CALIFORNIA ENERGY COMMISSION

California Energy Commission

Clean Transportation Program

FINAL PROJECT REPORT

In-situ Bio-methanation in Food Waste Digesters using CO2 and Catalytically-derived Hydrogen from Biogas

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TIS would also like to express our sincerest gratitude and appreciation to all our staff, vendors and partners for making this project a success.

PREFACE

Assembly Bill 118 (Núñez, Chapter 750, Statutes of 2007) created the Clean Transportation Program. The statute authorizes the California Energy Commission (CEC) to develop and deploy alternative and renewable fuels and advanced transportation technologies to help attain the state's climate change policies. Assembly Bill 8 (Perea, Chapter 401, Statutes of 2013) reauthorizes the Clean Transportation Program through January 1, 2024, and specifies that the CEC allocate up to $20 million per year (or up to 20 percent of each fiscal year's funds) in funding for hydrogen station development until at least 100 stations are operational.

The Clean Transportation Program has an annual budget of about $100 million and provides financial support for projects that:

- Reduce California's use and dependence on petroleum transportation fuels and increase the use of alternative and renewable fuels and advanced vehicle technologies.
- Produce sustainable alternative and renewable low-carbon fuels in California.
- Expand alternative fueling infrastructure and fueling stations.
- Improve the efficiency, performance and market viability of alternative light-, medium-, and heavy-duty vehicle technologies.
- Expand the alternative fueling infrastructure available to existing fleets, public transit, and transportation corridors.
- Establish workforce-training programs and conduct public outreach on the benefits of alternative transportation fuels and vehicle technologies.

To be eligible for funding under the Clean Transportation Program, a project must be consistent with the CEC's annual Clean Transportation Program Investment Plan Update. The CEC issued GFO-18-602 to provide funding opportunities under the Clean Transportation Program for demonstration-scale biofuels production facilities to fund low carbon biofuel production projects that scale-up, scale-out, and prove a technology or process at the first demonstration-scale biofuels production facilities at a site-specific location. In response to GFO-18-602, the recipient submitted an application which was proposed for funding in the CEC's notice of proposed awards January 18, 2019 and the agreement was executed as ARV-18-024 on May 15, 2019.

ABSTRACT

Technology & Investment Solutions LLC (TIS), in partnership with the University of Southern California (USC), was awarded by the California Energy Commission (CEC) with Project Grant No. ARV 18-024 to demonstrate a novel "*in-situ*" biological upgrading of biogas from the anaerobic digestion (AD) of liquid food waste and/or liquified food substrates. TIS developed the novel *in-situ* (internal) upgrading technique in order to address the challenges and the high expense associated with traditional upgrading processes for low-quality biogas into high-value fuel. Upgrading biogas to biomethane has many benefits which includes (but not limited to) the following:

- Allows for use as an alternative fuel to pipeline natural gas;
- Creates a renewable source of energy;
- Potential source of additional income to AD plant owners or operators; and
- Prevents methane emission to the atmosphere.

The demonstration of this system has shown that upgrading biogas directly within the AD reactor through biological processes is possible without the need for highly specialized and expensive external upgrading equipment such as membrane filters or PSA. The project also demonstrated that low-quality biogas can be upgraded through a relatively simple and economical manner which is especially important for small-scale AD plant owners and operators or those that produce less than 100,000 standard cubic feet (scf) of biogas daily. Further, TIS believes that with additional optimization of the system, commercial-scale implementation throughout the State of California and beyond can be realized.

Keywords: Bio-methanation, hydrogen, methane catalytic reforming, hydrogenotrophic methanation, archaea, food waste, anaerobic digestion, PSA.

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EXECUTIVE SUMMARY

The TIS project team, in partnership with USC, has successfully completed the CEC Project Grant No. ARV-18-024 and produced biomethane gas from the anaerobic digestion of food waste with improved methane content and energy value. The new *in-situ* (internal) biomethanation technique developed by TIS using catalytically-derived hydrogen gas from USC's proprietary CSR unit has been successfully demonstrated at the former Meadowbrook Dairy facility located in the unincorporated and disadvantaged community within the Phelan Piñon Hills Community Services District (PPHCSD) service area in San Bernardino County, California.

Traditional biogas upgrading or biomethanation methods are usually done externally (*ex-situ*) wherein the carbon dioxide (CO_2) component of the raw biogas is removed or separated using expensive and highly specialized equipment such as membrane filtration or PSA units. *Ex-situ* methods can be both technically and economically challenging, especially for small-scale AD plant owners and operators that lack resources. Through this grant, the TIS project team has successfully demonstrated the production of biomethane using the *in-situ* process wherein catalytically-derived hydrogen gas (H_2) was used to increase the methane (CH_4) content in the biogas through the enhanced hydrogenotrophic process within the AD reactor.

TIS' primary goal for this project was to demonstrate a relatively simple biomethanation process by directly producing high-quality renewable natural gas (RNG) without the need for separate biogas upgrading equipment like membrane or PSA. The demonstration project was able to produce hydrogen gas from a slip stream of raw biogas from the AD reactor using USC's proprietary catalytic steam reformer (CSR) unit by about 10.1 percent from the initial value of 56.3 percent on a volume basis (vol.) before the hydrogen injection to approximately 62 percent (vol.) after the upgrading process. The project was also able to demonstrate the production of biomethane gas with methane contents of 75 percent (vol.) or higher using only the enhanced biological processes within the AD reactor. The project team believes that with further improvements to the system, our final target of 90percent (vol.) methane and above can be achieved.

Upgrading the AD biogas into RNG can have several benefits including as a cleaner alternative to pipeline natural gas, as a potential source of additional revenue for the plant owners and operators, and as a more environment-friendly solution to flaring or venting the low-quality biogas to the atmosphere. The RNG produced from the TIS process can be used directly in an off-the-shelf natural gas engine-generators and produce electricity without the derating usually associated with using lower quality biogas as fuel. In addition and depending on the AD plant location, the upgraded biogas may be injected directly into existing natural gas pipelines as RNG and create carbon credits.

Ultimately, TIS aims to further optimize this biomethanation process so that it can be easily adopted by AD owners and operators throughout the State at any scale and create value to all constituents.

CHAPTER 1: Project Background & Objectives

Project Overview

Technology & Investment Solutions LLC (TIS), in partnership with the University of Southern California (USC), was awarded by the California Energy Commission (CEC) with Grant No. ARV 18-024 to demonstrate a novel in-situ biological upgrading of biogas from the anaerobic digestion (AD) of food waste and/or liquified food substrates. TIS has developed and tested an in-situ method of upgrading the quality of AD biogas, also referred to as "biomethanation", through the addition of catalytically-derived hydrogen gas (H_2) produced from the proprietary catalytic reactor (CR) technology designed and fabricated by USC. The upgraded AD biogas with hydrogen addition has been shown to increase the biomethane content from the typical 50%-60% vol. to at least 90% vol. or with a biogas energy value exceeding 900 btu/scf. The project team composed of AD and bio methanation experts Christian Tasser (President) and Froi Aquino (Project Manager and MSU PhD student) from TIS, biogas catalytic conversion experts Prof. Theodore Tsotsis and graduate students Razieh Etezadi and Linghao Zhao from USC, and organic waste industry veteran Mr. Kevin Sutton from Circle Green. The demo facility is located at the former Meadowbrook Dairy site in an unincorporated community near the City of El Mirage, California. Circle Green is leasing the project site from the Phelan Piñon Hills Community Services District (PPHCSD).

Project Goals & Objectives

The project's technical objective was to upgrade the methane content of the biogas generated in a food waste digester to produce renewable natural gas (RNG) of quality that meets or exceeds the vehicle fueling standards of 900 BTU/scf. To accomplish this goal, TIS constructed a demonstration-scale plant at the former Meadowbrook Dairy located within the disadvantaged community of El Mirage, CA and utilized a hybrid, electrically/waste-heat driven catalytic steam reformer (CSR) technology that was previously developed, field-tested, and patented by USC.

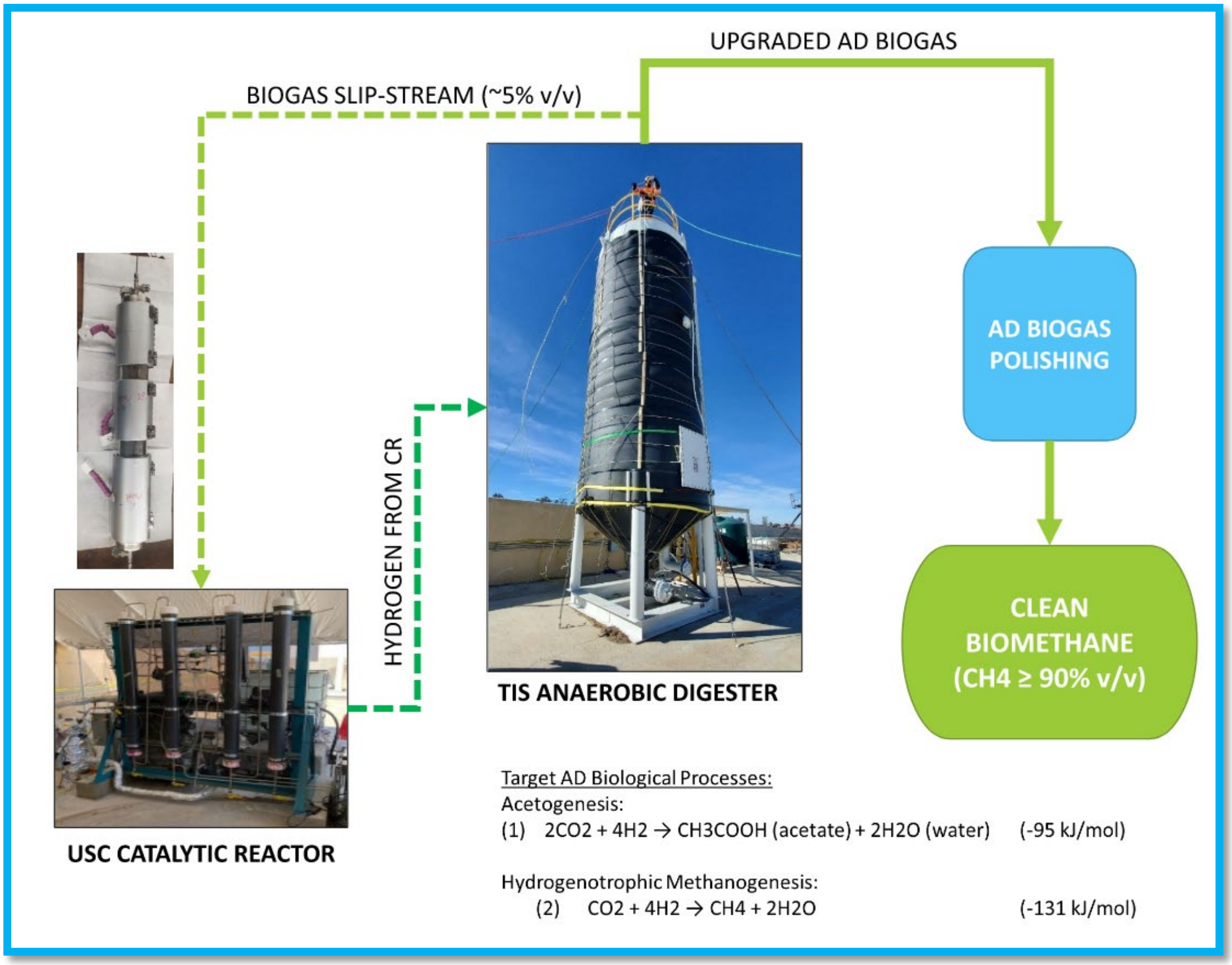
To achieve truck-fueling or pipeline quality AD biogas, further reduction of the CO_2 is typically required via the use CO_2-separation technologies such as membrane filters or pressure-swing adsorbers (PSA). This process has gained importance since the most recent air quality regulation in California no longer allows any biogas or waste-gas flaring except during emergency or equipment down-time. The result of the TIS in-situ technique eliminates the need for waste-gas flaring from a high BTU biogas stream entering an RNG upgrading system and instead returns any CO_2 gas from the biogas slipstream back to the anaerobic digester.

Overall Process Description

To accomplish the *in-situ* biomethanation of AD biogas in the presence of the hydrogen-rich syngas mixture from the CSR unit, TIS has constructed a demonstration-scale plant at the former Meadowbrook Dairy facility in El Mirage, California. **Figure 1** shows a simplified schematic of the overall in-situ biomethanation process.

During the project demonstration, a slipstream of the generated AD biogas from the food waste digester was directed to the USC CSR unit to produce a hydrogen-rich syngas mixture. After recuperating the heat from the CSR unit, the syngas was returned and dispersed inside the AD reactor tank where biochemical processes occur simultaneously to improve the composition of the final AD biogas.

Figure 1: Overall process schematic of the TIS in-situ biomethanation method



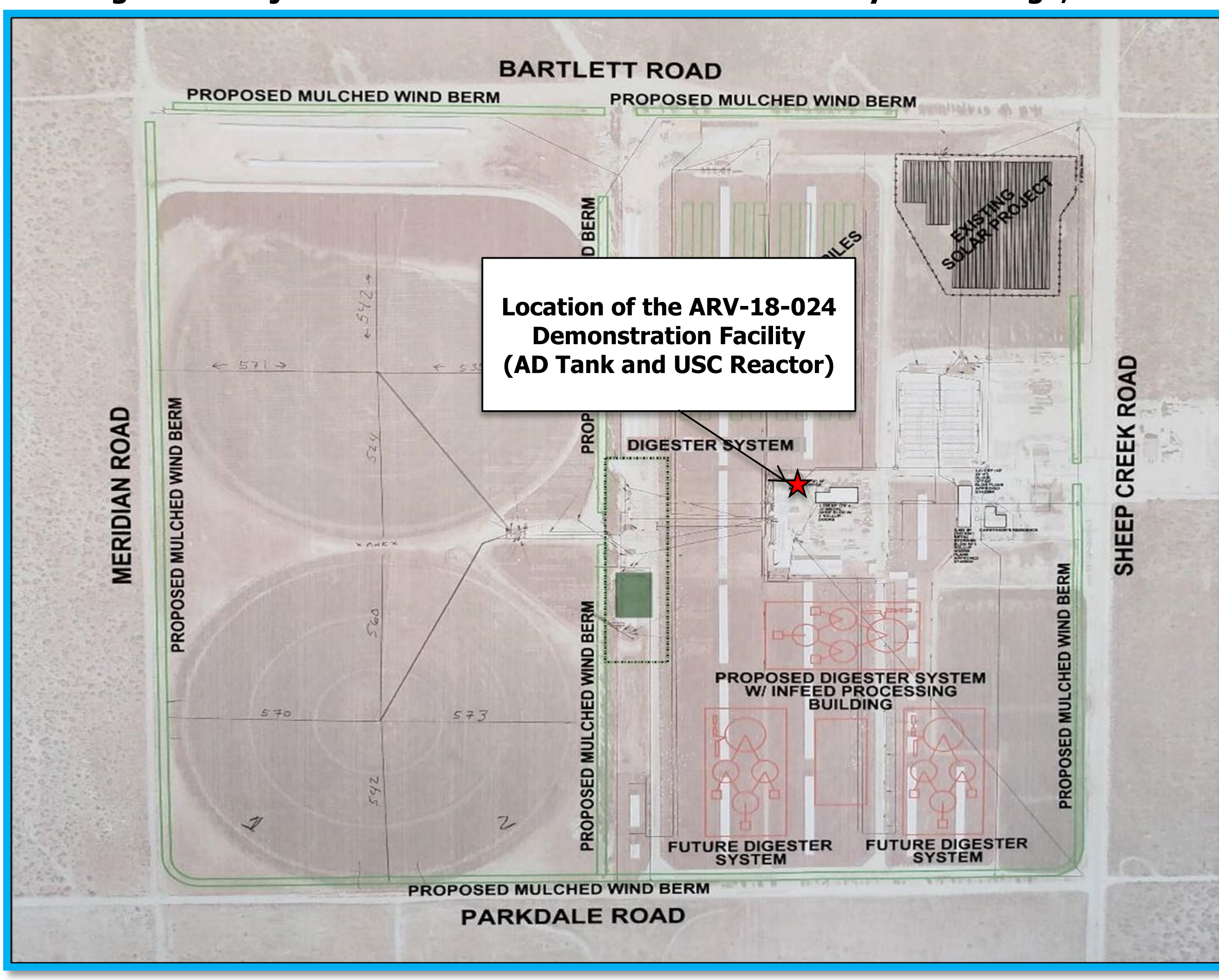
Source: Technology & Investment Solutions LLC

CHAPTER 2:
Site Preparation and Installation

Site Preparation and Construction

The project demonstration site was located at the former Meadowbrook Dairy, 17900 Sheep Creek Road, El Mirage, CA 92301 (**Figure 2**). To facilitate the proper installation of the new AD tank, the USC reactor skid, and all other plant components, necessary preparations were carried out at the site. First, TIS performed some minor repairs and routine site maintenance of the site and the existing building structure where operation and testing were conducted, including the installation of new doors, sealing of wall openings, and clearing the premises of junk materials. The indoor area received a fresh coat of paint, and new shelves were installed to promote proper organization of all materials and equipment. Next, TIS cleared the concrete pad area where the AD tank system and the CSR skid were installed, then set up a secured storage unit to provide safekeeping of the tools and equipment for the project.

Figure 2: Project site at the former Meadowbrook Dairy in El Mirage, CA



Source: Technology & Investment Solutions LLC

Equipment Installation

The project involved the acquisition and installation of a newly fabricated 15,000-gallon vertical steel tank that was used as the main AD reactor tank or also referred to as "AD tank or digester tank". The AD tank was successfully erected onsite in December 2022 using a 10-ton rated crane. The AD tank was securely anchored to the existing onsite concrete slab using steel cables and anchor bolts to ensure that the AD tank could withstand seismic load and strong winds. Finally, peripheral components such as access ladder with steel cage and the protective handrails were added as safeguards for accessing the top of the tank (**Figure 3**).

Figure 3: AD tank installation: side ladder with cage (left) & top handrail (right)

Source: Technology & Investment Solutions LLC

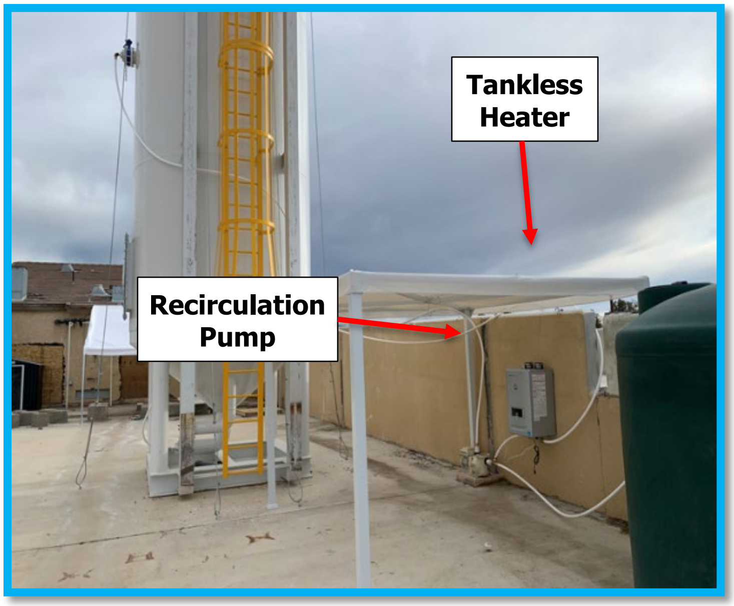
The AD tank also featured five (5) flanged connection ports: one (1) located on the side for the H2 gas inlet, two (2) located at the bottom for feed inlet, feed outlet, and two (2) located at the top for instrument and for biogas outlet. The bottom outlet was equipped with an 8-inch threaded flange, while the side has 6-inch threaded flanges. These flanges were drilled and threaded at one inch to accommodate the connections for the outlet and inlet lines.

The main recirculation pump was securely bolted to the concrete slab, while a tankless gas-fueled (e.g., propane or biogas) heater was installed on a nearby masonry wall. PVC pipes were utilized to connect the outlet and inlet of the digester tank to the circulation pump and tankless propane heater. A one-inch diameter plastic hose was employed and properly insulated to minimize heat losses (**Figure 4**). For the biogas system, a ¾-inch gas line was established, connecting the gas outlet at the top of the digester tank to the USC CSR unit. A safety release valve and a ball valve for isolation were also installed at the top of the digester. Furthermore, a ball valve was installed along the biogas outlet to regulate the flow of biogas.

Digital instruments were later installed and connected to the HMI (Human Machine Interface) board. These instruments include a circulation pump flow meter, digester tank level indicator, pressure indicator at the top of the tank, and a temperature indicator at the digester tank's feed outlet port.

To facilitate the supply of water and sludge, a 1,000-gallon day tank was connected to the digester tank, serving as an intermediate stage in the AD process.

Figure 4: Recirculation Pump and Heater



Source: Technology & Investment Solutions LLC

Figure 5: Tank supplying process water and organic substrates onsite

Source: Technology & Investment Solutions LLC

Site electrical work also proceeded in tandem with the installation of all system equipment. Electrical conduits were carefully placed, ensuring proper routing and organization for the electrical wiring. After laying out all the electrical wiring, the terminals were connected to the circuit breakers and the main electrical panels (**Figure 6**) to complete the plant's electrical infrastructure.

Figure 6: Main Electrical Panels

Source: Technology & Investment Solutions LLC

Anaerobic Digester Tank Preparation:

AD Tank Heating system

An efficient and reliable heating system is crucial to maintain the desired temperature range (in this case 35-55°C or 95-131°F) during the anaerobic digestion process. A suitable heating system design ensures that the digester tank will operate within the optimal temperature range to facilitate the digestion process effectively.

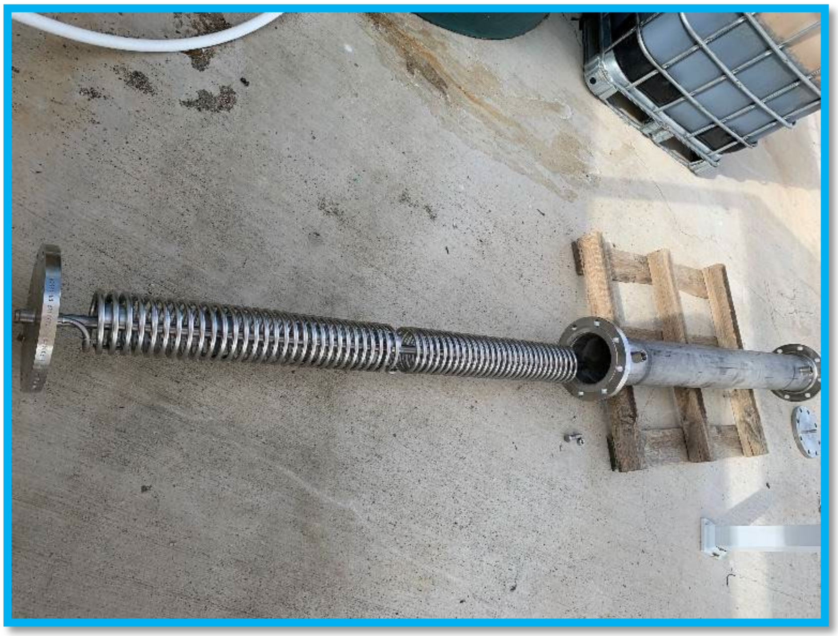
The overall AD tank heating system is comprised three (3) main parts:

1. AD Sludge Heating Loop
2. Heating Water Loop
3. Digester insulation

AD Sludge Heating Loop

The main component of the AD sludge heating loop is the shell-and-tube type heat exchanger (HX). TIS specifically designed and fabricated a well-suited HX (**Figure 7**) to prevent potential blockages in the heater screens and hose connections as the sludge is recirculated through the tubes. TIS also considered the expected sludge viscosity and the presence of other solid particles in the HX design. The HX facilitated the transfer of heat without contamination from the heating water loop to the AD sludge through indirect heating.

Figure 7: Shell-and-tube type heat exchanger



Source: Technology & Investment Solutions LLC

To ensure efficient operation and separation between the sludge and the heater, a clean water loop was integrated into the heat exchanger design. The clean water enters the stainless-steel coil, forming a hot, clean water loop within the heat exchanger. As a result, no sludge enters the heater, reducing the likelihood of any issues or blockages. The heat exchanger itself was designed using a 6-foot diameter stainless steel pipe, serving as the heat exchanger shell, which was sealed at both ends with bolted blind flanges. One end of the heat exchanger featured 2X ½ inch inlet and outlet welded connections, enabling the smooth flow of fluids through the system.

Heating Water Loop

A clean heating water loop was thoughtfully designed to optimize the heating process. This heating loop comprised several components, including a water supply tank, hot water circulation pump, pressure expansion tank, flow meter, pressure gauge, and a ball valve. All these components were strategically mounted and interconnected, forming a cohesive system that worked in conjunction with the tankless propane heater and a solar system.

Propane or natural gas heater: This heater utilizes the combustion of propane or natural gas to generate heat, which is then transferred to the water heating loop.

Solar thermal heating: Given the site's favorable conditions of long sunny days with clear skies, solar thermal sludge heating was identified as an ideal solution for the digester operations. A dedicated heating loop was designed specifically for this purpose, incorporating various equipment (**Figure 8**).

The equipment included a solar blanket, a small heat exchanger, a hot water circulation pump, a ball valve, a pressure gauge, a flowmeter, an expansion tank, and thermometers for measuring the inlet and outlet temperatures, enabling the calculation of heat exchanged.

The solar blanket loop proved highly effective in heating the digester tank, particularly during hot and sunny days. It was utilized extensively throughout the summer, either independently or in conjunction with propane heating, especially when solar heating alone was insufficient. This combination of solar and propane heating provided a dual benefit of clean thermal energy and significant savings in propane and electricity consumption.

Based on these positive results, further improvements were made. The size of the solar blanket was increased, and an additional set of solar blankets was installed to enhance heating capacity. Furthermore, the hot water circulation pump was upgraded to a higher capacity model, and a 6-gallon water supply tank was included in the loop to compensate for any water loss resulting from evaporation or unobservable leakage, ensuring a consistently reliable system operation.

Figure 8: Solar heating blankets for digester heating

Source: Technology & Investment Solutions LLC

Digester Tank Insulation

The significant challenge encountered in heating the digester and sludge stemmed from the rapid temperature drop experienced at night due to the high desert climate. These lower temperatures resulted in a considerable loss of heat content within the digester tank. To address this issue, a solution was implemented by covering the digester tank with foam insulation material. This insulation effectively prevented heat convection and radiation from escaping the tank, thereby retaining the heat within the liquid.

To accomplish this, a one-inch foam insulation material was procured and meticulously installed, covering over 95percent of the digester tank surface (**Figure 9**). This insulation proved highly effective, reducing heat loss by more than 50 percent. By employing this insulation method, the digester tank could maintain a more stable and optimal temperature, enhancing the overall efficiency of the heating process.

Figure 9: Digester Tank as delivered (left) and with exterior insulation (right)

Source: Technology & Investment Solutions LLC

AD Tank Operation with USC Catalytic Reformer

USC Catalytic Reformer

The catalytic steam reactor (CSR) system was designed and fabricated by the University of Southern California (USC) to carry out the catalytic steam reforming of a portion of the AD biogas. The AD biogas is reacted with an externally supplied steam within the CR unit, after which the methane and CO_2 in the biogas are converted into synthesis gas (syngas) which are composed mainly of hydrogen (H_2) and carbon monoxide (CO).

The CSR system (**Figure 12**) consisted of four (4) different subsystems. The following is a list of the subsystems which includes a short description of their functions.

1) Biogas Delivery and Purification Section

Since the biogas from the digester may contain impurities such as biomass fragments and water droplets, these are first removed with the aid of a water trap before the raw biogas enters the CSR system. Any water droplets that may have escaped are collected via a water trap. The biogas is then directed through a series of adsorption tanks for further treatment and purification. The biogas enters from the top of the filter columns and flows downwards through the column beds for all tanks. After exiting the biogas pretreatment stage, the composition of the gas is sampled through a sampling port using a solenoid valve.

2) Steam Generator (Boiler)

A steam generator (boiler) is used to provide the steam (H_2O) needed for the reforming reaction. For the complete conversion of the methane (CH_4) contained in the biogas into hydrogen gas (H_2), the catalyst requires a stoichiometric (H_2O/CH_4) molar ratio of two (2). However, in this study H_2O to CH_4 ratios higher than stoichiometric were utilized (base-value of 2.5) to help protect the reforming catalyst. Also, to ensure that there is no contamination of the feedwater to the boiler, purified water was used in most of the testing carried out in this project.

3) Catalytic Steam Reformer

The catalytic steam reformer is a tubular reactor with an outer diameter (OD) of 3-inch, a length of 22 inches and is made out of 316-type stainless steel (316 SS). A photograph of the reactor itself is shown in **Figure 10** below. The reactor is divided into two (2) parts: The bottom part with a length of 11 inches serves the role of a preheating and mixing section and is filled with stainless steel balls. The top of the reactor is filled with a reforming catalyst in the form of pellets. The syngas exiting the catalytic reformer is then directed into the digester.

Figure 10: Catalytic Reformer

Source: Technology & Investment Solutions LLC

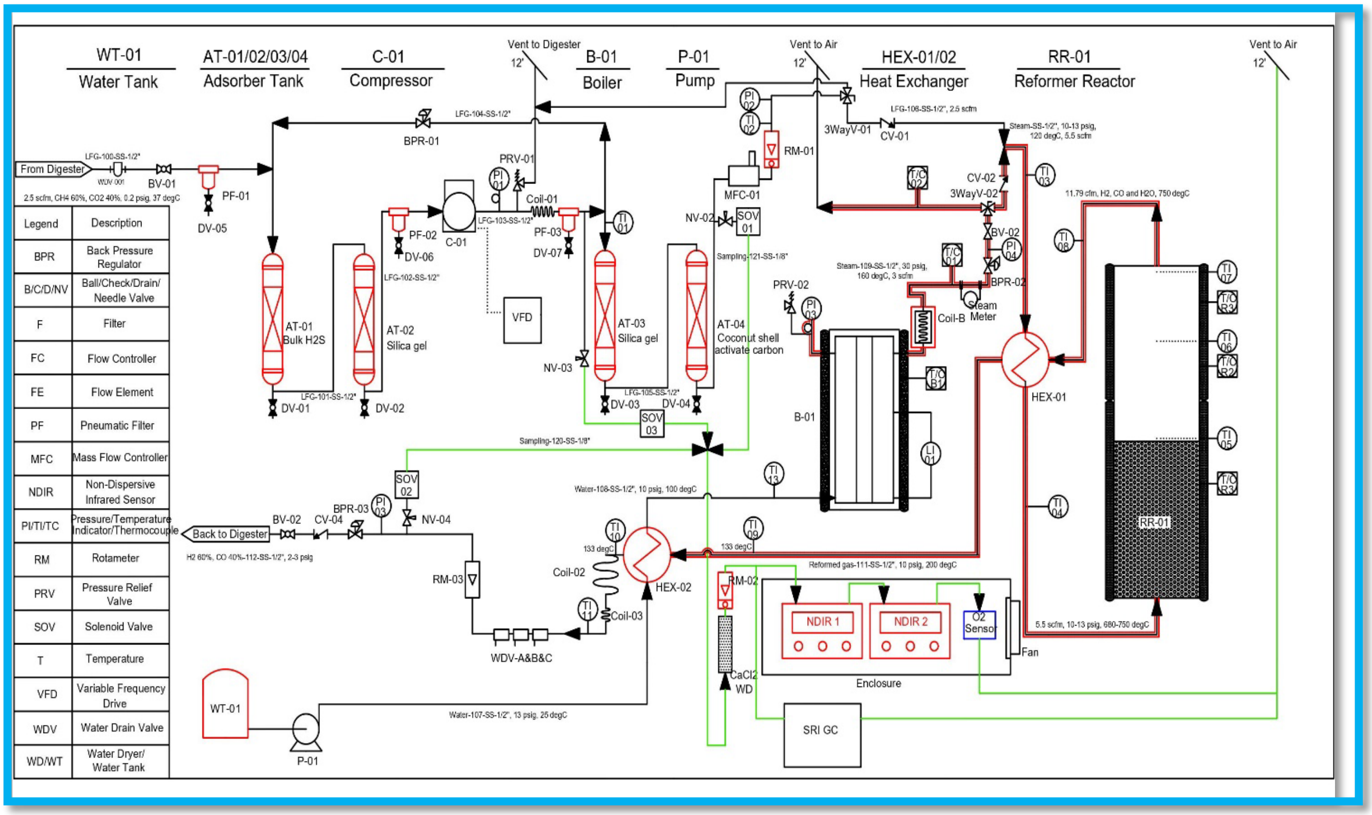
The syngas exiting the reformer will also contain a substantial amount of carbon monoxide (CO) gas. If needed, in order to increase the production rate of H_2, a second reactor may be added to the CSR system to convert the CO and unreacted steam into additional H_2 via the water gas shift (WGS) reaction.

4) Sampling/Analytical and Control Hardware

The CSR system is equipped with different analytical and control hardware including temperature sensors (thermocouples), pressure sensors (manual and automatic pressure gauges), flow meters and flow indicators, gas analyzers (gas chromatograph and FTIR sensors), and various types of solenoid valves and actuator valves. The system is also controlled through a program developed using the LabView software.

Figure 11 shows the process and instrumentation diagram (P&ID) of the CR system while **Figure 12** shows the whole CSR system currently installed at the project site.

Figure 11: USC Catalytic Reformer Process and Instrumentation Diagram



Source: University of Southern California

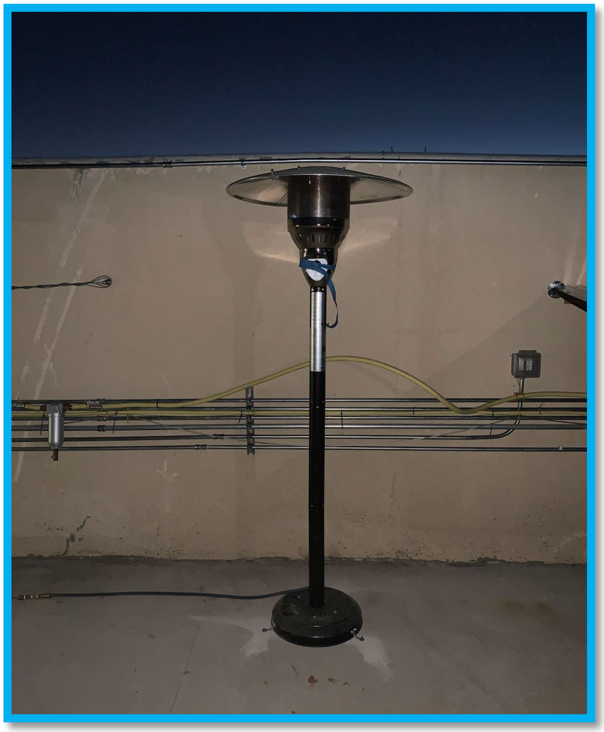
Figure 12: USC Catalytic Reformer deployed at the project site

Source: Technology & Investment Solutions LLC

Hydrogen Injection in the Digester

Once the digester modification and heating loop installation were completed, the testing and operation commenced at the site. To enhance AD biogas production efficiency, a representative mixture that resembled liquid food waste (i.e., combination of sludge, sugar, caustic soda, vinegar, and chicken soup) was added into the digester. The digester began producing biogas after a few hours where a small slipstream (1 to 3 scfm) of biogas was supplied to the CR unit. Notably, the biogas production persisted even when the CR unit was not in operation, necessitating a means to take care of the excess biogas by using a small gas flare (**Figure 13**).

Figure 13: Small Onsite Emergency Flare



Source: Technology & Investment Solutions LLC

Once the CR unit started producing syngas, the connection line to the digester was opened to slowly introduce hydrogen into the system. Initially, a hydrogen injection line was designed to add hydrogen into the digester tank's feed line using venturi effect. However, due to the high hydrogen feed flow rate from the CR unit and the low suction pressure at the venturi section, several adjustments were made to the injection setup (**Figure 14**).

Eventually, TIS decided to change the hydrogen injection method by feeding it directly into the digester tank. Modifications were implemented, allowing the hydrogen to be injected through the return line at the digester tank side flange. This revised approach proved to be more effective. Future modifications such as leak testing, and tube and fitting replacements took place during the hydrogen injection process.

To achieve proper mixing of hydrogen with the liquid in the reactor, a biogas recirculation process was introduced. This involved installing a biogas recirculation loop consisting of a compressor, stainless steel lines, and associated valves and fittings. The biogas inlet, equipped with a check valve, was connected to the sludge outlet line. The circulation process successfully operated at low digester tank pressure.

Figure 14: Hydrogen Injection System

Source: Technology & Investment Solutions LLC

Modified Hydrogen Injection Line

To enhance the surface contact between the sludge in the digester tank and the injected hydrogen, a carefully designed one-inch PVC schedule 80 piping system was implemented. This piping system was created in a rectangular shape, with a side length of 6 ft., and a cross connecting the four centers of the side length. The construction of the piping system began partially outside the tank and was completed inside it.

The pipes were drilled from various angles, starting from the bottom to facilitate sludge drainage and progressing to the top and sides for effective hydrogen injection. This drilling pattern ensured maximum surface contact between the gas and the liquid, optimizing the reaction between the injected hydrogen and the sludge.

To ensure the structural integrity of the piping system, all pipes were drilled extensively, with the total area of the drilled holes matching the cross-section of the main line. The PVC schedule 80 pipes, along with their connections and fittings, were chosen to withstand any potential forces or vibrations that may occur under the pressure of the injected gas.

Prior to closing the manhole and introducing the new sludge, the entire structure underwent a pressurization test. This test involved injecting water into the piping system to verify its integrity and performance.

By implementing this well-designed PVC schedule 80 piping system and conducting a rigorous testing process, the contact between the sludge and injected hydrogen was significantly optimized, ensuring efficient and effective operation of the digester tank.

CHAPTER 3: Project Results

Results

TIS has successfully completed the CEC demonstration project at the former Meadowbrook Dairy site which showcased the new *in-situ* biomethanation technique for upgrading AD biogas into high-value fuel. Through this project demonstration, TIS was able to produce biomethane from the anaerobic digestion of food waste with increased methane content and energy value.

With the use of the proprietary CSR reactor unit from USC, the TIS team was able to produce on-demand hydrogen gas (H_2) from a slipstream (1 – 3 scfm) of the raw biogas from the AD tank. The catalytically derived hydrogen gas was injected back into the digester to enhance the production of methane (CH_4) in the biogas by the hydrogenotrophic bacteria (hydrogenotrophs) through the following reaction:

$$4H_2\ (g) + CO_2\ (g) \rightarrow CH_4\ (g) + 2H_2O\ (l) \qquad (\Delta G^\circ = -131\ kJ)$$

In this conversion, four (4) moles of hydrogen gas are required to act as a donor to reduce the CO_2 into two (2) moles of water and one (1) mole of methane gas. The project team also found that the hydrogen content of the syngas produced by the CSR unit can be further optimized by varying the amount of steam injected in the CSR unit through the following reactions:

1. Methane Steam Reforming

$$\boldsymbol{CH_4 + H_2O \leftrightarrow CO + 3H_2} \quad (\Delta \boldsymbol{H = 225.4\ kJ/mol})$$

2. The Water Gas Shift Reaction

$$\boldsymbol{CO + H_2O \leftrightarrow CO_2 + H_2} \quad (\Delta \boldsymbol{H = -41.1\ kJ/mol})$$

For the complete conversion of the methane contained in the raw biogas into hydrogen gas, the catalyst used in the CSR unit required a stoichiometric steam-to-methane (H_2O/CH_4) molar ratio of two (2). The team also found that the higher the steam-to-carbon ratio, the more hydrogen can be produced by the CSR unit. Therefore, for this project, H_2O-to-CH_4 ratios higher than stoichiometric were utilized (base-value of 2.5) to ensure complete methane conversion to hydrogen and at the same time to protect the reforming catalyst from degradation.

The biomethane produced from the AD reactor after the injection of catalytically derived H_2 was tested using the on-site Fourier Transform Infrared (FTIR) detector. The reading for the CO_2 level of non-detect (ND) indicated the complete reaction of CO_2 with the hydrogen gas injected in the digester and the successful occurrence of hydrogenotrophic methanogenesis process within the AD reactor. This finding was also supported by the observed change in the archaea microorganism population measured via the Polymerase Chain Reaction (PCR) analysis conducted on the sludge sampled from the AD reactor. The PCR lab report which shows the graphical representation of the changes in the archaea cultures before and after the addition of hydrogen gas into the system can be found in Appendix A. The methane producing microorganisms were mostly comprised of the "M. soehngenii" species at the start of the test and then replaced by more thermophilic archaea types which favored hydrogenotrophic conversion of H_2 gas and CO_2 to methane gas. This conversion has resulted in the increase in the methane gas content (ca. 75 percent vol.) of the generated AD biogas.

Table 1 below summarizes the electrical consumption of each equipment that was monitored during the demonstration.

TIS Preliminary In-situ Biomethanation Results:

Before H_2 addition:
CH_4 = 44 to 57% v/v

After H_2 addition:
CH_4 = 72% v/v (Target = 90% v/v)

Table 1: AD System main equipment electrical consumption

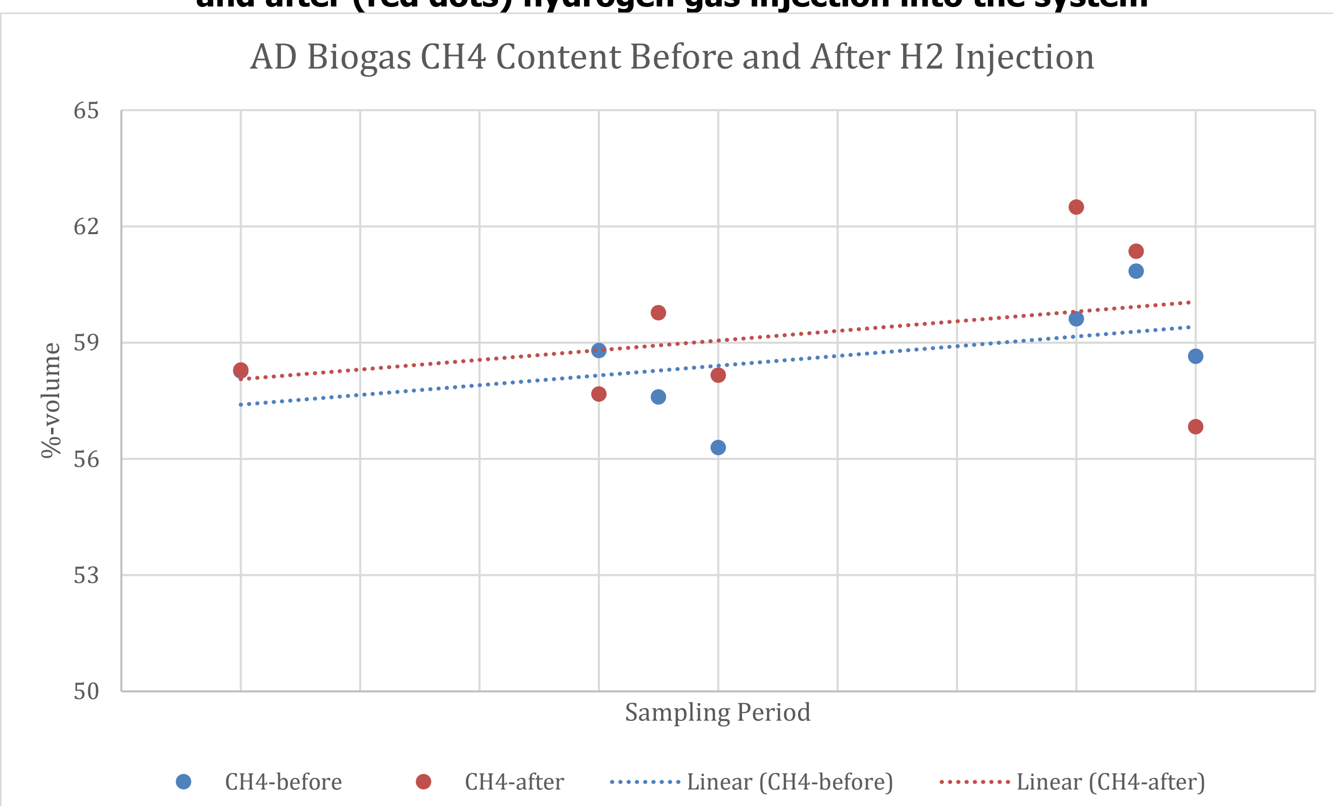
Equipment	Maximum capacity	Expected Normal Use
compressor	1 Hp	(%20 rpm) (0.15 KW)
boiler	4 x 1 KW	3.0 KW
Superheating section	2 x 150 W	0.3 KW
Reformer	3 x 2 KW	4.0 KW
Water Pump	1 x 75 W	0.075 KW
Total	12.12 KW	7.53 KW

The TIS project team has generated over six (6) months of operational data as part of our Monitoring and Verification (M&V) plan. The initial data did not immediately show the effects of the hydrogen gas injection to the AD reactor as the team worked on trying to optimize the entire process. As stated previously, the team made several modifications to the AD system as well as to the CSR unit from USC in order to optimize the whole system. **Table 2** below provides a summarized version of the data collected during the testing period.

Table 2: Summary of the measured methane (CH4) and carbon dioxide (CO2) contents of the AD biogas produced by the system before ("start") and after ("end") hydrogen (H¬2) gas injection

DATE	CH_4-start	CH_4-end	CO_2-start	CO_2-end
6/29/2022	47.00	46.20	20.30	22.50
6/30/2022	49.80	48.10	22.40	23.80
7/6/2022	52.50	55.20	23.60	23.70
7/7/2022	55.60	55.70	23.60	23.40
7/11/2022	50.80	57.20	22.00	23.90
7/12/2022	42.30	57.30	18.60	23.80
7/19/2022	43.70	64.40	19.30	21.80
7/20/2022	56.40	45.00	23.60	23.60
7/27/2022	57.00	46.50	23.50	22.00
8/9/2022	58.30	58.30	23.90	23.80
8/15/2022	58.90	60.90	19.10	18.10
8/16/2022	59.10	58.80	21.80	22.90
8/17/2022	57.50	60.50	25.00	20.50
8/18/2022	58.20	55.50	24.30	29.10
8/23/2022	58.60	62.50	25.40	19.40
8/24/2022	60.40	61.30	22.20	22.10
8/25/2022	58.00	57.10	24.10	29.50

Figure 15: Summary of the methane content of the AD biogas before (blue dots) and after (red dots) hydrogen gas injection into the system



Source: Technology & Investment Solutions LLC

As shown in **Figure 15** above, the lowest methane content in the AD biogas before hydrogen injection is approximately 56.3 percent vol. while the maximum methane content of 62percent vol. was measured after the hydrogen gas injection. This is equivalent to about a 10.1% increase in the methane content as a result of the hydrogen addition into the system. Although this result has been very encouraging, the team believes that there could be further improvements that could be employed into the system to achieve our target of 90percent vol. methane and above. The project team had learned several valuable lessons from this demonstration project and would recommend the following changes to similar future research:

1) Scale of the AD System– TIS had acquired a large 15,000-gal capacity AD reactor tank but had only utilized up to a quarter (25 percent) of its total capacity during the demo process. The huge scale made it very difficult to manage and precisely control the processes within the reactor which include heating, pH balancing and gas collection. The lack of available resources like power and water in the area also made it extra hard to operate the system. We had to bring water to the site from external sources.
2) Testing Sites – TIS had installed several sensors and instruments to measure usual parameters like flowrate, temperature, pH and pressure. However, some parameters like chemical oxygen demand (COD) and microbial analysis must be done in a properly equipped laboratory. TIS has invested in acquiring a COD analyzer but operating the unit also requires proper staff training and equipment maintenance. Having an accessible third-party technical laboratory to quickly send sample to would be beneficial when doing demonstration projects like this.
3) Extreme weather conditions – the selected location for the site is ideal for green projects because it already has some of the infrastructure existing at the site like concrete paving and building structures. However, the predominantly desert community also brought unique challenges especially to the operation of the AD system. For instance, during the wintertime, the ambient temperature could drop to below freezing during the day making it very difficult to heat the system. Recirculating through frozen pipes was also impossible. During the summertime, the lack of onsite water and the extreme heat can also make the plant operation very challenging. The strong wind at the site also means that the staff need to regularly maintain and clean every component from sand and dust.
4) Staff Availability – because of the remote location of the demo site, it became difficult to find technicians who are willing to travel to the site every day to operate and maintain the system.

Challenges

It is important to note that the former Meadowbrook Dairy site where the demo plant was installed did not have an existing electrical and water service connection. TIS initially explored the possibility of applying for a new electrical supply line at the site with the local utility provider, Southern California Edison, but immediately determined that doing so would be cost-prohibitive. In addition, the time it will take to complete the installation of the new electrical service will have detrimental impact on TIS ability to complete the project within the allotted project period.

TIS addressed the lack of onsite power supply by initially procuring and installing a 60-kW propane-fueled generator. The generator was integrated seamlessly through the main onsite electrical panel and provided the power needed to operate the AD system as well as the USC

CSR reactor skid. In order to provide sufficient fuel supply for the power generator, a 250-gallon propane tank was installed on-site.

During the installation and testing period, TIS also experienced several unexpected delays that had affected the project schedule. The COVID-19 pandemic has affected our operation through the passing of our plant operator in 2020. TIS hired a new staff as a replacement in 2021. TIS also experienced minor material and equipment supply issues (i.e., shipment delays and availability) on some of the plant components due to the effect of the COVID-19 pandemic on the domestic and international shipping and manufacturing industries.

Lastly, the unusually long and wet winter season in California towards the end of 2022 through the first quarter of 2023 also made continuous operation at the former Meadowbrook Dairy facility very challenging due to site's high elevation and remote location. Frequent freezing temperatures also made it impossible to sustain the heat required by the AD process to continue so TIS decided to temporarily stop operation and testing at the site until the local weather became more favorable.

Benefits

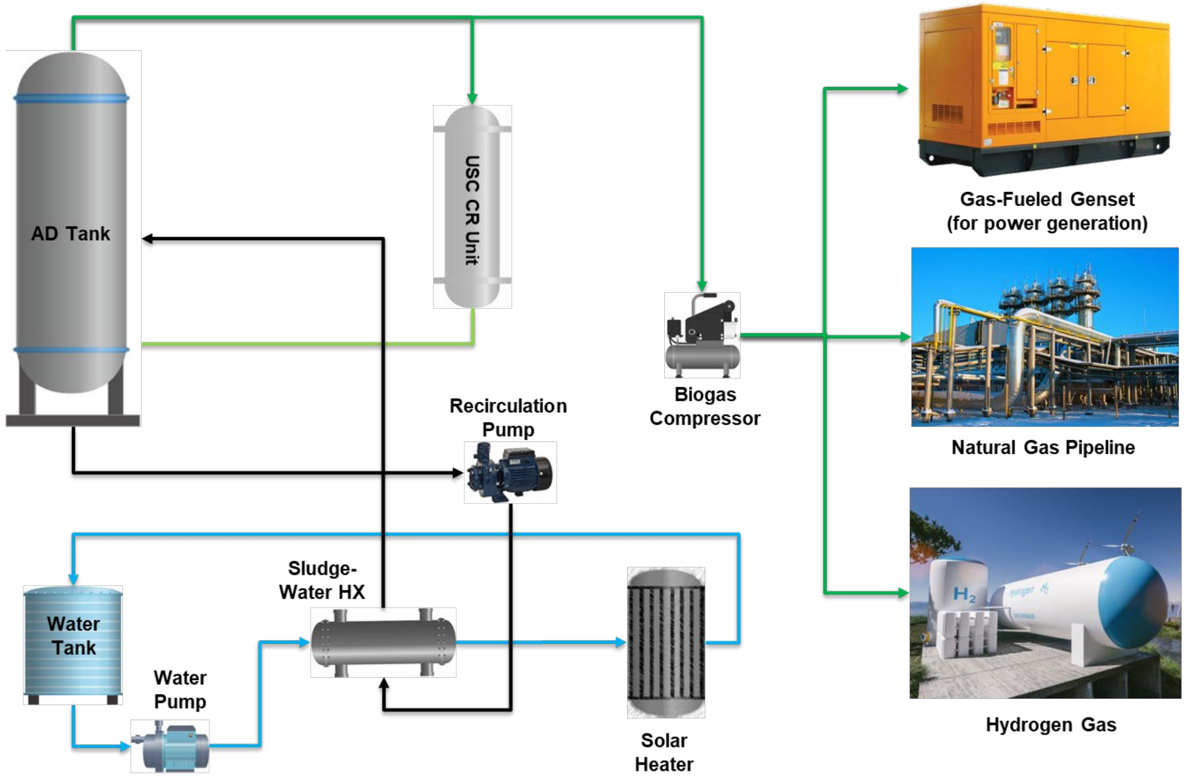
The TIS developed in-situ technique simplifies the biogas upgrading process by directly producing high-quality biogas without the need for separate upgrading equipment after the digester. Upgraded biogas or "biomethane" can become a potential source of additional revenue for the AD plant owners and operators as opposed to flaring or venting the low-quality biogas. The biomethane from the TIS in-situ process can be used directly in an off-the-shelf natural gas generators and produce electrical power without the derating usually associated with using lower quality biogas and without the need for operating highly specialized upgrading equipment like membrane or PSA. Depending on project location and other factors, the upgraded biogas may also be injected directly into existing natural gas pipelines creating additional revenue for the operators from both the sale of biomethane and the potential carbon offset as green biomethane. Upgrading the AD biogas creates new economic opportunities, especially for small to medium-scale biogas producers who could use their AD biogas to generate electricity either to offset their own electrical needs or to sell to the grid instead of flaring. There are also significant environmental benefits for doing so such as avoiding carbon emissions from venting or flaring the low-quality biogas directly into the atmosphere.

Scale-up and Commercialization

TIS plans to disseminate the knowledge and experience that the team has gained from this project through technology transfer and licensing activities to benefit small to medium-scale AD biogas facilities all around the State of California and beyond.

The next phase for the project at this site will be the conversion of the upgraded AD biogas or biomethane to produce high-purity hydrogen gas that can compete with the traditional steam-methane reforming process for producing hydrogen using natural gas, as part of our new project grant no. PIR 21-005. USC and TIS also plan to apply for a joint patent for the newly developed H_2 gas injection system design later.

Figure 16: Sample Uses of In-situ Upgraded Biomethane



Source: University of Southern California

GLOSSARY

ANAEROBIC DIGESTION (AD) — is a process through which bacteria break down organic matter—such as animal manure, wastewater biosolids, and food wastes—in the absence of oxygen. (Source: www.epa.gov; Accessed: July 5, 2023).

ARCHAEA - a group of microorganisms that are similar to, but evolutionarily distinct from bacteria. These microorganisms lack cell nuclei and are therefore prokaryotes.

BIOGAS — is a gaseous renewable energy source produced from raw materials such as agricultural waste, manure, municipal waste, plant material, sewage, green waste, wastewater, and food waste. Biogas is mainly composed of methane (CH_4) and carbon dioxide (CO_2) produced from anaerobic digesters, biodigesters or bioreactors.

BIOMETHANE - which is another term for this purified pipeline-quality fuel, refers to biogas that has been cleaned and conditioned to remove or reduce non-methane elements. (Source: https://afdc.energy.gov/fuels/natural_gas_renewable.html. Accessed: July 5, 2023)

BIOMETHANATION - a process by which organic material is microbiologically converted under anaerobic conditions to biogas. Three main physiological groups of microorganisms are involved: fermenting bacteria, organic acid oxidizing bacteria, and methanogenic archaea.

CALIFORNIA ENERGY COMMISSION (CEC)—The state agency established by the Warren-Alquist State Energy Resources Conservation and Development Act in 1974 (Public Resources Code, Sections 25000 et seq.) responsible for energy policy. The Energy Commission's five major areas of responsibilities are:

1. Forecasting future statewide energy needs
2. Licensing power plants sufficient to meet those needs
3. Promoting energy conservation and efficiency measures
4. Developing renewable and alternative energy resources, including providing assistance to develop clean transportation fuels
5. Planning for and directing state response to energy emergencies.

CATALYTIC STEAM REFORMING (CSR) – a method for producing syngas (hydrogen and carbon monoxide) by reaction of hydrocarbons with water with the aid of a catalyst. Natural gas is the common feedstock used but for this project we used AD biogas.

CIRCLE GREEN, INC. - Mr. Kevin Sutton is the CEO and owner of Circle Green, Inc. and the project developer of a new composting and green fuel production facility in Phelan, California. Circle Green is currently leasing the former Meadowbrook Dairy site from PPHCSD and allows TIS to use a small portion of the site to conduct the project demonstration.

COMPRESSED NATURAL GAS (CNG)—Natural gas that has been compressed under high pressure, typically between 2,000 and 3,600 pounds per square inch, held in a container. The gas expands when released for use as a fuel.

HYDROGENOTROPHS - organisms that are able to metabolize molecular hydrogen as a source of energy. An example of hydrogenotrophy is performed by carbon dioxide-reducing organisms which use CO_2 and H_2 to produce methane.

METHANOGENS - microorganisms that produce methane as a metabolic byproduct in hypoxic conditions. They belong to the domain Archaea and are members of the phylum Euryarchaeota.

MOJAVE DESERT AIR QUALITY MANAGEMENT DISTRICT (MDAQMD) - As the air pollution control agency for San Bernardino County's High Desert and Riverside County's Palo Verde Valley, the District has primary responsibility for regulating stationary sources of air pollution located within its jurisdictional boundaries. The District implements air quality programs required by state and federal mandates, enforces rules and regulations based on air pollution laws and educates businesses and residents about their role in protecting air quality and the risks of air pollution.

PRESSURE-SWING ADSORPTION (PSA) - a technique used to separate some gas species from a mixture of gases (typically air) under pressure according to the species' molecular characteristics and affinity for an adsorbent material.

PHELAN PINON HILLS COMMUNITY SERVICES DISTRICT (PPHCSD) – is a California Special District established in 2008 and governed by a five-member Board of Directors. The District operates and maintains the following services: Water, Parks & Recreation, Street Lighting, and Solid Waste & Recycling. PPHCSD is the owner of the former Meadowbrook Dairy site.

RENEWABLE NATURAL GAS (RNG) – see "BIOMETHANE"

SYNTHESIS GAS (SYNGAS) - is a mixture of hydrogen (H_2) and carbon monoxide (CO), in various ratios. The gas often contains some carbon dioxide and methane. Syngas is combustible and can be used as a fuel.

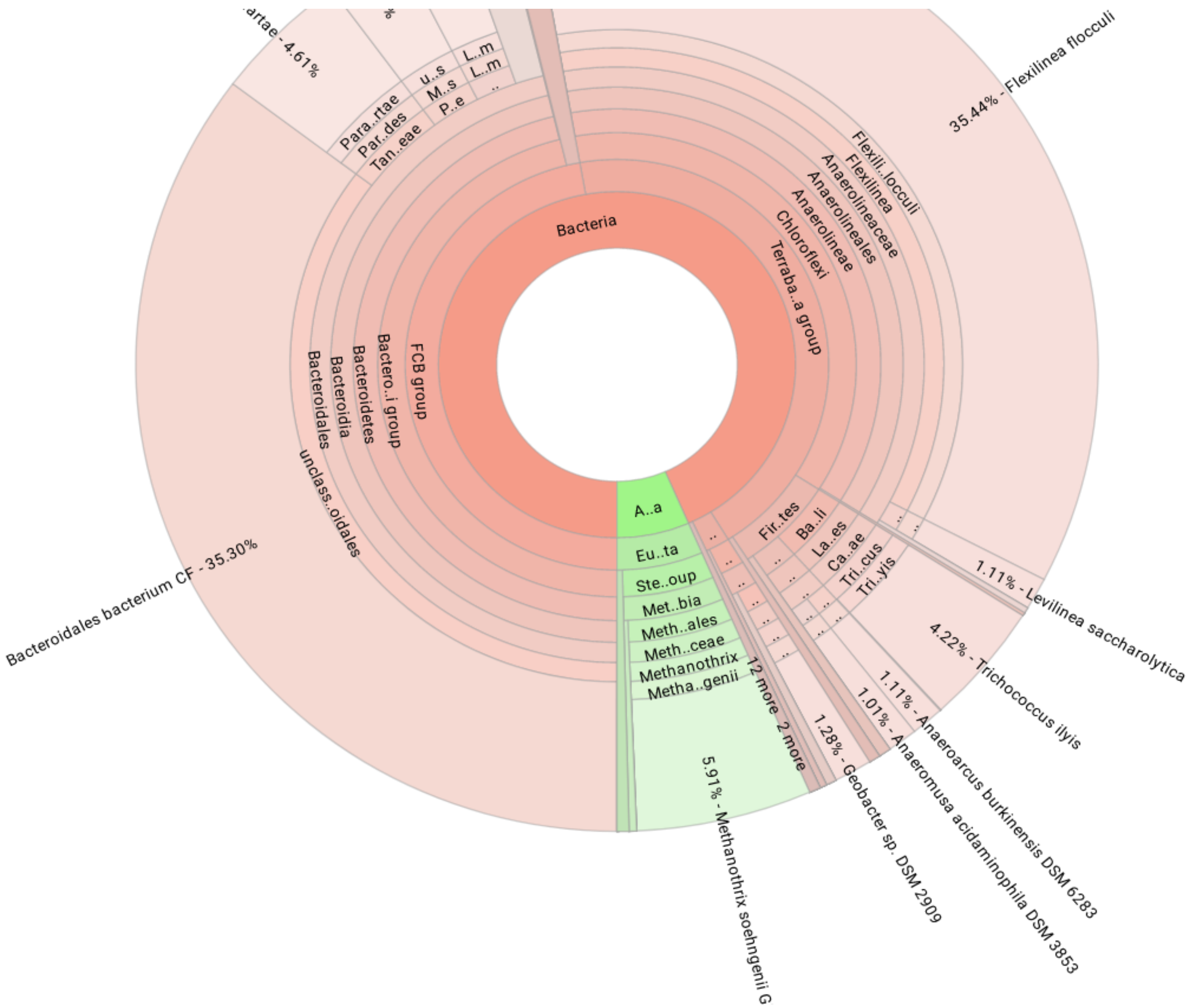
TECHNOLOGY & INVESTMENT SOLUTIONS LLC (TIS) - a Tustin, California based company established in 2015 to study and develop technology and projects in biogas & food waste digestion. TIS collaborates with the University of Southern California on a biomethanation reactor and digester system that is designed to carry out the catalytic steam reforming of biogas and produce hydrogen.

UNIVERSITY OF SOUTHERN CALIFORNIA (USC) – founded in 1880, is the oldest private research university in California with main campus located in Los Angeles, California. USC developed and patented the catalytic reforming technology used in this project.

APPENDIX A:
PCR Testing of Archaea

The polymerase chain reaction (PCR) lab reports show in a graphical presentation the change of the archaea cultures before and after addition of hydrogen. The methane formers soehngenii species dominated at start-up and changed to more archaea types for hydrogenotrophic conversion of H_2 and CO_2 to methane.

Figure A-1: Start-up conditions and Archaea Cultures



Source: Technology & Investment Solutions LLC

Figure A-2: Hydrogenotrophic conditions and Archaea Cultures

Source: Technology & Investment Solutions LLC