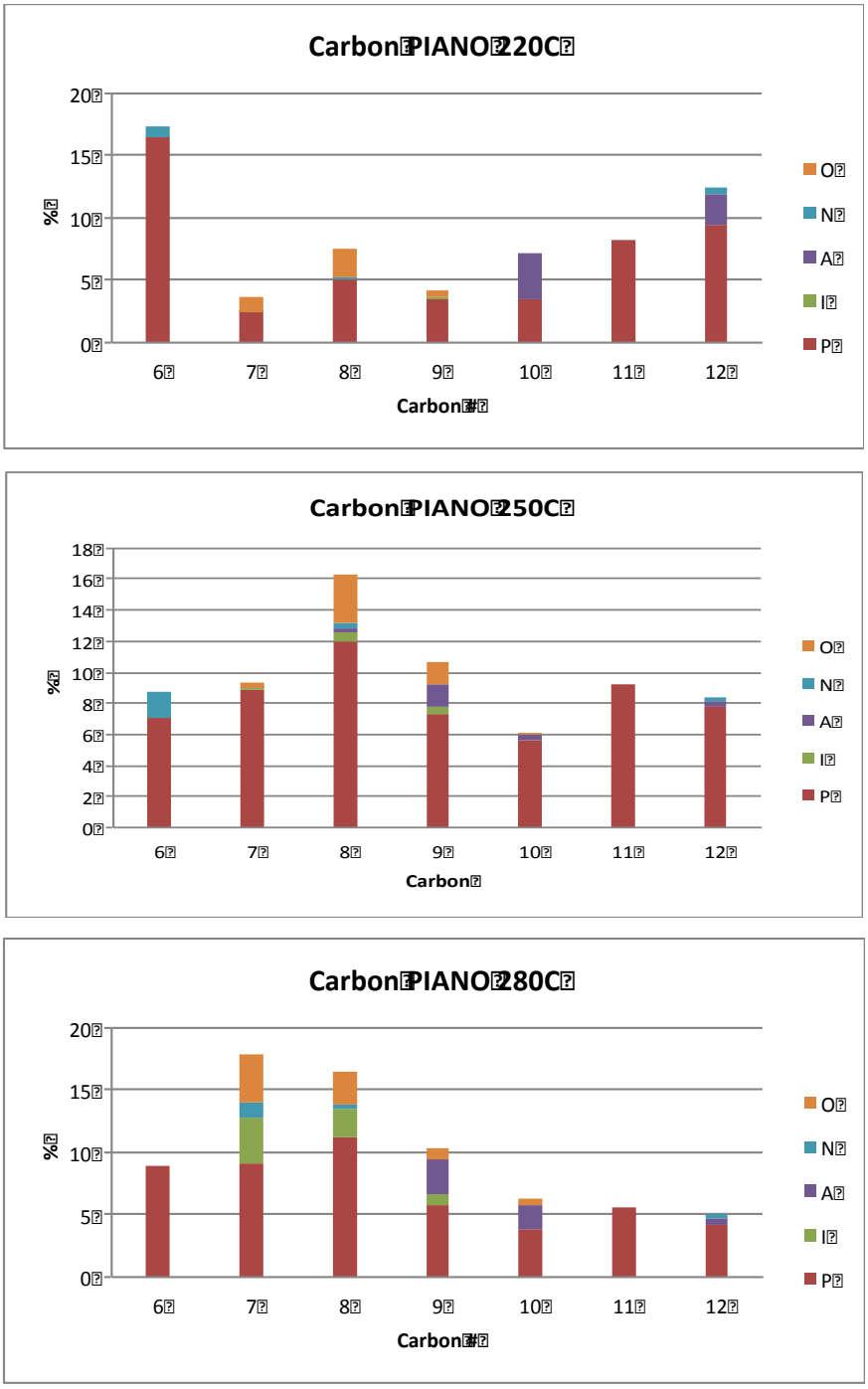


Figure 6-11: GC chromatogram of FTS liquid products



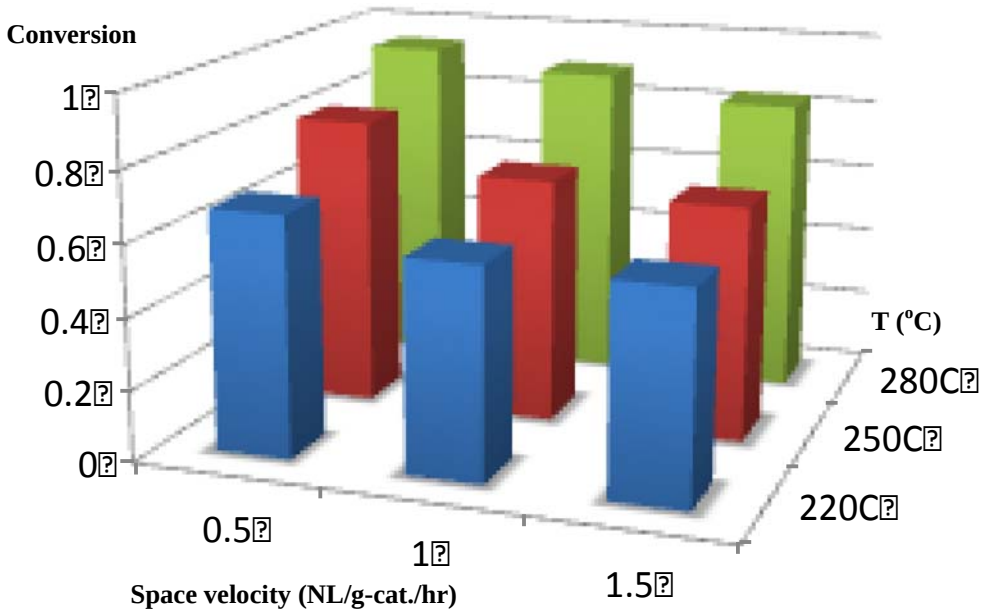
A detailed speciation of liquid product is achieved by PIANO analysis, where the content of paraffin (P), iso-paraffin (I), aromatics (A), naphthene (N), and olefin (O) in the liquid product is examined. The PIANO test results are shown in Figure 6-12. The reaction conditions are: H2/CO=2.1, P=180 psi, space velocity=0.5NL/g/h. It is observed from the figure that the main component of the product liquid is n-paraffin. However, n-paraffin content is reduced with increasing operating temperature. When temperature rises from 220°C to 280°C, iso-paraffin content is 0.362 percent, 1.229 percent, and 6.925 percent, respectively. Iso-paraffin is an important octane value booster; the significant increase of iso-paraffin content is also an indication of enhanced liquid octane value.

Figure 6-12: PIANO analysis results of F-T liquid sample with zeolite-shell catalyst at different temperatures. Reaction conditions: H_2/CO=2.1, P=180 psi, space velocity=0.5NL/g/h



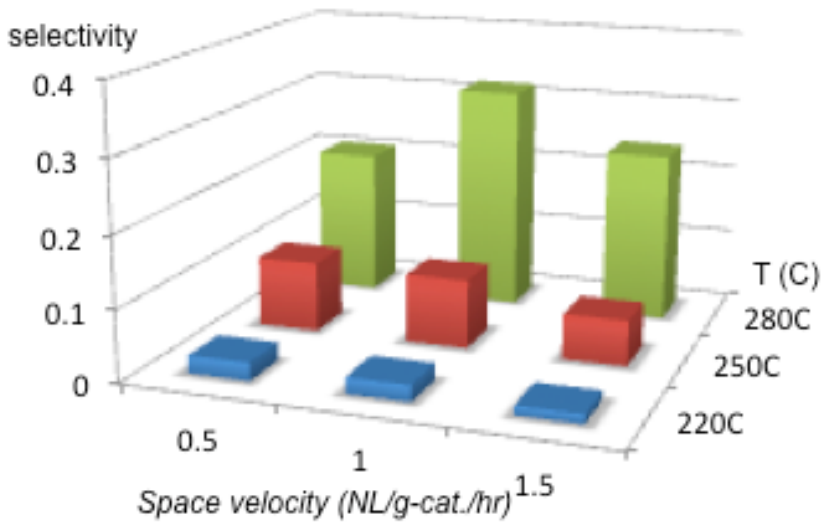
Besides liquid product analysis, gases analysis is also achieved. The change of CO conversion with temperature is shown in Figure 6-13. Reaction condition is $H_2/CO=2.1$, P=180 psi, space velocity (SV) are 0.5, 1, and 1.5NL/g/h. The experiment is carried out at 220, 250, and 280 degree C, respectively. It can be observed from the figure that, at fixed SV, CO conversion increases with increasing temperature; and CO conversion also shows an increasing trend with decreasing SV when temperature remains constant. For example, at SV=0.5, with increasing temperature from 220°C to 280°C, CO conversion was 62 percent, 86 percent, and 96 percent respectively.

Figure 6-13: CO conversion at different temperature and space velocity



In addition, the effects of SV and temperature on CH_4 selectivity are shown in Figure 6-14. From the figure it can be found that CH_4 selectivity will significantly increase with rising temperature. At 280°C, CH_4 selectivity is around 20 percent-30 percent; when temperature is at 250°C, CH_4 selectivity is reduced to less than 10 percent, and this number will be further decreased to less than 3 percent when temperature is at 220°C.

Figure 6-14: CH_4 selectivity at different temperature and space velocity



CHAPTER 7:
Summary of Results

All of the major technical objectives of this project were met. This section will summarize the results.

A PDU scale HTP was designed, built and demonstrated. The HTP produced a pumpable feedstock of comingled biomass and biosolids and met all of the target specification described in the performance objective. The most important result is that a feedstock of up to 40 percent solid loading (target was 30 percent) can be converted into the pumpable form with this technology. Carbon loss during the HTP process was less 4 percent (target was less 10 percent).

A PDU scale WGS process was also designed, built, integrated to SHR and successfully operated. The production of SNG with all the target specifications was successfully demonstrated. The SNGs production rate is 1.5 cubic meters per kilogram input of feed. The energy content of the producer gas was 15MJ per kilogram input of feedstock. The production of SNG at the temperature range of 650-750ºC, a H_2/C mole ratio of 1.0 and H_2O/feedstock mass ratio of 2 was successfully demonstrated. Composition of the SNG was 91 percent (mass) or 80 percent (mole) of CH_4 content with final separation of CO_2.

The preliminary design of a pilot plant at 5 tons per day capacity using the PDU technology was completed. A block flow diagram with process mass and energy balance and process & utility flow diagrams were developed as major deliverables of the project.

Preliminary process economic analyses were completed for a 3500 BDT/day SNG plant using biosolids and biomass as feedstock. It was estimated that the SNG production cost is $4.39/MMBTU with an IRR of 16.68 percent. This result together with the preliminary design basis for the pilot plant provides the confidence for moving forward to the pilot plant demonstration of this technology at the site of waste treatment plant.

Feasibility study of algae as a potential feedstock for SHR process was performed. It was estimated 2,216 barrels of liquid fuel can be produced from the 2,000 tons of algae feedstock.

Synthesis of gasoline from the modified FT catalyst was also performed. The research team successfully developed the new catalyst with zeolite encapsulation and demonstrated the production of gasoline ranged liquid fuel from renewable sources such as biomass and municipal waste.

The synthesized gasoline is a renewable gasoline, which is “carbon neutral”, and its usage needs no modification of existing infrastructure such as engines and pipelines. Renewable gasoline can be a solution for the both energy dependence issue and global climate change.

GLOSSARY

BDT	Bold Dry Tonne
Btu	British thermal unit
CEC	California Energy Commission
CE-CERT	College of Engineering-Center for Environmental Research and Technology
CH_4	Methane
CO	Carbon Monoxide
CO_2	Carbon Dioxide
DAFT	Dissolved Air Floatation Thickener
DOE	Department of Energy
FT	Fischer-Tropsch
GC	Gas Chromatography
GC-FID	Gas Chromatography with Flame Ionization Detector
GC-TCD	Gas Chromatography with Thermal Conductivity Detector
H_2	Hydrogen
HTP	Hydrothermal Pretreatment Process
HTR	Hydrothermal Reactor
H_2S	Hydrogen Sulfide
IRR	Internal Rate of Return
MAWP	Maximum Allowable Water Pressure
MAWT	Maximum Allowable Water Temperature
MAWL	Maximum Allowable Water Loading
MFC	Mass Flow Controller
MFM	Mass Flow Meter
MIT	Massachusetts Institute of Technology
mm	Millimeter
NiO	Nickel Oxide
NH_3	Ammonia
PDM	Pressure Display Module
PDU	Process Demonstration Unit
PPM	Parts Per Million
PR	Peng-Robinson
RPM	Round Per Minute
PWM	Pulse Width Modulation
SHR	Steam Hydrogasification Reactor
SLPM	Standard Liter Per Minute
SMR	Steam Methane Reformer
SOP	Standard Operation Procedure
SVM	Solenoid Valve Module
TPD	Tone Per Day
TDH	Transport Disengagement Height
UC	University of California

USA	United State of America
WGS	Water Gas Shift
ZnO	Zinc Oxide
ZnS	Zinc Sulfide