Gasification Technology Developed for the Production of Renewable Hydrogen

D. Dodd and J. Hazard

Sierra Energy
221 First St, Davis, CA, USA, info@sierraenergycorp.com

ABSTRACT

Sierra Energy's FastOx technology is a fixed-bed gasification system that breaks down waste at the molecular level by injecting oxygen and steam at highly-concentrated and rapid rates. The main product is a clean and high-quality syngas, which is an intermediate fuel used to produce valuable energy products, such as renewable hydrogen. The FastOx gasifier can produce hydrogen at a cost of \$1–\$5/kg(H2) with systems ranging from 12.5 MTPD to 100 MTPD. For vehicular transportation, a 100 MTPD system can produce hydrogen at an industry-leading \$0.43/GGE. Coupled with the benefits of eliminating waste, reducing greenhouse gas emissions, and fueling economic growth, the production of renewable hydrogen with FastOx gasification is a paradigm shift from conventional operations. This paper will introduce the FastOx gasification process, review the performance of the pilot system in comparison with conventional technologies, examine the process and economics of hydrogen production using FastOx and explain the environmental impact with a developed hydrogen case study using California waste.

Keywords: gasification, hydrogen, renewable hydrogen, greenhouse gases

1 INTRODUCTION

Hydrogen fuels from renewable sources are considered some of the most promising alternative fuels for reducing oil consumption, greenhouse gas emissions, and air pollution. Municipal solid waste (MSW) and other waste resources represent a distributed and renewable source of hydrogen capable of addressing multiple environmental concerns associated with energy generation while remaining cost competitive with conventional sources of hydrogen.

Sierra Energy's FastOx gasifier represents a new hybrid of waste gasification developed to directly address the limitations of conventional and plasma-arc systems. The FastOx technology is a fixed bed gasification system that breaks down feedstock at the molecular level by injecting oxygen and steam at highly-concentrated and rapid rates. The injections result in high temperatures, around 2,200°C, without capital-intensive plasma-arcs or difficult-to-operate molten baths. The FastOx gasifier has a cold gas efficiency of 66–79% and a parasitic load of 16–20%, which maximizes the output and minimizes natural resource inputs. FastOx gasification drives off 90% of the organic components in waste, directly reforming it to clean and high-quality syngas, typically in the region of 60% CO and 30% H2. The syngas is an intermediate fuel used to produce valuable energy products, such as electricity, renewable diesel, ethanol, methane, hydrogen and more. The high temperature of FastOx gasifiers allow the remaining 10% inorganic materials and toxic compounds in waste to be melted and recovered as recycled metal and inert stone (slag) that can be sold for reuse.

Sierra Energy's pilot gasification system was located at U.S. Department of Defense's Renewable Energy Testing Center (RETC) at the former McClellan Air Force Base, Sacramento, California. The gasifier, named Mark 4 (Mk4), is a functional pilot that was designed to test the conversion of multiple waste streams and the composition of the resulting syngas, to troubleshoot operational logistics, and to collect data for further system automation.

The production of hydrogen from waste materials via the FastOx process is very compelling, given that the FastOx technology can be deployed in small-scale, distributed production plants that could be located to solve multiple local municipal problems. This paper will introduce the FastOx gasification process, review the performance of the pilot system in comparison with conventional technologies, examine the process and economics of hydrogen production using FastOx and explain the environmental impact with a developed hydrogen case study using California MSW.

2 FASTOX GASIFICATION TECHNOLOGY

The FastOx process begins by feeding a waste material, such as municipal solid waste, medical waste, biomass, industrial waste or hazardous waste, into the top of the gasifier. The waste descends in the FastOx gasifier (by gravity) through four reaction zones inside the chamber (Figure 1):

Drying occurs when the hot, rising gases from the tuyere zone heat the waste in the top zone of the unit. The first reaction removes moisture (free water) from the waste material.

Devolatization is where the majority of the organic matter is driven off into syngas. The waste undergoes pyrolysis (heating in the absence of oxygen between 150°C and 500°C), during which the volatile matter is removed from the waste. The volatile matter is typically where a large amount of the chemical energy in the waste is released, as a mixture of light gases, hydrocarbons and condensable tars. Afterwards, the only remnants are char (or fixed carbon) and ash.

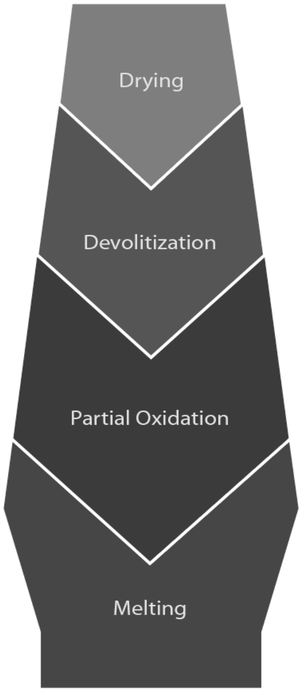

Figure 1. Reaction zones in a FastOx gasifier

Partial oxidation occurs when carbon-containing materials in the waste react with the injectants. In the lower regions of the FastOx gasifier, oxygen and steam are injected through the tuyeres to consume all of the remaining char material and convert it into syngas. This exothermic oxidation reaction raises the local temperatures to over 2,200°C and provides all of the energy for the self-sustaining FastOx process to occur.

Melting of inorganic compounds result from the high temperatures occurring in the partial oxidation zone. These compounds collect at the bottom of the unit and are continuously removed as inert stone (slag) and recycled metals.

Unlike conventional gasification which typically injects atmospheric air (composed of 80%vol. N2 that dilutes and impedes the reactions), the FastOx process injects solely oxygen and steam. In theory, this has several favorable effects on the gasification process:

- With the exclusion of nitrogen, the total gas volume inside the gasifier is significantly reduced, which increases the partial pressure of reacting species inside the vessel and shifts the reaction equilibrium to more products;
- Lower gas volumes also allow for smaller solid material sizing, which increases the total surface area and the number of reaction sites of the gasifiable material, causing an increase in reaction rates;
- Oxygen increases local temperatures, which are then moderated by the addition of steam, subsequently producing hydrogen which is a higher-diffusing molecule, increasing internal reaction rates;
- The presence of nitrogen interferes with the mass-transfer mechanisms of reactants and products. Therefore by excluding nitrogen, a significant increase in reaction rates is observed; and
- Sensible heat energy which is generally absorbed by inert nitrogen during conventional gasification, may instead be used for other endothermic reactions in the upper zones, allowing for more solid materials to be converted with FastOx, increasing the productivity.

3 SIERRA ENERGY'S VALIDATION TEST PLAN

A total of sixty-seven test runs were conducted on the Mk4 unit to establish an understanding of the FastOx gasifier's operability. For each test run, the syngas composition and the key operational measurements (i.e. temperature, pressures, and mass flows) were recorded during conventional compressed air gasification and then for oxygen-steam injection gasification. Additionally, slag samples collected from baseline test runs were sent to a third party laboratory to confirm non-leaching characteristics.

3.1 Feedstock Flexibility

During the Feedstock Variability Testing Campaign, a total of sixty-seven test runs were conducted to establish an understanding of the FastOx gasifier's operability with various feedstocks. Most of these runs generated baseline data from charcoal briquettes, lump charcoal, and biomass woodchips. In addition to these baseline feedstocks, the gasifier was also able to convert a variety of feedstock (e.g., plastics, glass, tires, ecopellets, walnut shells, metallurgical coke and oil shale) and synthetic municipal solid waste (sMSW) into a high-quality syngas. These feedstocks were tested because of their varying ash, moisture, and volatiles contents to help determine process requirements (Table 1).

Table 1. Proximate analysis for tested feedstock [%wt.]

Feedstock	Ash	Moisture	Volatiles
Briquettes	13.8	5.2	26.8
Lump Charcoal	9.1	6.1	30.1
Plastics	2.0	0.2	95.8
Glass	98.0	2.0	--
Tires	23.2	0.8	54.2
Woodchips	0.1-2.0	25.0-60.0	77.0-87.0
Ecopellets	1.5	7.1	71.2
Walnut shells	2.6	10.9	--
Met coke	5.0-9.0	--	--
Oil shale	59.8	0.05	41.0

Because it is difficult to obtain a consistent and pre-sized baseline MSW stream for direct run comparisons, Sierra Energy used a synthetic post Materials Recycling Facility's (MRF) MSW recipe developed by the University of California, Davis [1]. Sierra Energy adjusted the UC Davis recipe to replicate actual post-MRF MSW by including the inorganic fraction that the university removed from the recipe. The academic personnel were testing in a non-slagging gasifier and therefore wanted to limit the ash content of the waste material. Items that were difficult to obtain or unsafe to handle on the non-commercial pilot unit were replaced with chemically-compatible and easy to obtain alternatives. For example, 'Food scraps' were replaced with dog food pellets and grass or 'yard wastes' were replaced with alfalfa pellets. The final feed material composition used by Sierra Energy is shown in Table 2.

Table 2. Synthetic municipal solid waste recipe [%wt. Wet basis]

Ingredient Name	Fraction of sMSW
Paper	
Recycled paper	33%
Plastics	
PETE (polyethylene terephthalate)	7%
LDPE (low density polyethylene)	7%
PS (polystyrene)	4%
Glass	
Glass (recycling scrap from MRF)	2%
Organics	
Food waste (dog food)	13%
Grass (alfalfa pellets)	8%
Trimmings and lumber	15%
Metals	
Various metals (scraps from MRF)	4.5%
Aluminum pellets	0.5%
Other	
Construction and demolition concrete, soil and dirt (limestone)	6%

Results: The Mk4 processed feedstocks with high moisture content, such as fresh woodchips whose mass is approximately 50% moisture. Generally, feedstocks with high moisture content reduce the thermal efficiency of the gasifier and the syngas energy density (MJ/m3). The FastOx gasfier, however, is able to handle these moisture fluctuations due to the "updraft" configuration of the gasifier allowing volatiles and moisture to be driven off the material at the top of the gasifier before it descends into the zones where the main gasification and melting reactions take place. While there was a decrease in gasifier efficiency, the system was able to maintain steady-state operations with high moisture feedstocks, with no detrimental operational side effects.

Another feature of the FastOx gasifier is its ability to process feedstock with large ash contents (e.g., oxides and inorganics), which is known to affect slagging capabilities. The FastOx gasifier operates at a high enough temperature to melt and vitrify the ash. Consequently, the toxic ash is rendered chemically inert and exits the system as an inert slag.

3.2 Syngas Analysis

In order to compare and validate the syngas composition and heating value with conventional compressed air gasification, six test runs were employed for the Real Time Syngas Analysis Campaign. Each run lasted for 6 to 12 hours and the feedstock varied between lump charcoal and woodchips.

Syngas composition and quality were evaluated by installing a Wuhan Cubic Optoelectronic Model 3100P portable coal gas analyzer downstream of the FastOx gasifier. This analyzer uses multiple detectors to determine the composition of the major components found in syngas: A Non-Dispersive Infrared (NDIR) detector to measure CH4, CnHm, CO, and CO2, Electrochemical Detector (ECD) to measure O2, and a Thermal Conductivity Detector (TCD) to measure H2. However, since the TCD is not selective for hydrogen, the analyzer uses a software algorithm to correct the TCD reading for the other gases detected by the NDIR and ECD.

Results: Compared to the conventional compressed air gasification, FastOx gasification increased the quality and heating value of the syngas produced (Table 3). Testing indicated that there was a 215% increase in H2 and 108% increase in CO, respectively, which leads to a 118% increase in heating value. During compressed air mode operation, excess nitrogen acts as a diluent and lowers the heating value of the syngas. Because the FastOx process injects oxygen and not high-N2 air, a higher BTU value syngas is produced (12.23 MJ/Nm3), which allows for the syngas to be used in higher-efficiency thermodynamic power cycles.

Table 3. Averaged real time gas analysis results [%vol.]

Gasification Type	H_2	CO	CO_2	O_2	N_2
FastOx Gasification	27.70%	68.29%	2.90%	0.43%	0.04%
Compressed Air Gasification	8.79%	32.87%	2.63%	0.89%	55.37%
Percent Increase	215.01%	107.77%	--	--	--

3.3 Slag Analysis

To confirm the non leaching characteristics of the slag produced from the FastOx process, six test runs were conducted to produce sufficient slag samples. Each run was scheduled for 6 to 12 hours and the feedstock varied between lump charcoal and woodchips. Two slag samples were tested by third party laboratories and confirmed non-toxic by the EPA's Total Threshold Limit Concentration (TTLC) analysis and Toxicity Characteristic Leaching Procedure (TCLP). The TTLC analysis ensured that the materials were in compliance with Title 22 of the California Code of Regulations, while the TCLP analysis made sure the materials met federal guidelines.

Results: The TTLC results (Table 4) verify that the slag samples contain a variety of heavy metals; however, the concentrations of these components are significantly less than the regulatory levels. Furthermore, the TCLP results confirm that the leachability of these components are significantly less than the regulatory levels, and therefore, the slag samples are considered non-toxic to the environment and can be used for making cement clinkers, road base, bricks, and other construction material.

Table 4. TTLC results

Component	Concentration [mg/kg]	Regulatory Level [mg/kg]
Beryllium	2.0	75
Vanadium	590	2,400
Chromium	44	2,500
Cobalt	20	8,000
Nickel	420	2,000
Copper	55	2,500
Zinc	Not Detected	5,000
Arsenic	3.2	500
Selenium	Not Detected	100
Molybdenum	5.6	3,500
Silver	Not Detected	500
Cadmium	Not Detected	100
Antimony	Not Detected	500
Barium	1,500	10,000
Mercury	Not Detected	20
Thallium	Not Detected	700
Lead	Not Detected	1,000

3.4 Gasifier Performance Metrics

Various metrics were used to evaluate the gasifier's performance in both compressed air mode and FastOx mode by obtaining key process parameters (e.g., pressures, temperatures, mass flow rates and material throughput rates).

The 'specific productivity' of a blast furnace or gasifier is defined as the mass of material consumed per unit-time, per unit-internal volume. The 'oxidant productivity rate' is defined as the burden consumption per unit mass of oxidant.

Results: A selection of the testing data for the Mk4 operation in compressed air mode shows that the gasifier consumes the feedstock at a specific productivity of 176.8 kg/hr/m3. In comparison to the compressed air mode, the FastOx mode consumed the feedstock at a specific productivity of 381.6 kg/hr/m3, a 116% increase in specific productivity.

The FastOx process has an oxidant productivity rate of 0.52 kg (O_2)/kg, which is significantly lower than the conventional air-blown process of 1.50 kg(O_2)/kg. Fewer oxidant injectants are needed for the FastOx process because excess heat energy is used for additional endothermic reactions, rather than being absorbed by the large volume of nitrogen present in air injection.

3.5 Overall Findings

At this phase of testing and validation, the Mk4 has satisfied the following technical objectives:

- Verified the Mk4's operability with numerous feedstocks of varying ash and moisture content;
- Validated an increase in syngas quality through real time gas analysis, which demonstrated a 118% increase in the dry syngas energy density when compared to compressed air mode;
- Confirmed the non-leaching characteristics of the slag byproduct in accordance with the EPA's standard TCLP and TTLC test methods; and
- Analyzed the Mk4 gasifier's performance metrics, which indicated a 116% increase in specific productivity of operations and a 185% increase in oxidant productivity.

4 HYDROGEN PRODUCTION USING FASTOX GASIFICATION

The FastOx gasifier is able to produce low-cost hydrogen using the following systems in series:

- The FastOx gasifier
- Gas Cleaning, Water Gas Shift and H_2 Purification
- Hydrogen Fuel Cell

4.1 Gas Cleaning, Water Gas Shift and H_2 Purification

Additional gas conditioning and preparation is required for the production of hydrogen. This additional equipment is not required for the production of electricity using gas turbines, or reciprocating internal combustion engines. After additional cleanup, the syngas moves on to the gas conditioning and preparation unit, where it is compressed and mixed with high-pressure saturated steam and fed into the Water-Gas Shift (WGS) reactor where the following reaction takes place to maximize H_2 production:

$$CO + H_2O \rightarrow H_2 + CO_2 \qquad (1)$$

The WGS reaction is mildly exothermic, and excess heat is removed from the shifted syngas to makes high-pressure steam.

A hydrogen membrane module is used to remove the hydrogen from the post-WGS gas stream, before sending that hydrogen stream to a pressure swing adsorption (PSA) module to purify the hydrogen product stream to the very high purity requirements.

4.2 Hydrogen Fuel Cell

The purified hydrogen produced by the system is fed into a hydrogen fuel cell. A proton exchange membrane (PEM) fuel cell is an established, low temperature hydrogen-fueled technology with proven operational abilities converting conventional hydrogen sources into electricity. PEMs have a variety of end use applications (stationary, transportation), high electrical efficiency ranging from 40-60%, and no emissions other than heat and water.

4.3 CO_2 Recovery

After the syngas goes through the water gas shift and hydrogen membrane, a system upgrade can be added to include enhanced CO_2 recovery. Gas treatment to the off-gas at this point in the process (gases other than the hydrogen) can be installed to generate a purified stream of CO_2. At this stage, one of the several methods of converting CO_2 to transportation fuels becomes viable. The addition of this capability to a FastOx system will maximize the energy output and leave no wasted emissions.

5 HYDROGEN ECONOMIC ANALYSIS USING FASTOX GASIFICATION

The US Department of Energy (DOE) developed the Hydrogen Analysis Project (H2A) to model the unit cost of producing hydrogen from various industrial processes [2]. Sierra Energy used the H2A model and worked with experts from the DOE’s National Renewable Energy Laboratory (NREL) to calculate key metrics for the FastOx process. It was calculated that the FastOx gasifier can produce hydrogen at a cost of \$1–\$5/kg(H2) with systems ranging from 12.5 MTPD to 100 MTPD.

For vehicular transportation, proton exchange membrane (PEM) fuel cells that utilize hydrogen are significantly more efficient compared to internal combustion (IC) engines. A fuel cell can power a vehicle approximately 2.5 times as far as a gallon of gasoline in an IC engine. Therefore, 1 kg(H2) has the potential to replace 2.5 gallons of gasoline, which allows the hydrogen production cost of \$5.00/kg(H2) to be equivalent to \$2.00/gal(gasoline) or \$2.00/Gallon of Gasoline Equivalent (GGE).

A small-scale FastOx gasification system (12.5 MTPD) can produce hydrogen at \$1.94/GGE, while a 100 MTPD system can produce hydrogen at an industry-leading \$0.43/GGE. For comparison, see the Table 5 below:

Table 5. Hydrogen production cost comparison

Production Method	Production Cost	
FastOx Gasification (systems ranging from 12.5 to 100 MTPD)	\$1-\$5/kg(H_2)	\$0.40-\$2/GGE
Natural Gas (produced via steam reforming at fueling station)	\$4-\$5/kg(H_2)	\$1.60-\$2/GGE
Natural Gas (produced via steam reforming off-site)	\$6-\$8/kg(H_2)	\$2.40-\$3/GGE
Wind (via electrolysis)	\$8-\$10/kg(H_2)	\$3.20-\$4/GGE
Solar (via electrolysis)	\$10-\$12/kg(H_2)	\$4-\$4.80/GGE

6 CALIFORNIA CASE STUDY AND IMPACT

Sierra Energy has developed a ChemCAD model of the FastOx gasification process and has validated it against actual empirical data from Sierra Energy's pilot demonstration unit.

Using the waste composition of average California post-recycled MSW residual composition and the validated ChemCAD model, Sierra Energy created a case study examining the potential impacts associated with the production of hydrogen via FastOx gasification [3].

Table 6. Summary of california post-recycled msw residual composition

Item	[%wt. Dry basis]
Organics	30.3
Plastics	19.9
Electronics	1.3
Metals	6.6
Glass	2.7
Paper	37.8
Mixed Residue	0.7
Special Waste	0.7
TOTAL	100

In general, one metric ton of as-received California post-recycled MSW feedstock generates 0.73 metric tons of syngas with approximately 8.8 MJ of chemical energy. This syngas can be further converted into 58.0 kg of H_2. Table 7 shows the renewable energy potential and the climate warming impact using FastOx gasification [4].

Table 7. Climate Warming Impact of Califonia's Trash and Renewable Hydrogen Potential Using FastOx Gasification

Emission Data of California	
Waste Disposed of in California Landfills	30.4 MMT/yr
Climate Warming Impact	116.55 MMTCO2e/yr
Renewable Energy Potential with FastOx	
Hydrogen	1,562,749,200 kg(H_2)/yr
Gallons of Gasoline Equivalent	3,307,322,780 GGE/yr
Emissions Avoided	29.39 MMTCO_2e/yr

REFERENCES

[1] Cattolica, R. and Jenkins, B., "Research and Demonstartion Project for Bioenergy and Biofuels Production from Post-MRF Residuals," California Integrated Waste Management Board, 2009.

[2] DOE H2A Production Analysis, http://www.hydrogen.energy.gov/h2a_production.html.

[3] Beck, R., "Targeted Statewide Waste Characterization Study: Characterization and Quantification of Residuals from Materials Recovery Facilitie," California Integrated Waste Management Board, 2006

[4] Sierra Energy, "Waste to Hydrogen in California Using Sierra Energy's FastOx Gasification System," 2014. https://gallery.mailchimp.com/73ba9fcff85ec9b3768d2848c/files/California_Hydrogen_Report_rev2.pdf