CALIFORNIA ENERGY COMMISSION

California Energy Commission

Clean Transportation Program

FINAL PROJECT REPORT

The Generation of Synthetic Diesel and Other Synthetic Petroleum Products Through the Fischer-Tropsch Synthesis Process Via the Gasification of Dairy Manure Solids and Utilization of Biogas

Prepared for: California Energy Commission

Prepared by: Agricultural Waste Solutions, Inc.

Gavin Newsom, Governor

July 2020 | CEC-600-2020-043

California Energy Commission

Michael Bagtang
Steve McCorkle
Bruce Scott
Primary Authors

Agricultural Waste Solutions, Incorporated
4607 Lakeview Canyon Road #185
Westlake Village, CA 91361
Agricultural Waste Solutions website available at www.agwastesolutions.com

Scott Brothers Dairy Farms
18051 Gilman Springs Road
Moreno Valley, CA 92555
Scott Brothers Dairy Farms website available at www.scottbrothers.com

Agreement Number: ARV-10-043

Elyse Cheung-Sutton
Commission Agreement Manager

Elizabeth John
Office Manager
ADVANCED FUELS AND VEHICLE TECHNOLOGIES

John P. Butler II
Acting Deputy Director
FUELS AND TRANSPORTATION

Drew Bohan
Executive Director

ACKNOWLEDGEMENTS

Agricultural Waste Solutions would like to thank Bruce and Nanette Scott, and the Scott Brothers Dairy for their dedicated and innovative support of the GTL technology developed through this project. The Scott Brothers Dairy partnership made possible the technological developments that have the potential to make reductions of dairy solids and biogas discharge through the conversion into the cleanest burning diesel fuel on the planet.

Agricultural Waste Solutions would also like to thank the crew for their hard work and their families for their support.

PREFACE

Assembly Bill 118 (Núñez, Chapter 750, Statutes of 2007) created the Clean Transportation Program, formerly known as the Alternative and Renewable Fuel and Vehicle Technology 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.
- Retrofit medium- and heavy-duty on-road and nonroad vehicle fleets to alternative technologies or fuel use.
- 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 PON-09-604 for the development of new, California-based biofuel production plants to increase statewide biofuel production and reduce greenhouse gas emissions. In response to PON-09-604, the recipient submitted an application which was proposed for funding in the CEC's notice of proposed awards August 12, 2010 and the agreement was executed as ARV-10-043 on August 25, 2011.

ABSTRACT

The project at the Agricultural Waste Solutions-Scott Brothers Dairy Farms pilot facility is intended to produce renewable diesel from dairy manure waste at a volume and cost that demonstrates that a commercial-size facility can be economically sustainable. When integrated into the best dairy management practices described in the San Jacinto Watershed Integrated Regional Dairy Management Plan, the technology implemented can also make a substantial contribution to meeting the social and environmental goals of the San Jacinto Watershed and the Regional Dairy Management Plan.

This project utilized the synthetic gases generated from the pyrolysis of dairy solids to generate transportation diesel through Steam Methane Reformation and Fischer-Tropsch Synthesis processes. The project successfully created transportation diesel from dairy solids. This project also tested the potential to use biogas as a feedstock for the generation of transportation diesel. Municipal natural gas was used as a substitute for biogas during testing where transportation diesel was also successfully created.

During fabrication, designing, and configuring the pilot scale facility, the company evaluated the long-term sustainability of the equipment on site. It was determined that some design modifications will be required in order to optimize production due to the unique environment and long-term production needs; however, the pilot test was successful in qualifying the one-year pilot system as originally designed.

Keywords: Agricultural Waste Solutions, Scott Brothers Dairy Farms, renewable diesel, San Jacinto Watershed Integrated Regional Dairy Management Plan, synthetic gas pyrolysis, Steam Methane Reformation, Fischer-Tropsch Synthesis, biogas, natural gas.

Please use the following citation for this report:

Bagtang, Michael, Steve McCorkle and Bruce Scott. 2020. *The Generation of Synthetic Diesel and Other Synthetic Petroleum Products Through the Fischer-Tropsch Synthesis Process Via the Gasification of Dairy Manure Solids and Utilization of Biogas*. California Energy Commission. Publication Number: CEC-600-2020-043.

TABLE OF CONTENTS

Page

LIST OF FIGURES

LIST OF TABLES

EXECUTIVE SUMMARY

The Agricultural Waste Solutions, Inc. system is a skid mounted, scalable technology solution consisting of four key modules to process manure into clean water for irrigation and/or re-flushing, potable water when required, and a high-energy biological synthetic gas that can be converted into diesel fuel products and/or electricity.

Under CEC Award Number ARV-10-043, Agricultural Waste Solutions, Inc. agreed to produce renewable diesel products from dairy manure at the Agricultural Waste Solutions, Inc.-Scott Brothers Dairy Farms pilot facility that demonstrates the validity of the Agricultural Waste Solutions, Inc. system process and its technology. The renewable, almost no sulfur diesel products, were verified to be of the quality and performance characteristics that meet industry standards.

Agricultural Waste Solutions, Inc. has a process to take both liquid and dry manure, a regulated liability to dairies and other animal farmers, and turn them into valuable assets. Pioneers and partners in this technology are Scott Brothers Dairy Farms and Agricultural Waste Solutions, Inc.

The Agricultural Waste Solutions, Inc. system separates water from manure, recovering clean water for reuse on the facility for irrigation, flushing, or livestock watering, while providing a dry solids feedstock for use in the gasification process to produce clean, renewable energy in the form of diesel fuel products for on-farm use and/or off-farm sales. The goal of the first phase of the pilot project is to prove that the system can make clean water, fertilizer, and low-emission diesel fuel products of predictable qualities and predictable quantities for the California Energy Commission.

The Agricultural Waste Solutions, Inc. processes and system configurations consist of up to four modules that are already proven and in use in other industries. The modules are adapted to comply with Agricultural Waste Solutions, Inc.'s process patent and are patented as one apparatus patent by Agricultural Waste Solutions, Inc. The modules are patented by Agricultural Waste Solutions, Inc.'s key suppliers and are licensed to Agricultural Waste Solutions, Inc. for the agricultural industry.

Solids Recovery Module: Removes more than 98 percent of total suspended solids and 40 percent of total dissolved solids, 90 percent of phosphorus, 70 percent of total Kjeldahl nitrogen, and 40 percent of potassium and other salts. Note that total dissolved solids and nitrates (a nitrification products of ammonia and a component of total Kjeldahl nitrogen) are the primary pollutants of concern with regard to salt offset requirements.

Water Treatment Module: Cleans the discharge water from the Solids Recovery Module to further process it for beneficial on-farm reuse as well as to evaluate and demonstrate the potential to convert the cleaned water to potable water.

Gas Production Module: Economically creates large quantities of high-quality, high-British Thermal Unit bio synthetic gas from manure solids recovered in the Solids Recovery Module and other biomass, as well as a phosphorus-rich fertilizer ash by-product. Currently, Scott's system is permitted only for dairy waste; other waste streams will be evaluated later in the project.

Liquid Fuel Module: Converts the bio synthetic gas into clean, advanced biofuels—primarily renewable, low-emission diesel fuel. The raw bio synthetic gas will also be cleaned and used with a generator to create electricity for the operation.

Gas Cleaning Module: The bio synthetic gas is cleaned and conditioned to become an input for energy generation, either in the form of liquid fuels, electricity, or both.

The Agricultural Waste Solutions, Inc. system addresses both solid manure and wash water. In addition to removing total dissolved solids and nitrates from the water ultimately used for irrigation, it removes the nutrients of concern in the total maximum daily load—phosphorous and nitrogen. The added benefit of a bio synthetic gas by-product that can be converted to both electricity and diesel fuel, with a high-quality value fertilizer ash by-product that reduces the volume of solids by 80 percent and, therefore, can be easily used or locally sold. This project addresses total dissolved solids (TDS) salt offsets and total maximum daily load (TMDL) nutrient issues unlike other technologies like anaerobic digesters that produce large volumes of a wastewater stream that still contains most or all of the original odors, nutrients, salts, and other components. Much of the TDS and nutrients that enter the system are retained in the fertilizer ash, which is far easier to transport and control than the original manure or the types of waste streams produced using other technologies.

Chapter 1: Project Purpose and Approach

The project objective, to produce renewable diesel products from dairy manure waste at a volume and cost that demonstrates commercial sustainability, is a complex objective that requires innovative solutions. Agricultural Waste Solutions (AWS) is able to provide those innovate solutions that meet the specific aspects and traits the animal agricultural industry needs in order to implement viable technological results.

1.1 Task 2-Equipment Test Results Report

Task 2 establishes the system specifications for the pilot plant, ordering of equipment, assemblage of the modules in a skid-mounted fashion, and delivery onto the Scott Brothers Dairy site.

Primary equipment modules were shipped to the site at the end of June 2013. Updates and new tasks to the modules were completed in September 2013. The modifications were required to be completed by the manufacturer, and they were of high significance to our forward progress. Some progress on this task was made in November 2013 by the manufacturer; however, completion did not occur by the manufacturer until January 2014. Critical replacement parts were only available in Europe and included a long lead time due to made-to-order specialty to fit the application. Once the replacement parts became available, the manufacture sent technicians to initiate the replacement and installation in November 2013. Consequently, the primary technician to complete and finalize the install did not become available until January 2014 due to his scheduling constraints.

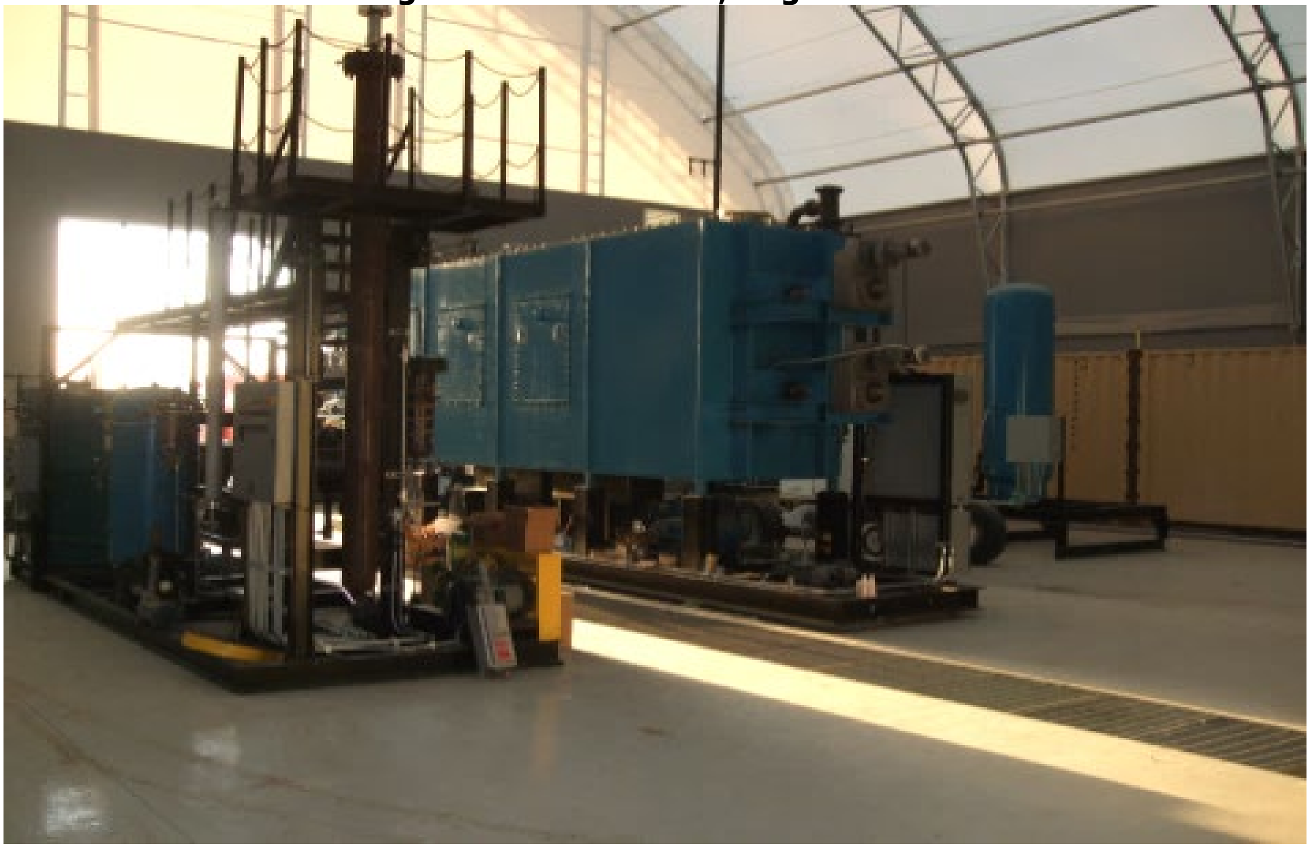
1.2 Task 4-Site Installation Completion Report

Task 4 details the preparation of the project site on Scott Brothers Dairy, receiving the modules, receiving auxiliary equipment, and creating the infrastructure to support the project.

The structural modifications required for building permit final inspection were completed by September 2013. Building permit inspection and approval was completed in November 2013.

A majority of the interior infrastructure such as the catwalk, affixing the utilities connections, and input/output piping to the equipment was completed December 2013. Figures 1-3 reflect the progress made in the installation of the catwalk and subsequent infrastructure tied to it.

Figure 1: Pre-Catwalk, August 2013



Source: AWS

Figure 2: Catwalk Construction, November 2013

Source: AWS

Figure 3: Installation Utilities and Piping, December 2013

Source: AWS

1.3 Task 5-Assembly Completion and Commissioning Report

Task 5 details the installation and integration of the AWS system modules at the Scott Dairy site. The full integration between the Solids Recovery Module, the Gas Production Module, the Gas Cleaning Skid, the Liquid Fuel Module and the Water Treatment Module was dependent upon equipment positioning to account for the overall safety of the operations staff and visitors as well as the overall process flow, the three primary flue exit points through the roof, feedstock access for both the liquid and solid manures, utility and input/output connections to the catwalk, demonstration points and walkway widths, maintenance access, and output solids and liquids storage and movement. Full integration also required assembly and installation of auxiliary equipment, including mixing and conveyance equipment for liquids and solids, flue stacks, compressors, glycol chilling, explosion proof electrical components and cabinets, tanks, boiler, heaters, condensers, etc. Perhaps most importantly, full integration of the modules and the auxiliary equipment required a sound building structure to support the full integration.

Two major wind and storm events, in February and May of 2014, exposed some design issues in this first of its kind building design that required a replacement of the entire roof covering and several design modifications and replacements to the roof support structure. This issue delayed completion of Task 5 until November 2014. The resulting structural design modifications and new roof covering, shown in Figure 4, have resulted in a building that has already withstood far stronger winds and storms than those that caused the damage and delays, and we are pleased to report that the building manufacturer has issued a complete warranty on the new structural design and covering.

Figure 4: Installation of Custom Exhaust Flues After Roof Structure Modifications and Re-covering, July 2014

Source: AWS

Figure 5: Steve McCorkle (AWS) Explains the Fischer-Tropsch Module After Installation and Integration of the AWS Modules, November 2014

Source: AWS

1.4 Task 6-Continuous Operations Report

Task 6 details the test and validation of the AWS system components of the project at Scott Brothers Dairy site. An initial test plan for continuous operations was submitted February 10, 2015. The test plan was later amended and updated to include recent collaborative agreements and grant opportunities on April 13, 2015.

Preparations for a validation of project equipment and generation of synthetic diesel products began with sourcing testing gases from a local supplier, installation of monitoring and analysis equipment, and finalizing the operational integrity of the equipment and modifications.

A summary of the test plan is as follows:

Synthetic gas (Syngas) generated by the gasifier was blended with natural gas and then fed into the steam methane reformer. That feed was slowly transitioned to a pure syngas feed into the steam methane reformer. The output gas composition was analyzed and supplemented to a composition recommended by consultants with experience with the AWS Fischer-Tropsch (FT) system and catalyst. That supplemented reformed syngas was fed into the FT to generate the desired synthetic diesel products.

1.5 Task 7-Project Operations Report

Testing commenced mid-April 2015. Chemical engineering and process consultants were engaged in during the initial commissioning and operation of the equipment to ensure safe operation and favorable results for the project.

1.6 Task 8-Data Collection and Analysis

The collection of data occurred during testing and operation. Multiple data parameters were taken, recorded and analyzed for overall system efficiency, energy use, and feasibility. Gas and fuel analysis were done by an independent contractor proficient with calibration, operation, and analysis of SRI's on site with Gas Chromatograph SRI Model 8610D and 310 units to test quality of the system's products.

Manure feed was tested for moisture content periodically during operation of the gasifier. Syngas output from the gasifier was tested during operation to track pyrolysis efficiency. Exhaust oxides of nitrogen, sulfur oxide, carbon monoxide, carbon dioxide, and temperature from the gasifier was checked intermittently as well to confirm efficiency of the burners. Stored syngas was tested in triplicate to confirm consistency of composition before it was fed to subsequent systems such as the steam methane reformer and the FT reactor.

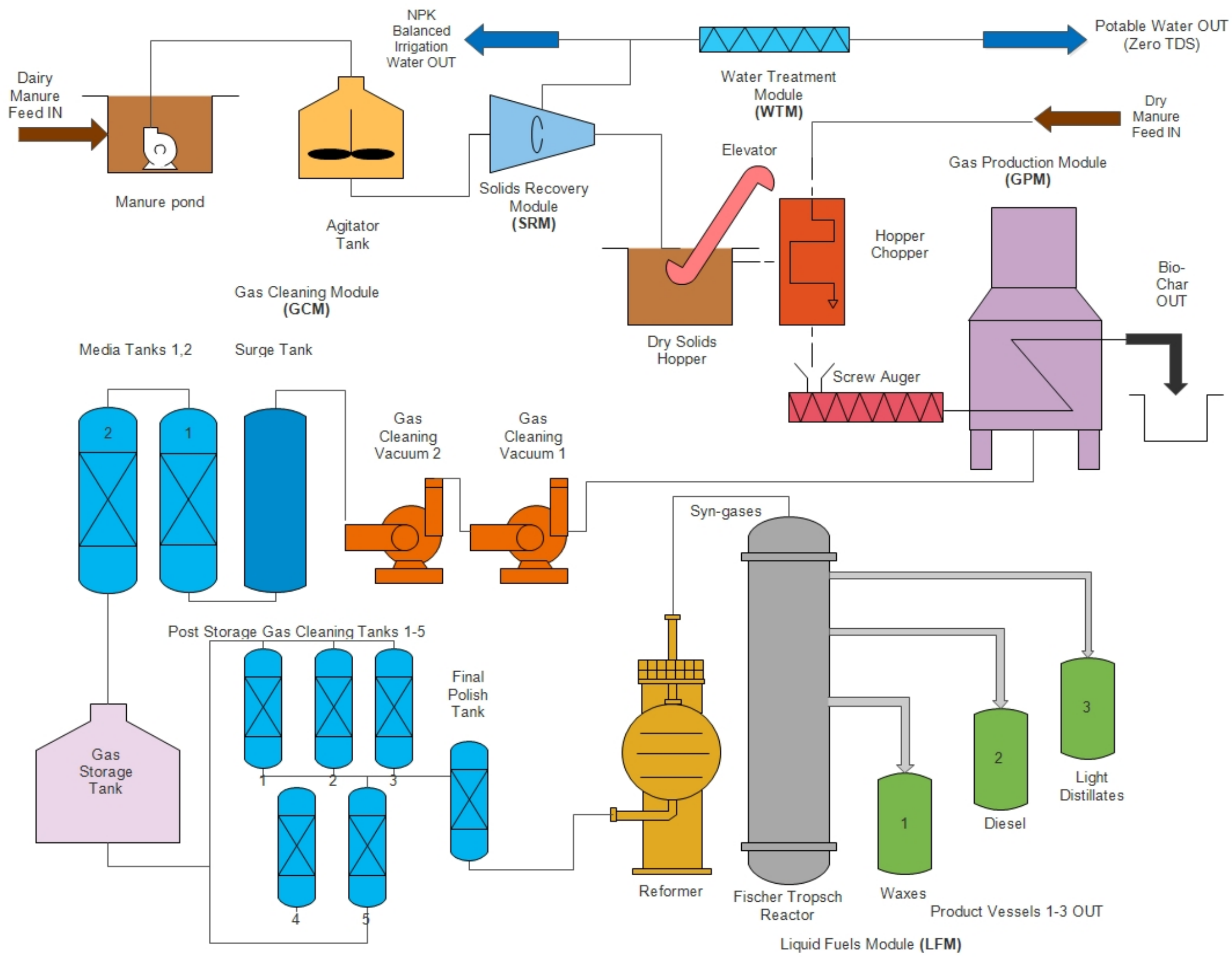
Blended feed to the steam methane reformer was sampled to confirm correct composition. Output of the steam methane reformer was sampled intermittently to track catalyst activity and conversion.

Tail gas output from the FT reactor was sampled every 30 minutes for overall syngas conversion and catalyst activity. Product output from the FT reactor was sampled and collected every hour as well to measure output per ratio feed, then analyzed for composition.

1.7 Process Description

A simple process flow diagram of the process is shown in Figure 6.

Figure 6: Simple Process Flow Diagram



Source: AWS

Flush water from the milking barn transports manure to where it is collected in the manure pond or sump. The manure flush water slurry is next degassed and homogenized in the agitator tank, and it is then processed through a centrifuge which separates the liquid and solids of the manure slurry. The liquid from the centrifuge is used for agricultural irrigation or further processed via microfiltration, for potable water quality when needed while the dry centrifuged solids are combined with dry manure from the dairy corral in the hopper chopper. The hopper chopper feeds the pyrolysis gasifier, where the combined manure solids undergo pyrolysis to generate syngases and char. Remaining solids from the gasifier are collected as biochar which can be land applied as a product added value fertilizer or exported off the farm. The syngases are cleaned of impurities through gas cleaning vacuums 1 & 2 and gas cleaning module media tanks 1 & 2. The syngases are stored until needed within the gas storage tank. The gases are filtered again for impurities before being processed in the reformer, which converts the syngases to the hydrogen to be processed in the FT reactor. From the FT reactor, sulfur-free diesel, waxes, heavy distillates and other synthetic petroleum products are produced.

Natural Gas would be fed through the final polish tank to remove traces of mercaptans, which are detrimental to catalyst activity in the reformer and FT Reactors. Once mercaptans are removed, the natural gas would be then processed by the reformer and FT Reactor, similar to use of syngas.

Chapter 2: Project Activities and Results

2.1 Instruments and Test Equipment

Gas composition will be tested using SRI Instruments Model 8160D Gas Chromatograph similar to what is shown in Figure 7. The results from the SRI Instruments Model 8160D Gas Chromatograph will show the constituents by volume percent of each of the component.

Figure 7: SRI Instruments Model 310 Liquid Chromatograph

Source: AWS

Fischer-Tropsch Liquid composition will be analyzed using an SRI Instrument Model 310 Liquid Chromatograph, shown in Figure 5 above, reporting hydrocarbons volume based on the length of their carbon chain.

2.2 Methods, Parameters, and Procedures

The gasifier will be used to generate syngases from the pyrolysis of dairy solids. These syngases will be run through the reformer and FT tower at operational parameters decided upon by chemical engineering consultants experienced with the specific reactor on site and the catalyst utilized. Recommended parameters for the reformer and FT reactors are made to fit the specific system on site and to match the business plan of AWS. Those subsequent ratios of Dihydrogen: Carbon monoxide will be varied to determine how the product (Fischer-Tropsch Liquid, light distillates, and waxes) yield changes with respect to the hydrogen gas to carbon monoxide ratio. The gas composition that exits the gasifier and the steam methane reformer will be analyzed, as well as the respective products composition from the FT reactor.

Gas and liquid ratio and compositions will be determined using SRI Instruments' gas chromatograph and liquid chromatograph, similar to what is shown in Figure 5. A Fischer-Tropsch Liquid sample will injected into a liquid chromatographic column, where the constituents of hydrocarbons are separated in the order of increased boiling points and detected by the Flame Ionization Detector. In a similar manner, a gas sample will be injected into a gas chromatographic column, and the components of the gas sample will be separated in order of molecular weight.

Procedures for running tests described in this plan will be similar to the following:

1. Purge the gas piping, gas lines, and process system equipment of atmospheric gases using an inert gas such as nitrogen.
2. Generate and collect synthetic petroleum product for syngas generated through pyrolysis gasification of dairy manure solids
3. Run analysis on the syngas and subsequent products from the pyrolysis gasification of dairy manure solids
4. Recirculate liquid fluid lines
5. Initiate the reformer and reactor warm up procedure until catalyst for both the reformer and reactor reaches activation state
6. Feed syngases at Dihydrogen: Carbon Monoxide ratio of 1.8:1
7. Generate and collect synthetic petroleum product
8. Run analysis on respective ratio's product
9. Vary Dihydrogen: Carbon Monoxide ratio
10. Generate and collect synthetic petroleum product for each subsequent ratio
11. Run analysis on each subsequent ratio's product

2.3 Project Results

Operation for this CEC test plan commenced on Monday, April 20th, 2015 with the pyrolysis of dairy manure. The gasifier operated for 15 hours and produced a synthesis gas (syngas) of a consistent composition. The syngas composition was tested periodically. The averaged composition of the output syngases is shown in Table 1.

Table 1: Average Composition of Gasifier Syngas Output

Component	Avg. Percent
Hydrogen	32.54
Oxygen	0.45
Nitrogen	3.04
Methane	12.53
Carbon Monoxide	17.28
Ethane	1.76
Carbon Dioxide	29.63
Ethylene	N/D
Propane	0.37
Iso-Butane	2.05
Butane	0.09
Isopentane	0.29
Pentane	0.02
Total	100.05

Source: AWS

Syngas was stored in a vessel purged with nitrogen to avoid any atmospheric contamination. Due to some residual nitrogen from the purge, the resulting composite sample analysis was altered as shown in Table 2.

Table 2: Composite Analysis of Stored Syngas Post Pyrolization

Component	Percent
Hydrogen	21.46
Oxygen	1.68
Nitrogen	19.77
Methane	8.26
Carbon Monoxide	15.43
Ethane	1.56
Carbon Dioxide	30.82
Ethylene	N/D
Propane	0.45
Iso-Butane	0.01
Butane	0.13
Isopentane	0.40
Pentane	0.03
Hexane	0.01
Total	100.00

Source: AWS

The nickel steam reforming catalyst had been exposed to moisture and air during storage. The catalyst was therefore conditioned for 24 hours prior to commencing reforming runs. The reformer vessel was first purged with nitrogen for 6-8 hours, at an elevated temperature of 700° to eliminate any moisture, grease, etc., that may have accumulated on the catalyst surface. The reactor was then fed hydrogen to reduce the oxidized metal surfaces back to the metallic state. This stage of catalyst reduction (also known as catalyst activation) lasted 16-18 hours.

Operation of the steam methane reformer commenced on Thursday, April 23rd. To simulate the commercial scenario of combining methane from biogas generation systems, such as anaerobic digesters or land fill gas that may be in close proximity to agricultural sites, natural gas was blended into the syngas feed into the reformer. The steam feed rate was established for an overall 2:1 Steam to Carbon molar ratio. The natural gas was treated by sulfur treat vessels to remove the mercaptan based odorous compounds added to natural gas for safety reasons by municipal gas providers.

The molar analysis of the reformate gas confirmed a greater than 95 percent carbon conversion rate to carbon oxides and hydrogen. The analysis of the reformate gas is given in Table 3.

Table 3: Average Reformed Syngas Composition

Component	Avg. Percent
Hydrogen	80.744
Oxygen	0.191
Nitrogen	3.660
Methane	4.815
CO	3.720
Ethane	0.008
CO2	9.988

Source: AWS

Reformed gas was stored in nitrogen purged storage tanks, after vacuum evacuation. The final composition average of the stored reformate gas is given in Table 4.

Table 4: Stored Reformed Syngas Composition

Component	Avg. Percent
Hydrogen	65.92
Oxygen	0.68
Nitrogen	6.80
Methane	10.98
CO	4.67
Ethane	0.02
CO2	10.86
Isopentane	0.08
Hexane	0.05
Total	100.07

Source: AWS

It was initially stated to the CEC that a Pressure Swing Absorption apparatus is necessary to create the gas ratios needed to utilize the current FT reactor in conjunction with the other modules present on site. Due to the high capital cost and lack of availability of rental Pressure Swing Absorption's, as well as not knowing the desired characteristic of a Pressure Swing Absorption before the syngas was actually created and measured for this environment, it was described to the CEC to use bottled gas for this round of testing to supplement the syngas generated by both the gasifier and steam methane reformer in order to create the needed gas composition for FT synthesis to occur creating the desired FT products. Bottled 99.9 percent CO and 99.9 percent Dihydrogen gases were purchased and were used to supplement and establish the desired ratios. The reformed syngas composition was supplemented to the levels shown in Table 5.

Table 5: Supplemented Reformed Syngas Composition

Component	Percent
Hydrogen	47.08
Oxygen	0.07
Nitrogen	7.93
Methane	3.08
CO	27.33
Ethane	0.57
CO2	12.49
Propane	0.16
iso-methane	0.51
Methane	0.05
iso-Pentane	0.14
Hexane	0.00

Source: AWS

The initial FT feed of supplemented reformed syngas has a molar Dihydrogen: Carbon monoxide ratio of 1.7:1 and was varied during FT operations to an end ratio of 1.5:1. The initial feed of 1.7:1 focused production of FT liquids which typically is characterized by a boiling point less than 660°F. These liquids characteristically carry the Fischer-Tropsch Liquid classification. These FT liquids have a pour point within ambient temperature ranges, and therefore are in a primarily liquid form during normal conditions.

As the ratio approached 1.5:1, the reactor produced liquids with a boiling point greater than 660°F. These liquids are generally classified as waxes with high pour points and usually take a solid form at normal ambient temperatures.

The FT liquid with a Boiling Point<660°F was analyzed through liquid chromatography and the molecular signature was compared to consumer available pump diesel, purchased at a retail location, whose composition was tested on the same machine. Their respective carbon chain numbers of the two samples are shown in Table 6.

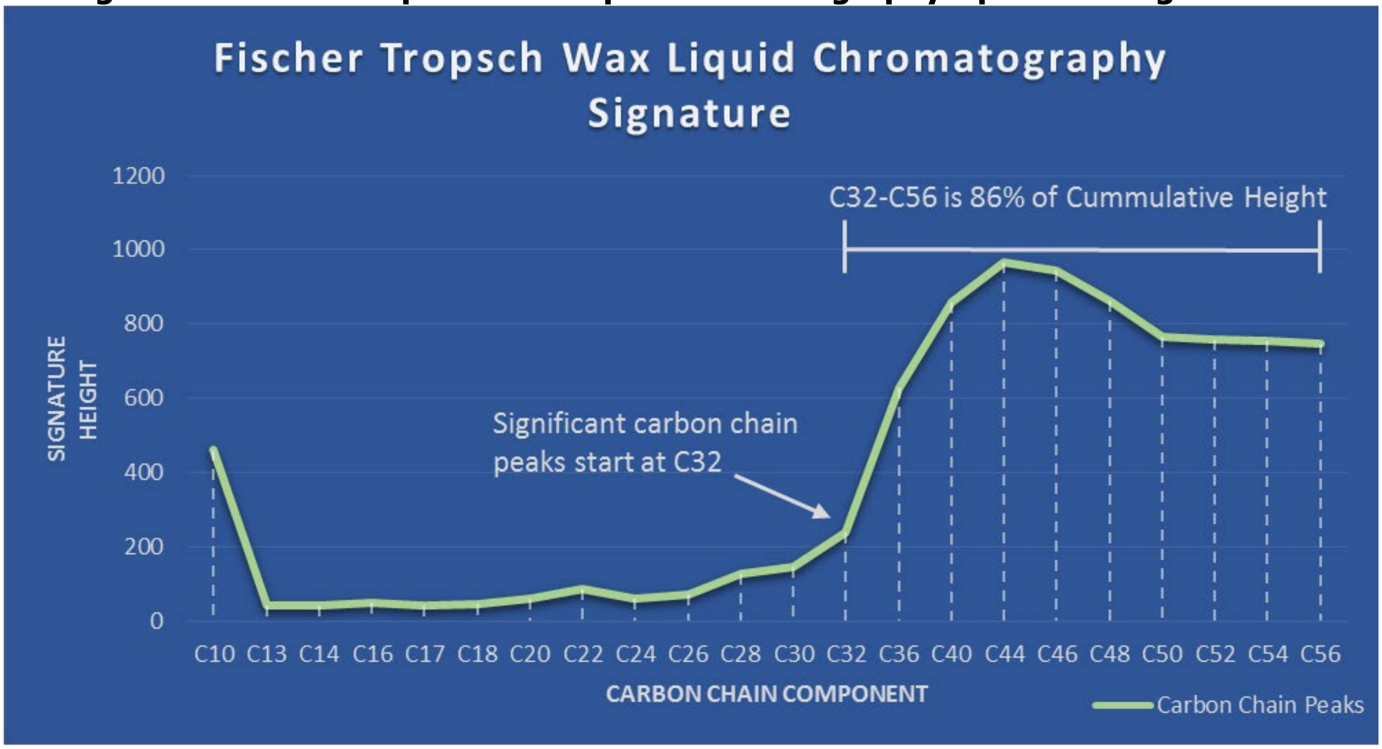
Table 6: Carbon Length Composition Pump Diesel vs Fischer-Tropsch Liquid

Sample	**Pump Diesel**	**FT Liquid**
Component	**Percent**	**Percent**
C10	8.99	13.37
C13	N/D	N/D
C14	26.31	49.28
C16	24.89	15.30
C17	N/D	N/D
C18	7.17	6.09
C20	8.62	4.87
C22	8.73	7.34
C24	5.62	1.53
C26	6.90	1.33
C28	2.77	0.87
C32	N/D	N/D
C36	N/D	N/D
C40	N/D	N/D
Diesel Carbon Fraction C13-C26 Percent	88.24	85.75

Source: AWS

The subsequent FT wax product generated was also tested via liquid chromatography. Its signature is shown in Figure 8.

Figure 8: Fischer-Tropsch Wax Liquid Chromatography Optimized Signature



Source: AWS

Figure 9: AWS and Scott Brothers Staff with Liquid and Diesel Products

Source: AWS. From left to right: Steve McCorkle with initial liquids produced by FT reactor, Michael Bagtang with wax product produced by FT reactor, and Bruce Scott with distilled diesel product.

2.4 Data Analysis

2.4.1 Gasification

The low oxygen percentage and the majority hydrogen, methane, carbon monoxide, and carbon dioxide percentages reflected in Table 1 indicates pyrolytic conversion of dairy manure occurred in the gasifier, which is to be expected. The consistency of syngas composition and production was tested incidentally by the varied feed rate from the inconsistent density of dairy manure from the storage batch, which had pockets of compaction. The manure in the feed reflected very consistent moisture content, determined from samples gathered during gasifier operations, validating the manure overall had a consistent British Thermal Unit value for pyrolysis.

2.4.2 Steam Methane Reforming

The high hydrogen percentage and relatively low methane percentage reflected in Table 3 indicates a near complete catalytic conversion of the feed natural gas, syngas, and steam to the hydrogen product in the steam methane reformer. The reformer, by design, does not provide carbon monoxide selectivity. Its design and catalyst are suitable to produce hydrogen gas as the main product in a water-gas shift reaction, achieving near 100 percent conversion.

2.4.3 Fischer-Tropsch Reactor

The product liquids generated by the FT reactor reflect a very similar composition to that of pump diesel, with a composition difference of less than 2.5 percent to that of consumer available pump diesel reflected in Table 6. The inevitable percentage of premature chain termination under the low Dihydrogen: Carbon monoxide ratio would result in the production of liquids of medium chain hydrocarbons, which is typical of the diesel fraction in FT liquids.

The product wax generated by the FT reactor has a liquid chromatography signature that favors carbon chains greater than Carbon 32, reflecting a high solid paraffin wax composition, as shown in Figure 6. Note on the LC signature in Figure 6 that peaks did not start to form until Carbon 28, and significant peaks started at Carbon 32. The largest area under the curve is in the Carbon 32-Carbon 56 range, indicating a composition of primarily paraffinic long chain hydrocarbons. By maintaining a low Dihydrogen: Carbon monoxide ratio, the reaction would be pushed towards hydrocarbon chain propagation and result in chain termination in the longer hydrocarbon chain range, such as waxes.

The approach (starting with a 1.72:1 Dihydrogen: Carbon monoxide ratio and ending toward a 1.55:1 Dihydrogen: Carbon monoxide ratio feeding the FT) was to assure the production of liquids and waxes in the shortest time available for the test run. By manually maintaining the temperature within a tight range +/- 3 Fahrenheit during the test (not easily done in an industrial practice on a large scale), we were able to study the selectivity and the chain spread probability due to variations in flow rates, fortuitously allowed to us by periodic slip of back pressure valves. Hydrogen exhibits a significantly different compressibility factor than other gases, including that of helium. The flow variance due to slight, but sudden pressure change will result in a magnified influence on hydrogen concentration and fugacity, consequently affecting the reactant mix and activity coefficients within the reactor. These changes were stepped, and the new values persisted for some period of time, resulting in observable differences in performance.

The collected data indicates a very good correlation between changes in hydrogen mole fractions and the minor change in flow rates resulting from pressure differentials. Combined with the sensitivity of the catalyst to hydrogen concentration and contact times, we were able to record a direct qualitative effect of critical parameter changes on the hydrocarbon chain spread probability of the syngas.

The initial flow rate was intentionally kept low to set the reactor up. This flow rate was below critical values, causing an inadequate probabilistic contact with the catalyst surface, and mostly generating methane due to the much higher mobility of hydrogen at the given temperature than exhibited by carbon monoxide. As the flow rate was increased towards the target 6 liters/hr-gm-catalyst, we produced liquids in the Carbon 14 to Carbon 26 range, as is expected with an increasing hydrogen mole fraction near the catalyst surface. Though not confirmed, it was postulated that this mole fraction to be suitable to give a local Dihydrogen: Carbon monoxide ratio of approximately 2.0. An accurate availability of this ratio at the catalyst surface produces liquids in the range as collected. Industrial slurry-based reactors vary in ratios due to residence times, and therefore produce a wide spectrum of liquids. As flow stabilized and reached the low Dihydrogen: Carbon monoxide ratio we initially started with, we observed a very consistent chain propagation into the paraffin wax range. We continued at these operating parameters until the end of the test run, resulting in a high yield of paraffin wax.

Chapter 3: Conclusion and Recommendations

3.1 Conclusions

Operation of the various components in the AWS system performed with excellent results. Each component's output was consistent, and the FT reaction yielded very high-quality products.

A quantitative summary interpretation of the Gas Chromatograph analysis from the FT operation can be made as follows:

- Throughout the test run, we were able to achieve >70 percent carbon conversions. In any catalytic reaction system, initial conversion rates typically drop within 4-6 hours of operation. Industrial average start rates are typically slightly lower than 65 percent and stabilize around 50 to 55 percent. During the test run, we did not see the conversion rate drop, but we can expect that it would have dropped over time to 55 percent-60 percent.
- During the initial part of the test, when flow rate was deliberately kept low, the system produced a spike in the methane mole fraction of the exit gas, as is expected from high hydrogen availability and simultaneous increase in space velocity, both deterrents to chain propagation.
- As flow reached and stayed within the ideal reaction range, we saw a period of liquid production very consistent with theoretical predictions.
- Soon after, the system started producing high molecular weight paraffin waxes.
- Overall liquid/wax production from converted carbon was 40 percent, which is on the higher end of industry average.
- Once the system stabilized, nominal amounts of methane were produced, consistent with what the chain propagation probability factor would predict.

Generally, we were successful in converting maximum syngas to medium and long chain hydrocarbons; however, we were also were fortunate to see benefits from some unexpected variations in the system performance. This experience will give us excellent insight on the design criteria for the larger scale commercial system.

3.2 Lessons Learned

There were many of lessons learned, per se, during the practical implementation of the process through both the primary equipment and overall system. The following is a list of hindsight epiphanies that intensive planning and multistage operational development previously either overlooked or underemphasized.

- Gasification
  - Need a method to immediately know and monitor how much material is being fed into the gasifier per cycle and per unit time
  - Need a faster way to cool the biochar when exiting the gasifier
  - Need a dust suppression system for when the char exits the gasifier and travels through the discharge auger
  - Need a position adjustable flame detector that follows the flame from the burner as it climbs or decreases so that a flame fault will not become present as often

  - Need a storage location for the biochar that will allow it to cool without it continuing to thermally decompose
  - Need a manure feed that maintains the same feed rate while auto-adjusting for consistency variability
  - Test ports and testing equipment should be readily available for each part of the process
  - Real time gas flow and gas volume records are very important
  - Pressure gauges on every vessel is needed
  - There were lessons learned in "you don't know what you need until you need it"
    - Have accounts set up with local suppliers to secure any critical items locally instead of waiting on shipping; inventory more critical parts
    - Budget overnight shipping on critical items
  - Contingency equipment is needed to always be in a ready state
- Steam Methane Reformation
  - A more detailed method of pressure testing piping should be implemented
  - A check list to verify that all components that are a part of a system have been verified for operation so that everyone is on the same page and nothing is overlooked
  - Flame height sensor needs variable positioning ability
  - Having temporary piping that is quickly implementable is excellent for contingencies
- FT Synthesis Reactor
  - Work done by outside contractors needs to be validated by internal personnel for correct installation
  - Piping inlet and outlets need to be verified for correct flow direction and correct medium transportation
  - Critical and/or specialty components such as compressors, heaters, catalyst, flow regulators, etc. should have replacements on-site and available for immediate replacement in the event primary components become inoperable.
- Gas Mixing
  - It was initially stated to the CEC that a Pressure Swing Absorption apparatus is normally necessary to create the gas ratios needed to utilize the current FT reactor in conjunction with the other modules on site. Due to the high capital cost and lack of availability of different Pressure Swing Absorptions to rent for the trials, as well as not knowing the optimum chemical ratios required for a PSA suited to our reactions, it was described to the CEC to use bottled gas for this round of testing to supplement the syngas generated by both the gasifier and steam methane reformer in order to create the needed gas composition for FT synthesis to occur to create the desired FT products. Textbooks and chemical engineering consultants supported the bottled gas supplementation idea for the following reasons:
    - Due to the high pressures of the syngas storage system, it would have a high enough entropy to create a well-mixed system
    - Volumetric flow calculations validated that the concept was feasible

        - The presence of a gas chromatograph in order to quickly test gas compositions stored and in-transit instilled confidence that we could determine what bottled gas supplement were needed
    - In practice, supplementing syngas composition with bottled gas created an issue with accurately analyzing the gas compositions. By feeding a much higher pressure, low volume bottled gas into the syngas storage system, which is at a relatively low pressure but considerably higher volume, we did not have a high enough entropy to create a well-mixed, homogenous composition. Accurate gas compositions were not capable of being tested until the gases were blended under their own pressures several hours later.
    - Supplemental gas would stratify towards the top of the tank, causing a spike in the needed ratios, and settle after several hours. Realizing this, it was conceived to spike the needed gas ratios to produce FT liquids, and as the ratios dropped over time due to settling and mixing, the lower ratios would feed the FT reactor, producing the more valuable wax product.
    - During the time of quote inquires for securing bottled gases, a quote was also requested for a gas mixing device. Although that the bottled gases could arrive in the needed timeframe, the gas mixing device would not arrive on time to meet this round of CEC testing. It is still desired to purchase a proper gas mixing device for future testing and operations.
    - It was realized that improper gas metering equipment was utilized since that the composition of the syngases would not correlate correctly to a flow meter designed for natural gas, air, or a number of standalone gases, causing some confusion with what was read versus what actually flowed.

3.3 Further Work

The recent passage of the National Institute of Food and Agriculture's Biomass Research and Development Initiative in March 2015 has created a joint program between the National Institute of Food and Agriculture and the U.S. Department of Energy to develop economically and environmentally sustainable sources of renewable fuels and bio-based productions. Funding comes from both the Department of Energy's Office of Energy Efficiency and Renewable Energy and the U.S. Department of Agriculture National Institute of Food and Agriculture. Agricultural Waste Solutions, Inc. has accepted a collaboration with researchers from Washington State University Center for Sustaining Agricultural and Natural Resources to represent gasification and renewable diesel conversion technology on a U.S. Department of Agriculture/U.S. Department of Energy Biomass Research and Development proposal from Washington State University utilizing the AWS-Scott Dairy pilot facility technology.

3.4 Commercialization Potential

The commercialization potential of the AWS technology solution demonstrated with this project is very high. The dairy industry alone has outlined requirements to implement over 2600 manure to renewable energy systems on U.S. farms by 2020 in order to meet their greenhouse gas emissions reduction commitments made to the White House for the Biogas Roadmap Plan. The entire worldwide animal agricultural industry is facing similar requirements to reduce the air, water and soil pollution created by excess quantities of manure, and incumbent technologies that generate electricity are facing increasing difficulties obtaining permits in the more stringent regulatory environments such as California and the European

Union. Electricity generation from farms is also experiencing decreasing feed-in tariff incentive rates as wind and solar projects populate the grid and Renewable Portfolio Standards goals are met. Diesel fuel is the most utilized form of energy on farms, and all of the by-products of the AWS solution can be either utilized on the farm or sold for high-value use and revenues off the farm. AWS intends to create new profit centers from manure in order to help farmers sustain the economic cycles of farming as well as lead and sustain environmental and social responsibilities. The demand for low carbon transportation fuels is rapidly increasingly worldwide, and the AWS solution converts one of the most polluting waste forms in the world into the cleanest burning diesel products available on the planet.

AWS plans to prove the commercial operational viability of the technology solution demonstrated with this project by enhancing the process controls and automation of the system in order to operate on a fully continuous basis for several months. AWS is planning larger scale commercial projects and will qualify and validate any technology and process enhancements required for the commercial projects at the AWS-Scott Brothers facility. AWS will apply for the CEC Commercial Solicitation in 2015 and, if successful, will utilize the grant proceeds to scale up the size of the FT system at Scott Brothers Dairy Farm to the same size as the gasifier, so that all of the manure at Scott Brothers Dairy Farm can be converted into FT diesel products and thereby demonstrate the economic viability of a small-scale AWS technology solution on an average sized farm such as Scott Brothers Dairy Farm.

Challenges facing the Agriculture/Dairy industry in California and how AWS's technology can solve problems and keep companies in California

- High standards for water and air quality in California
  - Standards in CA are most similar to European Union
    - European Union companies looking for technology that's successful in California
    - Other states too since they know their regulations will eventually catch up

GLOSSARY

AGRICULTURAL WASTE SOLUTIONS, INC. (AWS)–A company that allows global farmers to continue producing the world's safest food in a sustainable manner – socially, economically and environmentally. The AWS process creates a profit center for farmers while protecting the environment and improving the lives of those that connect or intersect with agriculture. AWS converts manure and ag wastes into renewable diesel, clean water and fertilizer.[1]

FISCHER-TROPSCH PROCESS (FT)–Converts carbon monoxide and hydrogen into oils or fuels that can be substituted for petroleum products. The reaction uses a catalyst based on iron or cobalt and is fueled by the partial oxidation of coal or wood-based fuels such as ethanol, methanol, or syngas, typically coming from an adjacent gasifier.[2]

SYNTHETIC GAS (SYNGAS)–A mixture comprising of carbon monoxide, carbon dioxide, and hydrogen. The syngas is produced by gasification of a carbon containing fuel to a gaseous product that has some heating value. Some of the examples of syngas production include gasification of coal emissions, waste emissions to energy gasification, and steam reforming of coke.[3]

---

[1] Agricultural Waste Solutions, Inc. is available at www.agwastesolutions.com/about-aws/

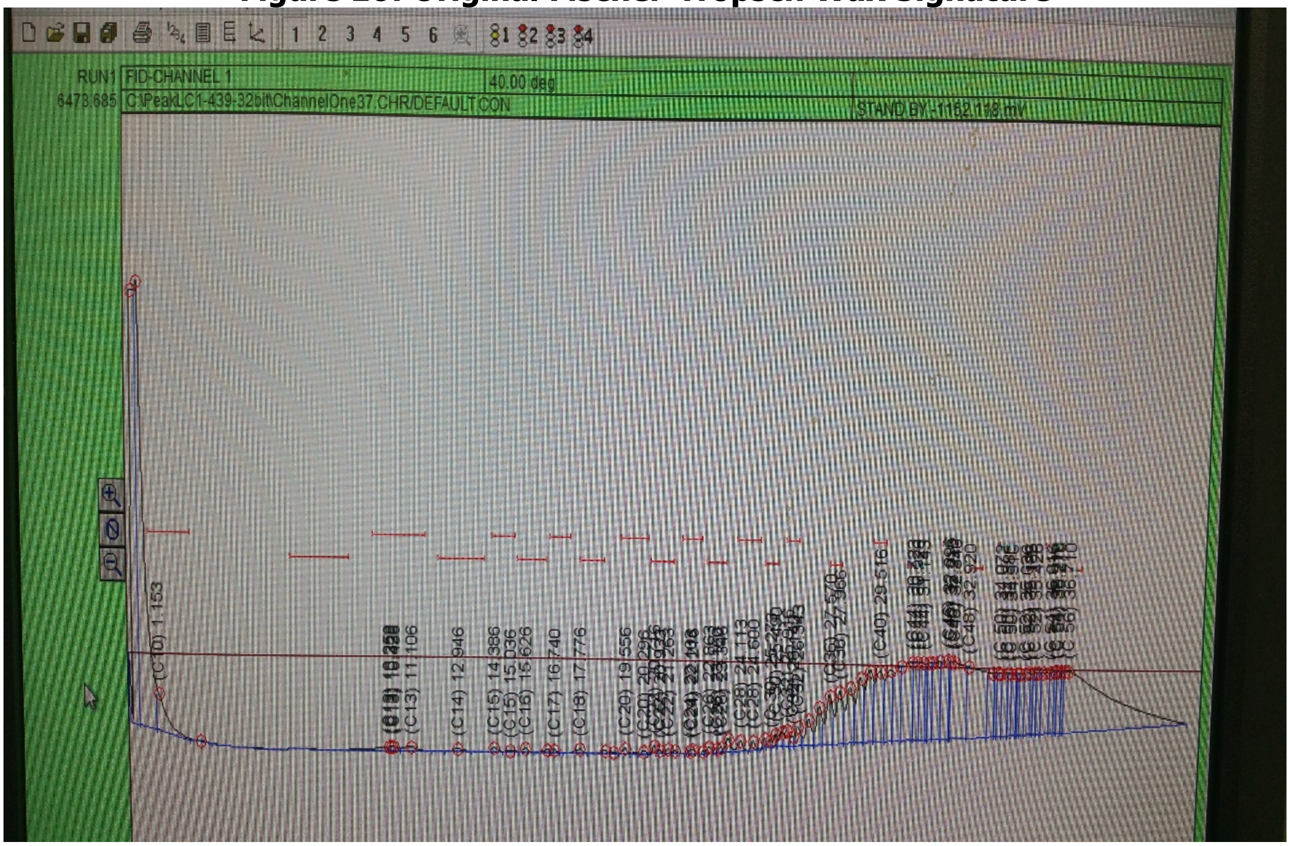
2 Fischer-Tropsch Process is available at https://www.sciencedirect.com/topics/engineering/fischer-tropsch-process

3 Synthetic Gas is available at http://biofuel.org.uk/what-is-syngas.html

APPENDIX A: Supplemental Photos

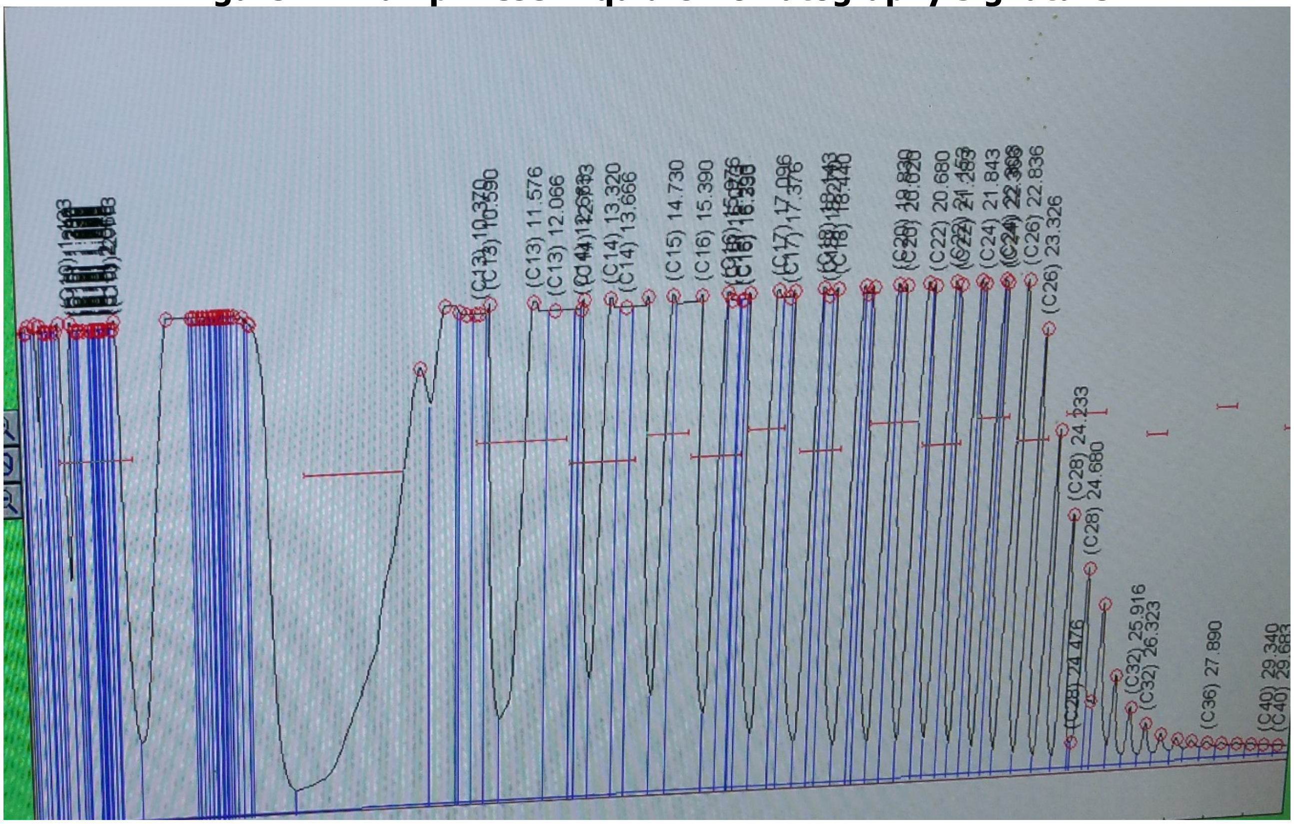
Figure 10, 11 and 12 are supplemental photos showing the original Fischer-Tropsch wax signature, pump diesel liquid chromatography signature, and the Fischer-Tropsch Liquid Chromatography signature.

Figure 10: Original Fischer-Tropsch Wax Signature



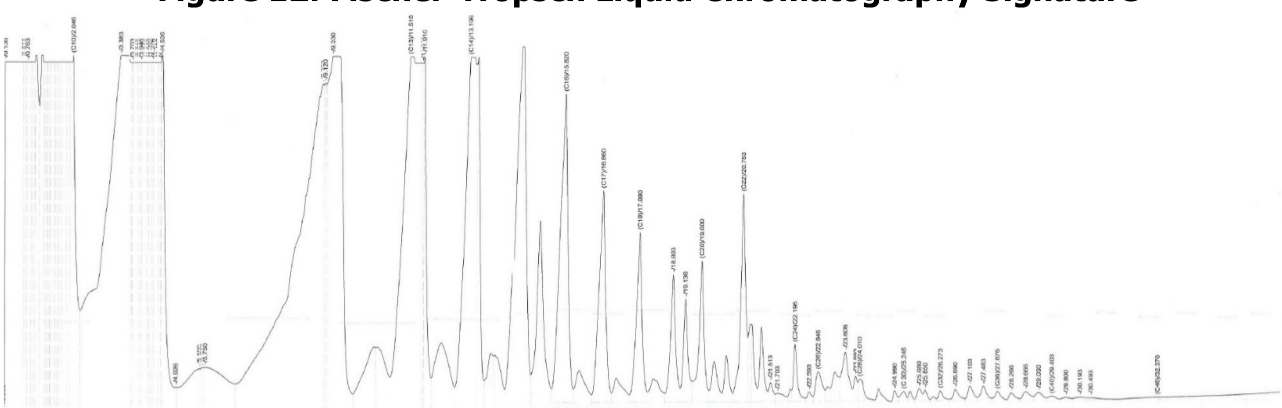
Source: AWS

Figure 11: Pump Diesel Liquid Chromatography Signature



Source: AWS

Figure 12: Fischer-Tropsch Liquid Chromatography Signature



Source: AWS