



ENERGY RESEARCH AND DEVELOPMENT DIVISION

FINAL PROJECT REPORT

Renewable Syngas Methanation

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PREFACE

The California Energy Commission's (CEC) Energy Research and Development Division manages the Gas Research and Development Program, which supports energy-related research, development, and demonstration not adequately provided by competitive and regulated markets. These natural gas research investments spur innovation in energy efficiency, renewable energy and advanced clean generation, energy-related environmental protection, energy transmission and distribution and transportation.

The Energy Research and Development Division conducts this public interest natural gasrelated energy research by partnering with RD&D entities, including individuals, businesses, utilities and public and private research institutions. This program promotes greater gas reliability, lower costs and increases safety for Californians and is focused in these areas:

- Buildings End-Use Energy Efficiency
- Industrial, Agriculture and Water Efficiency
- Renewable Energy and Advanced Generation
- Natural Gas Infrastructure Safety and Integrity
- Energy-Related Environmental Research
- Natural Gas-Related Transportation

Renewable Syngas Methanation is the final report for the Renewable Syngas Methanation Project (PIR-18-004) conducted by Taylor Energy. The information from this project contributes to the Energy Research and Development Division's Gas Research and Development Program.

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

ABSTRACT

The purpose of the project was to develop and demonstrate an autothermal-gasification pilotscale process to convert forest biomass, through a series of steps, into ultra-clean, pipelinequality renewable gas. The project team incorporated innovative pulse-detonation-derived acoustic power to intensify the gasification process, using Taylor Energy's Pilot-Scale Biomass Gasification Test-Facility, located at the University of California, Riverside, Center for Environmental and Research Technology. A forest biomass-to-syngas process was developed for economic production of pipeline-quality renewable gas, and the project team demonstrated key subsystems to advance the state of the art for gasification/reforming technology to produce syngas (synthesis gas) intended for upgrading to renewable gas.

Key Results:

- Biomass Gasification:
 - Thermo-catalytic intensification methods employing pulse-detonation-derived acoustic power resulted in increased specific throughput and improved energy conversion efficiency, and they are expected to reduce the installed capital cost.
- Gas Shift Reactor:
 - The project team identified a catalyst made of perovskite microfibers with oxide structures of the perovskite type as the most promising catalyst for advancing the state of the art for converting biogas-derived syngas.
- Syngas Methanation:
 - An 80 percent methane yield was achievable by reacting the shifted syngas slipstream in an adiabatic 3-stage nickel-based catalytic methanation process.

Keywords: forest biomass, syngas, gasification, methanation, renewable gas

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TABLE OF CONTENTS

| Acknowledgements | i |
|--|----------------------------------|
| Preface | ii |
| Abstract | iii |
| Executive Summary | 1 |
| Background Project Purpose and Approach Key Results and Implications for Future Commercialization Future Research Needs Anticipated Benefits for California Knowledge Transfer and Next Steps | 1 2 2 3 3 |
| CHAPTER 1: Introduction | 5 |
| Project Purpose Relevant Background Information Advancing a Technology Knowledge Gaps This Project Addresses Goals and Metrics That Demonstrate Success Market Factors That Contribute to Acceptance | 5 5 6 6 7 |
| CHAPTER 2: Project Approach | 8 |
| Project Partners, Technical Advisors, and Project Participants Technical Approach Specific Technology and Research Objectives Biomass Gasification Innovative Gasification Process Biomass Feeding Gas Shift Reactor Develop/Validate a Cryogenic Deep-cleaning Process to Enable Methane | 8 9 10 12 13 15 |
| Production | |
| Syngas Methanation Key Project Milestones | 18 21 |
| CHAPTER 3: Results | 22 |
| Specific Technology and Research Results Biomass Gasification Innovative Gasification Process Biomass Feeding Gas Shift Reactor Syngas Methanation | 22 22 23 26 29 30 |

| Specific Market and Policy Barriers Technology Approach Proposed to Achieve Economic Deployment at Medium Scale Public Outreach | 34 35 38 |
|---|----------------|
| CHAPTER 4: Conclusion | 39 |
| Importance to California's Clean Energy and Climate Goals Key Implications of the Project Outcomes for Commercial Markets Benefits of Lessons Learned: Future Development Opportunities | 39 39 40 |
| Glossary and List of Acronyms | 42 |
| References | 45 |
| Project Deliverables | 47 |
| APPENDIX A: Process Evaluations | A-1 |

LIST OF FIGURES

| Figure 1: Taylor Energy's Biomass Gasification Test Facility at UCR | 8 |
|--|----|
| Figure 2: Process Flow Diagram — Using Two Pulse Detonation Power Inputs | 10 |
| Figure 3: Mass and Energy Balance for the Biomass Gasification R&D System | 11 |
| Figure 4: Testing Pulse Detonation Methods Used to Generate Acoustic Power | 12 |
| Figure 5: Wood Shavings Supplied in 40-Pound Bales | 13 |
| Figure 6: Calibrating the Biomass Feed Rate, Measured in Pounds per Minute | 14 |
| Figure 7: A Komar Biomass Auger-Extrusion Type of Feeder | 14 |
| Figure 8: Feeding System: Auger-Extruder, Blower/Sawdust-Pump, Gas Ejector | 15 |
| Figure 9: Traditional Iron-Chromium Type High-Temperature Gas Shift Catalysts | 16 |
| Figure 10: Perovskite-type Materials | 16 |
| Figure 11: Water Gas Shift Reactor With Heat Recovery Steam Generator | 17 |
| Figure 12: Methanation System Design for Renewable Gas Production | |
| Figure 13: Methanation Catalyst Test System | 20 |
| Figure 14: Intensified by Mixing With Acoustic Power (Image Recorded at 7 Hz) | 22 |
| Figure 15: Detonation Cycle | 24 |
| Figure 16: Cyclic Detonations at 20 Hz | 24 |
| Figure 17: Amplitudes Combine (A) for Acoustic Waves at the Same Frequency | 25 |
| Figure 18: Acoustic Power Linkage With Carbon Particles Can Cause Dissociation | 26 |
| Figure 19: Steam Eductor Input Biomass Into the Base of the Gasification Reactor | 27 |

| Figure 20: Steam Eductor Input Biomass Into the Gasifier Main Body | 27 |
|---|----|
| Figure 21: System Design for Feeding Biomass Into 10-psig Kinetic Pressure | 28 |
| Figure 22: CO Conversion and Product Gas Composition (Dry Basis) From the Stage-1 Reactor at 662°F (350°C) for 100 Hours | 31 |
| Figure 23: CO Conversion and Product Gas Composition (Dry Basis) From the Stage-2 Reactor at 662°F (350°C) for 100 Hours | 32 |
| Figure 24: CO Conversion and Product Gas Composition (Dry Basis) From the Stage-3 Reactor at 662°F (350°C) for 100 Hours | 33 |
| Figure 25: CO Methanation Is an Exothermic Reaction | 33 |
| Figure 26: Feedstocks, Technology Paths, and Carbon Negative Energy Product | 34 |
| Figure 27: Two-Stage Conversion of Biomass to Syngas | 35 |
| Figure 28: Staged Conversion of Biomass \rightarrow Bio-slurry \rightarrow Syngas \rightarrow RNG | 35 |
| Figure 29: Staged Conversion of Biomass Into RG | 36 |
| Figure 30: High-Pressure Syngas Production Using Entrained Flow Gasification | 37 |
| Figure A-1: Feedstocks, Technology Paths, and Carbon Negative Energy Product A | -2 |
| Figure A-2: Total Levelized Operating Expenses (OPEX) Sensitives A | -3 |
| Figure A-3: Levelized Cost Profile for a 945-TPD Biomass-to-RG Project A | -3 |
| Figure A-4: Process Flow Diagram of the Taylor Energy Gasification System | -4 |
| Figure A-5: Gasifier Model in the Aspen Plus User Interface A | -1 |

LIST OF TABLES

| Table 1: Syngas Slipstream Composition for WGS Catalysts | 23 |
|---|-----|
| Table 2: Syngas Composition, Post-Gas-Shift Catalyst | 29 |
| Table 3: Syngas Composition After Minimizing Air Infiltration | 30 |
| Table 4: Gas Composition – Ratios Change After Each Methanation Stage | 31 |
| Table A-1: Summary Results for the Stockton Site-specific RG Study | A-1 |
| Table A-2: Global Warming Potentials of the Key GHGs | A-1 |
| Table A-3: WTT Results of the Life Cycle Assessment | A-2 |
| Table A-4: WTW Results of the Life Cycle Assessment | A-4 |
| Table A-5: Life Cycle Carbon Intensity for a Base Case RG Plant | A-5 |
| Table A-6: Life Cycle Analysis for GTI RG Plant With and Without Carbon Capture | A-6 |

Executive Summary

Background

Currently, fossil gas plays a major role in California's energy consumption; 90 percent of the gas consumed is imported via pipeline from out of state (CEC, n.d.). As a solution for reducing fossil gas usage, forest biomass can be converted through a series of steps into ultra-clean, pipeline-quality, renewable gas.

Forest biomass, such as dead trees, is a clean energy resource abundant throughout the state. The U.S. Forest Service reveals that "about 36.3 million trees across 2.6 million acres of federal, state, and private land died in California in 2022" due to conditions caused by drought, bark beetle infestation, and high tree densities (USDA Forest Service, 2023). By using dead tree biomass, the state of California can reduce wildfire damage and improve forest health. To help support the transition away from fossil gas and to build an industry that justifies the costs to collect and transport forest biomass, pipeline-quality renewable gas must be economical for utilities and end users. Currently the cost per million British thermal units (MMBtu) of fossil gas is \$3.70, whereas renewable gas exceeds \$7.00 (ICF, 2019). Therefore, breakthroughs are needed to enable techno-economic advances.

The project provides timely support for California's clean-energy and climate goals for achieving carbon negative biofuels production and addressing tree mortality, as stipulated in the "Proclamation of a State of Emergency" (Tree Mortality), issued by the Governor in 2015 (Brown, 2015).

Project Purpose and Approach

The project team developed a forest biomass-to-syngas process for economic production of pipeline-quality renewable gas using Taylor Energy's Pilot-Scale Biomass Gasification Test-Facility, located at the University of California, Riverside. Project goals included: demonstrating a slipstream with renewable gas quality that meets California investor-owned-utility standards, evaluating gas shift methods applied to biofuels, and validating a methane production process that can be scaled for commercial deployment.

The pilot-scale technology employed a low-pressure entrained flow gasifier with a reforming stage, followed by downstream cleaning systems, and a catalytic methanation process to make the pipeline-quality renewable gas. Taylor Energy incorporated innovative pulse-detonation-derived acoustics to intensify the gasification process. The pilot-scale throughput was 5 tons-per-day, feeding biomass recovered from forest waste. The team operated the gasification process for 500 cumulative hours, including two 8-hour runs, collecting engineering data on temperature, pressure, flow rates, etc. In addition to the demonstration and testing, the team prepared a material and energy balance, including energy efficiency calculations, a techno-economic analysis, and a life cycle analysis.

The successful scale-up demonstration of this system would be of interest to municipalities that want to provide pipeline-quality renewable gas to existing utility customers who are

presently consuming imported fossil gases. The system produced more than 25 standard cubic feet per minute (SCFM) of renewable syngas and more than 1.5 MMBtu per hour of heat output, which demonstrates success at pilot scale and provides the engineering base to design a larger biomass-to-renewable-gas demonstration plant that can meet gas pipeline specifications.

Key Results and Implications for Future Commercialization

- Biomass Gasification
 - Increased throughput, improved energy conversion efficiency, and reduced installed capital costs by intensifying thermo-catalytic gasification.
- Pulse Detonation
 - Achieved high-intensity mixing between gases, vapors, and solids at frequencies of 25 to 35 hertz by applying acoustic power in the frequency range of 7 to 20 hertz.
- Biomass Feeding
 - Provided a means of continuous biomass input by using a steam reductor to overcome the internal gasifier kinetic pressure, up to about 3 pounds per square inch gauge (psig).
- Gas Shift Reactor
 - Formed additional methane for the subsequent methanation process by cracking and or hydrogenating light olefins during the water gas equilibrium shift.
 - Converted approximately 50 percent by volume of the carbon monoxide content into hydrogen for methanation by using a single-stage, high-temperature, water gas shift.
 - Identified perovskite microfiber catalysts as the most promising type of emerging waste gas shift catalysts.
- Syngas Methanation
 - Maintained a 3 SCFM renewable gas slipstream during continuous tests without difficulty, from about 30 SCFM syngas from the gas shift reactor.
 - Achieved an 80 percent yield of methane by converting biomass derived syngas with a 3:1 hydrogen to carbon monoxide ratio using a 3-stage nickel-based catalyst.

Future Research Needs

• Prove the dissociative impact of acoustic power by measuring interactions between biomass particles and gases when acted upon by supersonic shocks at 35 hertz.

• Prove that feeding biomass directly into the detonation zone where supersonic shocks are administered can produce high-value carbon products.

Anticipated Benefits for California

Ultimately, this work will benefit ratepayers, the public, and the environment by providing:

- Economic benefits by reducing the cost of community-scale biomass gasification by more than 50 percent relative to present industry standards.
 - Co-production of high-value carbon products with engineered shapes, including carbon black and graphitic carbon products, will finally add significant value.
 - Potential cost savings coming from lower gas utility bills and future economic development in rural areas.
- Environmental benefits from using renewable feedstocks instead of fossil fuels.
 - Reduce forest fire and associated health risks by the removal of millions of tons of dead trees and forest-slash through sustainable forest management practices.
- Societal benefits of increased energy security from reducing reliance on pipelineimported fossil gas by using local resources and labor to produce sustainable energy infrastructure.

Knowledge Transfer and Next Steps

The team shared information with the following key individuals in academia, industry, and government institutions:

- University of Utah
- Kern Oil & Refining Co.
- Maersk Container Shipping
- Port of Los Angeles
- Port of Long Beach
- Department of Public Works, County of Los Angeles
- California Department of Conservation
- California Department of Forestry and Fire Protection (CalFire)
- Sims Resource Renewal
- U.S. Department of Agriculture, Small Business Innovation Research
- U.S. Department of Energy, Bioenergy Technologies Office
- CEMEX USA
- National Science Foundation

The research team developed the following recommendations:

• Further research is needed to resolve the remaining technical issues for biomass feeding and cracking tars to enable the economic scale-up and successful deployment of gasification technologies.

• Given the high capital cost relative to the perceived risk, both state and federal support will be needed for first-of-a-kind plants demonstrating advanced biomass gasification methods. Thereafter, the technology can be deployed by industry within California.

Takeaways from the research include:

- Pulse detonation power methods applied to biomass gasification can be used to solve tar formation and carbon/tar deposition problems.
- Biomass feeding problems persist with input of pulse-detonation-derived power.
- A path to cost-effective production of generic methanation catalysts was established.

Prospects for broader adoption and informing policy and planning include:

- Low-temperature applications of 932°F–1112°F (500°C–600°C) for bio-crude liquids using a second-stage entrained flow gasification system to produce high-pressure syngas.
- High-temperature applications of 1742°F–1922°F (950°C–1050°C) for hydrogen-rich syngas compressed from 2 atmospheres to 10 atmospheres for purification and pipeline use.
- Medium-temperature applications of 1382°F–1562°F (750° –850°C) for fuel-gas production, generating near-atmospheric-pressure renewable fuel gases that can serve as a reliable fuel source for cement kilns, calcining processes, and certain rotating power generation systems.

Where the research could go next:

- This research could support modular biomass-to-renewable gas systems as stand-alone units and medium-scale processing plants using flash-pyrolysis for biocrude liquids production, followed by high-pressure entrained flow gasification to make pipelinequality renewable gas.
- Pulse detonation technology can be developed for future high-pressure applications (300 psig to 1000 psig). For example, entrained flow gasification methods employing high-velocity oxygen/fuel burners could be replaced with pulse detonation burners.

CHAPTER 1: Introduction

Project Purpose

The project demonstrates pilot-scale testing of an autothermal-gasification process to convert forest biomass into pipeline-quality renewable gas (RG). It supports the advancement of biomass gasification technology towards market adoption, and it supports California's clean energy and climate goals, by producing carbon negative biofuels with carbon as a co-product that can be sequestered economically.

Relevant Background Information

The project provides support for California's clean-energy and climate goals for achieving carbon negative biofuels production and it addresses tree mortality as stipulated in the "Proclamation of a State of Emergency" (Tree Mortality), issued by the Governor in 2015 (Brown, 2015).

The quantity of dead trees in California increased from 130 million in 2018 to 160 million in 2020 (USDA Forest Service, 2023). The Forest Service report reveals that "about 36.3 million trees across 2.6 million acres of federal, state and private land died in California in 2022" due to conditions caused by drought, bark beetle infestation, and high tree densities. The average Ponderosa pine tree with a 12-inch diameter weighs 2,000 pounds (1 ton). Harvesting 10 percent of the dead trees each year as a biomass feed would amount to an available fuel resource of about 20 million tons per year, or approximately 55,000 tons per day.

Recent scientific developments and environmental changes are focused on life cycle analyses (LCA) performed around energy systems. Forest residues and other separated biomass energy feeds are projected to generate low carbon and negative carbon fuels, increasing the potential value of biomass residues. New policies adopted by California gas utilities commit to using renewable gases, thereby necessitating changes in the future of energy sources, generation methods, and renewable gas procurement, transmission, and delivery.

Advancing a Technology

Gasification is a mature technology; however, there are limitations when applied to low-density, low-value renewable feeds. Research and development (R&D) is required to scale down and optimize systems for smaller community scales ranging from 200 tons/day to 2,000 tons/day to convert biomass into RG economically.

Worldwide, as of 2022, there are 1,500 large-scale gasification systems in commercial operation, located at 700 refinery-scale facilities (Denton, 2022). Gasification technologies using traditional energy feeds (coal, petroleum coke, heavy residues) operate with little downtime and provide economic benefits. Biomass properties differ from refinery feedstocks and, therefore, conversion methods optimized for biomass are needed, downsized from refinery scale for community operations that process biomass sourced within about 50 miles of a biomass conversion plant, feeding from 200 tons per day (TPD) to 2000 TPD biomass, producing from 1.5 million standard cubic feet per day (MMSCFD) to 15 MMSCFD of RG.

Knowledge Gaps This Project Addresses

There are research gaps related to the economical use of forest biomass residues as a lowcost gasification feed in the 1.5 to 15 MMSCFD RG output range. This size range is overlooked by industry because it is small for major companies such as Air Products and Shell, while the R&D effort is complicated and costly for small businesses.

The lag in technology development has resulted in a real market need for forest biomass gasification methods. This project addresses that knowledge gap in the commercial readiness plan for developing a financially feasible biomass-to-renewable-gas project.

Goals and Metrics That Demonstrate Success

Goals:

- Demonstrate a gasification-reforming technology using forest biomass to produce biofuels that are converted into RGs.
- Demonstrate a slipstream with RG quality that meets gas standards in applicable California investor-owned utility (IOU) territory.
- Evaluate four gas shift methods applied to biofuels.
- Develop, test, and validate a cryogenic deep-cleaning process that enables methane production.
- Develop, test, and validate an RG production process that can be scaled for commercial deployment.

Metrics:

- A feed rate of 5 tons per day (TPD) or 7.3-pounds per minute of forest residues
- Four different sulfur-tolerant sour-gas shift catalysts
- Commercially available methanation technology using improved catalyst formulations for a 3-stage adiabatic syngas (synthesis gas) methanation process.

To achieve California's carbon negative goals and objectives, the scale at build-out is a modest 200 TPD plant capacity (1.5 MMSCFD RG), potentially increasing to a 2,000 TPD (15 MMSCFD RG) capacity for community-scale energy projects. The overall biomass supply chain must be designed for appropriate throughputs, at all levels.

Market Factors That Contribute to Acceptance

Interested audiences:

- Municipalities and gas providers wanting to provide pipeline-quality RG and phase out the use of imported fossil gases.
- Pipeline customers in the Sierra Nevada wanting to leverage this research into projects at the 200-TPD to 300-TPD scale for locally sourced renewable products.
 - Considering the need for free-standing biomass conversion systems in towns in the Sierra Nevada, projects would need to operate as profitable independent business units, which helps lift the economy and improve energy security.
 - Another market factor is the availability of forest biomass and the cost of collection and preparation as a feedstock.
 - Projects would provide jobs and a cleaner environment and would minimize the hazards of forest fires.

CHAPTER 2: Project Approach

Project Partners, Technical Advisors, and Project Participants

Donald Taylor served as Project Manager/Principal Investigator (PM/PI) for Taylor Energy and was responsible for making decisions on process, scientific, and technical issues, working in consultation with Technical Advisory Committee (TAC) members. Dr. Arun Raju served as the PI for the University of California, Riverside (UCR), and focused on process evaluations for the project. The TAC members, listed below, comprised academics and industry professionals who provided technical knowledge and recommendations to benefit the project:

- Kevin Whitty, Professor, University of Utah (Gasification Advisor)
- Frank Lu, Aerospace Engineering Professor, University of Texas at Arlington (Pulse Detonation Power Advisor)
- Brendan McDonnell, Chief Technology Officer (Sims Limited Waste Recycling Advisor)
- Prab Sethi, Energy Consultant (Renewable Energy Business Development)
- Evan Williams, Cambrian Energy (Renewable Gas Project Finance Advisor)
- Scott McKelvey, Business Consultant to PCI (Oxygen Systems Integration)

Technical Approach

The project team performed the work at the Center for Environmental Research and Technology (CE-CERT), a research and commercial testing center operated by UCR. CE-CERT brings together multiple disciplines to address environmental challenges in air quality, climate change, energy, and transportation; it is located in Southern California Gas Company's (SoCalGas) service territory. Taylor Energy's Biomass Gasification Test Facility is shown below (Figure 1).

Figure 1: Taylor Energy's Biomass Gasification Test Facility at UCR



The project team accomplished concurrent R&D objectives on parallel paths:

- Modified the gasifier/reformer for operation, using high purity oxygen and/or air enriched to 93 percent volume oxygen. Operated the system for 500 cumulative hours to test and optimize the use of acoustic power inputs.
- Developed pulse detonation methods to generate acoustic power in the 7 hertz (Hz) to 20 Hz range and applied them to gasification.
- Designed and installed a water gas shift (WGS) reactor to test catalytic conversion of carbon monoxide (CO) to hydrogen (H₂) using a slip stream.
- Constructed a 3-stage methanation system to test catalyst formulations for methane production.
- Obtained real time operating data using infrared analysis monitoring four gases, which included a gas conditioning system and a gas calibration system that was designed, constructed, and operated by UCR vendor Kurt Bumiller.

Specific Technology and Research Objectives

The system starts with woody biomass being fed into a low-pressure entrained flow gasifier to produce syngas. The syngas flows downstream to the gas shift reactor and the product stream is sent to a catalytic methanation process to make the pipeline-quality renewable gas. Taylor Energy incorporated innovative pulse detonation acoustics to intensify the gasification process.

Technical hurdles were overcome by verifying the integration and performance of the following key subsystems:

- Biomass Gasification
- Innovative Gasification Process
- Biomass Feeding
- Gas Shift Reactor
- Syngas Methanation

The objectives for the pilot demonstration were to:

- Convert forest residues into RG.
- Evaluate methane production catalysts and select an optimum catalyst.
- Produce a 2.5-standard cubic feet per minute (SCFM) slipstream demonstrating pipeline-quality gas composition suitable for injection into the subcontractor's gas grid.
- Produce renewable gases that are suitable for production of pipeline-quality gas and test system operation for 500 hours.
- Produce renewable gas with heat content between 990 and 1150 British thermal units per standard cubic feet (BTU/scf) with low sulfur content.

Biomass Gasification

The overall objectives were to develop, test, and demonstrate the conversion of woody forest biomass into RG using entrained flow gasification methods while operating near atmospheric pressure. A process flow diagram for the biomass gasification system and a mass and energy balance are presented below for the pilot R&D system (Figure 2 and Figure 3).



Figure 2: Process Flow Diagram — Using Two Pulse Detonation Power Inputs

Figure 3: Mass and Energy Balance for the Biomass Gasification R&D System



The team operated the gasification system for 500 cumulative hours, optimizing the conversion system for syngas production. Using a syngas slipstream, 2.5 SCFM of near-pipelinequality RG was produced by performing a single-stage water gas shift reaction followed by a 3-stage methanation process.

Innovative Gasification Process

Innovative to the gasification process was the input of acoustic power that intensified the thermo-catalytic gasification reactions. The acoustic power was generated with pulse detonation burners firing towards the center of the gasification reactor from both the bottom and the top directions. Compared to existing gasification methods, this technology has the capacity to increase specific throughput, improve energy conversion, and reduce installed capital cost by leveraging thermo-catalytic intensification methods with process modularization to reduce overall syngas production costs.

Pursuant to project objectives, Taylor Energy developed an oxygen/fuel/steam fired pulse detonation power system that produced superheated exhaust and acoustic power as input to the gasification process. Acoustic power imparts compression waves that flow through the biomass gasification process. The compression waves drive the comminution and ablation of friable solids within the entrained flow reactor, causing rapid particle-size reduction.

Acoustic power sound waves form tiny bubbles that quickly implode — releasing micro shockwaves producing heat energy and active radicals that can cause neighboring material to collapse. The power output was increased from 10 Hz to 20 Hz. However, operating above 20 Hz, the kinetic pressure caused feeding problems into the gasifier. A digital delay generator (DDG) was used to control five channels in sequence to 1 microsecond. Commercially available fuel injectors provide up to 40 Hz and spark ignitions for detonations effective up to 1000 Hz.

The researchers developed the use of commercially available fuel injection technology based on high-speed gas direct injection, known as GDI technology. Fuels tested for detonation properties were pressurized up to 1000 psig for use in GDI systems. Methanol, ethanol, propylene, propane, and dimethyl ether all performed similarly; however, propane was the most convenient and cost-effective fuel for pilot scale R&D (Figure 4).



Figure 4: Testing Pulse Detonation Methods Used to Generate Acoustic Power

For testing at pilot scale, liquid fuels are preferred due to their ease of measurement, whereas commercial operations would preferably use product gases. The system is designed to use self-generated fuel-gas products as detonation fuels. The use of gaseous fuels is disclosed in the technical literature and offers a final embodiment that would control gas flow through a critical orifice; no moving parts would be used to control oxy/fuel mixing. The team used a DDG with resolution to 1 nanosecond to precisely operate the detonation subsystems, particularly the fine control of the fuel injection timing, water injection timing, and spark ignition timing.

Biomass Feeding

Wood shavings made from Ponderosa pine, sourced in California and supplied in 40-pound bales, simplified the feeding tasks and the means for measuring the feed rate in bales per hour (Figure 5).



Figure 5: Wood Shavings Supplied in 40-Pound Bales

The feed rate was recorded by collecting and counting the number of bales consumed each hour. The Komar extrusion feeder was used to control the biomass input rate; the Komar rate control adjustment provided numerical settings from 1 to 10 on the control panel. Based on the feed properties, the team was able to feed using three mid-range power settings between approximately #4 control setting and #7 control setting (Figure 6). The control panel settings below correspond to the approximate feed rates, based on test calibration rates:

- #5 control setting = 5.5 pounds per minute
- #6 control setting = 7.3 pounds per minute
- #7 control setting = 12 pounds per minute

Source: Taylor Energy

Figure 6: Calibrating the Biomass Feed Rate, Measured in Pounds per Minute



Source: Taylor Energy

The gasifier operation included the addition of a mineral catalyst in powdered form, a dolomitic quick lime, calcium oxide (CaO), that served as an effective gasification catalyst. The input rate was 1 pound of CaO per 40 pounds of biomass feed, or about a 2.5 weight percentage. Below 617°F (325°C), CaO also served to react with acid gases present, for example, binding sulfur as calcium sulfide.

To test the benefits of acoustic power (which uses kinetic pressure fluctuations to improve the biomass conversion process), it was necessary to implement a new biomass feeding system able to input biomass against 3 pounds per square inch gauge (psig) internal kinetic pressure. Previous test systems (with acoustic power of only 7 Hz) employed a biomass auger-extrusion-feeder made by Komar that formed a plug seal used to isolate the reactor from the atmosphere (Figure 7).



Figure 7: A Komar Biomass Auger-Extrusion Type of Feeder

Source: Taylor Energy

However, in this case, the kinetic energy, transmitted as a high/low pressure flux, caused the biomass plug-seal to dissociate. To address the plug seal issues, the research team needed to change the approach to feeding biomass into a pulse-pressurized gasification reactor. A more elaborate feeding system was designed/implemented, with the objective of isolating the gasification reactor from an existing Komar auger-extrusion feeder used to control the throughput rate. In principle, the approach was validated within the limits of a single-stage steam

powered jet-ejector, which was used to input wood shavings against a maximum 3-psig pressure (Figure 8).



Figure 8: Feeding System: Auger-Extruder, Blower/Sawdust-Pump, Gas Ejector

Source: Taylor Energy

Gas Shift Reactor

The team developed and tested four different WGS methods that employed four different catalyst types in different forms and operated at different conditions. All four methods used materials for high-temperature WGS (HT-WGS) catalysts in the 752°F to 1112°F (400°C to 600°C) range. In that high-temperature range, the catalysts are more tolerant to trace contaminants that can be present in biomass derived syngas.

When evaluating the gas shift methods using different forms of catalyst, the team looked for both existing and emerging catalytic materials and their corresponding operational methods that could potentially simplify the overall syngas conversion process. For example, tolerance to sour gases containing sulfur compounds up to about 40 ppm would minimize the syngas precleaning stages. The team also considered the strategic availability of the minerals and metals needed to produce various catalysts. Traditional gas shift catalysts are iron based (Fe_3O_4/Cr_2O_3) and use chromium III oxide (Cr_2O_3) for stabilization to prevent catalyst sintering (Figure 9). However, both environmental and strategic sourcing concerns arise with chromium compounds, which prompted the search for alternative high-temperature catalyst types. Of the classic ironbased HT-WGS types, a new iron/cobalt formulation was available that seemed to resolve both the strategic sourcing and the potential environmental issues.

Figure 9: Traditional Iron-Chromium Type High-Temperature Gas Shift Catalysts



Source: Johnson Matthey (Screen, 2007)

An alternative to classic gas shift catalysts is emerging based on the perovskite type oxide (ABO₃) structures, with A and B being a large and a small cation. The compositional flexibility of perovskite structures using different combinations of A and B cations, and the various doping options on A-sites and B-sites with active elements enable new materials (Figure 10). Perovskites are an ideal material class to serve two purposes: the perovskite backbone for CO oxidation and to exsolve nanoparticles that migrate to the surface for water splitting activity. Perovskites are an ideal material to optimize both reactions at the same time.

Figure 10: Perovskite-type Materials



Source: Johnson Matthey (Screen, 2007)

Because the intended process path employed syngas methanation, the approach was to convert about half the CO present in biomass derived syngas into H_2 , so that the H_2 to CO ratio was adjusted to optimize for catalytic formation of methane (CH₄) via syngas reactions using a nickel-based methanation catalyst.

The first method employed a proprietary calcium-oxide/aluminum-oxide formulation, circulated in a draft-tube reactor that failed when integrated at full pilot-scale, because the co-current syngas flow regime selected for testing caused problems on the syngas discharge side. The

three other methods were tested at slipstream-scale using different catalyst formulations impregnated into three different substate types: monolith, pellets, and ceramic blanket, as follows:

- Catalyst -01: Iron-chromium oxide catalyst, Fe₃O₄/Cr₂O₃ active at 572°F to 842°F (300°C to 450°C)
 - Monolith with 2-mm x 2-mm square channels
- Catalyst -02: Emerging iron-cobalt catalyst (cobalt is also active for methanation)
 - o 3-mm x 7-mm pellets
- Catalyst -03: Cobalt-doped perovskite, Nd_{0.6}Ca_{0.4}Fe_{0.9} Co_{0.1}O₃
 - High-temperature fiber blanket

All three slipstream-scale HT-WGS catalyst methods were shown to increase the hydrogen content of biomass derived syngas to achieve a ratio of about 3:1 for H_2 :CO needed for the subsequent methanation reactions.

A slipstream-scale gas shift reactor was designed and constructed with the flexibility to test the different catalyst types. The process configuration for the gas shift reactor included a heat recovery steam generator, shown in Figure 11.







Source: Taylor Energy

The design throughput for the gas shift reactor allowed for a syngas flow rate of 30 SCFM. A project task specified 2.5 SCFM as the minimum throughput for an RG slipstream from a syngas methanation process. To amply supply the needs of a downstream methanation system, a catalyst volume of 3 cubic foot was selected for the gas shift reactor. The shift reactor was operated near atmospheric pressure, considering that the water gas shift reaction was not impacted by pressure due to the stoichiometry (CO + water [H₂O] \rightarrow H₂ + CO₂). Advanced technical targets for water gas shift catalysts are identified below:

| • | Gas-hourly space velocity (GHSV) | 30,000 h ⁻¹ |
|---|----------------------------------|------------------------|
| • | CO conversion | 90% |
| • | Selectivity | 99% |
| • | Lifetime | > 5000 h |
| • | Cost | <\$1/kWe |

Catalytic shift reactions are exothermic by nature (dH = -42.09 kJ/mol). The catalyst operating temperature was maintained within a narrow range by controlling the flow rate of CO-rich syngas into the gas shift reactor. The gas shift reactor was lined with an insulating-type castable refractory (Kaolite-45), providing a cylindrical chamber 12 inches in diameter and 48 inches in height and able to retain process heat while operating up to 850°C (1562°F), contacting gases with the catalyst materials. Catalyst testing was performed while operating near atmospheric pressure at 12-inches water column, which is less than $\frac{1}{2}$ -psig internal pressure.

The Fe-Cr-based (Catalyst-01) and the Fe-Co-based (Catalyst-02) shift catalysts were chemically reduced prior to evaluation of the catalytic activity. This was done by treating them with producer gas at 482°F (250°C). The catalysts were reduced using producer gas without requiring the use of pure hydrogen as a reducing agent. The perovskite type (Catalyst-03) employs an oxidized material in the form of ABO3 that was pretreated by calcining at 1112°F (600°C), using a bottom-mounted preheat burner firing with air.

For testing, the gas shift catalyst bed was heated to approximately 788°F (420°C) as the starting point for both the Fe-Cr and the Fe-Co shift catalysts. The catalyst bed was maintained at approximate 752°F (400°C) to 842°F (450°C) during testing. The research team found that fiber-based catalysts (made from alumina microfibers produced at 1832°F (1000°C) were attractive as an emerging alternative to classic gas shift catalysts.

Develop/Validate a Cryogenic Deep-cleaning Process to Enable Methane Production

The project budget was depleted due to COVID-19 issues; therefore, validation testing was not completed. Instead, the project completed a conceptual study on two cryogenic deepcleaning cycles: an historic Joule-Thompson cryocooling cycle and an emerging state-of-the art thermoacoustic cryocooling cycle. Both cycles could achieve hydrogen liquefaction temperatures.

Syngas Methanation

After performing a catalytic water gas shift, the syngas slipstream was directed to a three-stage methanation system used to produce more than 2.5 SCFM of RG, containing mostly CH_4 with H_2

as the major diluent. The team designed a methane production system to upgrade the syngas to pipeline quality renewable gas. Researchers chose a 3-stage fixed-bed reactor for methane production, which included heat-tracing the reactors to start-up at 446°F (230°C). The reactors and the piping connections were water-cooled and refrigerant-cooled to remove the heat of sequential methanation reactions; 3- SCFM of near pipeline-quality RG was produced.

The methanation reactor was designed for top-to-bottom syngas flow. The methanation system was designed for operation at 200 psig and 482°F (250°C). Each of the three reactor stages was temperature-controlled to operate at 482°F (250°C) to provide uniform heating. A 3-inch-thick ceramic fiber blanked was wrapped around each methanation stage from top to bottom.

The product gases left the reactors at different temperatures, in descending order: 1076°F (580°C), 824°F (440°C), and 500°F (260°C). The first-stage reactor was the hottest, because the largest amount of H2 and CO2 was converted to methane via exothermic reactions. After each stage, a recycle gas stream was added to the syngas product stream, which was then cooled to 446°F (230°C) via heat exchange, with a small amount of CO2 refrigerant allowed to flow through 1/8" copper coils surrounding the flexible metal-bellows hoses connecting the three stages, cooling the syngas to 446°F (230°C) before entering a subsequent stage.

The research team developed and tested a set of nickel-based catalysts for syngas methanation. The formulations and the catalyst production recipes were based on depositing nickel on gamma alumina. Among other validation testing, the team tested the CO conversion activities of the catalysts — the process objective being the conversion of half the CO present into an excess of H_2 (Figure 12 and Figure 13).



Figure 12: Methanation System Design for Renewable Gas Production



Figure 13: Methanation Catalyst Test System

Source: Taylor Energy

The syngas feed was pretreated by passing it through a shallow fixed-bed composed of calcium oxide granules maintained at 482°F (250°C) to react with sulfur compounds. All catalysts tested in this study exhibited excellent methanation activity in the temperature range of 623 degrees kelvin (K) (662°F [350°C]) to 723°K (842°F [450°C]). For all the methanation catalysts prepared, catalytic stability was well maintained for 100-hours at 623°K (662°F [350°C]) when operating at the slipstream reaction conditions.

A slipstream of 3-SCFM renewable gas was maintained during continuous tests without difficulty, by drawing the syngas volume through the methanation system that was generated by the gas shift reactor processing up to 30 SCFM.

Factors for successful methanation catalysts activity and selectivity were selected as follows:

- To avoid an excessive reactor temperature increase, catalyst activity grading from lower to medium to high activity by increasing the content of nickel species was performed as the stage sequence increased.
- To avoid catalyst deactivation by sintering and coke deposition, CeO₂ was selected as the promoter to improve textural stability and oxygen transfer capability. First- and second-stage catalysts were prepared by impregnation.
- To avoid formation of inactive NiAl2O4 spinel species, the third-stage catalyst with large nickel content was prepared as a physical mixture of NiTiO3 of perovskite structure and commercial grade alumina powder, which was pelletized for use.

Key Project Milestones

- Selection and design of catalysts for methanation:
 - Developed and tested a set of nickel-based catalysts for 3-stage syngas methanation.
- Pulse detonation system:
 - Optimized an oxy/fuel/water pulse detonation burner (one US patent issued in 2022). Taylor Energy developed an oxygen/fuel/H₂O fired pulse detonation power system that produced superheated exhaust and acoustic power as input to the gasification process.
- Feeder:
 - Optimized the feeder for biomass for input of wood shavings against a maximum 3-psig pressure.
- HT-WGS:
 - Developed an HT-WGS reactor to test catalysts in the 752°F (400°C) to 1112°F (600°C) range that increased the hydrogen content of biomass derived syngas to achieve a 3:1 ratio for H₂:CO.
- Syngas slipstream methanation:
 - Designed a methane production system to upgrade the syngas to pipeline-quality renewable gas. Chose a 3-stage fixed-bed reactor system for methane production.
- LCA:
 - Performed an LCA of the process. An LCA is a methodology for assessing environmental impacts associated with all the stages of the process.
- Economic analysis:
 - Studied the techno-economic performance of biomass-to-RG systems.
- Gases, Regulated Emissions, and Energy Use in Transportation (CA-GREET) analysis:
 - Projected a low-carbon footprint of 10.1 kilograms (kg) of carbon dioxide equivalent per million British Thermal Unit (CO₂e/MMBtu) fuel, compared to a baseline of 82.1 kg CO₂e/MMBtu fuel for the North American fossil gas case under the California Low Carbon Fuel Standard.
- Evaluation of public benefits:
 - Evaluated the public benefits of the process.
- Technology transfer:
 - Communicated the findings to universities, the public and private sectors.

CHAPTER 3: Results

Specific Technology and Research Results

Biomass Gasification

The project results indicate that the technology innovation will likely increase throughput and improve energy conversion efficiency, while reducing the installed capital cost for biomass gasification systems. The reaction rate for biomass materials was limited by both heat and mass transfer into particle cores because structured carbon-oxygen polymer layers provided insulation and fiber strength.

Acoustic power input into the bottom of the reactor appeared to intensify the gasification process through rapid comminution and via intensified gas/solids mixing. For example, inspection of video data showed sound waves interacting with feed materials, seeming to improve reaction kinetics. Interactions between soundwaves and biomass solids were recorded as the rapid circular movement of glowing feed particles that were elutriated from the reactor. Looking down into the gasification reactor through a top viewport, the circular motion of glowing carbon particles (biomass particles being partially oxidized) was recorded on video, which showed the angular momentum imparted by acoustic pressure waves (Figure 14).

Figure 14: Intensified by Mixing With Acoustic Power (Image Recorded at 7 Hz)



Source: Taylor Energy

The gasifier operated at 5-ton/day scale feeding wood-shavings. For comparison, modular shop-fabricated commercial scale systems would process 200 ton/day to 300 ton/day of bio-mass wastes. The pilot scale test system produced 80 SCFM to 100 SCFM of syngas during biomass gasification research and development; the gas composition varied somewhat due to the moisture content in the feed, which increased from time to time due to occasional rain infiltration.

The gasifier was operated to produce a consistent slipstream used for testing different gas shift catalysts (Table 1), operating at 850°C (1562°F) to 950°C (1742°F), feeding biomass at a constant rate of 5 pounds per minute.

| Syngas Composition | Percent by Volume |
|---|---------------------------------------|
| СО | 9% – 12% |
| H ₂ | 8% - 10% |
| CH4 | 4% – 5% |
| C _x H _y | 7% – 8% |
| C ₂ H ₄ , C ₂ H ₂ , C ₃ H ₆ | 4% – 5% |
| CO ₂ | 18% – 22% |
| N ₂ | 37% – 42% |
| H ₂ O (inherent) | 10% – 12% (saturated at 122°F [50°C]) |
| H ₂ O (low-pressure, added) 1.2 steam-to-syngas volumetrie | |

Table 1: Syngas Slipstream Composition for WGS Catalysts

Source: Taylor Energy

Technical Barriers and Challenges

The processing and removal of heavy bio-tar fractions has been a persistent problem for biomass gasification systems. The gasifier typically operated at 1382°F (750°C) to 1922°F (1050°C). However, due to low temperature excursions into the pyrolysis range (842°F [450°C] to 1202°F [650°C]), biocrude liquids and heavy bio-tars were produced during transition periods. During temperature transitions through the pyrolysis range, high molecular weight condensed-crosslinked biopolymers were formed, known collectively as heavy bio-tars. Project results indicated that formation of a heavy bio-tar fraction during transition periods was not prohibitive but remained a concern. Most heavy bio-tars were formed during transitions, but they can be minimized by establishing careful heating procedures for start-ups and shut-downs. Pulse detonation power methods applied to biomass gasification can be used to solve the persistent problem of heavy bio-tar formation (and consequent tar deposition problems) by minimizing heavy tar formation during biomass devolatilization. This can occur by minimizing the aggregation of carbon char particles, which serve as catalysts for tar formation by causing large polyaromatic rings to form through successive polymerizations. In theory, minimizing carbon char formation helps minimize the formation of heavy bio-tar.

Innovative Gasification Process

The pulse detonation burner designed for the high-output condition was developed and operated successfully as an external power device for generating intense acoustic energy. Based on several trials, the high-output condition proved too powerful for the project needs. Project results indicated that using two low-output condition burners firing in a "constructive" mode at the same frequency would provide maximum kinetic pressure with the minimum inputs. The project resulted in the design, fabrication, and operational testing of multiple prototype pulse detonation burners. Figure 15 shows the principle of operation, with the cycle consisting of a fill, a detonate, and a purge. Figure 16 shows the successful prototype detonation burner operating at 20 Hz, which was used in the project. Extremely rapid mixing of the inputs (oxygen, water, and propane) was accomplished using a proprietary cyclonic mixing-head developed for the project and designed specially to form micro-vortices, which cause such high-shearing action that sonic power is generated: An intense shrill-whistle is sure evidence of a successful mixing head. On the other hand, the absence of an intense shrill-whistle indicates a lack of high-shear mixing (through the action of micro-vortices), limiting detonations to about 5 Hz.





Source: Taylor Energy

Figure 16: Cyclic Detonations at 20 Hz



Source: Taylor Energy

Proof-of-concept testing demonstrated cumulative benefits that enable cost reductions, including lower gasification hardware costs. For example, one detonation burner would replace multiple systems needed for fluidized bed gasification, eliminating the entire gas fluidization manifold and the external gas preheat system while providing the superheated steam input needed for thermochemical processing (steam-to-carbon ratio [S/C] >0.5).

Simplicity, durability, and low-cost hardware are inherent advantages of the oxy-fuel-water pulse detonation system employed to generate acoustic power used to intensify Taylor Energy's biomass gasification process. The hardware is low-cost to construct and operate.

Solids comminution and improved gas/solids mixing are two mechanisms identified that were observed to increase the mass and heat transfer rates.

By using an opposed-firing method, the amplitude of acoustic waves was increased (combined) when the frequency was synchronized, as shown below (Figure 17).



Figure 17: Amplitudes Combine (A) for Acoustic Waves at the Same Frequency

Source: (Waikato 2019)

One of the gasification test objectives was to use the acoustic power of detonation-derived sound waves as the means to intensify the deconstruction of organic molecules, rather than relying on the high-peak temperatures achieved through cyclic detonations. Dr. Sergey Frolov's team at the Semenov Federal Center for Chemical Physics, Moscow, has used the high-temperature aspect of pulse detonation power to enable conversion of organic wastes into high quality syngas by exploiting peak operating temperatures around 2777°F (1525°C), well in excess of the biomass ash-fusion temperature (Frolov, 2021) When the process objective is to minimize capital cost for modular community-scale deployments, excessively high temperatures (that melt the mineral ashes to form a low viscosity fluid) are considered less desirable. However, the effort to use acoustic power for low-pressure gasification — to be accomplished below the ash softening temperature — was complicated by the unique way in which pulse detonations generate kinetic pressure.

Preliminary operational testing and research of the technical literature indicated that, to fully realize the benefits of pulse detonation shocks (that are input to the gasification process as high-intensity sound waves), the optimum frequency is about 35 Hz. Production of shocks must be practiced in the range of 20 Hz to 40 Hz to achieve measurable linkage with carbon particles; that is, to blow the carbon particles apart requires selecting a best frequency.

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Technical Barriers and Challenges

Initial tests confirmed literature references that indicated the need for greater pulse power output to achieve project performance objectives that relate to intensification of the biomass gasification process. Submicron carbon particles derived from biomass pyrolysis are most directly impacted by high-intensity sound waves at about 35 Hz (Göktepe, 2015). To intensify the biomass gasification process, the research team increased the acoustic power output by increasing the pulse detonation frequency from 7 Hz to 30 Hz. This is because the acoustic power output is directly proportional to the detonation frequency. Figure 18 shows the linkage between acoustic power and the dispersion of carbon particles. Particle dispersion is evident (right) when the frequency is between 30 Hz and 40 Hz.

Figure 18: Acoustic Power Linkage With Carbon Particles Can Cause Dissociation





Source: Göktepe, 2015

Biomass Feeding

Moisture content of the feed was the variable that most directly impacted operations. The drier the biomass feed, the better the performance for thermo-catalytic conversion to syngas. Biomass variables that can also impact the process include the carbon-to-hydrogen ratio, carbon-to-oxygen ratio, and total alkali ash content. Testing was performed using wood shavings as feed, which exhibited some variability due to occasional rain infiltration into the bales on hand.

The addition of a rotary blower (sawdust pump) and a steam-eductor both served as pass throughput devices that did not impact the feed rate. Their import to the gasification system was to overcome the kinetic pressure component that consisted of rapid 3-psig pressure spikes. This was accomplished with some difficulties. Future embodiments will need improvements to use either: (1) a two-stage steam-eductor operated at relatively high motive pressure (>300 psig), or (2) an isolation device, such as a rotary star valve used in combination with a steam/gas eductor system. Figure 19 shows an example of this configuration.

Figure 19: Steam Eductor Input Biomass Into the Base of the Gasification Reactor



Source: Taylor Energy

Technical Barriers and Challenges

When operating with pulse detonation power input, the gasification reactor developed higher internal (kinetic) pressure, from ½ psig to 3 psig, which is not detrimental to the process and can be desirable. However, the research team was not prepared to feed into a pressurized system. Previously the biomass gasification system was operated with low internal pressure, near atmospheric pressure, with the capacity to increase process suction by turning up an induction blower.

A determination was made to engineer and test a steam jet eductor designed to overcome the kinetic pressure, up to about 3 psig, thereby providing a means of continuous biomass input using a consumable (steam) that must be input to the gasification process (S/C ratio = 0.05).

Two locations were considered, and both were tested. Biomass was input continuously into the main body of the gasification reactor using a 4-inch x 1.5-inch x 8-inch eductor (Figure 20).



Figure 20: Steam Eductor Input Biomass Into the Gasifier Main Body

Biomass was also input continuously into the bottom of the gasification reactor using a singlestage ejector, 8 feet in length, that was tested using 300 psig CO₂ for development purposes and then operated using saturated steam at 300 psig. This system was just able to feed against 3psig internal kinetic pressure spikes that were pulsing at 20 Hz (Figure 19).

Operating experience proved that (by increasing the pulse frequency) the pulse-detonationderived kinetic pressure was quick to generate more internal pressure than could be overcome by a single-stage jet ejector. A two-stage ejector would likely serve to overcome the 5 psig internal pressure, and the addition of a rotary isolation valve would likely increase capability to 10 psig. The layout for a future embodiment shows the location of a multi-component feeding system designed to feed into kinetic pressure provided by two low-output condition detonation burners, firing at the same frequency to achieve constructive wave interference (Figure 21).





Gas Shift Reactor

Heat generation from runaway reactions is possible within the gas shift reactor because some forms of catalysts are active for reforming, for water gas shifting, and for methanation. The gas shift reactor product stream contained 18–21 volume percentage (vol-%) H_2 as compared to 8–10 vol-% H_2 from the gasifier when operated using a means of pneumatic feeding that allowed air input.

The results are reported in Table 2. The gas composition included N2 in the balance and other minor gas fractions not shown. When the gas shift catalysts were tested, the feeding system was operated with air input through the sawdust pump. The pressure swing adsorption (PSA) type of O_2 supply also contributed N2. The gas shift catalyst tests show that about 50 vol-% CO was converted into H₂, which is the desired outcome intended for the downstream methanation process.

| Component | Catalyst-01 Range, %-vol | Catalyst-02 Range, %-vol | Catalyst-03 Range, %-vol |
|-----------------|-----------------------------|-----------------------------|-----------------------------|
| CO | 7 | 4.5 | 6 |
| H ₂ | 18 | 20 | 21 |
| CH ₄ | 8 | 7 | 9 |
| Light HCs | <1 | <1 | <1 |
| CO ₂ | 28 | 26 | 31 |

Table 2: Syngas Composition, Post-Gas-Shift Catalyst

Source: Taylor Energy

The nickel-based methanation catalysts intended for use as syngas methanation catalysts are typically very sensitive to light olefines, which can result in carbon deposition, blinding active sites. Therefore, the syngas pretreatment process was influenced to select HT-WGS catalysts with relatively low sensitivity to light olefins, particularly including the emerging (engineered) perovskite structural catalysts that operate as stable metal oxides at about 1112°F (600°C); this includes the iron-chromium type catalysts that are well proven industrially and available commercially. Emerging iron-cobalt formulations are said to offer some important advantages.

At the syngas condition tested, catalyst-03 operating at 1112°F (600°C) to 1148°F (620°C) exhibited no evidence of carbon deposition in the form of "whiskers," which are characteristic of the carbon deposits that result from light olefin content. Both catalyst-01 and catalyat-02 exhibited some soot discoloration after three test sequences, each lasting 8 hours, but no carbon "whiskers" were seen to form. The gas shift data indicated that light olefins are cracked and/or hydrogenated during the water gas equilibrium shift, resulting in the formation of additional methane content that is beneficial in preparing for the subsequent methanation process.

Technical Barriers and Challenges

In performing the subject biomass gasification research, another project focus was to evaluate syngas pretreatment methods that would enable process cost saving and generally improve

syngas pretreatment operations, if possible, by using fewer processing stages. An objective was to evaluate gas shift catalysts that are tolerant to trace contaminants typically found in biomass derived syngas, including tolerance to sulfur compounds and unsaturated hydrocarbons. The research team found that fiber-based catalysts (made from alumina microfibers produced at 1832°F [1000°C]), are attractive as an emerging alternative to classic gas shift catalysts.

The classical catalysts are iron-based, for example, Fe_3O_4/Cr_2O_3 , with Cr_2O_3 used for stabilization to prevent catalyst sintering. However, environmental concerns about chromium compounds have prompted the search for replacements for chromium in high-temperature catalysts. Catalyst poisons for the iron-chromium catalyst are inorganic salts, boron, oils, phosphorus compounds, liquid water, and sulfur compounds (Popovic, 2022)

Syngas Methanation

The results of this study meet the requirement for deploying nickel-based catalysts to be used in the development of a syngas methanation process for operation at pilot plant scale. The results reported in Table 3 show the syngas composition after air infiltration was minimized by using steam input to the feeding system. Note that the N2 content of 7 vol-% to 15 vol-% was still input by the PSA oxygen unit and resulted from air input through the feeding system.

| Syngas Composition | Percent by Volume |
|--------------------|-------------------|
| H ₂ | 39%–55% |
| СО | 37%–15% |
| $CH_4 - C_2H_6$ | 0%–15% |
| CO ₂ | 17%–0% |
| N ₂ | 7%–15% |

Table 3: Syngas Composition After Minimizing Air Infiltration

Source: Taylor Energy

The syngas feed composition for each catalytic reactor stage (stage-1, stage-2, and stage-3) changed because of the previous methanation stage. After pretreatment for acid gas removal, following each sequential methane production stage the syngas ratios of H_2/CO and H_2O/CO were adjusted. Average inputs and outputs for the three stages are shown in Table 4.

| | | Stage-1 Inlet | Stage-2 Inlet | Stage-2 Outlet | Stage-3 Inlet | Stage-3 Outlet |
|--------------|---------------------|------------------|------------------|-------------------|------------------|-------------------|
| Temp., | °C | 270 | 300 | 450 | 260 | 315 |
| Flow rate, I | Nm³/h | 18.2 | 96.0 | 89.6 | 8.2 | 7.9 |
| | CO2 | 13.0 | 19.3 | 21.5 | 21.5 | 21.3 |
| | со | 15.5 | 4.3 | 0.4 | 0.4 | 0.05 |
| Gas | H₂ | 60.1 | 21.3 | 7.7 | 7.7 | 0.7 |
| composition, | CH₄ | 10.3 | 53.3 | 68.4 | 68.4 | 75.9 |
| V01% | C ₂ + | 0.2 | 0.1 | 0.05 | 0.05 | 0.05 |
| | N ₂ , Ar | 0.9 | 1.7 | 2.0 | 2.0 | 2.0 |

Table 4: Gas Composition – Ratios Change After Each Methanation Stage

Source: Taylor Energy

Three nickel-based catalyst formulations were tested, each having been engineered with nickel content and surface area selected for the staged CO conversion activity required. Each of the three catalysts were tested for operational stability. The stage-1 catalyst stability was maintained for 100 hours at 662°F (350°C). Conversion of CO was maintained at approximately 86 percent. CH₄ in the product gas was approximately 30.4 percent on a dry basis. The gas input for a stage-2 catalyst contained 53.1 percent H₂, 5.8 percent CO and 8.4 percent CO₂ on a dry basis (Figure 22).





Source: Taylor Energy

The gas feed to the stage-2 methane production catalyst contained approximately 30 percent CH₄ and 50 percent H₂, among other product gases, as shown in Figure 23. The stage-2 catalyst stability was maintained for 100 hours at 662°F (350°C). Conversion of CO was more than 95 percent, while H₂ decreased to approximately 25 percent. CH₄ in the product gas increased to approximately 66 percent after the stage-2 methanation catalyst.





Source: Taylor Energy

The gas feed to the stage-3 methane production catalyst (resulting from stage-2 output) contained approximately 66 percent CH_4 and 25 percent H_2 , among other product gases, as shown in Figure 24. The steam-to-carbon molar ratio of the feed was approximately 1, reflecting the CO consumption and the water formation following the second methanation stage. The stage-3 catalyst stability was maintained for 100 hours at 662°F (350°C); the conversion of CO was about 95 percent. Methane (CH₄) in the product gas reached approximately 80 percent.

Figure 24: CO Conversion and Product Gas Composition (Dry Basis) From the Stage-3 Reactor at 662°F (350°C) for 100 Hours



Source: Taylor Energy

The CH₄ yield increased with each of the three methanation stages, achieving 80 percent CH₄. CO conversion and CH₄ yield increased with each of the three methanation stages. The heat content in the product gas stream reached 820 Btu/scf (measured as total combustibles content), which was a lower heating value compared to the project objective of between 990 Btu/scf and 1150 Btu/scf. However, by separating 80 vol% of the residual H₂ for recycle to the process and removing 95 vol% of unreacted CO₂, an RG energy content of 950 Btu/scf, approaching pipeline-quality for energy content, would be sustained without upgrading the RG heat content by adding a small gas fraction with higher energy density.

Technical Barriers and Challenges

Technology challenges are associated with the highly exothermic nature of the methanation reaction. Catalyst deactivation can occur very quickly because of hot spots, coking, and catalyst sintering. The primary reaction is the hydrogenation of carbon monoxide, which is an exothermic reaction (Figure 25). Existing commercial 3-state catalytic methanation processes are available for conversion of high-pressure syngas into high-quality renewable gas. The challenge is in producing high-pressure syngas using low-value separated biomass energy feeds.

Figure 25: CO Methanation Is an Exothermic Reaction

CO Methanation
CO +
$$3H_2 \rightarrow CH_4 + H_2O \qquad \Delta H^\circ = -206 \text{ kJ/mol}$$

Specific Market and Policy Barriers

Presently, the market barriers for biomass-to-syngas, followed by syngas-to-RG or syngas-to- H_2 , are the overall high cost for system installations and the modest economic performance after installation. Both the installed capital cost and the system operating cost need to be reduced by 50 percent. The project results served to increase awareness and support opportunities to reduce overall installed cost for biomass gasification systems by 50 percent based on preliminary engineering, with the opportunity to achieve greater overall reductions in system cost.

The project results indicate that technoeconomic performance for biomass-to-syngas can be optimized and improved compared to state-of-the-art system performance, compared, for example, with GTI's high-pressure fluidized bed steam/oxygen biomass-to-syngas process.

The research team evaluated multiple technology paths that would use these innovative gasification methods to improve thermal conversion process outcomes. The graphic below (Figure 26) identifies carbon negative feedstocks (1, 2, 3, 4) and processing paths that can use the low-pressure thermo-catalytic conversion methods tested (6, 7, 8) that lead to key energy applications and key energy products (9, 10, 11, 12, 13, 14). Note that the color-codes below indicate technical readiness; dark green is commercially ready, whereas red requires more R&D. For example, path $7 \rightarrow 10 \rightarrow 14$ is an optimum path that leads to high-pressure syngas enabling production of high-value products, such as pipeline-ready RG.



Figure 26: Feedstocks, Technology Paths, and Carbon Negative Energy Product

Technology Approach Proposed to Achieve Economic Deployment at Medium Scale

The research team believes that an important solution to the key problem of feeding biomass residues into a high-pressure gasifier is solved by exploiting low-pressure thermal conversion of biomass into a pumpable liquid-slurry to serve as an intermediate energy carrier of higher density; the liquid-slurry can be stored and used to continuously feed a high-pressure entrained flow gasification plant scaled for pipeline RNG applications (Figure 27).





Pyrolysis of biomass typically refers to its thermal decomposition by heating in a (mostly) inert atmosphere. Enhanced by pulse-detonation-derived acoustic power, biomass decomposes into solids (char), water, carbon oxides, hydrogen, and light hydrocarbons, as well as myriad liquid-range organic molecules (Figure 28).



Figure 28: Staged Conversion of Biomass→Bio-slurry→Syngas→RNG

Source: Taylor Energy

The biomass-to-RG system includes three processing islands, as shown in Figure 29.

Source: Villanueva, 2011



Figure 29: Staged Conversion of Biomass Into RG

Source: Taylor Energy

RD8

The near-term commercialization efforts would focus on using high-pressure entrained flow gasification methods enabled by producing a low-pressure pumpable liquid-slurry feed using pulse detonation methods to generate acoustic power for process intensification.

The entrained flow gasification process shown below is commercially available to use with any biocrude or bio-slurry that is pumpable to high pressure for injection (Figure 30).





Source: Eberhard, 2020

To achieve California's carbon management goals, scale at build-out must be large, although the development program was based on a modest projection of a 200-TPD plant capacity. The overall forest biomass supply chain must be designed for appropriate throughputs, at all levels. A site-specific project feasibility study would confirm or alter the 200-TPD proposed scale planned for ultimate deployment. At present, liquid-slurry production would be accomplished at a scale of 200 TPD to 300 TPD, considering the need for free-standing biomass conversion systems to operate as profitable independent business units.

The vision for biomass-to-RG business units is that waste biomass would be supplied by Cal Fire and other forest-thinning operations, collected from within a radius of approximately 50 miles. A liquid-slurry plant would produce pumpable liquids and biocarbon products. Thermal conversion business units would also produce carbon negative H₂, used as fuel for biomass collection and for product delivery in tractor trailers, which significantly improves the LCA.

A centralized biomass gasification plant, operating continuously at high pressure, processing the equivalent of 1500 TPD to 2000 TPD of biomass liquids, would achieve >90 percent online availability; this is possible using an entrained flow gasifier operating with a pumpable liquidslurry feed. For example, oxygen plants that supply the O_2 for partial oxidation operate with 98 percent online availability. Depending on the energy offtake agreement, within budget, one spare entrained flow gasifier train may be provided for backup. The gasification of bio-slurry to produce syngas for high-purity RG production is best accomplished at community scale, where the technology would be scaled down significantly from the much larger refiner applications.

Public Outreach

- University of Utah: Collaboration in developing the 2-stage pyrolysis/gasification.
- Kern Oil & Refining: Collaboration responding to a Sierra Nevada Biofuels solicitation.
- Maersk Shipping/Port of Los Angeles: Presentation(s) about green methanol.
- California Department of Conservation: Biomass-to-Hydrogen Sierra Nevada Proposal.
- CalFire: Biomass-to-Hydrogen Proposal for testing and development.
- Sims Resource Renewal: Potential collaboration in waste-to-energy in California.
- UDSA SBIR: Biomass-to-Hydrogen proposal.
- CEMEX USA: Presentation(s) about renewable energy for Victorville Cement Plant.
- Website development: Blog posts, videos, and PowerPoint Presentations.

CHAPTER 4: Conclusion

Importance to California's Clean Energy and Climate Goals

Taylor Energy developed and demonstrated a pilot-scale woody forest biomass gasification process intensified using a specially developed acoustic power system. The syngas compositions were ideal for catalytic methanation methods used to make RG. Project results support the conclusion that thermo-catalytic gasification methods can be scaled up and used to convert forest biomass residues into carbon negative energy products, including RG.

The results indicate that, when the technology is scaled up for community-scale projects, then direct ratepayer benefits could include cost savings from lower gas utility bills, future economic development in rural areas, and lower environmental impacts, both local and state-wide.

Environmental benefits include decreased impacts by using renewable feedstocks instead of fossil fuels. Benefits include reduced fire risk and reduced health risks due to minimizing forest fires, particularly including the removal of millions of tons of dead trees and forest-slash to accomplish sustainable forest management practices.

Societal benefits include increased energy security for local communities and ratepayers. Security benefits include reduced reliance on imported fossil gas by using local resources and local labor to produce sustainable energy infrastructure.

Key Implications of the Project Outcomes for Commercial Markets

Worldwide, there are no modular scale systems that convert low-cost biomass residues into high-value RG using thermo-catalytic methods (Whitty, 2022). Biomass gasification systems typically produce low-energy content synthetic gases that are unable to directly meet IOU pipeline specifications without further processing. Therefore, biomass derived fuel-gases are typically used by adjacent or over-the-fence end users, which lowers the value of biomass derived synthetic gases.

Taylor Energy asserts that the syngas quality can be upgraded to meet IOU pipeline specifications with minor modifications to the process, including the use of air enriched to 99 percent oxygen. The project results indicate that modular scale systems, which up-grade biomass derived syngas to pipeline quality, are feasible using the innovations tested; these were shown to enhance the conversion of biomass into syngas (H₂+CO) by applying acoustic power methods that intensified a low-pressure entrain flow gasification process. The scale of the system tested was 5 TPD, which should be scalable to a 50-TPD biomass gasification throughput.

The project results indicate that the simplified process hardware and a modular scale design with means for intensification should reduce syngas production costs. RG produced from waste biomass can be low-cost, because feedstock costs can be near zero for all early separated biomass conversion projects.

Benefits of Lessons Learned: Future Development Opportunities

Takeaways from the research include:

- Achieving IOU pipeline-quality RG specifications is expected to be feasible using the two-stage high-pressure biomass gasification process outlined in the project results.
- The project results continue to support the concept that modular shop-fabricated biomass-to-biofuel plants can operate as stand-alone profit centers at medium scale.
- The economic evaluations identified an optimum approach for utility-scale RG production using a pumpable bio-crude/carbon slurry as feed for a well-proven entrained flow gasification system, serving as a cost-effective pretreatment system that operates at low pressure.
- Project results support the concept that the core technology can scale to 2000 TPD by using the 2-stage pyrolysis/gasification approach. Initial commercial development would be accomplished at 50-TPD scale (about two tractor trailer loads per day) able to produce more than 5 TPD of RG, and then scaled to 200 TPD. The flash-pyrolysis technology would not need to be scaled above about 300 TPD, which capacity is eminently feasible for deployment of an oxidative type of pyrolysis process as the first stage used to feed a high pressure entrained flow gasifier.
- Project results indicate that the (kinetically) pressurized gasifier operation is both desirable and feasible: Pulse detonation technology is potentially applicable for much higher kinetic-pressure applications. For example, entrained flow gasification uses highvelocity oxygen/fuel burners as their key technology to enable rapid reaction rates. Detonation burners that generate much higher kinetic pressure could be used to further enhance the high pressure entrained flow gasification process in the future.
- State-of-the-art thermoacoustic cryocooling methods can be improved by integrating the use of pulse detonation power to replace linear-electric pulse power inputs.

Where the research could go next:

- Develop modular biomass-to-RG as stand-alone medium scale processing plants.
- Develop modular biomass flash-pyrolysis methods using pulse-detonation-derived acoustic power for carbon-slurry production, supplying "pumpable liquids" for use in high-pressure entrained flow gasification systems that produce RG at utility scale.
- The flash pyrolysis application of the innovation tested is particularly suited for detonation-derived acoustic power because optimum thermal cracking is performed at 500°C, where heat transfer via convection is relatively slow, whereas flash-pyrolysis methods are improved by increasing heat rates.
- Initial development of the pulse detonation gasification system would be accomplished at 50-TPD scale (two tractor trailers per day) and then scaled to 200 TPD.

- Develop low-cost RG sources with LCAs that are carbon negative, which provides value to both society and customers. To deliver these values to the market requires modular biomass-to-RG systems. Fundamental improvements to the biomass-to-syngas process are needed to enable cost reductions resulting from process simplifications.
- Increase in size slowly: the core technology is intended for scaling, potentially up to 2000 TPD in single trains. However, initial development must be accomplished at 50-TPD scale (about two tractor trailer loads per day) and then scaled to about 200 TPD.
- A flash-pyrolysis version using the pulse detonation technology may not need to scale above 300 TPD, which capacity is eminently feasible for deployment of an oxidative type of pyrolysis process.

GLOSSARY AND LIST OF ACRONYMS

| Term | Definition | | |
|--------------------------------|--|--|--|
| \$/MMBtu | US dollar per million British Thermal Unit | | |
| \$MM | million US dollars | | |
| \$MM/yr | million US dollars per year | | |
| ABO ₃ | perovskite type oxide | | |
| BCF/yr | billion cubic feet per year | | |
| BFB | bubbling fluidized bed | | |
| Btu | British Thermal Units | | |
| CalFire | California Department of Forestry and Fire Protection | | |
| CaO | calcium oxide | | |
| CE-CERT | Center for Environmental Research & Technology | | |
| Cents/MJ | cents per millijoule | | |
| CeO ₂ | cerium oxide | | |
| CFC-12 | chlorofluorocarbons | | |
| CH ₄ | methane | | |
| CI | carbon intensity | | |
| СО | carbon monoxide | | |
| CO ₂ | carbon dioxide | | |
| CO ₂ e | carbon dioxide equivalent | | |
| Cr ₂ O ₃ | chromium III oxide | | |
| DDG | digital delay generator | | |
| DOE | Department of Energy | | |
| Fe ₃ O ₄ | iron oxide | | |
| g/MJ | gram per millijoule | | |
| gCO _{2e} /MJ | gram of carbon dioxide equivalent per millijoule | | |
| GDI | gas direct injection | | |
| GHG | greenhouse gas | | |
| GHSV | gas-hourly space velocity | | |
| GREET | Gases, Regulated Emissions, and Energy Use in Transportation | | |
| GTI | Gas Technology Institute | | |
| GWP | Global Warming Potential | | |
| H ₂ | hydrogen | | |

| Term | Definition | | |
|----------------------|---|--|--|
| HFC-123a | hydrofluorocarbons | | |
| HI-WGS | high-temperature water gas shift | | |
| Hz | hertz | | |
| ICF | Inner City Fund | | |
| IOU | investor-owned utility | | |
| IPCC | Intergovernmental Panel on Climate Change | | |
| К | Kelvin | | |
| kg | kilogram | | |
| kj/mol | kilojoules per mole | | |
| kW | kilowatt | | |
| kWe | kilowatt equivalent | | |
| kWh | kilowatt-hour | | |
| lb | pound | | |
| Lb/MMBtu | pound per million British Thermal Unit | | |
| LCA | life cycle analysis | | |
| MMBtu | million British thermal units | | |
| MMm ³ /Yr | million meters cubed per year | | |
| MMSCFD | million standard cubic feet per day | | |
| NOx | nitrous oxide | | |
| OPEX | operating expenses | | |
| PDB | pulse detonation burners | | |
| PM | particulate matter | | |
| PM ₁₀ | particulate matter 10 microns | | |
| PM2.5 | particulate matter 2.5 microns | | |
| PSA | pressure swing adsorption | | |
| psig | pounds per square inch gauge | | |
| RG | renewable gas | | |
| S/C | steam-to-carbon ratio | | |
| scf | standard cubic foot | | |
| scfm | standard cubic feet per minute | | |
| SO ₂ | Sulfur dioxide | | |
| SO _x | sulfur oxides | | |

| Term | Definition | | | |
|---------|---|--|--|--|
| TAC | Technical Advisory Committee | | | |
| TPD | tons per day | | | |
| Tons/yr | tons per year | | | |
| UCR | University of California, Riverside | | | |
| USDA | United States Department of Agriculture | | | |
| VOC | volatile organic compounds | | | |
| vol-% | volume percentage | | | |
| WGS | water gas shift | | | |
| WTT | well to tank | | | |
| WTW | well to wheel | | | |

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Project Deliverables

- Progress Reports
- TAC Meeting Schedule (draft and final)
- TAC Meeting Agendas (draft and final)
- TAC Meeting Back-up Materials
- TAC Meeting Summaries
- Site Readiness Verification Document(s)
- M&V Plan (draft and final)
- Methanation Catalyst Design Report (draft and final)
- Micro-oxy/fuel Pulse-detonation Burner Fabrication Report (draft and final)
- Gasifier Performance Report (draft and final)
- CPR Report #1
- Cryogenic Syngas Purification System Report (draft and final)
- Methane Production System Report (draft and final)
- Pilot-Scale Testing Report (draft and final)
- CPR Report #2
- Process Evaluation Report (draft and final)
- Kick-off Meeting Benefits Questionnaire
- Mid-term Benefits Questionnaire
- Final Meeting Benefits Questionnaire
- Initial Fact Sheet (draft and final)
- Final Project Fact Sheet (draft and final)
- Final Report Outline (draft and final)
- Final Report (draft and final)
- Presentation Materials (draft and final)
- High Quality Digital Photographs
- Technology/Knowledge Transfer Plan (draft and final)
- Technology/Knowledge Transfer Report (draft and final)
- Production Readiness Plan (draft and final)

Project deliverables, including interim project reports, are available upon request by submitting an email to <u>ERDDpubs@energy.ca.gov</u>.





ENERGY RESEARCH AND DEVELOPMENT DIVISION

Appendix A: Process Evaluations

June 2024 | CEC-500-2024-072



APPENDIX A: Process Evaluations

Introduction

This task involves the techno-economic analysis and life cycle analysis of the renewable syngas methanation process.

Techno-economic Analysis:

The Gas Technology Institute (GTI) performed an economic feasibility study in 2019 that served as the base case. The GTI project was based on a high-pressure processing plant designed to gasify 945 tons per day (TPD) of wood wastes, producing 8.7 million standard cubic feet per day (MMSCFD) of renewable gas (RG) using oxygen/steam in a high-pressure bubbling fluidized bed (BFB) gasification system deployed at a brownfield power plant site located near Stockton, California (Table A-1).

| - | - |
|---|-----------------|
| Biomass Input Annually, tons/yr (17 | 310,000 |
| Plant Capacity (base case), MMm ³ /y | 82 (2.9) |
| All-in capital cost, \$MM | 340 (± 30%) |
| Annual OPEX, \$MM/yr | 39.3 |
| Cost of RNG Production, cents/MJ (| 1.2-1.4 (13-15) |
| GREET® Life cycle carbon intensit | 16.8* |
| | 0 (0) |
| | 0.002 (0.005) |
| Criteria Pollutant Emissions, | 0.0001 (0.0003) |
| g/MJ (lb/MMBTU) | 0.0009 (0.002) |

Table A-1: Summary Results for the Stockton Site-specific RG Study

*California GREET® 3.0 CI = 17 gCO₂e/MJ

Tons/yr = tons per year; MMm³/yr = million meters cubed per year; BCF/yr = billion cubic feet year; \$MM = Million US Dollar; \$MM = Million US Dollar per year; cents/MJ = cents per millijoule; \$/MMBTU = US Dollar per million British Thermal Unit; CI = carbon intensity; gCO_{2e}/MJ = grams of carbon dioxide equivalent per millijoule; g/MJ = gram per millijoule; lb/MMBTU = pound per million British Thermal Units; PM = particulate matter; VOC = volatile organic compounds; SO₂ = sulfur dioxide; NO_x = nitrous oxide

Source: GTI, 2019

This feasibility study is a good source of economic data based on a pressurized oxygen/steam gasification process; it achieved similar results as proposed by employing methods 7, 10, and 14 in Figure A-1, which will result in the near-term large-scale production of high-pressure RG using waste feeds.



Figure A-1: Feedstocks, Technology Paths, and Carbon Negative Energy Product

Source: Taylor Energy

The capital required for a high-pressure BFB biomass conversion facility designed to produce about 3 billion cubic feet (BCF) per year of RNG is projected to be \$340 million. We believe the GTI capital cost projections for a pressurized BFB at the Stockton site represent the upper limit for biomass-to-RG system costs. Using a low-pressure flash pyrolysis process integrated with a high-pressure entrained flow gasifier, the process is assumed to scale down 1:1, so that a 200-TPD embodiment is expected to cost significantly less than \$71.4 million.

The research team asserts that the capital and operating costs shown in Table A-1 represent the upper limits for the proposed Taylor Energy technology deployment, because combining methods 7, 10, and 14 (Figure A-1) is expected to be significantly less capital intensive. For example, methods 10 and 14 use well-proven systems that have been commercially available for decades.

These high-pressure conversion subsystems (10 and 14) can be engineered, procured, and constructed with standard wrap-around process performance guarantees that enable cost-effective financing packages in the \$150 million range. Methods 10 and 14 (Figure A-1) are proven to be cost-effective processes. Only operation #7, low-pressure flash pyrolysis for conversion of forest biomass into biocrude (liquids that can be pumped to high-pressure, such as carbon slurry) requires further development; this would entail some minor scale-up uncertainty and a limited financial risk. Excluding capital repayment costs, the production cost estimates for GTI's biomass-to-RG plant is in the range of \$13 per MMBtu to \$15 per MMBtu (Figure A-2).



Figure A-2: Total Levelized Operating Expenses (OPEX) Sensitives

Source: GTI, 2019

The operating cost profile estimated for GTI's Stockton project is presented in Figure A-3.





Source: GTI, 2019

An Aspen Plus process model has been developed, and it can be used to predict process behavior and estimate material and energy balances. Aspen Plus is a well-known simulation tool that can handle nonconventional feedstocks and process streams using built-in process units and physical/chemical property databases. A brief description of the process model used to perform the simulations is given in the process flow diagram in Figure A-4. (A detailed description of the conversion technology, including unique advantages, is discussed in the original proposal.) The feedstock is supplied to the gasifier through an extruder feeder and the gasification process is enhanced by using acoustic power generated by pulse detonation burners (PDBs).

The product stream from the gasifier passes through an integrated reformer stage that is intensified using acoustic power. The gas stream from the reformer goes through conventional gas cleanup/upgrading steps, including ash/char separation, filtration, and gas cooling.



Figure A-4: Process Flow Diagram of the Taylor Energy Gasification System

The basic parameters for the integrated gasification/reforming process include:

- Temperature Air input Power for compression of primary air Power for oxygen production (enrichment to 93%) Fuel-gas heating value Fuel-gas density Fuel-gas production Efficiency (gasification and reforming)
- 1472°F–1742°F (800°C–950°C) 6.25 scf/lb-wet-feed 15.8 kWh/ton-dry-feed 41.6 kWh/ton-dry-feed 227 Btu/scf 20.3 scf/lb 26.9 scf/lb-wet-feed 72.9%

Description of Aspen Plus Simulation

The solid feedstock is fed into the gasifier on a steady basis at predetermined feed/air ratios. The model simulates the gasifier using decomposition and gasification units. These units are based on built-in Aspen reactor blocks and calculate the equilibrium composition in the reactor under the given conditions by means of Gibbs free energy minimization. The model uses the Peng-Robinson equation of state for thermodynamic calculations. The user interface for the gasifier model in the Aspen Plus is shown Figure A-5.



Figure A-5: Gasifier Model in the Aspen Plus User Interface

The decomposition block converts nonconventional feedstocks such as biomass into its basic elements on the basis of yield information using the RYIELD block. The components are then sent to the gasification block, which calculates the equilibrium product gas composition using the Gibbs free energy minimization approach.

The carbon conversion information, feed flow rates and compositions, and reactor operating conditions are supplied by the user based on existing experimental data. The ash and unreacted char are removed from the reactor in a solids stream and the product gas is subjected to gas cleanup in order to remove contaminants.

The clean gas stream is cooled down in two quench steps and sent to gas storage. The syngas is then converted to renewable methane using a catalytic conversion technology. Experimental work on the methanation catalyst is included in the report.

The methanation simulations are based on equilibrium assumptions and, while the simulation results can be used to perform heat and mass balances, to design experiments, and to understand process behavior, it must be noted that experiments conducted in the laboratory or in pilot scale reactors may not be under equilibrium.

Based on the process model, the net thermal efficiency of the process was estimated to be 56.5 percent, with 50 percent of the feedstock energy being converted to renewable methane. The efficiency is influenced by several factors and is particularly sensitive to the process parameters, including operating temperature, feed composition, and pressure.

Life Cycle Assessment

Two of the most important criteria used for the technological evaluation of industrial systems are the total energy consumption and the net emissions of the desired pathway. Conventional methods of evaluation often focus on a limited number of steps in a production pathway and are inadequate in their ability to quantify the "cradle-to-grave" energy use and emissions. Life cycle assessment (LCA) models iteratively calculate the energy use and emissions associated with specific pathways using large databases consisting of information on various stages of the pathways and some user-specified input values. An LCA of the forest biomass gasification process for RG production was conducted, and the results are given below.

Greenhouse gases. The key greenhouse gases (GHGs) considered by the LCA, and their Global Warming Potential (GWP) compared to CO₂, are given in Table A-2. The GWPs are the 100-year warming potential values published by the Intergovernmental Panel on Climate Change (IPCC) and are often referred to as the IPCC 2007 GWPs. The GHG emissions for each pathway are calculated for each GHG and are reported on a carbon dioxide equivalent (CO₂e) basis using the GWPs.

| GHG Name | 100 Year GWP |
|-----------------------------------|--------------|
| Carbon dioxide (CO ₂) | 1 |
| Methane (CH ₄) | 25 |

Table A-2: Global Warming Potentials of the Key GHGs

| GHG Name | 100 Year GWP |
|----------------------------------|--------------|
| Nitrous oxide (N ₂ O) | 298 |
| Chlorofluorocarbons (CFC-12) | 10,900 |
| Hydrofluorocarbons (HFC-134a) | 1,430 |

Source: Taylor Energy

The categories of energy use are listed below.

- Total fossil energy per unit of energy produced for each stage of fuel production
- Total energy used per kilometer driven for the fuel used in vehicles
- Fossil energy used per kilometer driven for the fuel used in vehicles
- The proportions of types of energy used for each stage of the fuel production cycle

A number of software packages are available that include extensive databases and 'pathways' that can be used to evaluate most of existing technology/pathway options. The Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation (GREET) model is one such model that is widely used in academic studies, especially in the United States. This study is conducted using the CA-GREET 3.0. The CA-GREET model is a modified version of the GREET model consisting of California-specific assumptions.

The well to tank (WTT) results of the life cycle analysis are presented in Table A-3. The total and fossil energy use is listed, including specific petroleum, coal, and natural gas. The table also presents the GHG emissions in CO₂ equivalent values. The GHG emissions of the baseline case, fossil North American natural gas, is 82.1 kg CO₂e/MMBtu fuel, while the GHG emission for the gasification based renewable methane pathway is 10.1 kg CO₂e/MMBtu fuel.

| Thom | Energy Usage, Water Consumption or Emissions (Btu/MMBtu or gallon/MMBtu or g/MMBtu) | | | |
|------------------------------------|--|---|--|--|
| Item | Baseline Fossil Natural Gas | Gasification-based Renewable Methane | | |
| Total Energy | 1,179,953.36 | 1,876,071.01 | | |
| Fossil Fuels | 1,159,935.04 | 112,068.81 | | |
| Coal | 5,910.87 | 26,388.82 | | |
| Natural Gas | 1,149,635.99 | 42,534.27 | | |
| Petroleum | 4,388.19 | 43,145.72 | | |
| Water Consumption | 11.53 | 36.62 | | |
| CO ₂ (w/ C in VOC & CO) | 71,067.06 | 8,696.41 | | |
| CH ₄ | 338.12 | 20.79 | | |
| N ₂ O | 3.33 | 1.52 | | |
| GHGs | 82,085.42 | 10,012.80 | | |

| Table A-3: WTT Results of the Life Cycle Assessi |
|--|
|--|

| Itom | Energy Usage, Water Consu (Btu/MMBtu or gallon/MI | Imption or Emissions MBtu or g/MMBtu) | |
|--------------|--|--|--|
| Item | Baseline Fossil Natural Gas | Gasification-based Renewable Methane | |
| VOC: Total | 52.96 | 8.75 | |
| CO: Total | 658.63 | 151.75 | |
| NOx: Total | 75.95 | 51.45 | |
| PM10: Total | 6.49 | 6.25 | |
| PM2.5: Total | 2.92 | 2.14 | |
| SOx: Total | 12.49 | 22.05 | |

VOC = volatile organic compounds; CO = carbon monoxide; PM10 = particulate matter 10 microns; PM2.5 = particulate matter 2.5 microns; SO_x = sulfur oxides.

Source: Taylor Energy.

The basic assumptions used in model are listed below:

- Analysis year: 2024
- Feedstock: Biomass gasification pathway using forest residues
- CAMX grid (California-Mexico grid regional electricity mix for utility supply).
- CA Crude is selected for regional crude oil.
- Fossil gas feedstock is considered as North American natural gas (NG).
- Co-product credits: none
- Steam/electricity export credits: none

The well to wheel (WTW) results presented in Table A-4 below show the total energy use per mile driven, using the specified fuel and the GHG emissions. As anticipated, the WTW analysis shows that the biomass gasification pathway uses a higher amount of energy per mile of the vehicle driven. However, the GHG emission baseline is 341.8 gCO₂e/mile for vehicles using fossil gas, while it is 35.8 gCO₂e/mile driven for the biomass conversion.

Carbon Sequestration Feasibility Analysis

Some fraction of biocarbon is necessarily produced when using thermal conversion methods. A techno-economic study of carbon sequestration methods is needed to select the best alternative from available methods:

- Geologic carbon impounds, such as an engineered monofil
- Soil amendments, building carbon content in the forest floors, and soils in the valley
- Engineered carbon: carbon black, graphitic carbons, and nanocarbon particles
- Engineered cement products, cement castings, structural sequestration products

A future demonstration-scale project will focus on the use of biocarbon as a soil amendment, evaluating the techno-economics and certifications required to employ biocarbon for sequestration in soil building applications. Additionally, a future demonstration project will evaluate recovery of CO_2 from the gasification system as a solid or as a compressed and refrigerated

liquid; both are commercial forms of CO₂ used industrially that can be transported to wet-mix cement plants for addition to cement, forming permanent carbon sequestration structures.

Ultimately, thermal conversion methods will include production high-value carbon products, for example, graphene structures that, like diamond fragments, are strong and conductive of electrons; such products are a future adjunct to the present technical approach. Discussion of high-value structured carbon intended as high-value co-products that sequester carbon is not included in this report.

| | Energy Usage, Water Consumption or Emissions (Btu/mile or gallon/mile or g/mile) | | | | | | | |
|-------------------------------------|---|-------|----------------------|---|-----------|-------|----------------------|-------|
| Item | Baseline Fossil Gas | | | Gasification-based Renewable Methane | | | | |
| | Feedstock | Fuel | Vehicle Operation | Total | Feedstock | Fuel | Vehicle Operation | Total |
| Total Energy | 523.83 | 225.5 | 4,164.17 | 4,913 | 104.88 | 3,026 | 3,574.24 | 6,705 |
| Fossil Fuels | 518.61 | 147.3 | 4,164.17 | 4,830 | 103.41 | 297 | 0.00 | 400 |
| Coal | 1.54 | 23.08 | 0.00 | 24.61 | 1.77 | 92.55 | 0.00 | 94 |
| Natural Gas | 499.81 | 123.3 | 4,164.17 | 4,787 | 15.32 | 136 | 0.00 | 152 |
| Petroleum | 17.26 | 1.01 | 0.00 | 18.27 | 86.33 | 67.89 | 0.00 | 154 |
| Water Consumption | 0.02 | 0.03 | 0.00 | 0.05 | 0.00 | 0.13 | 0.00 | 0.13 |
| CO ₂ (w/ C in VOC CO) | 31.56 | 17.19 | 247.19 | 295 | 7.63 | 22.58 | 0.88 | 31.08 |
| CH ₄ | 1.29 | 0.04 | 0.08 | 1.41 | 0.02 | 0.06 | 0.00 | 0.07 |
| N ₂ O | 0.01 | 0.00 | 0.00 | 0.01 | 0.00 | 0.00 | 0.00 | 0.01 |
| GHGs | 65.34 | 18.21 | 258.27 | 341 | 8.38 | 24.19 | 3.22 | 35.79 |
| VOC: Total | 0.05 | 0.00 | 0.17 | 0.22 | 0.00 | 0.00 | 0.02 | 0.03 |
| CO: Total | 0.17 | 0.00 | 2.57 | 2.74 | 0.01 | 0.02 | 0.51 | 0.54 |
| NOx: Total | 0.20 | 0.01 | 0.11 | 0.32 | 0.03 | 0.04 | 0.11 | 0.18 |
| PM10: Total | 0.00 | 0.00 | 0.02 | 0.03 | 0.00 | 0.00 | 0.02 | 0.02 |
| PM2.5: Total | 0.00 | 0.00 | 0.01 | 0.01 | 0.00 | 0.00 | 0.01 | 0.01 |
| SOx: Total | 0.05 | 0.00 | 0.00 | 0.05 | 0.00 | 0.08 | 0.00 | 0.08 |

Table A-4: WTW Results of the Life Cycle Assessment

Source: Taylor Energy

Path-forward Improvements That Impact the LCA

The path forward model for commercial deployment is expected to offer the greatest degree of carbon negativity concurrent with the most favorable economic feasibility: Forest biomass

thinnings (destined for air-curtain combustion or slow organic devolatilization and then decomposition) are shredded to $1\frac{1}{2}$ -inch minus and then are warm-air dried in the forest to <17.5 percent moisture for bulk-transport to a 200-TPD pyrolysis facility located within a radius of 50 miles. Additionally, a means of producing gaseous hydrogen at each pyrolysis plant site using emerging fuel cell technology in the proton-pump configuration in included in the development plant, but it is not included in the life cycle analysis. Biomass pyrolysis plants (that necessarily produce gases, liquids, and carbons) will provide a small remote source of the fuel-grade compressed H₂ needed for negative carbon transport of biomass and biocrude to their points of economic use, which will serve to further decrease the LCA.

The life cycle analysis informs a vision for advancing the use of biomass, It is to be collected, dried, and transformed into biocrude and carbon offsets, transported for centralized transformation into high-purity RG for pipeline distribution through the existing utility pipeline system and converted into carbon-negative fuels for both heat and power. Processes for biomass-to-RNG via gasification presently range between negative-200-gCO₂eq/MJ to positive-200-gCO₂eq/MJ, depending on how biomass is sourced and how much grid power is used. For example, the carbon intensity projected for the GTI waste wood gasification facility for RNG production planned for deployment near Stockton, California, is projected to have CA-GREET of 17.0 gCO₂e/MJ, as shown in Table A-5.

| GREET® Life cycle carbon intensity, gCO ₂ e/MJ | 16.8* |
|---|-----------------|
| PM, g/MJ (lb/MMBtu) | 0 (0) |
| VOC, g/MJ (lb/MMBtu) | 0.002 (0.005) |
| SO ₂ , g/MJ (lb/MMBtu) | 0.0001 (0.0003) |
| NOx, g/MJ (lb/MMBtu) | 0.0009 (0.002) |

Table A-5: Life Cycle Carbon Intensity for a Base Case RG Plant

*California GREET® 3.0 CI for base case = $17 \text{ gCO}_2\text{e/MJ}$

Source: Taylor Energy

The deployment of a biomass-to-RG process provides substantial environmental benefits, reducing criteria pollutants by approximately 99 percent and producing a very low carbon fuel in the base case and below zero in the case including carbon sequestration technologies. The life cycle analysis for a demonstration-scale project will consider the emissions impact using a carbon sequestration or CO₂ capture cycle. The addition of CO₂ capture on the GTI-Stockton, California, life cycle analysis reduces the impact to -60.6 gCO₂e/MJ (Table A-6).

| Cases | Base ⁺ | Case 1 ⁺ |
|--|-------------------|---------------------|
| Feedstock transportation and treatment | 6.47 | 6.47 |
| Gasification | 8.43 | 8.43 |
| Residual transportation | 0.0850 | 0.0850 |
| Syngas cleanup | 5.99 | 5.99 |
| RNG production | 0.0418 | 0.0418 |
| Miscellaneous [¶] | 3.54 | 3.54 |
| Electricity displacement [¥] | -8.60 | -8.60 |
| RNG transportation | 0.856 | 0.856 |
| Carbon capture | 0 | -77.4 |
| Carbon Intensity (CI) | 16.8 | -60.6 |

Table A-6: Life Cycle Analysis for GTI RG Plant With and Without Carbon Capture

Source: Taylor Energy

Critical Elements for Successful Techno-Economic Deployment

• Project scale, site analysis, due diligence, and permitting.

A future project would engineer, construct, and operate a commercial demonstration system intended to enable the wise and rapid development of large-scale carbon negative RG plants using forest residues (or separated urban biomass) as the energy feed. An initial feasibility study would include site analysis, identifying a location for a demonstration project consisting of a 200-TPD biomass thermal conversion plant (method #7, Figure A-1) integrated with a 200-TPD entrained flow gasification plant (method #10, Figure A-1); products would include carbon negative RG (method #14, Figure A-1) intended for pipeline distribution at high pressure, and biocarbon products engineered for long-term use or designed for sequestration.

An economic assessment would require site readiness tasks as part of the due diligence work; these would:

- Identify access to an existing gas pipeline, with an NG pipeline agreeable to a gas utility.
- Perform all activities to complete and submit California Environmental Quality Act (CEQA) and National Environmental Policy Act (NEPA) documentation.
- Identify and perform studies relating to resources, biological, botanical, aquatic, soil, hydrologic, wildlife, and timber surveys.
- Site analysis and due diligence (land purchase and utilities recruitment).

The land and facility requirements must be specified, and the project utility requirements must be identified with their sources to further define economic projections. Site permitting issues

must be reviewed and summarized, and the preliminary engineering elements required for permits must be identified. A feasibility study must be completed with all elements in preparation for a demonstration project, including project financial partners, equipment layouts, and operating plans with projected materials and energy balance. A detailed LCA must be prepared disclosing the plan to produce carbon negative RG. These are preliminary engineering feasibility tasks.