Arnold Schwarzenegger
Governor

AIR INDEPENDENT INTERNAL OXIDATION STEAM GENERATOR

INDEPENDENT ASSESSMENT REPORT

Prepared For:

California Energy Commission
Public Interest Energy Research Program
Energy Innovations Small Grants Program

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Prepared By:
San Diego State University Research Foundation
Rob Queen
5250 Campanile Drive
San Diego, CA, 92182-1858
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Public Interest Energy Research (PIER) Program
California Energy Commission

Matt Coldwell
Program Manager
Energy Innovations Small Grant Program

Mike Gravely
Manager
Energy Systems Research Office

Thom Kelly, Ph.D.
Deputy Director
Energy Research and Development Division

Melissa Jones
Executive Director

Preface

The Public Interest Energy Research (PIER) Program supports public interest energy research and development that will help improve the quality of life in California by bringing environmentally safe, affordable, and reliable energy services and products to the marketplace. PIER funding efforts focus on the following research, development, and demonstration (RD&D) program areas:

- Building End-Use Energy Efficiency
- Industrial/Agricultural/Water End-Use Energy Efficiency
- Renewable Energy Technologies
- Environmentally Preferred Advanced Generation
- Energy-Related Environmental Research
- Energy Systems Integration
- Transportation
- Energy Innovations Small Grant Program

The PIER Program, managed by the California Energy Commission (Energy Commission), annually awards up to $62 million, five percent of which is allocated to the Energy Innovation Small Grant (EISG) Program. The EISG Program is administered by the San Diego State University Research Foundation through the California State University, under contract with the California Energy Commission.

The EISG Program conducts up to six solicitations a year and awards grants for promising proof-of-concept energy research.

The EISG Program Administrator prepares an Independent Assessment Report (IAR) on all completed grant projects. The IAR provides a concise summary and independent assessment of the grant project to provide the California Energy Commission and the general public with information that would assist in making subsequent funding decisions. The IAR is organized into the following sections:

- Introduction
- Project Objectives
- Project Outcomes (relative to objectives)
- Conclusions
- Recommendations
- Benefits to California
- Overall Technology Assessment
- Attachments
    - Attachment A: Final Report (under separate cover)
    - Attachment B: Grantee Rebuttal to Independent Assessment (grantee option)

For more information on the EISG Program or to download a copy of the IAR, please visit the EISG program page on the California Energy Commission's website at: http://www.energy.ca.gov/research/innovations or contact the EISG Program Administrator at (619) 594-1049, or e-mail at: eisgp@energy.state.ca.us.

For more information on the overall PIER Program, please visit the California Energy Commission's website at http://www.energy.ca.gov/research/index.html.

Abstract

This research determined the feasibility of an air independent internal oxidation (AIIO) process using metal oxides/peroxides to convert fuel to electricity and/or heat. The researchers evaluated existing research, created flow sheet models, and built a laboratory scale test reactor to generate data for a wide range of candidate metal oxides/peroxides and fuels. They then created preliminary designs at pilot and prototype scales.

Researchers carried out extensive testing and analysis on a laboratory scale test reactor in the High Temperature Gas Dynamics Laboratory at Stanford University. Results indicated such an AIIO system is feasible. Of the six candidates, copper oxide ranked highest due to its low fuel/oxide ratio, lack of undesirable species, non-toxicity, and easy handling/availability.

Analysis and experimental data indicated that zero gaseous pollutant and greenhouse gas emissions are feasible. Calculations suggest AIIO has the potential to capture over 90 percent of fuel energy to produce work and/or process heat, well above that of existing boilers.

Keywords: Air independent internal oxidation, AIIO, oxygen carrier, carbon capture, CO_2 capture, chemical looping, copper oxidation, biomass, coal

Introduction

Electricity generation and organic waste disposal create significant air quality issues since they release large quantities of greenhouse gases. Present biomass-driven generation provides a partial solution, but costs are high and sequestration of resultant greenhouse gases is typically incomplete.

A process that would yield heat energy for generation at lower costs with little or no greenhouse gas emissions would provide both economic and environmental benefits to California ratepayers, as well as the state as a whole.

The researchers proposed to demonstrate feasibility of an air independent internal oxidation power plant with zero pollutant and greenhouse gas emissions using a variety of fuels, including selected biomass materials, at better heat rates than existing boilers.

Objectives

The goal of this project was to determine the feasibility of an air independent internal oxidation (AIIO) system using metal oxides/peroxides[1] to convert fuel[2] to electricity and/or heat. The researchers established the following project objectives:

1. Identify and report: adiabatic reaction temperature; heat available to power (electricity + heat); flow rate of oxidant; flow rates and properties of oxidation products; oxygen carrier available for regeneration; CO_2 emitted or available for capture; air pollutant formation; and material handling, safety, and cost issues.
2. Determine and report: reaction completion; heat release/adiabatic temperature; side reaction products; material safety, stability, durability, and handling.
3. Develop and report a candidate fuel/oxygen carrier (OC) matrix and a rationale for choices.
4. Develop and report process requirements from flow sheet analysis: state points, temperatures, pressures, flow rates, enthalpies.
5. Design and build bench scale test facility.
6. Checkout and start-up test equipment.
7. Perform experimental screening and report results.
8. Confirm and report the feasibility of zero gaseous pollutants and GHG emissions.
9. Determine and report analytical functions and process models, and experimental parameter determination and validation.
10. Develop a design for next stage product testing.

1. Initial candidates were Fe_2O_3-Fe_3O_4, BaO_2-BaO, NiO-Ni, Mn_2O_3-Mn_3O_4, CuO-Cu, SrO_2-SrO, CaO-CAO_2, CaS-$CaSO_4$, CoO-Co_3O_4, Co+Ni
2. Candidate fuels were Priority 1: natural gas, rice straw, corn stover, coal, and Priority 2: ethanol, used cooking oil, biodiesel, and wood waste.

11. Develop and report a prototype design including: process one line flow chart, process interconnect and instrumentation diagram, bill of materials, capital and O&M cost projections, and projected performance.

Outcomes

1. The researchers determined open loop reactor equilibrium results for the candidate oxygen carriers and indicated that a single oxygen carrier system was adequate for all Priority 1 fuels. CO_2 emissions were less than 1 ppmv for all systems, and greater than 90% of CO_2 was available for capture. Researchers predicted CO, SO_2, and SO_3 to be essentially zero. They did not predict NO_x formation at the modeled bed operating temperatures.
2. The researchers analyzed a full two reactor closed loop system with a commercial software package for 24 possible pairings of candidate metal oxides and fuels. They selected this method over an open loop approach to obtain more accurate mass, species, and energy balances. This step generated the data necessary to meet Objectives 2–4 as planned.
3. Researchers used data from literature research, open loop equilibrium analysis (Objective 1), and closed loop equilibrium flow sheet analysis (Objective 2) to screen out four of the initial oxygen carrier candidates for cost, pollutant formation, or regeneration potential. They ranked the remaining six as follows: Fe_2O_3-Fe_3O_4, BaO_2-BaO, NiO-Ni, Mn_2O_3-Mn_3O_4, CuO-Cu, SrO_2-SrO.
4. Parameters from Objective 2 led to a final ranking of three oxygen carrier candidates as viable for further study: CuO-Cu, Fe_2O_3-Fe_3O_4, Mn_2O_3-Mn_3O_4.[3] All three had similar combined work and heat outputs across an 800–1000 degree centigrade range of fuel oxidation reactor temperatures. The final ranking of copper over iron reflects its much lower metal oxide to fuel mass ratio.
5. The researchers designed and built a laboratory scale reactor in the High Temperature Gasdynamics Laboratory at Stanford University.
6. They completed check-out and start-up of the test equipment.
7. Testing using CuO-Cu and Fe_2O_3-Fe_3O_4 yielded data for temperature, flow rate, and gas composition. The researchers performed additional experimental work using thermo-gravametric analysis, x-ray diffractonmetry, and scanning electron microscopy to verify and enhance test data. They did not test Mn_2O_3-Mn_3O_4 further due to material safety handling issues and discovery of a potential side reaction of carbide formation.[4]
8. Researchers demonstrated the copper and iron oxygen carriers to be capable of producing power and/or heat with zero gaseous pollutants and GHG emissions

3. Rejected candidates: BaO_2-BaO due to formation of high quantities of side reaction products at maximum operating temperatures, SrO_2-SrO due to very high pressures required for regeneration, and NiO-Ni due to carcinogenic properties.
4. The issue of potential carbide formation is an item for future study.

using corn stover, rice straw, coal, and methane. They found both carriers to be capable of reduction and regeneration without significant material loss.

9. The researchers conducted an analysis of reactors, turbines, compressors, pumps, and heat exchangers operating with a copper oxygen carrier and rice straw as fuel. For a 5 MWe plant, analysis suggested a net plant efficiency of 25% (13,648 Btu/kWh heat rate), including energy required for CO_2 liquefaction. Present biomass plants are likely only to match this efficiency if they do not include energy for CO_2 capture.
10. The researchers designed a detailed pilot scale test unit, including two reaction chambers, two cyclone separators to allow the bed material to be switched between reactors as gas products are exhausted, and capability to add make-up bed material.
11. The researchers completed a preliminary prototype design study, including a one line flow chart, interconnect and instrumentation diagrams, and bill of materials for major equipment. They did not complete the planned cost projections and performance projections.

Conclusions

The research proved the feasibility of an air independent internal oxidation system using metal oxides/peroxides to convert fuel to electricity and/or heat. Top candidates were the copper and iron oxides, which were shown to yield zero gaseous pollutants and GHG emissions at projected heat rates better than current biomass plants.

Preliminary modeling and screening successfully identified three of the initial oxygen carrier candidates as viable for further testing. The researchers expected at least 90% of the CO_2 created to be available for capture in the process.

The researchers confirmed their hypothesis by showing at least two of the candidate oxygen carriers were capable of producing power and/or heat with zero gaseous pollutants and GHG emissions with several fuels. These results were obtained with CuO-Cu and Fe_2O_3-Fe_3O_4 after screening out Mn_2O_3-Mn_3O_4 (due to material handling safety issues), and using corn stover, rice straw, coal, and methane. The analysis of a 5MWe plant using copper and rice straw suggested a heat rate superior to that of present biomass plants when such plants include energy for CO_2 sequestration.

The detailed pilot scale test unit design and preliminary prototype design study provided useful information for future research and economic analysis. Although the researchers did not estimate projected capital and O&M costs and plant performance, given the early stage of prototype development, this would have of necessity been a very general projection and is not a significant omission.

Recommendations

The Program Administrator recommends moving forward to a pilot-scale demonstration. As this is done, selection of the fuel(s) to be used should include weighting for their quantities in California and attendant waste-disposal difficulties.

After taking into consideration (a) research findings in the grant project, (b) overall development status, and (c) relevance of the technology to California and the PIER program, the Program Administrator has determined that the proposed technology should be considered for subsequent funding within the PIER program.

Receiving subsequent funding ultimately depends upon (a) availability of funds, (b) submission of a proposal in response to an invitation or solicitation, and (c) successful evaluation of the proposal.

Benefits to California

Public benefits derived from PIER research and development projects are assessed within the following context:

- Reduced environmental impacts of the California electricity supply or transmission or distribution system
- Increased public safety of the California electricity system
- Increased reliability of the California electricity system
- Increased affordability of electricity in California

The primary benefit to the ratepayer from this research is reduced environmental impacts of the California electricity supply. These benefits accrue from the expected higher efficiency of an AIIO plant over conventional boilers, and its ability to allow conversion of biomass fuels such as rice straw and wood waste to useful energy while sequestering virtually all of the CO_2 produced.

Technology Transition Assessment

As the basis for this assessment, the Program Administrator reviewed the researchers' overall development effort, which includes all activities related to a coordinated development effort, not just the work performed with EISG grant funds.

Marketing/Connection to the Market

Clean EnGen Group, LLC plans to sell and install its power generation systems at its customers' sites. There is no evidence they plan to engage any other marketing organization. The researchers indicated they intended to partner with established CHP installers.

Engineering/Technical

The researchers indicated they could move from this proof of feasibility project directly to a pilot scale test in a two to three year time frame. They saw no engineering barriers to this plan.

The researchers indicated the pilot scale plant was needed before a full demonstration product could be built.

Legal/Contractual

The researchers indicated a patent application has been filed. If the process operates as intended, no additional legal barriers appear likely to arise.

Environmental, Safety, Risk Assessments/ Quality Plans

The researchers' recommendation for proceeding to a pilot-scale demonstration project is the logical next step and can address issues of reliability and safety.

Production Readiness/Commercialization

The researchers intend to commercialize the technology in partnership with an established combined heat and power installer. A period of two to three years to complete pilot testing and ready the process for commercialization is highly aggressive and dependent on timely additional research and development funding.

Attachment A: Final Report (under separate cover)

Attachment B: Grantee Rebuttal to Independent Assessment (none submitted)

Attachment A – Grantee Report

Air Independent Internal Oxidation Steam Generator

Prepared By:

George Touchton
35134 Millwood Court
Newark, CA 94560
Phone: 510-579-7878
Email: cleanengengroup@gmail.com

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Contract No. 500-98-014

Prepared For:
San Diego State
University Research Foundation
5250 Campanile Drive
San Diego, CA, 92182-1858