Test results for fuel cell operation on anaerobic digester gas

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Abstract

EPA, in conjunction with ONSI, embarked on a project to define, design, test, and assess a fuel cell energy recovery system for application at anaerobic digester waste water (sewage) treatment plants. Anaerobic digester gas (ADG) is produced at these plants during the process of treating sewage anaerobically to reduce solids. ADG is primarily comprised of methane (57–66%), carbon dioxide (33–39%), nitrogen (1–10%), and a small amount of oxygen ($< 0.5\%$). Additionally, ADG contains trace amounts of fuel cell catalyst contaminants consisting of sulfur-bearing compounds (principally hydrogen sulfide) and halogen compounds (chlorides). The project has addressed two major issues: development of a cleanup system to remove fuel cell contaminants from the gas and testing/assessing of a modified ONSI PC25 C fuel cell power plant operating on the cleaned, but dilute, ADG. Results to date demonstrate that the ADG fuel cell power plant can, depending on the energy content of the gas, produce electrical output levels close to full power (200 kW) with measured air emissions comparable to those obtained by a natural gas fuel cell. The cleanup system results show that the hydrogen sulfide levels are reduced to below 10 ppbv and halides to approximately 30 ppbv. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

Many wastewater treatment (WWT) plants use anaerobic digesters [1] to treat sewage in order to reduce solids. Digesters are large enclosed concrete containers that are heated to enhance the rate of digestion of the influent (sewage/sludge), which processes their proceeds via a natural, biological reaction whereby microbes consume the organic matter in the absence of oxygen. Typically, about 40% of the solids is converted to gas containing methane in the range of 57–66%. If collected and utilized, this gas represents a valuable form of renewable energy. Most of this gas is presently either vented to the atmosphere or combusted in flares. In either case, the release of these gases [methane and carbon dioxide (CO_2)] can possibly affect global climate by trapping radiation from the sun and enhancing atmospheric heating.

There has been emphasis at some WWT plants to use the anaerobic digester gas (ADG) for heat recovery (boilers), especially to heat the digesters to enhance the

digestion process. Additionally, there has been minimal electricity production using engine generators and natural gas production by treating the ADG to remove CO_2 and other contaminants. Because of siting problems relating to noise and air emissions, e.g., of nitrogen oxides (NO_x) and carbon monoxide (CO) associated with internal combustion engines, the utilization of ADG to produce electricity in an environmentally acceptable manner will require the development of new technologies. In this regard, fuel cells are an emerging technology that may ultimately improve the outlook for clean, efficient, and economical energy use of ADG. Recently, the EPA embarked on a project to establish the conceptual design of a fuel cell energy recovery system for application at anaerobic digester WWT plants [2,3], and to validate the conceptual design with site-specific hardware. For the assessment, a 200-kW phosphoric acid power plant, manufactured by ONSI, a subsidiary of International Fuel Cells, was sited at a WWT plant in Yonkers, NY. Funding for the fuel cell was provided by the NY Power Authority, in conjunction with the Electric Power Research Institute and the U.S. Department of Energy. The ONSI fuel cell is the only commercial fuel cell currently available on the market; there are approximately 170 natural-gas-fueled units in operation

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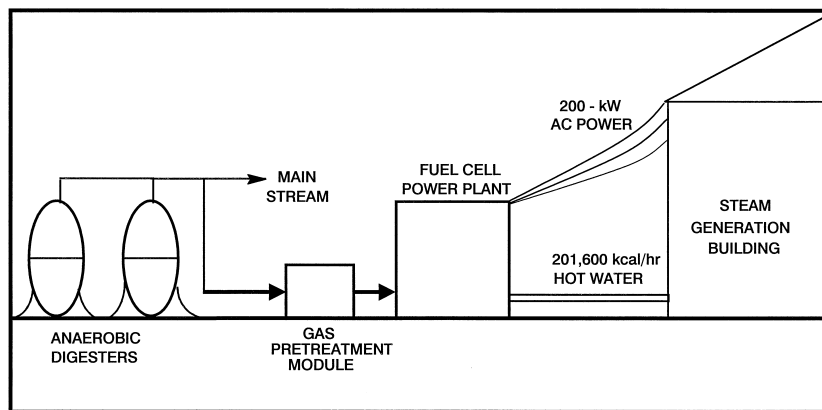* Corresponding author. Fax: +1-919-541-7885; e-mail: spiegel.ronald@epa.gov

Fig. 1. Fuel cell/digester energy recovery concept.

throughout the world, mostly in the U.S. and Japan. This application represents the first operation of a fuel cell on ADG from a WWT plant in North America. Additionally, there has been some activity in Japan to utilize ADG, especially at beer breweries [4].

Fig. 1 is a simplified diagram of the conceptual design consisting of digesters, a gas pretreatment module, and a fuel cell power plant. The processed ADG is fed to the fuel cell, and the resulting power produced is used at the Yonkers plant. None of the power produced is fed to the electrical grid because the load at the WWT plant is greater than the amount of energy produced by the fuel cell.

This paper describes test results on the system that removes sulfur compounds and halides from the ADG. Some fuel cell operational data will also be given.

2. ADG pretreatment system

2.1. ADG characteristics

Data [2] show that the major constituents in ADG are methane (57–66%), CO_2 (33–39%), nitrogen (N_2), (1–

10%), and a small amount of oxygen (O_2) (< 0.5%). The minor constituents include sulfur-bearing compounds, principally hydrogen sulfide (H_2S), and trace amounts of halogen compounds (chlorides) and nonmethane organic compounds (NMOCs). The sulfur levels can range from around 6 to 200 ppmv. Halogen compounds range from 0 to 4 ppmv. In addition, ADG is typically saturated with water vapor at a temperature of about 35°C; bacteria may be present in the gas as well. The heating value of ADG ranges from about 5.34 to 6.23 kcal/l (dry basis). This volumetric heat content is significantly lower than that of natural gas (8.72–9.34 kcal/l) due to the large amount of diluents, chiefly CO_2.

2.2. Pretreatment requirements and system design

Table 1 lists the ADG contaminants, the maximum allowable fuel cell contaminant limits, and the issues or concerns for satisfactory fuel cell operation. The implication of the levels of the contaminants in the ADG is the need to focus the pretreatment system design on removal of H_2S. The halide levels are sufficiently low so as to allow them to be removed in the fuel cell power plant fuel processor with a halogen guard bed on a site-specific basis.

Table 1
ADG fuel contaminant limits for fuel cell applications

ADG contaminant	Fuel cell power plant requirements[a]	Issue/concern
Sulfur (H_2S)	< 4 ppmv[b]	Poison to fuel processor reforming catalyst
Halogens (F, Cl, Br)	< 4 ppmv[c]	Corrosion of fuel processor components
NMOCs	< 0.5% olefins	Poison to fuel processor shift catalysts
O_2	< 4%[d]	Overtemperature of fuel processor beds due to excessive oxidation
	< 0.5%[e]	
NH_3	< 1 ppmv	Fuel cell stack performance
H_2O	Remove moisture and condensate	Damage to fuel control valves. Transport of bacterial phosphates
Bacteria/solids	Remove all bacteria/solids	Fouling of fuel processor piping/beds

[a] Operating on ADG (nominal composition: 60% CH_4; 40% CO_2).
[b] With zinc oxide sulfur guard bed.
[c] With optional halogen guard bed in fuel processor.
[d] With peak shave option.
[e] Without peak shave option.

Table 2
Pretreatment requirements — commercial ADG fuel cell application

ADG contaminant	Contaminant concentration range	Pretreatment requirements
Sulfur (H_2S)	< 200 ppmv	Reduce sulfur content to < 4 ppmv
Halogens (F, Cl, Br)	< 4 ppmv	No pretreatment requirement, providing optional halogen guard bed is used
NMOCs (olefins)	ppb → low ppm range	None
O_2	< 0.5%	None
	> 0.5%	Requires peak shave option
NH_3	None	None
N_2	< 4.0%	None
H_2O	Saturated at 35–43°C	Remove condensate/droplets from gas stream. Prevent further condensation in downstream piping
Bacteria/solids	May be present in ADG gas	Provide for removing solids and moisture carryover, prevent condensation, and keep ADG flowing

Other possible contaminants in the ADG that need to be eliminated are solids, liquid water and condensate, and bacteria.

Table 2 defines the pretreatment requirements, with the patented system design [5] depicted in Fig. 2. The system's main feature is a nonregenerable sulfur absorption bed for H_2S removal. This desulfurizer bed operates at ambient temperature and pressure, and converts H_2S to elemental sulfur and water via the Claus reaction ($H_2S + 1/2O_2 \rightarrow H_2O + S$). Elemental sulfur produced in the reaction is absorbed by the carbon bed. An air injection system is required to control O_2 levels within the desulfurizer to about 0.3–0.5% volume. A blower conveys the ADG through the pretreatment module and delivers it to the fuel cell at the required pressure. In addition, a coalescing filter upstream of the blower precludes the possibility of solids, liquid carryover, and bacteria entering the pretreatment module and fuel cell.

The absorbent material for H_2S removal is a potassium-hydroxide-impregnated activated carbon absorbent which is commercially available. This material had been previously tested in a landfill gas cleanup system [6,7]. The data revealed high absorption capacities and high efficiencies for removing sulfur compounds while operating at ambient temperature and pressure, with essentially 100% H_2S removal. Short residence times corresponding to gas velocities of 15–18 m/min (space velocities of 5300/h) through the bed were demonstrated. Since the mechanism for H_2S removal is oxidation of H_2S to elemental sulfur, some level of O_2 is required in the ADG feed gas. Tests indicated that a minimal O_2 concentration of 0.1% may be sufficient to initiate H_2S via the described absorption process.

Laboratory-based breakthrough testing was performed at 0.3% O_2 using a simulated digester gas stream consisting of CO_2 and methane containing 200 ppmv H_2S. A 10
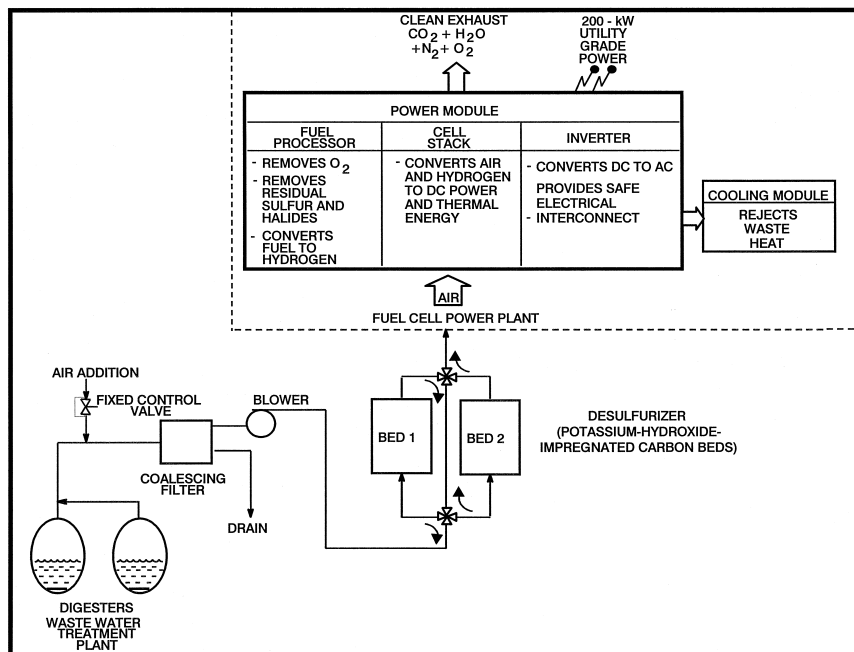

Fig. 2. Process schematic of commercial ADG pretreatment system.

ppmv breakthrough was achieved after 1322.6 h of testing. At a gas flow rate of 1450 cm^3/min, the breakthrough capacity of the impregnated carbon was determined to be equivalent to 0.62 g sulfur/g carbon. Following the breakthrough test, the elemental sulfur deposited on the carbon was chemically extracted and removed. A sulfur loading at 0.51 g sulfur/g carbon, or 33.8% weight defined as grams of sulfur divided by the weight of carbon plus the weight of sulfur times 100%, was ascertained. These numbers are in good agreement with, and therefore confirm, the H_2S breakthrough tests. As these tests utilized pure compounds, it is to be expected that the presence of other adsorbable compounds in ADG may have a tendency to reduce the capacity of the material for sulfur removal in actual field applications.

Operating costs associated with the activated carbon bed are low. Based on the measured H_2S loadings, 100 ppmv H_2S in the gas stream, and material costs of about US$5/kg for the adsorbent, the operating and maintenance cost estimates are less than US$0.15/kW h. The pretreatment system capital cost estimate is US$500/kW.

The size of the pretreatment module desulfurizer bed is dictated by three key variables: the sulfur content in the ADG, the maximum permitted loading of the absorbent bed, and the desired time interval between bed changeouts. Because sulfur levels in the ADG are fairly high, a single-bed approach is not practical: it would require a large bed and frequent changeouts. As shown in Fig. 2, the approach taken is to use two beds piped in series with directional control valves. The valving and piping permit operation of the two beds in series with reversing capability. This design also provides the capability to operate on a single bed while the other bed is being changed out. This arrangement permits the use of relatively small beds, and allows for longer time intervals between bed changeout operations. For a 200-kW fuel cell application, two cylinders, 0.6 m in diameter by 1.5 m high, were utilized. This size estimate is based on a typical sulfur feed content of 100 ppmv, absorbent bed loading of 35% by weight, and a changeout interval of 1 year. For ADG with 200 ppmv H_2S content, the same-sized beds would necessitate a reduced bed changeout interval of 6 months.

3. Fuel cell power plant

The PC25 C power plant is designed to operate on natural gas fuel with a net electrical power output of 200 kW. Operation on waste methane fuel, such as ADG, requires that the power plant accommodate a reduced heating value fuel containing up to 35–43% diluents (CO_2) by volume. This translates to significantly higher mass and volume fuel flow rates, with corresponding changes to the power plant process operating conditions. This can generally be achieved without major technology changes to the power plant. Required modifications to operate on ADG

are primarily related to resizing fuel inlet valves and plumbing to reduce pressure drop and increase fuel flow capacity. The power plant controller settings require adjustment tailored for ADG operation in order to maintain the proper level of process fuel, reformer steam, and burner air.

A result of using the dilute ADG is an increase in the heat rate of the power plant by approximately 5% relative to the natural-gas-fueled power plant. Because the effective fuel cost is relatively low, this decrease in power plant efficiency will not have significant impact on the overall plant economics.

To remove halides from the ADG, a halide scrubber has been incorporated into the reactant supply system of the fuel cell, between the hydrodesulfurizer (hot zinc oxide bed) and reformer. It consists of a vessel with a metal oxide supported on alumina.

4. Field test assessment

4.1. Scope of measurements

The contaminant removal process, comprising of a pretreatment system and halide guard, has been monitored by periodic gas sampling and analyses over a period approaching a year. Additionally, fuel cell exhaust air pollutant emissions were monitored during a 3-day period. The sampling locations are indicated on the schematics presented in Fig. 3. At locations 1, 2, and 3, the sampling ports consist of gate valves with Swagelok connectors. At these ports, glass-lined steel containers, fitted out with stainless steel valves to regulate flow, have been utilized to gather samples over approximately 34 h. The gas samples were sent to Air Toxics, Folsom, CA, for laboratory analysis. The system contaminant removal measurements and emission measurements for the pertinent sampling locations are described below.

(1) The inlet gas (raw ADG) was analyzed for sulfur compounds, halide compounds, and gas composition (methane, N_2, O_2, and CO_2). Canister samples were analyzed for halide and other volatile organic compounds (VOCs) by gas chromatography/mass spectrometry (GC/MS) according to EPA Method TO-14 and gas composition according to a modified ASTM Method D-3416. A gas chromatography/flame photometric detector (GC/FPD) was used to analyze sulfur compounds via a modified EPA Method 16.

(2) The pretreatment module outlet gas (pretreated ADG) was analyzed for the same gas constituents described for the raw ADG.

(3) The halide guard in the fuel cell was analyzed for VOCs and halide compounds via GC/MS according to EPA Method TO-14.

(4) Fuel cell power plant emissions were monitored for SO_2, NO_x, CO, CO_2, and NMOCs for 10 h/day over a
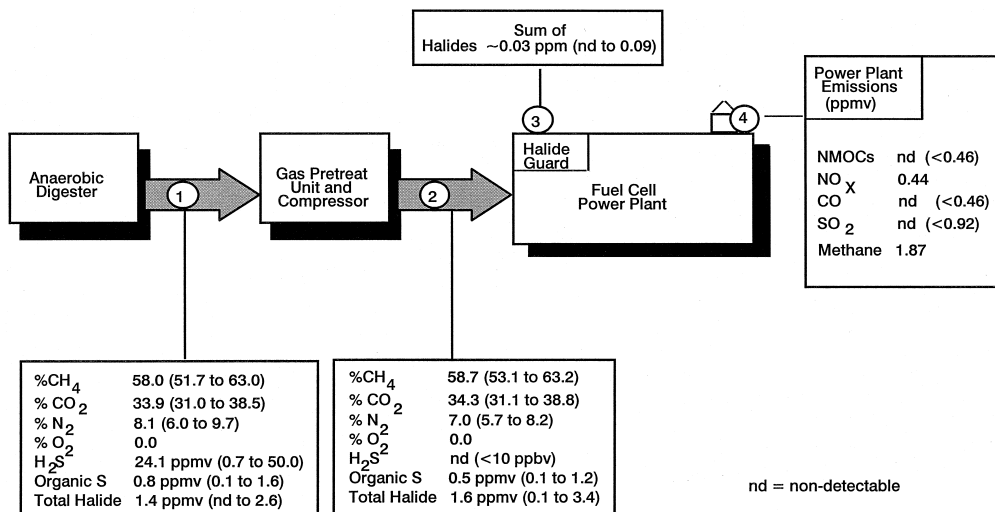
Fig. 3. Summary of anaerobic digester gas composition and contaminants, plus fuel cell emissions.

3-day period according to EPA Methods 6C, 7E, 10, 3A, and 25A, respectively. Exhaust flow rates were monitored concurrently with the continuous emissions measurements according to EPA Methods 1, 2, and 4.

4.2. Emissions

The fuel cell power plant emissions (location 4 in Fig. 3), when operating on ADG, are listed in Fig. 3. The average emissions (ppmv) are as follows: $NO_x = 0.44$; $CO = < 0.46$; $SO_2 = < 0.92$; NMOCs $= < 0.46$; and methane $= 1.87$. All readings are reported as parts per million, dry gas, corrected to 15% O_2. The values were measured via continuous emission monitors which were calibrated before and after each test for zero and span drift. The results of the emissions testing conducted over the three 10-h periods should be representative of longer term continuous testing, since the fuel cell power plant controller continuously adjusts the fuel and air to maintain constant temperature inside the reformer burner where the CO and NO_x are generated. In addition, the results for the ADG-fueled power plant are in good agreement with other emissions data on the PC25 C fueled with natural gas. The slightly lower NO_x emissions are likely to be a result of lower reformer burner flame temperatures associated with the lower heating value of the ADG fuel.

4.3. Pretreatment system

The results of the field testing of the pretreatment system and halide guard are listed at locations 2 and 3, respectively, on Fig. 3. The raw input ADG's composition is shown at location 1. All these values are based on the average of three samples which were collected and analyzed according to the procedures described above. One sample at each location was gathered each month over a 3-month period.

Total sulfur was reduced from 24.9 ppmv at the inlet of the pretreatment system to 0.5 ppmv at the outlet, or a removal efficiency of 98%. The pretreatment system is extremely effective in removing H_2S, with output levels nondetectable to the detection limit of 10 ppbv. The remaining organic sulfur (0.5 ppmv) is eliminated in the hydrodesulfurizer in the fuel cell power plant.

The total halides were reduced from 1.6 ppmv at inlet to the halide guard (location 3) to 0.03 ppmv at the outlet. This represents a removal efficiency slightly greater than 98%.

5. Conclusions

The equipment required to clean the ADG was successfully designed, constructed, and tested. It was documented that total sulfur and halide contaminants were removed with efficiencies greater than 98%. The removal levels would be likely to protect the power plant's fuel processor for its catalyst life of 5 years (40,000 h).

The fuel cell power plant has operated successfully and reliably on ADG for several thousand hours. It has consistently achieved an output of 150 kW, and has reached as high as 200 kW. The fuel cell is operated at the lower level primarily because the methane content in the ADG can vary by as much as $\pm 10\%$, while the controller in the fuel cell is designed for natural gas with a variation of $\pm 3\%$. Thus, if the fuel cell is operating at essentially full output at of 200 kW, and the fuel (methane) content of the ADG drops, the controller will not be able to adjust the necessary parameters to the new operating conditions and the power plant will shut off. A conservative operating point (150 kW) helps eliminate this possibility. Present work is being directed to modifying the control software to handle the larger methane variations associated with the lower heating value ADG.

Pollutants emissions in the exhaust of the power plant are minimal, and are below all Federal and State emission levels in the U.S. Consequently, this ultra clean technology can be sited virtually anywhere in the U.S.

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