



Energy Research and Development Division

FINAL PROJECT REPORT

Enhancement of Substituted Natural Gas Production

Sorption-Enhanced Steam Hydrogasification Process with In Situ Carbon Dioxide Capture

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PREFACE

The California Energy Commission's (CEC) Public Interest Energy Research (PIER) Program supports public interest energy research and development that will help improve the quality of life in California by bringing environmentally safe, affordable, and reliable energy services and products to the marketplace.

The PIER Program conducts public interest research, development, and demonstration (RD&D) projects to benefit California.

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- Transportation

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For more information about the Energy Research and Development Division, please visit the <u>CEC's research website</u> (www.energy.ca.gov/research/) or contact the CEC at 916-327-1551.

ABSTRACT

The California Energy Commission has identified renewable natural gas as an important alternative fuel that can contribute to achieving California's goals related to replacing conventional fuel and reducing emissions in the transportation sector.

The University of California, Riverside recently developed a new process to remove carbon dioxide (CO₂) and increase the energetic gas (hydrogen and methane) yield from renewable natural gas, called sorption enhanced steam hydrogasification. Results from a laboratory-scale bench reactor showed that adding a sorbent (a material used to adsorb liquids or gases) such as calcium oxide could remove CO₂ in steam hydrogasification and increase hydrogen and methane production from different kinds of feedstock. The amount of hydrogen, in particular, increased dramatically, by as much as 60 percent compared to production without the addition of sorbent. The hydrogen content in the gas produced by the process was enough to maintain a self-sustained supply back to the steam hydrogasification when the ratio of calcium oxide to carbon was larger than 0.29.

Researchers developed a bench-scale circulating fluidized bed reactor through the mockup test. The results showed a 76 percent carbon-to-gas conversion. Process simulation software used the bench-scale demonstration results to perform a technoeconomic analysis that included a detailed heat and mass balance for renewable natural gas production. Compared to other production processes, the sorption enhanced steam hydrogasification process had the lowest CO₂ footprint (43.6 kilograms per million British Thermal Units) and lowest production costs (\$14.8 per million British Thermal Units) among other processes.

The project team completed a preliminary design for a pilot plant that could produce approximately 20,000 diesel gallon equivalents per year of fuel grade renewable natural gas using 0.8 dry metric tons per day feed throughput from commingled green waste and biosolids.

Keywords: California Energy Commission, Public Interest Energy Research, renewable natural gas, sorption enhanced steam hydrogasification, substitute natural gas water gas shift, circulated fluidized bed reactor

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EXECUTIVE SUMMARY

Introduction

The California Energy Commission (CEC) has identified renewable natural gas as an important alternative fuel that can contribute to the state's goals to reduce fossil fuel use and greenhouse gas and other emissions in the transportation sector. State policy measures that have identified specific targets include Assembly Bill 1007 (Pavley, Chapter 371, Statutes of 2005), Senate Bill 1250 (Perata, Chapter 512, Statutes of 2006), the Bioenergy Action Plan, and the Low Carbon Fuels Standard. The Alternative and Renewable Fuel and Vehicle Technology Program, created by the CEC under Assembly Bill 118 (Nuñez, Chapter 750, Statutes of 2007), expedites the development and deployment of alternative fuels and advanced transportation technologies.

Residential or small commercial natural gas customers in California account for around 40 percent of the natural gas delivered by California utilities. Large customers, like electric generators and industrial users, make up the remaining 60 percent. In 2008, total natural gas consumption in California was 2,405,266 million cubic feet. Only 13 percent of natural gas used in California comes from sources within the state, with 46 percent from sources located in the Southwest, 22 percent from the Rocky Mountains, and 19 percent from Canada.

Substitute natural gas produced from renewable sources offers a viable alternative to fossil fuel-based natural gas and has significant greenhouse gas benefits. However, there are technical and economic limitations to using conventional substituted natural gas production processes — such as anaerobic-digestion and conventional methanation of gasification product gas — to produce natural gas from sustainable biomass (organic matter) resources.

The technology developed in this project can use California's renewable biomass resources to replace 30 percent of the total fossil-based natural gas consumed in the state each year with no increase in greenhouse gases and could, in fact, displace around 50 million tons of greenhouse gases.

Project Purpose

The purpose of this project was to develop and demonstrate a highly efficient thermochemical process that combines a carbon dioxide sorption-enhanced steam hydrogasification reaction with a water gas shift reactor to produce a large amount of substituted or renewable natural gas using biomass resources from California.

Renewable natural gas can be produced from carbonaceous and renewable feedstocks through technologies like anaerobic digestion, landfill waste decomposition, gasification, and pyrolysis. These methods, however, are often inefficient and produce gas of inferior quality compared to fossil natural gas. Technologies are needed that can produce cost-competitive renewable natural gas more efficiently. A new gasification technology that uses steam and recycled hydrogen as the gasifying agents, known as steam hydrogasification, has been under development at the University of California, Riverside for more than a decade.

By developing a new sorption enhanced steam hydrogasification reaction process with the addition of calcined dolomite as a sorbent (a material used to absorb liquids or gases), this

project could considerably reduce the amount of carbon dioxide in renewable natural gas while increasing production of hydrogen and methane.

Project Process

University of California, Riverside has been involved for some time in developing a new gasification technology based on the steam hydrogasification reaction to produce substitute or renewable natural gas from biomass (carbon-based) feedstocks. These feedstocks include green waste and organic wastes from landfills, biosolids from wastewater treatment facilities, and agricultural residues. The steam hydrogasification reaction can handle wet feedstocks, does not require expensive oxygen plants, and operates at a lower temperature than any other conventional gasification processes. This technology was intensively reviewed by the United States Department of Energy's National Energy Technology Laboratory and shown to be an efficient and economic process compared to existing technologies.

Substitute natural gas from biomass feedstocks can be used to generate electricity or as an alternative transportation fuel. Conventional processes to produce substitute natural gas require additional steps such as methanation (conversion of carbon monoxide or carbon dioxide into methane) of the gas, which limit the efficiency of the process. In this project, the research team used a new and more-efficient way to produce substitute natural gas by combining the water gas shift process into the steam hydrogasification reaction process. The water gas shift is used to convert carbon monoxide to carbon dioxide and hydrogen through a reaction with water. The results from the bench-scale process demonstration show very promising results for the next step, which is demonstration of the technology in a pilot plant.

The research team improved the process by enhancing the steam hydrogasification reaction using dolime (dolomitic lime). The dolime can be produced from the water gas shift process as spent sorbent for carbon dioxide capture. The captured carbon dioxide can be used as a source for algae growth or chemicals production.

Project Results

Results from the laboratory-scale bench reactor show that adding sorbent could remove carbon dioxide within the steam hydrogasification reaction and increase production of energetic gas (hydrogen and methane) from different kinds of feedstock. In particular, the amount of hydrogen increased dramatically, as much as 60 percent in yield compared to production without adding sorbent. The hydrogen in the gas produced was enough to maintain a self-sustained supply back to the steam hydrogasification reaction. The researchers developed a bench-scale circulated fluidized bed reactor through the mockup test that showed a 76 percent carbon-to-gas conversion.

Using a process mass and heat balance study, the researchers estimated the carbon use efficiency of sorption-enhanced steam hydrogasification reaction as a carbon to methane conversion. In the conventional steam hydrogasification reaction process, only 22 percent of the carbon was distributed to the final product as methane, compared to about 40 percent from the sorption enhanced steam hydrogasification reaction-based process. If the sorption-enhanced steam hydrogasification is integrated with methanation process, it has almost zero carbon in the form of carbon dioxide in the form of gaseous exhaust.

Process simulation software used the bench-scale demonstration results to perform a technoeconomic analysis and a detailed heat and mass balance for renewable natural gas production. Compared to other processes, the sorption enhanced steam hydrogasification reaction has the lowest carbon dioxide footprint (43.6 kilograms per million British thermal units) and lowest production costs (\$14.8 per million British thermal units).

The project team completed a preliminary design of a pilot plant that could produce around 20,000 diesel gallon equivalents per year of fuel-grade renewable natural gas using 0.8 dry metric tons per day feed throughput of green waste and biosolids.

Benefits to California

The successful demonstration of the sorption enhanced steam hydrogasification reaction process will improve scalable production of renewable natural gas in plants customized for locally available feedstocks. This improvement will create opportunities for producing renewable natural gas from locally available feedstocks that will create jobs, provide new economic opportunities, and reduce dependence on foreign sources of energy.

A pilot plant demonstration will complete the critical next step in the development of this technology. The project provides the process and engineering data necessary for the design of a pilot plant as well as construction and operation of a commercial plant. Thus, the successful completion of the proposed project will enable a new, low-cost, efficient gasification technology for renewable natural gas production to move towards commercialization.

Project Tasks and Goals

Tasks within this project included:

- Task 2: Demonstrate and validate the production of substitute natural gas (SNG) with the sorption enhanced steam hydrogasification reaction (SE-SHR) process. The demonstration was performed at the bench-scale SE-SHR circulating fluidized bed (CFB) reactor. The goal was to design, fabricate, and operate the laboratory bench scale SE-SHR CFB reactor to produce SNG with the following target specifications:
 - \circ Producer gas yield (carbon conversion efficiency into SNG): Above 65 percent
 - Producer gas composition dry basis (pre clean-up), hydrogen (H₂)-free basis
 - Carbon monoxide (CO): 5 percent to 20 percent volume (vol percent)
 - Methane (CH₄): 65-80 vol percent
 - Carbon dioxide (CO₂): < 25 vol percent
 - Tars: < 3 milligrams per cubic meter (mg/m³)
 - Sulfur: < 150 parts per million by volume (ppmv)
 - Ammonia (NH₃): < 0.05 vol percent</p>
- Task 3: Evaluate the process economics and energy balances by developing an integrated process flow and economic model with in-house engineering software packages. The goals of this task were to (1) develop the integrated process flow sheet using ASPEN Plus Equilibrium modeling software adjusted by laboratory results; and (2) evaluate the process economics using ASPEN ICARUS with in-house modifications.
- Task 4: Complete a basic engineering design for a pilot plant using key information developed during the project. The goal of this task was to develop the basic engineering design of the pilot plant to process one-to-five tons per day of feedstock of comingled city biomass waste with biosolids in California. The basic engineering design of the pilot plant would allow both technical and economic feasibility analyses of a commercial-scale process. This task included life cycle comparison with other processes for SNG production.

Technical Performance Objectives

The objectives of this agreement were to:

- Validate the production and quality of SNG from the SE-SHR process under optimum operating conditions.
- Meet target specifications for the producer gas composition with specified biomass feedstock (pine wood).
- Evaluate the process economics with the assistance of the Aspen Economic Analyzer, which can predict the return on investment. Knowing the return on investment will help

the contractor evaluate the economic impact of the process and compare the life cycle energy production cost of different technologies.

• Develop the basic engineering design of the pilot plant. The design will allow both technical and economic feasibility analyses of a commercial scale process

Technical Task Deliverables

Table 1 identifies sections in the report that describe the performance and outcome of project deliverables relating to technical tasks in the contract.

Table 1. Floject Deliverables and Related Report Section					
Task	Deliverables	Report Section			
2	 SE-SHR Demonstration Test Plan 	Chapter 2			
	 SE-SHR Detailed Design Flowsheet 				
	Process Mass and Energy Balance Report				
	Process Performance Results Report				
3	 Integrated Process Flow Sheet 	Chapter 3			
	 Process Economics Report 				
4	Block Flow Diagram	Chapters 3 and 4 (Life			
	 Process and Utility Flow Diagrams 	Cycle Analysis)			
	Pilot Plant Design Report				
	Life Cycle Comparison Report				

Table 1: Project Deliverables and Related Report Section

Source: University of California, Riverside

Steam Hydrogasification Reaction

Introduction

The new steam hydrogasification reaction (SHR) process combines hydrogen and steam as the gasification agents. This technology can significantly enhance the rate of methane formation.¹ It can also use lower energy content and high moisture feedstock such as lignite, biomass waste, biosolids, and microalgae. Green waste and biosolids are common municipal wastes that are usually disposed of in a landfill. Microalgal bloom resulted from eutrophication (excessive nutrients in a body of water from runoff) is a significant cause of water quality deterioration in some lakes and streams in United States (such as the Salton Sea in California). The SHR process can convert these problematic wastes to valuable fuels and chemicals without drying, which saves energy on pretreatment.

SHR can be coupled with steam methane reforming (SMR) or water gas shift (WGS) to generate enough hydrogen to recycle back to the SHR, thus eliminating the need for an external source of hydrogen. The details of related research and patents were published in 2009.²

The major advantages of the process are:

- The SHR feed method uses slurry. Thus, feedstock with high moisture content can be used directly, reducing the feedstock drying cost.
- SHR does not need a catalyst and can be operated at moderate temperature and pressure, reducing capital and operation costs. Also, adding steam dramatically increases the rate of CH₄ formation.
- The process is self-sustainable on H_2 supply with a closed-loop cycle, eliminating the need for external H_2 .
- Varying the steam to feedstock ratio and H₂ to carbon ratio in the SHR gasifier can control the H₂ to carbon monoxide (CO) ratio of the synthesis gas.
- The process is feasible and economic for small- and medium-scale facilities that use local feedstocks, which can reduce high feedstock transportation costs. Low rank coal, biosolids and municipal solid waste, including green waste, are suitable and favorable

¹ Jeon SK, Park CS, Hackett CE, Norbeck JM. Characteristics of steam hydrogasification of wood using a microbatch reactor. Fuel. 2007; 86: 2817-3.

² Raju ASK, Park CS, Norbeck JM. Synthesis gas production using steam hydrogasification and steam reforming. Fuel Process Technol. 2009; 90:330-6.

for this process.³ By contrast, conventional gasification plants are not economically viable on a small scale because of the high capital cost of oxygen separation.

In 2010, the National Energy Technology Laboratory (NETL) completed an independent technical and economic assessment of the SHR process for coproduction of power and Fischer-Tropsch (FT) fuel.⁴ The report concludes that SHR process has a 12 percent higher efficiency with 18 percent fewer capital costs compared to the most up-to-date mainstream gasification technologies.⁵

Steam Hydrogasification Reaction Process for Liquid Fuel Production and Carbon Dioxide Capture

In the case of synthetic fuel production like FT, SHR can be coupled with SMR. The flow diagram is shown in Figure 1.



Sand

Source: University of California, Riverside

In this process, the wet feedstock is first pretreated under 220°C by the hydrothermal reaction to produce a pumpable slurry.⁶ The feedstock is then gasified in the presence of steam and hydrogen to obtain a methane-rich output gas (SHR). The gasifier temperature is usually 750°C and the reactor type could be circulating fluidized bed using silica sand as the bed material. The circulating fluidized bed can provide good mixing of feedstock and gasification agents, improving heat and mass transfer. This type of gasifier could operate at a comparatively lower temperature that is suitable for gasifying reactive feedstocks like biomass.

³ Lu XM. Development and application of advanced models for steam hydrogasification: process design and economic evaluation. University of California Riverside; 2012.

⁴ The Fischer-Tropsch process was developed by Franz Fischer and Hans Tropsch in the early 1920s and is a series of chemical reactions that involve conversion of hydrogen and carbon monoxide into liquid hydrocarbons by using a catalyst.

⁵ Rath L, Shelton W, Summers M, Winer J. Hydrogasification/F-T production with electricity and electricity only cases CERT-1 thru CERT-6, Conceptual Study. NETL Technical report (Report No.: DOE/NETL-401/CRADA). 2010.

⁶ He W, Park CS, Norbeck JM. Rheological study of comingled biomass and coal slurries with hydrothermal pretreatment. Energ Fuel. 2009; 23: 4763-7.

The leftover char in the gasifier is delivered to the combustor along with the sand for extra heat supply. Impurities such as sulfur species (H_2S and carbonyl sulfide, for example) are removed from the product gas by warm gas cleanup at 350°C. Also, the water can still be kept in the form of steam under this temperature for the SMR step. SMR is the reaction between steam and methane to generate H_2 and CO. SMR then converts most CH_4 into a mixture of H_2 and CO at 850°C, making enough extra H_2 to recycle in the SHR gasifier. The quantity of H_2 can be reduced by H_2 separation to achieve a H_2 -to-CO ratio of 1:1 or 2:1 depending on whether an iron catalyst or cobalt catalyst was used in the FT reactor.

 CO_2 comes from two main streams in this process, flue gas from the regenerator and syngas from the SMR. For example, for FT fuel production, the CO_2 in the regenerator flue gas and SMR syngas occupies 18 percent and 22 percent of the carbon in the feeding of typical biomass, respectively. The CO_2 -lean syngas is then sent to the FT reactor.

Steam Hydrogasification Reaction Process for Substitute Natural Gas Production and Carbon Dioxide Capture

The SHR process for SNG production is based on the combination of the SHR and the WGS processes. This process also has enough hydrogen remaining to recycle to the SHR. The process flow diagram is shown in Figure 2. Like the process for FT synfuel production, the wet feedstock is first converted to a pumpable slurry and then gasified in the SHR reactor. The remaining char is burned in the combustor to provide heat for the gasifier, with impurities removed during the warm gas cleanup step. The majority of CO in the synthesis gas is converted to H_2 and CO_2 via WGS using two shift reactors in tandem loaded with high temperature catalyst and low temperature catalyst, respectively. This step produces enough H_2 amount for cyclic use. H_2 and CO_2 are then separated from the main stream for recycling and other use such as enhanced oil recovery and algae growth. The final output gas is SNG.



Figure 2: Steam Hydrogasification Reaction Process for Substitute Natural Gas Production

Source: University of California, Riverside

The CO₂ during SNG production comes from two main streams, flue gas from the regenerator and raw SNG from the WGS reactor. Like FT liquid fuel production, amine-based absorber/stripper configuration is used for CO₂ removal in the raw SNG at high pressure, and the Fluor Economine FG Plus CO₂ recovery process can be an option for regenerator flue gas.

Sorption Enhanced Steam Hydrogasification Reaction Using In-Situ Carbon Dioxide Capture Technology

In-Situ Carbon Dioxide Capture Technology

One unique technique in the pre-combustion system that has attracted much attention in the past several years is in-situ CO₂ capture, illustrated in Figure 3.



Figure 3: Illustration of In-Situ Capture Technique

Source: University of California, Riverside

This technique uses a chemical sorbent such as CaO to capture CO₂ directly in the reactor such as shift reactor or gasifier. CO₂ is removed quickly as it forms by the sorbent mixed with carrier materials or catalysts, which can change the equilibrium to promote even more energetic production than otherwise possible. This technology has great potential to lower CO₂ emissions, mitigating the greenhouse gas effect and increase energy production to satisfy the ascending demand for energy simultaneously. This process is also called sorption enhanced (SE) process. SE related studies are mainly focused on WGS, SMR, and gasification.⁷

Sorption enhanced steam gasification has been extensively studied over the past ten years. A remarkable enhancement of hydrogen production and a dramatic decrease of CO₂ were observed with the addition of CaO containing sorbent using different types of feedstock such as coal, biomass waste and oil waste. Some researchers have also shown that the combined

⁷ Selow ER, Cobden PD, Van den Brink RW, Hufton JR, Wright A. Carbon capture by sorption-enhanced water-gas shift reaction process using hydrotalcite-based material. Ind Eng Chem Res. 2009; 48: 4184-3.

use of a commercial catalyst like nickel and calcium-based sorbent results in higher purity hydrogen.⁸ The sorbent also contributed in tar reduction to some extent.⁹

Sorption Enhanced Steam Hydrogasification Reaction Processes for Synthetic Fuel Production

A new concept named SE-SHR is proposed here. SE-SHR combines sorption enhanced principles and steam hydrogasification reaction. The new block flow diagram for FT synthetic fuel production is shown in Figure 4.



Figure 4: Sorption Enhanced Steam Hydrogasification Reaction Process for Fischer-Tropsch Synthetic Fuel Production

It was expected that SE-SHR could produce enough H_2 for recycled use, while capturing most of the CO₂. The process is like the conventional SHR-based process; however, besides sand, sorbent (such as CaO) is also used in the fluidized bed. Sorbent can be used singly or mixed with sand because CaO and silica sand have similar densities and heat capacities. The used sorbent is calcined in the regenerator and sent back to the gasifier for reuse. The released CO₂ stream is for other use. It was expected that sorption enhanced technology could generate more energetic gas like H_2 and CH_4 . Consequently, there is more CH_4 fed to the SMR, which most likely leads to more CO produced via SMR. This could improve the subsequent FT fuel yield due to increased carbon input. The new block flow diagrams of two SE-SHR processes for SNG production are shown in Figure 5.

These two processes are SE-SHR coupled with WGS and SE-SHR coupled with methanation. High H_2 yield and low CO_2 concentration were expected from the SE-SHR gasifier. The sorbent from the gasifier is calcined in the regenerator and returned to the gasifier for cyclic use. The process of SE-SHR with WGS is shown in Figure 5(a). It is like the conventional process combining SHR with WGS, but the process based on SE-SHR was expected to produce less CO_2 and more CH₄. The process of SE-SHR with methanation is depicted in Figure 5(b). Since

Source: University of California, Riverside

⁸ Felice LD, Courson C, Jand N, Gallucci K, Foscolo PU, Kiennemann A. Catalytic biomass gasification: Simultaneous hydrocarbons steam reforming and CO2 capture in a fluidised bed reactor. Chem Eng J. 2009; 154: 375-3.

⁹ Guan YW, Luo SY, Liu SM, Xiao B, Cai L. Steam catalytic gasification of municipal solid waste for producing tarfree fuel gas. Int J Hydrogen Energ. 2009; 34: 9341-6.

the process can produce more H_2 than the recycle amount needed for SHR, additional H_2 can be used to react with residual CO and CO₂ in the producer gas via methanation to maximize the CH₄ production.





Source: University of California, Riverside

Sorption Enhanced Steam Hydrogasification Reaction Demonstration Test Plan

Introduction

To demonstrate the SE-SHR process, two independent tests were planned. First, the preliminary SE-SHR performance would be evaluated with the increase of CaO to carbon molar ratio (CaO/C) in the laboratory scale, batch type, continuously stirred tank reactor (CSTR). The relationship between the increase of energetic gas and captured CO_2 amount would then be established. The effect of temperature, sorbent particle size, and the combined effect of steam to carbon molar ratio (Steam/C) and hydrogen to carbon molar ratio (H₂/C) was also evaluated. Additionally, SE-SHR and sorption enhanced hydrogasification (SE-HG) was

compared. Second, the bench scale continuous feeding circulated fluidized bed (CFB) reactor was designed and demonstrated.

Laboratory Batch Continuously Stirred Tank Reactor Demonstration

The experiments were carried out in an CSTR. The reactor sketch and dimensions are shown in Figure 6. The system included a batch vessel with 230cc made of Inconel, a ceramic radiative heater, a magnetic driven impeller, a gas purge/release system, and a product gas collection system. Pressure and temperature in the vessel were measured by an Omega px303 pressure sensor and a K type thermocouple, respectively. All data was recorded and processed using LabView[®].





1.Magnetic agitator driven by belt 2.Cooling coils 3.Inconel reactor 4.Radiative heater 5.Impeller coupled with agitator 6.Gas purge and release system 7.Thermocouple and pressure gauge linked with LabView[®] 8.Gas collection system)

3

Source: University of California, Riverside

Pinewood sawdust, microalgae, wastewater treatment sludge (biosolids) and lignite were selected as typical samples for this task, which characteristics can be seen in Table 2. Most feedstock has high moisture content suitable for SHR. The pinewood sawdust is a typical green waste and F.M. Brown pinewood sawdust was used. The specific microalgae genus used was Chlorella vulgaris because it is one of the most notable bloom forming factors. Chlorella vulgaris was purchased from NOW Foods. In addition, the disposal of biosolids is always an environmental issue in most countries. The sewage sludge selected was received from Riverside wastewater quality control plant.

Analysis	Elements	Lignite	Pinewood	Algae	Sludge
	Volatile Matter	50.2	86.4	79.53	69.01
Proximate Analysis (wt%	Fixed Carbon	42.4	13.33	15.88	8.45
	Ash	7.4	0.27	4.59	22.54
Ultimate Analysis (wt% dry	Carbon	59.85	50.89	49.19	37.22
	Hydrogen	4.64	9.37	7.06	5.47
	Nitrogen	2.83	5.34	9.3	11.03
basis)	Sulphur, Organic	1.5	0.01	0.61	1.3
	Oxygen	23.78	34.12	29.25	22.44
	Balance	7.4	0.27	4.59	22.54
Moisture in raw sample H ₂ O (wt% wet basis)		60	10	90	92

 Table 2: Composition Analysis of Feedstock

Source: University of California, Riverside

All feedstock was dried and ground to pass the sieve of 150μ m. A mass of 0.5g sample was used for all experiments. Water was mixed with dry feedstock first to simulate the wet feedstock slurry with the desired moisture content in the reactor. In the case of SE-SHR experiment, sorbent was added and mixed with the feedstock in the vessel. Quicklime was used as the sorbent due to its widespread availability and low cost, which was obtained from ChemLime Co. (Fort Worth, Texas). The CaO composition was over 98 percent (wt. percent dry basis). The sorbent was also ground and sieved to the specific range.

The initial drying was only for the lab-scale study to control the experimental accuracy. For large scale practical operation, the wet feedstock such as biosolids or microalgae is directly blended with wood waste by the optimum ratio to form a pumpable slurry via hydrothermal pretreatment.¹⁰ The empirical moisture content of pretreated feedstock slurry with an acceptable viscosity is 66.7 percent (that is, the steam to feedstock mass ratio is 2).

Commingled biomass-biosolids, commingled biomass-microalgae and lignite were used for this study. The design of experimental condition is listed in Table 3.

¹⁰ He W, Park CS, Norbeck JM. Rheological study of comingled biomass and coal slurries with hydrothermal pretreatment. Energ Fuel. 2009; 23: 4763-7.

Feedstock	Item	Parameter Value	Steam/C (molar ratio)	H ₂ /C (molar ratio)	CaO/C (molar ratio)	Temp (°C)	Sorbent Particle Size (mm)
Pinewood and sludge (83% and 17% dry wt basis)		0, 0.88	2.74	1	/	750	0.075-0.15
Pinewood and algae (80% and 20% dry wt basis)	Effect of CaO/C (molar ratio)	0, 0.85	2.64	1	/	750	0.075-0.15
		0, 0.12, 0.29, 0.57, 0.86, 1.14	2.22	1.08	/	750	0.075-0.15
	Effect of temperature	650, 700, 750, 800	2.22	1.08	0.57	/	0.075-0.15
Lignite	Effect of sorbent particle size (mm)	<0.038, 0.075-0.15, 1.7-2	2.22	1.08	0.57	750	/
	Effect of steam/C (molar ratio)	1.67, 2.22, 2.78	/	0.63, 1.08, 1.59	0.36	750	0.075-0.15
	Effect of H ₂ /C (molar ratio)	0.63, 1.08, 1.59	1.67, 2.22, 2.78	/	0.36	750	0.075-0.15
	Reaction system	HG, SHR	For HG, 0; for SHR, 2.22	1.08	0.57	750	0.075-0.15

Table 3: Design of Experiment for Sorption Enhanced Steam Hydrogasification Reaction Performance Evaluation

Source: University of California, Riverside

The reactor was heated to the desired temperature with heating rate of 30°C/min. The reaction was not terminated until the inside pressure was stable. Then the reactor was cooled to below 100°C very quickly to stop the reaction from proceeding via air convection. The dry product gas was collected in a Tedlar[®] bag for analysis. The molar concentrations of carbon monoxide, carbon dioxide, hydrogen and methane were obtained via a gas analyzer (Cirrus[™] bench-top residual gas analyzer, MKS Instruments). The total molar amount of the dry product gas was estimated by the Virial equation at the collection temperature of 90°C. The molar amount of each gas was the product of the percentage and the total amount. In order to calculate how much CO₂ was captured by the sorbent, the remainder was immersed in dilute hydrochloric acid to decompose the carbonate thoroughly. The absorbed CO₂ amount was then obtained by weight difference. The amount of char and sulfur was calculated based on the corresponding elemental analysis of the residue with CO₂ released. Sulfur retained percentage was obtained by dividing the residual sulfur amount by the initial sulfur amount. Some feedstock and residues were selected for characterization using a D8 Advance X-ray Diffractometer from Germany BRUKER/AXSCo., Ltd. The crystalline compounds were determined through computer system aiding, which was presented by an intensity-2 θ format.

Continuous Bench-Scale Circulating Fluidized Bed Demonstration

The bubbling fluidized bed (BFB) type bench scale continuous gasifier, which was developed by the previous PIER program, is utilized for the CFB demonstration task.

Since the details of BFB gasifier can be found in the previous PIER report,¹¹ the newly added part for conversion of CFB gasifier is described in this report. The water gas shift reactor (WGS) process which locates in the downstream of the CFB reactor is identical to the previous project.

The design flowsheet of CFB demonstration unit is provided in Figure 7. Hot-sand circulation loop is added to existing BFB together with the redesign of the cyclone separator part. Circulated sand is heated by kiln type horizontal reactor with the mechanical screw feed. Table 4 summarizes the details of reactor conversion by each part.

¹¹ *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.

Section Name	Specifications	Description	Material
Sand circulation assembly 1	4" OD tube, 19" in length with 4" 300# raised faced flanges, welded 45 degree 2" OD tube with 300# raised face flange	PDU extension and sand return inlet	Inconel 600, stainless steel
PDU KILN Connector	Flexible double graided hose with 2" raised face flanges connected to 2" raised face flange with 2" to 1" reducer	Couples the KILN to sand circulation assembly 1	Stainless steel
Sand circulation assembly 2	13' of 1" turbine consisting of 3 pieces joined together by two 1" unions	Couples cyclone exit to KILN inlet	Stainless steel
KILN	3.5" OD tube, 86" in length with a 2" auger inside	Heats sand and pushes sand pack to the PDU	Inconel 600
Inlet Nozzle	¹ / ₂ " tube with ¹ / ₄ " tube inside, both have 150 micron filter on one end and the other has swagelok fitting to connect gas and steam feeds	Gas and steam inlet	Stainless steel
KILN Heater 1	8.5" OD, 3.5" ID Semicylindrical, 29" in length, 1800W 240V	Coupled with 2 to heat the front of the KILN	Ceramic
KILN Heater 2	8.5" OD, 3.5" ID Semicylindrical, 29" in length, 1800W 240V	Coupled with 1 to heat the front of the KILN	Ceramic
KILN Heater 3	8.5" OD, 3.5" ID Semicylindrical, 29" in length, 1800W 240V	Coupled with 4 to heat the front of the KILN	Ceramic
KILN Heater 4	8.5" OD, 3.5" ID Semicylindrical, 29" in length, 1800W 240V	Coupled with 3 to heat the front of the KILN	Ceramic
PDU extension heaters 1	Band heaters 4" OD 1000W 120V	Heat the PDU extension piece, Top Stainless steel	
PDU extension heaters 2	Band heaters 4" OD 1000W 120V	Heat the PDU extension piece, Stainless steel Bottom	

Table 4: Details of the Bubbling Fluidized Bed Modification to Circulating Fluidized Bed

Source: University of California, Riverside



Source: University of California, Riverside

For the optimum design of the CFB, an acrylic mockup was developed and attached to the existing BFB. Optimum gas flow rate which gives sand circulation was measured against the pressure difference across the reactor. To run the experiment, two acrylic pieces had to be made. The first piece was an extension of the existing BFB that would allow the external sand heater (Kiln) to return sand back to the main reactor. The second piece is called a loop seal,

this piece was added to control the direction of the gas flow so the sand circulation can take place. The fluidizing gases were fed in at two different inlets. Inlet A is located at the bottom of the process development unit (PDU) and inlet B is located at the loop seal. Also, the pressure differences across the reactor were measured. All locations used for the experiment are labeled in Figure 7.

By varying flow rates for both inlets and the Kiln's auger speed, the optimum input conditions required to achieve sand circulation were found to be 600 SCFH at inlet A, 250 SCFH at inlet B and an auger speed of 2 Hz. The combined flow rate for both inlets A and B is about 400 L/min which gives an air speed of 1.07 m/s at the bottom of the PDU. The pressure differences across the reactor in this input condition are summarized in the Table 5. Figure 8 shows the final modification of BFB in to CFB.

Table 5: Pressure Differences Across the Reactor During Circulating Fluidized Bed Mode

Delta P between location	Delta P between location 2	Delta P between
1 and 2	and 3	location 3 and 4
0.50-0.53	0.60-0.72	0.018

Source: University of California, Riverside

Figure 8: Bench Scale Circulating Fluidized Bed Reactor



Source: University of California, Riverside

Process Performance Results

Laboratory Batch Continuously Stirred Tank Reactor Results

Effect of Calcium Oxide / Carbon Molar Ratio

The preliminary effect of CaO addition on the steam hydrogasification of three aforementioned feedstock types was evaluated first. A certain amount of sorbent (CaO/C \approx 0.86) was added into the reactor. The SE-SHR performance was compared to the conventional SHR without sorbent introduced, which is shown in Figure 9.

There was almost no CO₂ in the product gas when sorbent was added. In addition, H₂ increased dramatically with the sorbent introduced. The initial H₂ input for lignite, pinewood-sludge (pwd-slg) and pinewood-microalgae (pwd-alg) was 0.027 mol, 0.02 mol and 0.021 mol, respectively, which is shown in terms of "H₂ recycle baseline" in the figure. H₂ yield was beyond corresponding baseline in SE-SHR and produced more than enough to send back to the gasifier for these feedstocks. However, the H₂ amount in the conventional SHR was lower than the baseline. Moreover, CH₄ was increased and CO was decreased in SE-SHR.



Figure 9: Effect of Sorbent Addition on Different Feedstock Types

Source: University of California, Riverside

The performance of SE-SHR with the gradual increase of CaO/C was further investigated. The effect of CaO/C on carbon conversion distribution (CH₄, CO, CO₂, CO₂ captured, C₂₊) is shown in Figure 10. The data presented shows the results with the baseline being no sorbent to the ratio of 1.14. The increase of CaO/C had a positive effect on the overall conversion of char and CO₂ removal. The char percentage decreased from 52 percent to 4 percent when the ratio was raised to 1.14. Due to the increase of CaO added, more CO₂ was removed and fixed in the sorbent, so less CO₂ was present in the gas phase. CO₂ was reduced to essentially zero (about 0.05 percent). Meanwhile, the methane percentage increased gradually as more sorbent was added. Hydrocarbon (C₂₊) percentage in particular was reduced most likely due to the catalytic effect of sorbent on components with higher molecular weight like tar.¹² The percentage decreased from 20 percent with no sorbent to 4 percent at the CaO/C of 0.86 and then leveled

¹² Guan YW, Luo SY, Liu SM, Xiao B, Cai L. Steam catalytic gasification of municipal solid waste for producing tarfree fuel gas. Int J Hydrogen Energ. 2009; 34: 9341-6.

off. Only a marginal change in the carbon conversion was noted after the ratio of 1.14 and is not shown here.





Source: University of California, Riverside

The gas production on a dry mole basis with CaO/C molar ratio is shown in Figure 11. Also shown in Figure 11 is the hydrogen recycle baseline required to maintain the sustained performance of SHR. Two trends were observed. First, the yield of H₂ and CH₄ increased with sorbent and second, the output of CO and CO₂ decreased. Especially for H₂, the production was enhanced by about 61 percent at the ratio of 1.14 compared to the case without sorbent. The increase in H₂ yield relates to the increase of CO₂ captured shown in Figure 10, which will be discussed later. Also, the required H₂ amount was 0.027mol, which is represented by the "H₂ recycle baseline" in Figure 11. Assuming the majority of H₂ could be separated, the H₂ production was acceptable for recycle use when the CaO/C was 0.29 or greater. Thus, to guarantee that sufficient H₂ was generated to sustain the steam hydrogasification reaction, the CaO/C should be at least 0.29. Besides, hydrogen sulfide was the main sulfur species existing in the SHR process.¹³ As can be seen in Figure 11, the sorbent contributed to the capture of

¹³ "Experimental Study of Gaseous Sulfur Species Formation during the Steam Hydrogasification of Coal" Energy Fuels, Article ASAP DOI: 10.1021/ef4021087

sulfur. The sulfur retained percentage was increased from 20 percent to over 90 percent with the CaO/C increased from 0.12 to 1.14.





Source: University of California, Riverside

These results clearly demonstrated the potential merits of the process coupling steam hydrogasification and sorption enhanced technology. The enhanced performance was primarily the consequence of the instant removal of CO_2 . When the product CO_2 was removed from the system by the sorbent, reactions were moved forward to get higher yields of the other product gases like H_2 . With more sorbent introduced, more CO_2 were captured and more energetic gases were produced.

Summarily, the result was that the SE-SHR improved the production of H_2 and CH_4 with the abatement of CO, H_2S and CO_2 and more sorbent led to more H_2 .

X-ray diffraction was used to characterize the samples with different CaO/C ratio before and after gasification. Feedstock-CaO mixture with CaO/C of 0.29 and 0.86, and their corresponding gasification residues were selected as the sample. The X-ray diffraction patterns are shown in Figure 12.

There was no crystalline structure detected in feedstock and its residue due to its amorphous species. When CaO was mixed with the feedstock, it was identified in the form of Ca(OH)₂. It was because CaO is very easy to get hydrated on its surface during storage. In Figure 12, plot 4 and 5 show that Ca(CO)₃ was formed in SE-SHR. Especially for the case with more CaO addition (CaO/C=0.86), there was some CaO left in the gasification residue in the form of

 $Ca(OH)_2$. It indicated that CaO loading was over the CO_2 amount generated in SE-SHR. Additionally, the amount of char was found in terms of carbon by measure the amount of carbon.





1. Feedstock 2. Feedstock-CaO mixture with CaO/C=0.29 3. feedstock-CaO mixture with CaO/C=0.86 4. feedstock-CaO gasification residue with CaO/C=0.29 5. feedstock-CaO gasification residue with CaO/C=0.86 6. gasification residue)

Source: University of California, Riverside

Relationship Between Energetic Gas Increment and Captured Carbon Dioxide Amount

The relationship between energetic gas increment (H_2 and CH_4) and captured CO_2 amount is depicted in Figure 13 and Figure 14. Figure 13 shows that the increase of H_2 was a function of the amount of captured CO_2 . Linear regression analysis was conducted on these data, the equation of which was shown as below. The correlation coefficient was 0.9922.

$$H_2$$
 (Increment) = 0.72CO₂ (Captured) + 0.0004 (mol)

This intimate relationship indicated that some reactions having both H_2 and CO_2 as product, such as WGS and water gas, were actively involved in the SE-SHR.

As shown in Figure 14, CH₄ ascended gradually with the increase of captured CO₂ amount. The linear equation fitted for these points is listed below. The correlation coefficient was 0.9113.



Source: University of California, Riverside

Figure 14: Relationship Between Methane Increment and Carbon Dioxide Captured Amount



Source: University of California, Riverside
The relationship between CH_4 and CO_2 was not as good as that between H_2 and CO_2 . It was most likely because the increase of CH_4 was enhanced by hydrogenation reaction during SE-SHR. Hydrogenation is comparatively slower than the other reactions with regard to steam. Thus, the CH_4 increment was limited. Additionally, the final pressure in the reactor did not increase too much. The pressure could not favor the hydrogenation to produce more CH_4 .

Effect of Temperature

Temperature is an important variable in gasification. The temperature of the reactor was varied from 650°C to 800°C with and without the sorbent. The effect of temperature on carbon conversion and gas production are shown in Figure 15 and Figure 16, respectively. From both figures, notice that an increase in temperature enhanced the conversion percentage and production of CH₄ with or without the sorbent. At each reaction temperature, adding the sorbent reduced the CO₂ significantly and also increased the H₂ when compared without sorbent. It can be seen that the conversion percentages of char and C₂₊ decreased after the introduction of sorbent. Additionally, when the temperature was raised, there was also a simultaneous increase in the percentage of CO₂ captured and H₂ yield which supported the positive influence on the shift conversions. However, due to the enhancement of water gas reaction, too high temperature like 800°C would produce more CO₂ which was over the capacity of the sorbent loading. The optimum temperature should be around 750°C, with the consideration of improving CH_4 production and minimizing CO_2 emission. Furthermore, the H_2 production with sorbent addition was higher than the minimum recycle requirement at each temperature, showing that the reaction temperature could be reduced to as much as 700°C to get enough recycled H_2 disregarding to the other gas yields.





Source: University of California, Riverside



Source: University of California, Riverside

Effect of Sorbent Particle Size

The particle size of sorbent is another important factor influencing the SE performance. The change in gas production with the increase of the sorbent particle size is shown in Figure 17.



Figure 17: Effect of Temperature on Gas Production

Source: University of California, Riverside

 CO_2 could be reduced to almost zero regardless of the particle size. Although the production of H_2 decreased slightly with the increase of particle size, H_2 could still meet the recycle requirement when particle size was increased to the range of 1.7-2 mm. In the meantime, CH_4 and CO decreased slightly. Because large particle possessed less surface area, there were comparatively limited sites for the gas solid reaction to proceed. This made less CaO react with CO_2 , mitigating the increment of H_2 via shift reaction.

Comparison of Sorption Enhanced Steam Hydrogasification Reactor and Sorption Enhanced Hydrogasification

The SE performances of HG and SHR are compared in Figure 18. Without sorbent addition, the H_2 yield of HG was less than that of SHR. SHR produced more CH_4 and CO_2 than HG did. It was mainly due to the enhancement by steam addition, improving the water gas reaction. When sorbent was added into the reactor (CaO/C=0.56), for both reaction types, CO_2 was hardly seen in the product gas and the yields of H_2 and CH_4 were increased compared without sorbent. However, even with sorbent addition, SE-HG could not generate enough H_2 over the recycle baseline. Only SE-SHR could make it. This implied that steam played an important role in improving the H_2 yield in SE-SHR.

Figure 18: Comparison of Gas Production Between Sorption Enhanced Hydrogasification and Sorption Enhanced Steam Hydrogasification Reactor



Source: University of California, Riverside

Effect of Hydrogen/Carbon Ratio

Figure 19 shows the combined effect of Steam/C and H_2/C molar ratios on the H_2 yield. For both SE-SHR and SHR, at each Steam/C of 1.67, 2.22 and 2.78, the H_2 yield was enhanced

with the increase of H₂/C. It was mainly due to more initial H₂ input. Excess amount of H₂ still remained in the reactor. The H₂ amount reached the maximum 0.042mol when H₂/C and Steam/C were set at 1.59 and 2.78, respectively. The H₂ recycle baseline is plotted in terms of dotted line in Figure 19, which represents the initial H₂ input of 0.0158 mol, 0.0271 mol, and 0.0398 mol, corresponding to each gasification condition. Except for the condition with H₂/C of 1.59 and Steam/C of 1.67, H₂ yields in SE-SHR all exceeded their corresponding baselines. It indicated that H₂ amount was already enough for recycle use in the gasifier and extra H₂ (the amount beyond the baseline) could be used for downstream processes like methanation. In particular, under the excluded condition aforementioned, lower steam input could not produce enough H₂ for cyclic use, implying that steam played a very important role in H₂ production. Thus, when Steam/C was increased to 2.22, the H₂ production was beyond the baseline. By contrast, H₂ yields in SHR did not exceed the recycle baseline.

By integrating the results of SE-SHR and SHR in Figure 19, the percentage increase in H_2 production was obtained and is shown in Figure 20. At each Steam/C, the percentage increase was descending with the ascent of H_2/C . It meant that more H_2 input lessened steam gasification during SE-SHR. This made less CO₂ generated, which mitigated the SE-SHR performance. Because less CO₂ was captured, less extra H_2 was generated.

Figure 19: Combined Effect of Steam/Carbon and Hydrogen/Carbon Ratios on Hydrogen Production



Source: University of California, Riverside

Figure 20: Percentage Increase in Hydrogen Production with Sorbent Addition



Source: University of California, Riverside

The data of CH_4 is shown in Figure 21. At each Steam/C, for both SE-SHR and SHR, the CH_4 yield was improved with the increase of H_2/C . It indicated that hydrogenation was enhanced with higher H_2 input and the hydrogasification gradually became predominant. Additionally, it can be seen that the CH_4 yield of SE-SHR was higher than that of SHR under the same gasification condition.

The results of CO and CO₂ are presented in Figure 22 and Figure 23, respectively. The increase of H_2/C in both SE-SHR and SHR reduced the yields of CO and CO₂ at each Steam/C. It implied that some CO and CO₂ related reactions (e.g. water gas reaction) were affected by more H_2 input. Besides, the CO and CO₂ yields of SE-SHR were lower than those of SHR.

Figure 21: Combined Effect of Steam/Carbon and Hydrogen/Carbon Ratios on Methane Production



Source: University of California, Riverside

Figure 22: Combined Effect of Steam/Carbon and Hydrogen/Carbon Ratios on Carbon Monoxide Production



Source: University of California, Riverside

Figure 23: Combined Effect of Steam/Carbon and Hydrogen/Carbon Ratios on Carbon Dioxide Production



Source: University of California, Riverside

By integrating the results of SE-SHR and SHR in Figure 23, the percentage decrease in CO₂ production is depicted in Fig.2.18. More CO₂ was captured with the increase of H₂/C at each Steam/C. Also, when Steam/C was set at 1.67, the decrease percentage could reach highest. All percentages were over 90 percent at three different H₂/C ratios. It was mainly due to less CO₂ being produced in a high H₂ containing environment. The fixed amount of sorbent (CaO/C=0.36) was sufficient for CO₂ capture with Steam/C of 1.67.



Figure 24 Percentage Decrease in Carbon Dioxide Production with Sorbent Addition

Source: University of California, Riverside

Summarily, with the increase of H_2/C at each Steam/C, the production of H_2 and CH_4 was enhanced while that of CO and CO_2 was decreased. The increase of H_2 was mainly because of more H_2 input. The enhancement of CH_4 production was mostly due to the improved hydrogenation with higher H_2/C . Also, SMRs were possibly affected by more H_2 . Therefore, less CH_4 was consumed. In particular, the enhancement of CH_4 production in SE-SHR was partially contributed from more H_2 due to SE.

Effect of Steam/Carbon Ratio

In Figure 19, when H_2/C was fixed at 0.63, 1.08 and 1.59, the increase of Steam/C enhanced the H_2 production gradually. It implied that steam gasification resulted in more H_2 yield. When steam input was increased, sufficient H_2 amount could be guaranteed for recycled use. Especially for the condition with H_2/C of 1.59, the extra H_2 production was enhanced from negative to positive by increasing Steam/C. The increase percentage in H_2 production is shown in Figure 20. The increase of Steam/C could produce more extra H_2 when Steam/C was increased to 2.78.

The production of CH₄ had different trend between SE-SHR and SHR. Figure 21(a) shows that the increase of Steam/C did not affect the CH₄ production during SE-SHR, while Figure 21(b) shows that the CH₄ production decreased slightly during SHR. For both SE-SHR and SHR, SMR

could be improved with more steam input, leading to less CH₄. In particular, the consumption of CH₄ during SE-SHR was most likely offset by other reactions at the same time, resulting in the insensitive behavior to the Steam/C change. This will be discussed later.

Besides, the increase of steam enhanced the yields of CO and CO₂ remarkably at each H₂/C shown in Figure 22 and Figure 23. This was primarily due to the domination of steam gasification. In addition, more CO₂ could not be captured during SE-SHR with higher steam input because the CO₂ amount was already beyond the limited capacity of sorbent loaded. Correspondingly, in Figure 24 the decrease percentage in CO₂ production was reduced with the increase of Steam/C at each H₂/C. CO₂ yield reached highest when H₂/C was 0.63 and Steam/C was 2.78. Thus, more sorbent should be added under higher Steam/C.

Summary

The performance of SE-SHR was evaluated by varying different gasification parameters. The main findings are listed below.

- 1. It was found that the addition of sorbent could remove CO_2 within SHR and increase the energetic gas (H₂ and CH₄) production for different kinds of feedstock. In particular, the amount of H₂ increased dramatically producing enough for recycled use over for a CaO/C molar ratio of 0.29.
- 2. Sorbent addition improved the H₂ production with CO₂ captured at different temperatures and the reaction temperature could be reduced to 700°C to get enough recyclable hydrogen. Higher temperature favored higher energetic gas yield, but too high temperature (e.g. 800°C) would produce more CO₂3. Sorbent with different particle size had the same positive effect on CO₂ removal and H₂ enhancement. In particular, small particle size could produce more energetic gases than larger size did.
- 3. With sorbent addition, hydrogasification could minimize the CO₂ production but could not increase enough H₂ yield for recycle use. Only SHR with sorbent addition could meet the H₂ recycle requirement. 5. When H₂/C was increased, the production of H₂ and CH₄ was increased and that of CO and CO₂ was decreased. This could be explained as hydrogasification was favored over steam gasification.
- 4. When Steam/C was increased, the yield of H₂, CO and CO₂ was improved. It was because steam gasification was predominant. Particularly, since more H₂ was produced during SE-SHR, the consumption of CH₄ was compensated by hydrogenation and CH₄ production had little change.

Bench Circulating Fluidized Bed Results

Feedstock

This section describes the CFB process operation result. The feedstock tested were biosolids comingled with woody biomass. 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: 75μ m- 90μ m, 150μ m- 180μ m and 355μ m- 425μ m. The particles with certain particle size range are then dried in a vacuum oven at 70° C 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 analysis 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 6. 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.

Analysis	Compound	Pinewood Weight %	Biosolids Sample #1ª Weight %	Biosolids Sample #2 ^b Weight %
	Moisture, M	5.65	94.8	95.2
	Volatile Matter, VM	81.52	3.65	3.45
Prox. Anal.	Fixed Carbon, FC	12.58	0.44	0.36
	Ash	0.26	1.11	0.99
	HHV (Btu/lb)	8093	N/A	N/A
Ult. Anal.	С	47.56	40.80	40.93
	Н	6.31	6.22	6.69
	0	45.81	23.12	23.02
	Ν	0.05	7.47	7.66
	S	0.01	1.04	1.07

Table 6: Results of Proximate and Ultimate Analysis (Dry Basis)on Pine Wood and Biosolids

Source: University of California, Riverside

Comingled feedstock, which consists of biosolid and biomass was prepared exactly same way as the previous report.¹⁴ The fixed carbon content of feedstocks 1^a and 2^b were 44 and 36 percent respectively.

Circulating Fluidized Bed Operation

Like the previous BFB test, the CFB 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.

The temperature of the reactor was gradually increased to 750°C to avoid the thermal shock. Nitrogen was used for the circulating fluidizing gas and purge gas during this stage, and the pressure of the reactor was maintained at 150 psi. The gas flow rate required to maintain the sand circulation was determined by the pressure difference across the reactor, which was measured in the previous mockup test. The slurry feedstock was fed into the reactor using a progressive cavity pump when the reactor temperature reaches steady state. Then, nitrogen

¹⁴ Production of Substituted Natural Gas from the Wet Organic Waste by utilizing PDU-scale Steam Hydrogasification Process is the final report for the project, chapter 3 (contract number 500-11-004, conducted by University of California, Riverside.

gas was switched to hydrogen gas to keep pressurizing and circulating 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 a Non-Dispersive Infrared (NDIR) spectrometer. Table 7 summarizes the input conditions and output concentration of the product gas.

Conditions and Results	Biosolids Comingled with Pinewood
Slurry feed rate (g/min)	48.63
Percentage of Carbon (%)	45.37
Rate of Carbon input (mole/min)	0.47
Moisture content (%)	76
Total flow rate of product gas (Liter/min)	10.05
Total flow rate of product gas (mole/min)	0.648
Final CH₄ vol %	66.8
Final CO ₂ vol %	10.1
Final CO vol %	23.1

Table 7:	Experimental Results from Steam Hydrogasification Reactor Only
	Operation Using the Different Feedstock

Source: University of California, Riverside

The typical process log for the CFB operation is provided in Figure 25. In this log, gas evolutions along the process operation time (in second) was recorded. The process is started by starting the SHR process first. Once SHR process reaches steady state, the WGS process is started. The decrease of CO and increase of CO_2 gas flow is clearly seen from the process log. Feedstock was co-mingled biosolid with biomass with 5 lb/hr feed rate. Temperature and pressure of the gasifier are 750C, 150 ps. For the WGS, HT WGS catalyst was used at 350C and 150 psi process condition, Final Gas Composition: 73 percent CH4, 27 percent CO (after CO_2 Separation). Carbon conversion to the gas species is estimated to be 76 percent.

Although the result shows the significant increase of the CH_4 concentration without increase of concentration of CO_2 , there is still room to further increase the CH_4 concentration by increasing the residence time of the SE-SHR reactor. Due to the physical limitation of the reactor, further increasing of the CH_4 concentration could not be possible. However, additional methanation process in the downstream can increase the CH_4 concentration from the CO conversion. This additional process is discussed in the Chapter 5, Life Cycle comparison.



Figure 25: Substitute Natural Gas Production Result

Source: University of California, Riverside

Process Mass and Energy Balance

Introduction

This section evaluates the sorption enhanced SHR processes for SNG production proposed with the ASPEN process simulation model to provide the process mass and heat balance. The optimum gasification condition of each process is determined based on the self-sustainability of hydrogen and the maximum production of SNG. The SE-SHR based processes are compared to the corresponding conventional SHR based processes.

Process Design Methodology

Aspen Plus version 8.0 was used for the process simulation. Aspen Plus is the core product of Aspen Technology. This software provides a market-leading process modeling environment for conceptual design and optimization in both chemical and power industries. One outstanding feature of Aspen Plus is the excellent performance in handling non-conventional solid materials like biomass.

The modeling included solid, liquid and gas phases, which required various packages to represent different chemical properties exactly. The feedstock used in the SE-SHR process was defined as non-conventional component. HCOALGEN and DCOALIGT were set as the enthalpy model and density model of feedstock, respectively. For liquid and gas phases, all properties were retrieved from the default database.

The process modeling for SNG production was divided into six main sections, which were feedstock pretreatment, gasification with combustion or regeneration, warm gas cleanup, downstream gas processing (WGS or methanation), H₂ separation and CO₂ removal.

The major operation models used in the above two processes are listed in Table 8.

In particular, feedstock was assumed to be first decomposed to elemental components before gasification by decomposition unit using RYield model. The decomposer temperature was 500°C. These elements were sent to the RGibbs reactor for gasification calculation.

The char leftover data was obtained experimentally from the batch CSTR test. These data were used to set the inert char percentage in the gasifier Gibbs model. The temperature and pressure in the gasifier were the same for all simulations. Sand was used for conventional SHR and quicklime was used for SE-SHR. Both feed rates were the same as feedstock rate at 400 tonnes per day. It should be noted here that 400 tonnes of sand or sorbent per day was for simplifying the simulation on a daily basis. This sorbent loading made CaO/C molar ratio at 0.36 in the gasifier. However, it did not mean the practical inventory of bed materials circulating in the fluidized bed should be 400 tonnes.

The practical inventory depends on the hydrodynamics performance in the circulating system. Based on the preliminary hydrodynamics study, the optimum bed inventory to feedstock mass ratio in the circulating fluidized bed is about 250 for SHR system.¹⁵ Assuming the residence time of feedstock in the gasifier is 30 seconds, the feedstock mass in the gasifier is 0.14

¹⁵ Yun MY, Bae DH, Park CS, Norbek JM. Development of circulating fluidized bed reactor for the steam hydrogasification of low ranked fuel. US-Korea Conference on Science, Technology and Entrepreneurship. 2012

tonnes as for the feeding rate of 400 tonnes/day. Therefore, the total bed inventory is 35 tonnes.

Operation Unit	Aspen Plus Model	Specification
Decomposition	RYield	Feedstock is decomposed to elemental C, H, O, N, S, Cl
Gasification	RGibbs	Possible products are specified including H ₂ , Cl ₂ , H ₂ O, HCl, C, CO, CO ₂ , CH ₄ , COS, H ₂ S, CS ₂ , CaO, CaCO ₃ , ash
Combustor	RGibbs	Char and air combustion
Regenerator	RGibbs	Char and air combustion with CaCO3 decomposition
Burner	RGibbs	Optional for extra energetic gas combustion to supply heat
Solid separation	Sep	Product gas with sand or sorbent separation
Warm gas cleanup	Sep	H ₂ S and chloride removal
H ₂ separation	Sep	H ₂ split from the product gas
SMR	Equilibrium	Methane-rich product gas reforming
WGS	Equilibrium	Converting CO to H ₂ and CO ₂
Methanation	Equilibrium	Converting CO and CO ₂ to CH ₄
FT	Ryield	Empirical simulation of FT fuel distribution
CO ₂ removal	Sep	CO ₂ split from the product gas

Table 8: Aspen Plus Specification of Operation Unit

Source: University of California, Riverside

If the system uses the mixture of sand (0.25mm average diameter) and CaO (0.15mm average diameter), the sorbent inventory should be 0.14 tonnes (CaO/C=0.36) and the sand inventory is 34.86 tonnes. However, due to attrition, elutriation and sintering issues, there is continuous loss in sorbent mass and CO_2 capture capacity. The particle size of used sorbent will become smaller. Then it cannot be captured by the cyclone and will leave the system. Thus, the sorbent should be refilled continuously to maintain 0.14 tonnes sorbent inventory and refresh the capture capacity.

In the process for SNG production, the product gas after warm gas cleanup was used for WGS or methanation. WGS section was simulated by using two built-in equilibrium blocks in series adiabatically under the pressure of 2.2MPa. The product gas was sent to the first WGS reactor packed with high temperature catalyst. Before entering the second WGS reactor, the gas was cooled down to 190°C for further low temperature catalytic synthesis. The reaction expected in the reactor is as below.

$$CO + H_2O = H_2 + CO_2 \qquad \varDelta H = -41kJ/mol$$

In the case of SE-SHR with methanation, methanation section was simulated by using two built-in equilibrium blocks in series adiabatically. The pressure was set at 2.2MPa. The gas was cooled down to 300°C before entering the methanation unit. The reactions in the methanation process are given below.

$$3H_2 + CO = CH_4 + H_2O$$
 $\Delta H = -206kJ/mol$

$$4H_2 + CO_2 = CH_4 + 2H_2O$$
 $\Delta H = -165kJ/mol$
 $CO + H_2O = H_2 + CO_2$ $\Delta H = -41kJ/mol$

In addition, some reactor models and input parameters were controlled by calculator and design specification. These FORTRAN routines could automatically adjust related dependent variables when independent variables were changed, instead of manual adjustment of them every time. Calculator block was applied to the decomposition reactor and the FT reactor. Design specification was applied to steam input, H_2 input, H_2 recycle separation, H_2 /CO syngas ratio, and air input for combustor/regenerator.

Process Evaluation Method

The primary standard for process evaluation is the self-sustainability of H_2 . If the H_2 could not meet the recycle requirement, the corresponding process was considered unfeasible. The mass balance of each process was conducted first to check the mass flow of each product. When the primary standard was satisfied, the maximum production of synfuel determines which process was the optimum. Lastly, the heat analysis was carried out to see if the optimum process could be self-sustainable on heat supply.

CO conversion percentage of WGS and methanation in the SNG production was calculated. CO_2 conversion percentage of methanation was also calculated. The process with highest CH₄ yield was considered optimum. The conversion percentage of CH₄, CO and CO₂ were the ratio of the output from the reactor over the input to the reactor.

In particular, the SNG quality was evaluated in terms of overall energy efficiency, methane conversion efficiency and Wobbe Index (WI). The overall energy efficiency was defined as followed:

Overall energy efficiency = Higher Heating Value (HHV)_{SNG}/HHV_{feed}

Where, HHV_{SNG} was the sum of H_2 , CH_4 and CO, of which HHV are 141.89, 55.62 and 10.09MJ/kg at 25°C respectively. The HHV_{feed} value (dry basis) of co-mingled feedstock is 25.8MJ/kg.

Methane conversion efficiency can be defined as:

CH₄ Conversion percent = CH₄ moles in the final SNG/Carbon moles in the feedstock

WI is the most efficient and robust single index and measure of gas interchangeability for practical operation, which is defined as the HHV of the fuel gas divided by the square root of its specific gravity with respect to air.

Results and Discussion

The block flow diagram of SHR-WGS based and SE-SHR-WGS based processes was shown in Figure 26. The process was simulated using pretreatment section, decomposition section, gasification section, and combustor or regenerator section. After the producer gas was cleaned up, it was sent to the WGS section to convert CO to H_2 and CO_2 . Then 99 percent of H_2 and CO_2 were removed from the output gas. Water was separated from the product by condensation. The remained product gas was SNG.

The process based on SE-SHR-Methanation was a little bit different from the above two processes, which block flow diagram is shown in Figure 27. The difference was in the downstream processing unit. Methanator was used instead of WGS, in which CO and CO_2 reacted with extra H₂ to make more CH₄. Accordingly, only H₂ required separation from the gas product.

Figure 26: Aspen Simulation for Substitute Natural Gas Production Based on Steam Hydrogasification Reactor-Water Gas Shift or Sorption Enhanced Steam Hydrogasification Reactor-Water Gas Shift



Source: University of California, Riverside

Figure 27: Aspen Simulation for Substitute Natural Gas Production Based on Sorption Enhanced Steam Hydrogasification Reactor-Methanation



Source: University of California, Riverside

The production of H₂ and CH₄ from WGS of SHR based process is depicted in Figure 28. The H₂ recycle baselines are plotted in the figure, which represent the H₂/C of 0.63, 1.08 and 1.59. The H₂ yield from the WGS reactor under some gasification conditions could not meet the recycle requirement, such as H₂/C of 1.59. Due to the enhancement of steam gasification, CH₄ production decreased with the increase of Steam/C. The maximum CH₄ yield was obtained with enough recycle H₂ under the gasification condition (H₂/C-Steam/C) of 1.08-2.22.

Figure 28: Production of Hydrogen and Methane from Water Gas Shift of Steam Hydrogasification Based Process for Substitute Natural Gas Production



Source: University of California, Riverside

The production of H_2 and CH_4 from WGS of SE-SHR based process is shown in Figure 29. All H_2 yields from the WGS reactor were beyond corresponding recycle baseline. It meant the process under these gasification conditions could be self-sustainable on H_2 supply. Due to the enhancement of steam gasification, CH_4 production decreased a little bit. The maximum CH_4 yield was produced under the gasification condition (H_2/C -Steam/C) of 1.59-1.67.



Figure 29: Production of Hydrogen and Methane from Water Gas Shift

The production of H₂ and CH₄ from methanation of SE-SHR based process is shown in Figure 30. Only the H2 yield from the methanator under the gasification conditions of 0.63-1.67, 0.63-2.22, 1.08-1.67 and 1.08-2.22 could meet the recycle requirement. Due to the enhancement of steam gasification, more CO and CO2 were produced in the producer gas, which contributed to the further CH₄ synthesis. Consequently, CH₄ yield increased with the increase of Steam/C. The maximum CH₄ yield was produced under the gasification condition (H₂/C-Steam/C) of 1.08-2.22.

Source: University of California, Riverside



Source: University of California, Riverside

The production of CO and CO₂ from WGS of SHR based process and SE-SHR based process is shown in Figure 31 and Figure 32, respectively. Besides, CO conversion percentage of WGS is also depicted in these figures. At each H₂/C, the yield of CO and CO₂ was enhanced with the increase of Steam/C during both processes. This trend was in accordance with the trend in the gasifier. The CO₂ production from WGS of SE-SHR based process was much less than that of SHR based process. The CO₂ production was reduced at least by 50 percent. The CO conversion percentage was close to 100 percent for both processes. It was because of two WGS reactors set in series, high temperature shift and low temperature shift, as mentioned earlier.





Source: University of California, Riverside

Figure 32: Production of Carbon Monoxide and Carbon Dioxide with Carbon Monoxide Conversion Percentage from Water Gas Shift of Sorption Enhanced Steam Hydrogasification Reactor Based Process for Substitute Natural Gas Production



Source: University of California, Riverside

The production of CO and CO₂ with conversion percentage from methanation of SE-SHR based process is shown in Figure 33. At each H_2/C the yield of CO and CO₂ was increased when the steam input was raised. However, the final yield of these two gases was extremely low and could be neglected in the SNG product. The conversion percentage of CO and CO₂ was very high due to two methanators in series.





Source: University of California, Riverside

The corresponding mass and heat analysis of above three optimum processes is depicted in Figure 34, Figure 35, and Figure 36. The mass balance of these processes is shown in Figure 34(a), Figure 35(a) and Figure 3636(a), respectively. 4335kmol, 7779kmol and 6470kmol carbon was converted to CH₄ in the gasifier in the SHR-WGS based, SE-SHR-WGS based and SE-SHR-Methanation based processes, respectively. The carbon in the form of CO₂ released from the combustor or the regenerator in these three processes was 11720kmol, 11675kmol and 11993kmol, respectively. No more carbon was distributed to CH₄ after WGS for SHR-WGS based and SE-SHR-WGS based processes. But more carbon was converted to CH₄ via methanation in the SE-SHR-Methanation based process. So the CH₄ production in the final SNG product was 7939kmol. Less CO entered the WGS reactor in the SE-SHR-WGS based process and process. It indicated the potential to reduce the WGS reactor size. Besides, 3869kmol CO₂ needed to be separated from the final product gas in the SHR-WGS based process and almost no CO₂ existed in the SNG of the SE-SHR-Methanation based process in the SNG of the SE-SHR-MGS based process. This substantially reduced the cost for CO₂ separation.

The corresponding heat balance of the three optimum processes is shown in Figure 34(b), Figure 35(b) and Figure 36(b). In SHR-WGS based process, the energy recovered from the combustor and the flue gas cooling was enough for the heat requirement of the gasifier, the air preheating, and the pretreatment. Besides, there was more energy output from the cooling of gas cleanup and WGS. In the case of SE-SHR-WGS and SE-SHR-Methanation based processes, the energy from the flue gas cooling could supply all the heat required by the air pretreating, the regenerator, and the gasifier. The heat from the cooling of gas cleanup section and the WGS/Methanation section could be used for the pretreatment. There was very limited net energy output from two SE-SHR based processes, though the heat demand and the heat supply could be paired. A bit of the final SNG product (e.g. 5 percent) could be used for extra heat supply if necessary. This would not affect the higher production.



Figure 34: Mass and Heat Balance of Main Processing Units of Steam Hydrogasification Reactor-Water Gas Shift Based Process for Substitute Natural Gas Production

Source: University of California, Riverside

Figure 35: Mass and Heat Balance of Main Processing Units of Sorption Enhanced Steam Hydrogasification Reactor-Water Gas Shift Based Process for Substitute Natural Gas Production



Source: University of California, Riverside



Source: University of California, Riverside

The carbon balance of each process is depicted in Figure 37. It shows that about 60 percent carbon went to the combustor or the regenerator flue gas in these processes. Only 22 percent carbon was distributed to CH_4 in the SHR-WGS based process. By contrast, about 40 percent carbon was converted to CH_4 in the two SE-SHR based processes. In particular, SE-SHR-Methanation based process had almost zero carbon in the form of CO_2 in the end.

Figure 37: Carbon Balance of Steam Hydrogasification Reactor Based and Sorption Enhanced Steam Hydrogasification Reactor Based Processes for Substitute Natural Gas Production



(a) Based on steam hydrogasification reactor-water gas shift, (b) based on sorption enhanced steam hydrogasification reactor-water gas shift, and (c) based on sorption enhanced steam hydrogasification reactor-methanation.

Source: University of California, Riverside

The comparison of SNG quality among SHR based and SE-SHR based processes is shown in Table 9.

Table 9: Comparison of Substitute Natural Gas Quality Among SteamHydrogasification Reactor Based and Sorption Enhanced Steam HydrogasificationReactor Based Processes

ltem	SHR WGS	SE-SHR WGS	SE-SHR Methanation	
CH ₄ (vol%)	94.1	95.85	97.33	
H ₂ (vol%)	4.88	4.07	2.67	
CO (vol%)	0.17	0.02	≈0	
CO ₂ (vol%)	0.85	0.06	≈0	
Energy Efficiency%	38.02	67.99	69.06	
CH ₄ Conversion%	21.75	39.03	39.83	
WI (MJ/Nm ³)	47.12	48.03	48.26	

Source: University of California, Riverside

The table shows that SE-SHR-Methanation based process had comparatively higher CH_4 percent and lower CO_2 percent. The two SE-SHR based processes had much higher overall energy efficiency, which percentage was almost 70 percent. Additionally, the CH_4 conversion efficiency of the two SE-SHR based processes was almost two times higher than that of the SHR based process.

The absolute minimum and maximum number of WI in most United States cities are 44.8MJ/Nm³ and 52.9MJ/Nm³, respectively.¹⁶ According to the Wobbe numbers in Table 9, these three SNG products could fit the standard range perfectly as a qualified interchangeable fuel. They could be burned satisfactorily in most appliances, boilers, burners, power plants and turbines with negligible change in burner performance without the need for special adjustment.

Summary

The performance of SE-SHR based processes for both FT synthetic fuel and SNG production was evaluated. The performance was compared to the conventional SHR based processes. The main results were summarized as below.

- 1. The optimum gasification condition (H₂/C-Steam/C) for FT synthetic fuel production using SHR based process and SE-SHR based process was 1.59-2.22 and 1.59-2.78, respectively.
- 2. The optimum SE-SHR based process for FT synthetic fuel production had comparatively lower total CO₂ emissions with higher FT product yield.

¹⁶ Klassen M. White paper on natural gas interchangeability and non-combustion end use. NGC+Interchangeability Work Group. 2005

- 3. The optimum gasification condition (H₂/C-Steam/C) for SNG production using SHR-WGS based, SE-SHR-WGS based and SE-SHR-Methanation based processes was 1.08-2.22, 1.59-1.67 and 1.08-2.22, respectively.
- 4. The two optimum SE-SHR based processes for SNG production had much lower total CO_2 emissions with higher SNG yield compared to the SHR based process. The optimum SE-SHR-Methanation based process had the highest CH_4 percent with near zero CO_2 percent in the SNG.
- 5. The WGS reactor size in the SE-SHR-WGS based process could be reduced to save cost due to lower CO input compared to the SHR-WGS based process.

CHAPTER 3: Evaluation of Process Economics and Life Cycle Comparison

Background and Methods

The conventional gasification process for renewable SNG (or RNG) production (Case A) is based on the developing process by ECN¹⁷ for production of SNG from biomass. The plant for Case A consists of eight major sections : (1) pretreatment of feedstock, (2) gasifier (circulated fluidized bed type), (3) gas cooler, (4) dust removal, (5) tar removal, (6) gas cleaning and conditioning, (7) methanation, and (8) upgrading and compression.

The steam hydrogasification process for SNG production (Case B) is based on the developing process by UCR for production of SNG from biomass. The plant for Case B consists of eight major sections: (1) pretreatment of feedstock, (2) SHR reactor, (3) heat recovery, (4) gas cleaning, (5) water gas shift, (6) H_2 separation and recycling, CO₂ separation, (7) methanation, and (8) dry and compression.

The anaerobic digestion process for renewable SNG production (Case C) is based on the conventional process which is well known for production of biogas. The plant for Case C consists of six major sections: (1) pretreatment of feedstock, (2) hydrolysis, (3) digester (mesophilic), (4) biogas tank (post digester), (5) digester reservoir, and (6) biogas upgrade (CO₂ separation).

Case A and the Case B were investigated using Aspen Plus software (ver. 7.3). The gasification section of Case A and Case B was simulated by decomposition and gasification units in the ASPEN block. The gasification block in Case A and Case B calculated the equilibrium product gas composition under the given conditions by means of Gibbs free minimization using the RGIBBS block. For Case B, the experimental results of the carbon conversion from CSTR batch reactor were used to simulate the equilibrium product gas composition of the gasification section.

The anaerobic digestion process for RNG production (Case C) was simulated using the data obtained from the wastewater treatment plants in reference.¹⁸ Figure 38 shows the block flow diagram of three cases.

^{17 &}quot;Production of Synthetic Natural Gas(SNG) from Biomass, Development and operation of an integrated bio-SNG system" R.W.R. Zwart, H. Boerrigter, E.P. Deurwaarder, C.M. van der Meijden, S.V.B. van Paasen. ECN-E--06-018, 2006

¹⁸ Anaerobic Digester Methane to Energy, A Statewide Assessment, Prepared For Focus On Energy, Prepared By Thomas E. Vik, P.E. DEE, McMahon Associates, Inc. 2003

Figure 38: Diagram of Renewable Natural Gas Processes



A. Conventional gasification process(developing process)

Source: University of California, Riverside

The process economic analysis was estimated by the spreadsheet, which was developed inhouse. The cost estimation has an expected accuracy of roughly -20~-50 percent in the lower ranges and 30~100 percent in higher ranges, since the level of the accuracy required for the program is for the feasibility purpose, which can be defined as "Class 5" in the AACE(Association for the Advancement of Cost Engineering International). All capital costs and O&M costs were estimated as "overnight costs" expressed in 2014 \$. The economic analysis was estimated for two cases with different capacity of feedstock, one is for the capacity of 200 TPD, and other is for the capacity of 400 TPD.

A 50/50 Debt/Equity financing was assumed with 8 percent and 10 percent discount rate, respectively for the capacity of 200 TPD. For the capacity of 400 TPD, a 50/50 Debt/Equity financing was assumed with 6 percent and 8 percent discount rate, respectively. The life time of the plant was assumed to be 20 years in all cases. O&M cost was assumed to be 4 percent of TCI (Total Capital Investment) for the 200 TPD of feedstock capacity and 3 percent of TCI for the 400 TPC of feedstock capacity.

Result and Discussion

Plant Capacity of 200 Tons Per Day

200 ton per day plant was designed and simulated with the following process conditions.

- Case A:
 - Gasifier condition: 850°C, 7 bar
- Case B:
 - H2O/feedstock ratio (slurry, wt. basis): 1

- Steam/feedstock ratio (wt. basis): 0.5
- Gasifier condition: 750°C, 400 psia
- Carbon conversion: 82.1 percent
- Case C:
 - Volatile: 75 percent
 - Volatile solids to digestion: 50 percent

Process economic assumptions used for this simulation were:

- Average inflation: 3.0 percent
- Discount rate (debt): 8 percent, Discount rate (equity): 10 percent
- Ratio of debt: 50 percent
- Economic life: 20 years
- Operation cost: 4 percent of TCI (Total Capital Investment)
- Feedstock cost: 20 \$/ton
- Annual Operation day: 333 days

Table 10 shows the plant throughput for each different case scenarios.

	Case	Case A Conventional Gasification	Case B Steam Hydrogasification	Case C Anaerobic Digestion
	Production (ton/d)	39.09	58.54	32.63
	CO (mol %)	0.3	8ppm	
Renewable	H ₂ (mol %)	0.8	1.4	0.1
Natural Gas	CO ₂ (mol %)	0.4	0.2	0.6
	CH4 (mol %)	98.1	98.3	99.3
	H ₂ O (mol %)	0.2	0.1	
	HHV (MMBtu/d)	2,250.7	3,370.6	1,878.8
CO2 Production (ton/d)		189.82	145.13	138
CO2 Production/RNG (kg/MMBtu)		84.34	43.06	73.45

Table 10: Plant Throughput, 200 Tons Per Day

Source: University of California, Riverside

The cost estimation of the total plant cost (TPC) including the operation cost is summarized in Table 11. It shows Case A and Case B have the higher plant cost than Case C.

Cost	Case A	Case B	Case C		
Total plant cost	65.42	79.53	33.22		
Operation cost	2.62	3.18	1.33		
Production cost (\$/MMBtu)	25.64	20.50	35.15		

 Table 11: Cost Estimation (\$ million)

Source: University of California, Riverside

However, the production cost shows the Case B has lowest number, since Case B has the highest RNG production efficiency. The broken down, categorized cost estimation is also summarized in Figure 39.





Source: University of California, Riverside

Plant Capacity of 400 Tons Per Day

Process condition of 400 ton per day plant was identical to the 200 TPD Plant. However, process economic assumptions used for this 400 TPD simulation are slight different due to the size of the plant.

- Average inflation: 3.0 percent
- Discount rate (debt): 6 percent, discount rate (equity): 8 percent
- Ratio of debt: 50 percent
- Economic life: 20 years

- Operation cost: 3 percent of TCI (total capital investment)
- Feedstock cost: 20 \$/ton
- Annual operation days: 333 days

Table 12 shows the plant throughput for each different case scenario.

Table 12: Plant Inroughput, 400 Tons Per Day				
Case		Case A Conventional Gasification	Case B Steam Hydrogasification	Case C Anaerobic Digestion
RNG	Production (ton/d)	78.18	117.08	65.26

Source: University of California, Riverside

In Table 13, cost estimation of total plant cost (TPC) together with the operation cost is summarized. It also shows Case A and Case B have higher plant cost than the Case C. However, like the 200 TPD plant, the production cost shows that Case B has the lowest number, since Case B has the highest RNG production efficiency. The broken-down categorized cost estimation is also summarized in Figure 40.

Table 13: Cost Estimation (million \$)

Cost	Case A	Case B	Case C
Total plant cost	108.50	131.91	71.81
Operation cost	3.26	3.96	2.15
Production cost (\$/MMBtu)	18.63	14.80	28.56

Source: University of California, Riverside

Figure 40: Plant Cost, Renewable Natural Gas Production Throughput and Production Cost, 400 Tons Per Day



Source: University of California, Riverside

Sensitivity analysis study shows the feedstock cost has highest influence on the RNG production cost. Case B has lowest sensitivity on this variable among three scenarios as shown in Figure 41.



Figure 41: Sensitivity Analysis of Production Cost on Feedstock Cost

Source: University of California, Riverside
CHAPTER 4: Development of Basic Engineering Design for Pilot

Plant

The pilot scale plant in a 0.8 dry metric TPD dry basis feed throughput, CFB reactor system without external heaters was designed. The plant will use a commingled green waste and biosolids feedstock. In this chapter, Preliminary Engineering design of the pilot plant was presented

The quantifiable design basis of the pilot plant is:

- Process higher heating value (HHV) efficiency above 63 percent.
- Convert 700 tons per year of co-mingled biosolids and biomass waste, (wet basis, 60 percent moisture) into 20,000 diesel gallon equivalents per year of RNG.

The proposed plant, if successful, will complete the critical next step in the development of this technology. The pilot plant will provide the process and engineering data necessary for the design, construction, and operation of a commercial plant.

In Figure 42 through Figure 47, block flow diagrams detailing the pilot plant process and utility flow are presented. This basic engineering work was done by Aaron Engineering Co. Ltd. The entire block flow diagram can be divided into 3 sections.

Feedstock Pretreatment Section

Co-mingled feedstock is converted into the pumpable form of the slurry. The detail process condition of the process fully described in the Chapter 3 of the previous report.¹⁹

Two vessels labeled as MAT-01 and MAT-03 provide the feed into the hydrothermal pretreatment reactor labeled as MAT-02. A progressive cavity pump, (P-02) is used for feeding the feedstock into the gasification reactor.

Gasification Section

Steam Hydrogasification Reactor is labeled as E-01, it has side feeding slurry port and bottom port for the fluidizing gas. It also has side feeding port for hot sand from sand combustor (C-03). Producer gas exits the gasifier from the top section. Producer gas will pass the double cyclone filter (C-01 and C-02). Retained sand will feed into the sand combustor (C-03). At the sand combustor, air and auxiliary fuel line provide the combustion reaction, together with the char byproduct coming from the gasifier. Hot sand will pass the loop seal (T-01), then feed

¹⁹ 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.

into the gasifier (E-01). Combustion exhaust gas will pass the exhaust cyclone (F-03), then, exhaust to outside.

Gas Conditioning Section

After cooling down the producer gas by the series of heat exchangers (EX-01, EX-02), the gas temperature will be around 350C, which is still above the bubbling point of the steam. Two water gas shift reactors consisting of high temperature (350C, HTS-01) and low temperature (220C, LTS-01) are placed to convert CO and water into hydrogen and methane.

Then the exit producer gas of LTS passes the warm gas cleanup unit (REM-01), to remove the sulfur species for the protection of the catalyst in the downstream processes. Cleaned gas is fed into the storage tanks (T-02, BU-02). Alternatively, the product gas can pass the series of sampling tanks (S-03 thru S-15) for analysis.



Figure 42: Block Flow Diagram with Process and Utility Flow (1)



Figure 43: Block Flow Diagram with Process and Utility Flow (2)



Figure 44: Block Flow Diagram with Process and Utility Flow (3)



Figure 45: Block Flow Diagram with Process and Utility Flow (4)



Figure 46: Block Flow Diagram with Process and Utility Flow (5)



Figure 47: Block Flow Diagram with Process and Utility Flow (6)

CHAPTER 5: Summary of Results

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

Table 12 below 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.

Task	Deliverables	Report Section
2	SE-SHR Demonstration Test Plan	Chapter 2
	 SE-SHR Detailed Design Flowsheet 	
	 Process Mass and Energy Balance Report 	
	 Process Performance Results Report 	
3	 Integrated Process Flow Sheet 	Chapter 3
	Process Economics Report	
4	Block Flow Diagram	Chapter 4 and
	 Process and Utility Flow Diagrams 	Chapter 3 (Life Cycle
	Pilot Plant Design Report	Analysis)
	Life Cycle Comparison Report	

Table 14: Project Deliverables and Related Report Section

Source: University of California, Riverside

Result from the laboratory scale bench reactor shows that the addition of sorbent could remove CO_2 within SHR and increase the energetic gas (H₂ and CH₄) production for different kinds of feedstock. In particular, the amount of H₂ was increased dramatically and enough for recycle use over the CaO/C molar ratio of 0.29. The hydrogen yield was increased by 60 percent when the calcium oxide to carbon molar ratio was increased to 0.86 as compared to the results without the sorbent. The hydrogen in the product gas was sufficient to maintain a self-sustained supply back to the SHR when the calcium oxide to carbon molar ratio oxide to carbon molar ratio was over 0.29.

The bench-scale CFB reactor was developed through the mockup test. The result shows a 76 percent carbon to gas conversion.

The techno-economic analysis with the detailed heat and mass balance for the RNG production was performed by process simulation software together with the bench scale demonstration result. The result was compared to the other processes that can produce the RNG. It shows SE-SHR process has the lowest CO_2 footprint (43.6 kg/ MMBTU) and also shows the lowest production cost (\$14.8/MMBTU) among other processes.

A preliminary design of a pilot plant was completed. The pilot plant is designed to produce approximately 20,000 diesel gallon equivalents (DGE) per year of fuel grade RNG using 0.8 dry metric Tons Per Day (TPD) feed throughput of commingled green waste and biosolids.

The pilot plant demonstration will complete the critical next step in the development of this technology. The project would provide process and engineering data necessary for the design, construction, and operation of a commercial plant. Thus, the successful completion of the proposed project will enable a new, low cost, efficient gasification technology for RNG production to move towards commercialization.

LIST OF ACRONYMS

Term	Definition
ARFVTP	Alternative and Renewable Fuel and Vehicle Technology Program
BDT	Bold Dry Tonne
BFB	Bubbling Fluidized Bed
Btu	British Thermal Unit
С	Carbon
C+	Hydrocarbon
CaO	Calcium oxide
CEC	California Energy Commission
CE-CERT	College of Engineering – Center for Environmental Research and Technology
CFB	Circulating Fluidized Bed
CH ₄	Methane
СО	Carbon monoxide
CO ₂	Carbon dioxide
CSTR	Continuous-Stirred Tank Reactor
DAFT	Dissolved Air Floatation Thickener
DGE	Diesel gallon equivalent
DOE	Department of Energy
FT	Fischer-Tropsch
GC-FID	Gas Chromatography with Flame Ionization Detector
GC-TCD	Gas Chromatography with Thermal Conductivity Detector
H ₂	Hydrogen
HHV	Higher Heating Value
HTP	Hydrothermal Pretreatment Process
HTR	Hydrothermal Reactor
H ₂ S	Hydrogen Sulfide
IRR	Internal Rate of Return
LCFS	Low Carbon Fuel Standard

Term	Definition
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
MMBtu	Million British Thermal Unit
NDIR	Non Dispersive Infra-red
NETL	Natural Energy Technology Laboratory
NiO	Nickel Oxide
NH ₃	Ammonia
NG	Natural Gas
PDU	Process Development Unit
PPM	Parts Per Million
PWG-ALG	Pinewood algae
PWG-SLG	Pinewood sludge
RNG	Renewable Natural Gas
RPM	Round Per Minute
PWM	Pulse Width Modulation
SE	Sorption Enhanced
SE-SHR	Sorption Enhanced Steam Hydrogasification Reactor
SHR	Steam Hydrogasification Reactor
SLPM	Standard Liter Per Minute
SMR	Steam Methane Reformer
SNG	Substituted Natural Gas
SOP	Standard Operation Procedure
SVM	Solenoid Valve Module
TPD	Tonne Per Day

Term	Definition
TDH	Transport Disengagement Height
UCR	University of California, Riverside
WGS	Water Gas Shift
WI	Wobbe Index; a measure of gas interchangeability for practical operation
ZnO	Zinc Oxide
ZnS	Zinc Sulfide
Sorbent	Material or molecule used to absorb liquids or gasses