Production of Synthetic Fuel from Anaerobic Digester Gas

Lyman J Frost, Joseph J Hartvigsen, S. Elango Elangovan Ceramatec, Inc., Salt Lake City, UT 84119 USA <u>lfrost@ceramatec.com</u>, <u>jjh@ceramatec.com</u>, <u>elango@ceramatec.com</u>

ABSTRACT

This paper discusses research conducted at Ceramatec related to small scale Fischer Tropsch (FT). The system designed and tested by Ceramatec indicates the ability to produce a modular, road-transportable system for the same capital as large plants. Ceramatec has used its non-thermal plasma catalyzed autothermal reformer to reform anaerobic digester gas and generate synthesis gas as feedstock for this FT design. In combination, the unit provides the ability to generate synthetic fuels at remote locations from waste products.

Keywords: Fischer Tropsch, synthetic fuel, biofuel, modular synthetic fuel plants

INTRODUCTION

Ceramatec has been involved in research associated with synthetic fuels for a significant period of time. It has demonstrated the ability to produce Fischer Tropsch (FT) fuels from a variety of feedstock sources (e.g. coelectrolysis of steam and carbon dioxide, gas output by an anaerobic digester, natural gas, and heavier hydrocarbons). Ceramatec started not with a technology but with an objective to design a system that could eventually be built on a small scale for the same operating and capital cost that large, world-class FT plants are built. Since there are limited sites that can provide the volumes of natural gas needed for these larger plants, a solution to smaller volumes of hydrocarbons to liquids was needed.

The energy industry has developed a model for economies of scale of building very large, very efficient, and permanently sited synthetic fuels plants. In order to process the diverse, dispersed, and small field resources that are available, a different model is required. The Ceramatec vision is a mass-produced modular unit that is sized to be road transportable, constructed of normally available materials in a factory, and designed for minimum capital and operating cost. What is lost in plant size is made up for in number of plants produced, and by mass manufacturing of innovative designs developed using modeling tools and developed around advanced catalysts and supports. The economics simply don't work for one-ofa-kind designs, built on-site for a small and transient feedstock. Ceramatec's reactor design philosophy attempts to reduce the costs and risks associated with reactor design, fabrication and operation by the following means:

- Using fixed bed reactors
- Limiting reactor train module size to 12"x12"x48" for over the road mobility
- Employing removable catalyst bed elements for offsite catalyst service
- Designing pressure boundary components fabricated from standard industrial piping and fittings
- Design for thermal management based on high activity catalysts
- Simplify the process scheme to minimize capital
- Achieve low thermal variation in reactor radial and axial profiles

TECHNICAL

Ceramatec successfully demonstrated a XTL reactor element at 43mm diameter and expanded this to a 100mm diameter reactor. Reactors are interoperable with a variety of structured reactor inserts and can be charged with highly active conventional or hybrid catalysts.

A Comsol multi-physics model was used to maximize the total reactor production rate by varying seven parameters defining the profile geometry. The total catalyst volume productivity was maximized subject to a constraint on the limiting temperature within the domain. A Monte-Carlo technique was used to find starting points for subsequent Nelder-Mead optimization to converge on local optima. This approach yielded some non-intuitive reverse taper fin solutions where heat gathering surface area was more critical than heat (Figure 1).



Figure 1: Insert for thermal transfer

Ceramatec has an established synthetic fuels laboratory infrastructure with sufficient syngas generation and compression capacity to supply a 2 BPD reactor. The current laboratory implementation of this reactor is a ¹/₄ length implementation of the 100mm reactor with a removable catalyst tube and a fixed cooling jacket. The cooling jacket features dual mode cooling with a forced convection pass on an annular zone in direct contact with the catalyst tube, surrounded by a boiling coolant outer shell. The forced convection pass coolant is held above the saturation pressure while the outer shell coolant is at saturation pressure. As the thermal stability of the 100mm diameter reactor is now proven, a 7-tube, ¹/₄ length, 1 BPD reactor is in design to demonstrate a larger number of reactor tube elements.

The ¹/₄ BPD GTL laboratory system is fed by a three (3) inch natural gas pipeline. After passing through a sulfur guard bed to remove any sulfur compounds, the synthesis gas is generated by a Ceramatec designed non-thermal plasma catalyzed reformer. This reformer is capable of processing up to 100 MSCF per day of high-BTU natural gas (i.e. enough for ~ 10 BPD of FT liquids). Figure 2 shows the reformer (~8' high; ~2' diameter).



Figure 2: 10 BPD Plasma Natural Gas Reformer

After production, the synthesis gas (CO and H_2) goes through several stages of compression. The first compression step uses a two-stage compressor with cooling to condense moisture after each stage (Figure 3). The synthesis gas exits the compressor at about 200 psig and is piped to an intermediate storage facility located external to the laboratory. When the intermediate storage in a 240 gallon 200 psig tank. When the tank is full, a second step of compression increases synthesis gas pressure to 800 psig and stores the material in two 500 gallon tanks (Figure 4). This serves as a buffer feedstock to the Fischer Tropsch reactor located within the laboratory.



Figure 3: Two-stage compression with cooling



Figure 4: Syngas storage (800 psig) and compressor

Each of the compression steps is sufficient to provide enough pressurized synthesis gas for ~ 2 BPD of FT liquids. The synthesis gas is then ready to be fed to the FT reactor. The reactor input is regulated to about 300 psig and is preheated prior to introduction into the FT reactor.

The FT reactor (Figure 5) operates at ~ 300 psig and ~225[°] C with internal heat transfer media to produce an even catalyst bed temperature in both axial and radial directions. The internal heat transfer structures have demonstrated the capability to maintain bed temperatures in a 4" reactor with a Co-Ru catalyst that varies by $< 10^{\circ}$ C.



Figure 5: FT reactor system (yellow skid)

The reactor has automated product collection for both light and heavy hydrocarbons (green skid in Figure 5). The

system has a dual cooling system with integral cooling. A synthesis gas recycle system is also used to optimize utilization. The recycled synthesis gas is re-pressurized prior to mixing with the fresh feedstock. The cooling loop operates at atmospheric pressure by use of a synthetic coolant. At full production with a catalyst of appropriate activity the FT reactor (\sim 5' high and 4" diameter) is capable of producing \sim ¼ BPD of FT liquids.

The carbon number distribution depends on the particular catalyst and the operating conditions of the reactor. Figure 6 shows the carbon distribution with two different catalysts. The distribution in blue is with a standard Ceramatec Co-Ru catalyst and the distribution in red is with a hybrid catalyst that is designed to terminate carbon polymerization. The hybrid has a special support structure.



Figure 6: C distribution standard & hybrid catalyst

The reactor has shown very stable operation and the catalyst used has demonstrated repeatable performance. The reactor was run for five hundred (500) hours and multiple product samples taken. The results tracked very well over time (Figure 7).



The stability of the reactor and catalyst has encouraged Ceramatec to design a 10 BPD pilot plant using the same components. The design was done in conjunction with an engineering and construction firm experienced in pilot plant construction. The 10 BPD pilot consists of three skids (skid 1 - 12'x12'x36'; skid 2 - 12'x12'x30'; skid 3 - 12'x12'x24') and a container for the synthesis gas

compression. The plant is designed to operate on natural gas that has been largely cleaned of any sulfur compounds. The reformer operates in an autothermal mode using air and steam as oxidants. An artist's rendition of the facility is shown as Figure 8.



Figure 8: Proposed 10 BPD GTL facility

The compact size of the unit is made possible by the design of the FT reactor, operation of the reformer on air instead of oxygen, and the compact size of the reformer.

Anaerobic Digester Gas

Ceramatec has used gas (~ 75% CH₄, 24% CO₂, other gases 1%) from an anaerobic digester as input to its plasma catalyzed reformer. The overall product flow is shown in Figure 9.

Anaerobic Digester Gas \rightarrow Fuels



Figure 9: Anaerobic digester gas to FT liquids

The biogas is combined with steam and preheated prior to entry to the plasma reformer. Since the reformer is insensitive to sulfur, any H_2S or organic sulfur does not have to be removed prior to the conversion to synthesis gas. Additional steam and air are provided to the reformer by separate piping. The synthesis gas does have to be cleaned of sulfur prior to entry to the FT reactor since FT catalysts are quite sensitive to sulfur. The sulfur is removed used an adsorption process. Values for one anaerobic digester gas are shown in Figure 10 and compared to the values for pipeline quality natural gas. As can be seen, the major difference is in the amount of input CO2. This particular gas had undergone sulfur removal before entry to the reformer. A zinc oxide guard bed was still used prior to entry to the FT reactor.

Inputs to the system	Natural Gas	Digester Gas
Methane (CH ₄)	98%	58.3%
	(pipeline	(volume)
	quality)	
Oxygen	Varies	Varies
Air	Varies	Varies
Water	Varies	Varies
CO_2	2% (volume)	39.8%
		(volume)
Outputs from the	Typical	Typical
reformer	Volume %	Volume %
Hydrogen (H ₂)	51.6	42.3
Nitrogen (N ₂)	15.3	15.3
Methane (CH_4)	1.2	.1
C2+	.0	.0
Carbon monoxide (CO)	23.9	23.4
Carbon dioxide (CO ₂)	8.0	18.9

Figure 10: Comparison of digester gas and natural gas

In October, 2015 the United States Department of Agriculture reported that there were 88.5 million head of cattle in the United States. A 2014 Purdue University report indicates that each 1000 pounds of animal produces biomass sufficient for ~ 22 SCF of CH₄ per day. If 50% of this manure can be used, this is equivalent to ~ 78 MBPD of FT liquids.

A simulation of a large feedlot operation capable of providing ~ 1 MMSCFD of anaerobic digester gas (~75% CH4, 24% CO2) was done with VMGSim ®. A special FT module was utilized to obtain the expected product yields. The results showed the generation of ~ 100 BPD of FT liquids using a cobalt hybrid FT catalyst. The same system generated about 230 BPD of produced water. The simulation flow is shown in Figure 11. Unconverted tail gas is used to provide heat energy to the reformer for generation of steam and preheat of entering feed elements.



SUMMARY

Ceramatec has been conducting research in the design of systems for the production of FT liquids. Most of the research has been done using natural gas as a convenient feedstock. Other feedstock options have been tried, including anaerobic digester gas, synthesis gas from the coelectrolysis of steam and carbon dioxide, and various reformed heavy hydrocarbons. The results demonstrate the ability to construct a modular, transportable system that is cost effective. Current laboratory data indicates that it is possible to build FT systems in this size range that will match the efficiency, capital cost per BPD capacity, and operating cost of larger FT plants. This provides the capability to utilize hydrocarbon sources that are not presently cost effective.

ACKNOWLEDGEMENTS

Portions of the FT reactor testing and catalyst design have been supported by the State of Wyoming and by the Office of Naval Research. A majority of the funding has come from private sources.