Removal of Synthesis Gas Pollutants and Liquid Fuel Synthesis

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CERAMATEC
TOMORROW'S CERAMIC SYSTEMS

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EXECUTIVE SUMMARY ABSTRACT

The Fischer Tropsch process for the conversion of synthesis gas into liquid fuels was first developed and commercialized by the Germans 75 years ago, and has been practiced continuously in South Africa for 60 years. However, numerous prior attempts in the US have failed to proceed to commercialization due to several major technical and economic barriers. The technical challenges stem from the fact that effective thermal management of the exothermic FT reaction requires the use of small reactor tubes and complex cooling strategies. The resultant FT reactors were large and complex to construct and operate. The solutions to address the technical challenge relied on economy of scale to make the process commercially viable. Making FT plants that are smaller to match available resource and thus more suited for distributed production of fuel is even more difficult to achieve. Under the program (UWSER49372CERAM) managed by the School of Energy Resource at the University of Wyoming, Ceramatec has demonstrated production of liquid hydrocarbon fuel from syngas using a modular Fischer Tropsch unit.

Ceramatec has teamed with the Western Research Institute to demonstrate a novel FT reactor system that will convert coal-derived syngas to liquid hydrocarbon fuel. Under this project, with support from the State of Wyoming and the Department of Navy, Ceramatec has designed a modular FT reactor that specifically addresses the challenges outlined above. The reactor was demonstrated to produce liquid hydrocarbon fuel at Ceramatec's laboratory. The Ceramatec reactor was also tested at the Western Research Institute using a methanation catalyst to produce synthetic methane from coal-derived syngas.

GENERAL TECHNOLOGY DESCRIPTION

Gasification

Gasification of coal is a process that can provide a highly efficient and environmentally friendly method for coal utilization. Western Research Institute (WRI) owns and operates a pilot-scale fluidized bed gasifier at its Advanced Technology Center in Laramie, Wyoming. The gasifier is a bubbling fluidized bed system specifically designed for the gasification of low-rank coals and can use either air or oxygen as an oxidizer. WRI has operated the device on several Wyoming coals with Wyodak coal being the most common.

The fluidized bed is contained within a refractory-lined vessel into which the coal is added via a lock-hopper system at a rate of 20-50 lb/hr. Ash and unconverted carbon (char) exit the vessel through a discharge pipe and the fines are collected in a cyclone downstream of a disengagement section. The operating temperature range of the gasifier is 1250-1800°F (700-1000°C) with a pressure range of 0-50 psig (0-3.4 barg). Typical syngas (dry basis) characteristics of the fluidized-bed gasifier appear in Table 1 below.

Table 1. Syngas composition from PRB coal, for air- and oxygen-blown conditions

	Air-Blown	**O_2-Blown**
H_2	19.7%	38.5%
CO	14.5%	28.5%
CO_2	13.3%	26.1%
CH_4	1.4%	2.8%
N_2	51.0%	4.0%
BTU/dscf	117	230

The system will work across a broad range of temperature and pressure conditions to allow for flexible test plans. The system can provide syngas for testing at temperatures between 5 ^{o}C and 200 ^{o}C, and pressures of up to 300 psig after subsequent compression.

A second gasifier located and operated at WRI is somewhat different in that it does not directly contact the coal with either air or oxygen. This feature prevents dilution of synthesis gas with nitrogen and eliminates the need for a costly oxygen plant. The design is based on staged, indirectly heated gasification (i.e. pyrolysis), which allows greatly improved control of the temperature and then the resulting synthesis gas. The gasifier is designed to control the oxidation of the feed material to produce higher quality synthesis gas without significant carbon dioxide.

Fischer Tropsch

Fischer Tropsch (FT) is a process for synthesis of fuels from carbon monoxide and hydrogen that was first used on a production basis by the Germans during WWII. FT synthesis is a polymerization process where a CH_X species is added to a growing aliphatic chain. Most FT facilities built today (e.g. the Oryx gas to liquids plant built in Qatar) are very large, expensive facilities that entail large capital expenditures and associated risk.[1]

Ceramatec has two unique technologies that are being offered as part of this project. The first is a catalyst that is projected to produce high yields in the desirable range of hydrocarbon chains. This catalyst is under development with Department of Defense funding. The second unique technology is a compact, transportable fixed bed FT process. This process has also been proven at a laboratory scale and operated for substantial periods of time. Under the current project, Ceramatec has modified the system to include improved liquid product collection system, recycling of unreacted syngas, and demonstrated unattended extended operation. In addition, a multi-tube FT reactor with vastly improved thermal management configuration has been designed and built. The unit, consisting 12 tubes, can be operated in a modular fashion i.e. one or more tubes at a time to provide a high turn down ratio.

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1. André Steynberg, Mark Dry, Fischer-Tropsch Technology, Elsevier Science, 2004.

Selective yield FT catalyst

In the traditional Fischer-Tropsch method, synthesis gas (mixture of CO and H_2) is reacted in the presence of either iron or cobalt-based catalysts, to produce paraffinic hydrocarbons, containing typically up to 50 carbon atoms in their molecules, along with small amounts of oxygenates and olefins. Other metals and metal oxides besides iron (Fe) and cobalt (Co) based catalysts have been studied for the FT reactions (e.g. ruthenium). Reaction products are formed on FT catalysts by chain growth (*i.e.*, polymerization) of surface methylenes formed from adsorbed CO. FT reaction pressures are higher than atmospheric (i.e.15-40 atmospheres pressure). These reactions are highly exothermic and temperatures throughout the FT catalytic bed must be maintained at a relatively even and low (230 -250 °C) temperature to insure the formation of the desired longer chain hydrocarbons.

Because of the broad hydrocarbon distribution obtained by standard FT processes, the product stream usually requires upgrading through a series of oil refining processes to obtain conventional transportation fuels. However, products displaying molecular weight distributions narrower than standard FT products have been obtained upon contacting synthesis gas over mixtures of hybrid or composite catalysts such as mixtures of standard FT catalysts and promoted support structures. The narrower molecular weight distribution is attributed to hydrocracking and isomerization of the FT products.

Ceramatec Background FT Technology

Ceramatec has been working with personnel at Brigham Young University to develop catalysts for the selective production of JP5 range diesel fuels (C_9-C_{16}). Standard FT catalysts and reaction conditions result in a broad distribution of products. Catalyst performance is dependent on both composition and microstructure, and microstructure is the result of processing history. Controlled processing is being used to vary the catalyst support, and the deposition of the iron or cobalt upon the support structure. The indications are that this will produce a catalyst that is more selective, active, and stable.

The catalyst is shown in Figure 1 and some of the liquid hydrocarbon product produced during initial runs of the FT unit at Ceramatec is shown in Figure 2.

Figure 1. FeCuK FT catalyst on La promoted 8 mm alumina rings

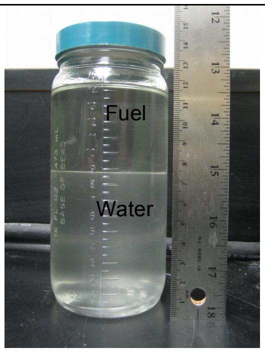

Figure 2. Liquid hydrocarbon product yielded from FT reactor (235 ^{O}C)

The FT reaction as previously mentioned is a surface catalyzed polymerization reaction of methylenes. The general reaction is: $CO + 2 H_2 \rightarrow -CH_2- + H_2O$

In Figure 2, there are two distinct phases present. The liquid hydrocarbons are the top portion and the water is in the lower portion of the bottle. The two products are relatively equal in volume in the shown yield as would be expected based on the reaction chemistry. In addition to the liquid products, the FT reactor yields some gaseous products and solid waxes that are collected and can either be processed or recycled to increase the desired liquid yields. Improvement in the liquid yields generated is affected by a number of the operating parameters of the FT reactor in addition to the effect of the catalyst itself. The ratio of hydrogen to carbon monoxide, bed temperatures, gas mixing, etc., all contribute to the product distribution that is obtained. Work is continuing on improving the yields in the liquids range by catalyst modification and careful control of the applicable parameters.

Compact fixed bed FT unit

Ceramatec’s FT reactor tubes are 18mm ID, with a catalyst-loaded length of approximately 1.8 meters in each tube. The stainless steel reactor tubes, heating elements and cooling passages are embedded in a block of cast or extruded material such as aluminum or ZAMAC (Zinc-Aluminum-Magnesium-Copper) die casting alloy to facilitate thermal management and modularity as shown in Figure 3. Pictures of the modular FT unit in a laboratory arrangement are shown in Figure 4.

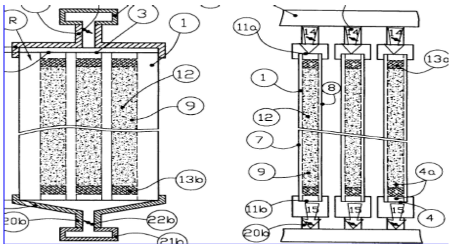

Figure 3. Drawing of FT system from patent

Figure 4. Compact modular FT unit in laboratory environment

DESCRIPTION PROGRESS UNDER WY FUNDING

Syngas System

Ceramatec completed installation of a syngas generation, compression, storage, and delivery system for the synfuels laboratory as part of an ONR project. This facility had not been operated prior to Wyoming project under contract number UWSER49372CERAM. Startup, commissioning and operability enhancements work was conducted jointly with this and the ONR projects. Activities addressed issues of maintenance and operability, increasing capacity, and enhanced automation safeguards in anticipation of unattended operation. The motivation for these latter two areas were to support the greater syngas demand of the larger multi-tube reactors being developed for this project. Ceramatec's original 18mm FT reactor consumes syngas at the rate of about 0.1 SCFM with an iron catalyst, and perhaps as high as 0.6 SCFM using a Co catalyst. The initial syngas production and compression rate of 3 SCFM was sufficient to run the FT reactor with the production system operating at a 20% duty cycle (~34 hours per week).

Figure 5. Low Pressure Compressor and Chillers

However, each tube of the new modular reactor has a catalyst volume five times greater than the 18mm reactor. Therefore, with the larger reactor and highest projected catalyst activity, a continuous syngas production rate of over 3 SCFM will be required even for single tube reactor operation. The lower activity of Fe-based catalyst could allow multi-tube operation at this same syngas production rate. Estimated syngas system operations in 2010 have exceeded 800 hours, with over 150 kscf of syngas produced.

Catalyst Preparation and Characterization

A total of eleven batches of FT catalyst have been prepared during this project in addition to a catalyst that was prepared on an earlier project (FeCuK, aqueous process on 4x6mm low surface area rings) which was the first catalyst tested using the new syngas system. Both FeCuK and CoRu formulations have been prepared using a traditional aqueous co-precipitation method and a proprietary dry process. A variety of high surface area gamma alumina support forms have been used including 1mm cylinder and 1.3mm trilobe extrudates from Saint Gobain, nano powder for microfiber entrapment (with Intramicron STTR from ONR), and an intermediate particle size produced from crushed and classified pellets. All but two of these supports were processed to provide lanthana promotion as is known in the literature. A typical batch size was 200g, though a large batch (1007-1) of FeCuK on lanthana promoted trilobes was produced in sufficient quantity for testing in both the 18mm reactor and the larger 38mm reactor.

These catalyst samples have been characterized using a variety of analytical methods including BET surface area (method of Brunauer, Emmett and Teller), XRD, TGA – both temperature programmed reduction (TPR) and temperature programmed oxidation (TPO), and hydrogen uptake. A data reduction methodology for the TPR/TPA was transported to MATLAB to generate the idealized constant rate temperature schedule for reduction or calcination.

FT Reactor Balance of Plant Development

A number of additions and refinements were made to the existing FT reactor system. Here the FT BOP refers to the system components downstream of the syngas generation and storage system. Some changes, such as installing larger tubing, a higher capacity mass flow controller and larger code stamp product collection vessels, were implemented in anticipation of operating the larger modular reactor design being produced for this project. Other changes were motivated by the need for a greater degree of autonomous operation with remote monitoring and control of the system. Further modifications fell under the categories of improving the reactor stability, safety, data quality, simplicity and economy of operation. The capacity expansion factors were derived by straightforward calculations using data from early runs while the need for most other changes were recognized either by issues arising from our own operating experience or suggestions by FT research experts from a global energy company.

Modification to existing FT reactor

- Gas pressure controlled stainless diaphragm valve backpressure regulator replaced a spring loaded pressure relief valve for reactor operating pressure control.
- A high pressure coalescing filter and blow-down valve was installed to prevent product liquid mist from interfering with the backpressure regulator.
- Microchannel GC hard plumbed to FT inlet and outlet to enable online gas composition monitoring.
- A W-hr meter was installed on the reactor heating circuit to enable calorimetry measurements during operation.

- New LabView application for FT interfacing and testing developed and tested.
- High pressure vane pump specified, ordered, and installed for reactor recycle operation. This pump is too large for the 18mm reactor, but will be used with the larger FT module.
- Refrigerated cooling bath circulation system implemented for chilled product collection
- A high temperature heat transfer fluid pumpled cooling loop (Therminol 59) with a plate fin heat exchanger has been designed. The piping manifolds are being fabricated.
- New hot and chilled product collection vessels of ~20 liter capacity replaced the original ~1 liter vessels. These new vessels were large enough to require being designed and fabricated as code stamped pressure vessels.
- Higher capacity mass flow meters sized for large reactors installed (6-300 SLPM, 25 bar)
- A digital backpressure regulator was installed and tuned. In addition to providing pressure control within the control system software or by remote operator, overall reactor pressure stability was enhanced compared to the spring loaded relief valve and stainless diaphragm backpressure regulators used previously.

Photos of the single tube FT reactor and BOP are shown in Figure 6- Figure 8 below.

	
Figure 6. Ceramatec 18mm single tube FT reactor and system BOP	Figure 7. Recycle pump, chiller circulating pump and backpressure regulation

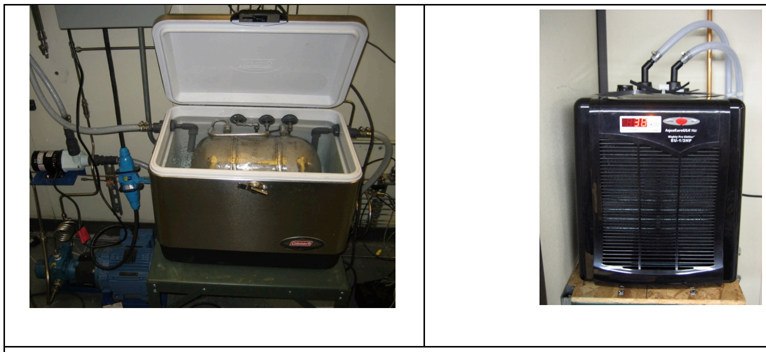

Figure 8. Chilled FT collection vessel (left) and FT product chiller

Five runs have been made with the FT reactor. The liquid and wax product distribution of atypical run is shown in Figure 9 below with a combined liquid-wax distribution and a comparison with JP-8 and off-highway diesel distillate fractions. As can be seen, the combined FT product generated closely matches the carbon number distribution of JP fuels.

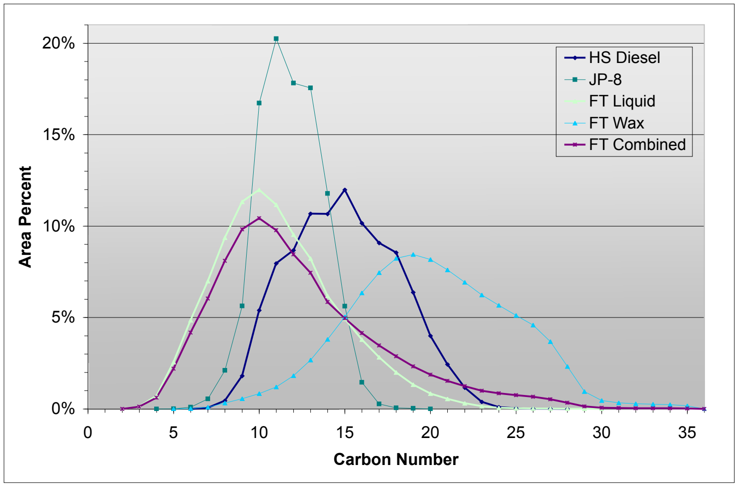

Figure 9. GC Analysis of FT product fractions and comparison with petroleum distillates.

The combined liquid and wax data were used to extract the alpha value for the ASF product distribution. For this sample an alpha value of 0.85 to 0.88 is obtained if species near the high end of the GC resolution are included. If they are excluded, a better fit is obtained which suggests a value of 0.90 to 0.93.

FT Reactor Operation and Catalyst Testing Summary

- Five batches of FeCuK catalyst have been run in the 18mm reactor.

- Catalyst reduction and activation process carried out in the FT reactor
- Over 4 months of reactor operating experience has been gained.
- Collected several liters of FT liquids
- Developing GC methods for analysis of non-condensate gases and liquid products.

Reactor Design and Fabrication

The basis of the reactor design was the reaction cooling duty requirement calculated using the process modeling tool VMGSim with the private FT unit operation module produced by the BYU FT consortium. A volumetric heat generation rate was calculated from the overall cooling duty, which was then used in a 2-D finite element multi-physics model. This model, implemented in Comsol-MP was used to evaluate cooling channel locations and the fin effectiveness of different configurations of the reactor's internal cooling structure.

The objective of the COMSOL multi-physics modeling is to understand the best configuration for the FT reactor cooling structures in order to remove heat efficiently. In order to model the heat transfer in the system, the heat generated in each tube is estimated first. The FT reactor tube is 1 ½" schedule 10 stainless pipe with an overall length of 7' with an active length of 2m. The syngas is fed into FT tube at hourly space velocity of approximately 4,250.

A process model of the FT reactor system has been started using the VMGSim modeling package. As we obtain catalyst activity data and product distribution data we can better define the rigorous FT reactor unit operation inputs for this model to predict the performance of the larger FT reactor being built as a deliverable on this project. The VMGSim process model using the private FT unit operation module (BYU FT Consortium Member access) was used to generate inputs to the COMSOL model. The objective of the design is to obtain a uniform temperature distribution inside a tube and between tubes. The temperature difference inside a tube decreases to 10^{o}C and the temperature distribution between tubes are uniform compared with the configuration shown in Figure 10.

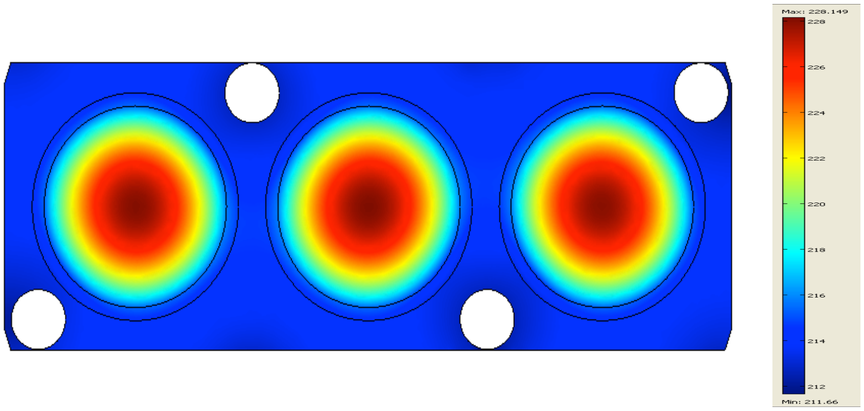

Figure 10. Temperature profile (^{o} C) of the configuration of 4 cooling tubes

Since a significant temperature gradient can develop within the catalyst bed due to the highly exothermic nature of the reaction, and since temperature variations broaden the product distribution, an internal cooling structure, which occupies about 20% of the cross sectional area, was also designed. A thermal model of the revised cooling block and internal fin predicts an internal temperature gradient of only 3°C.

TECHNICAL PROGRESS AT WRI

During the project duration, Ceramatec reactor was operated for a total of 183.5 hours at the Western Research Institute (WRI) Advanced Technology Center. This testing was performed utilizing coal-derived syngas from a fluidized-bed gasifier, and the reactor was loaded with 4 separate batches of methanation catalyst.

The purpose of testing was to stress the reactor thermal management system, and to test a small-scale sulfur removal system for syngas cleanup. The reactor heat management system was equipped with a temperature controlled blower that passes room-temperature air through the non-utilized reactor tubes. This system was wired to the hottest thermocouple in the reactor to prevent thermal runaway of the synthesis system.

Gas analysis was performed online with an SRI Multigas GC utilizing a ShinCarbon column and TCD-type detector.

Figure 11. WRI Fluidized-Bed Gasifier

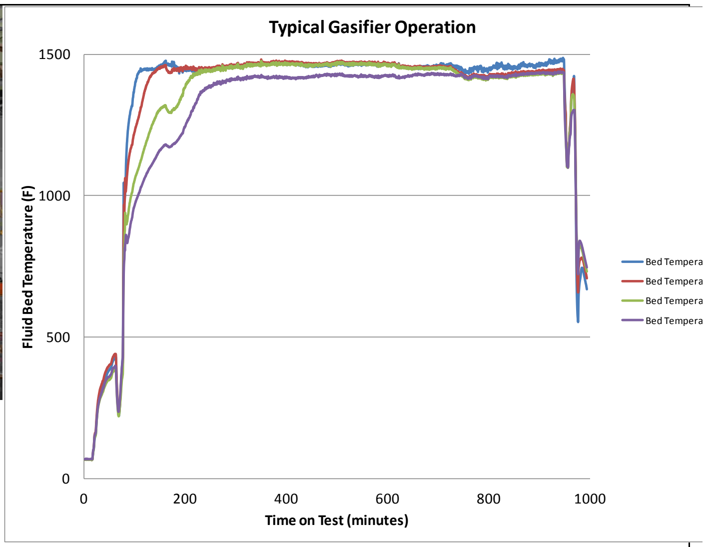

Figure 12. Typical Gasifier Bed Temperatures

Reactor Installation

The reactor and sulfur removal system were shipped from Ceramatec to WRI in February 2011. The reactor was installed adjacent to the fluid bed gasifier and all electrical and process connections were attached. An image of the installed reactor follows in Figure 13.

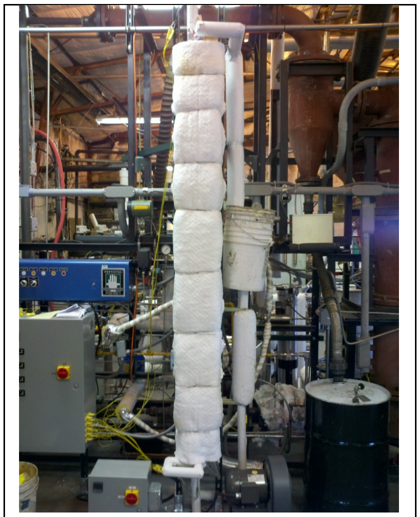

Figure 13. Ceramatec Reactor Installation

As seen in the picture, the small vessel to the left of the reactor is the sulfur removal system. This is a temperature controlled bed packed with two Haldor-Topsoe catalysts. The first was TK-550 CoMo hydrodesulphurization catalyst, and the second was HTZ3 ZnO sulfur sorbent.

The purpose of the testing was to stress the thermal management system of the Ceramatec reactor. Over the course of testing, axial temperature distribution in the reactor was not ideal, and it was not possible to keep the reactor at or near isothermal conditions throughout the catalyst bed. Though the reactor transferred heat quickly, the air used for cooling the reactor block was inadequate for removing the quantity of heat generated. It is recommended that a water- or oil-based heat transfer system be utilized for future iterations of this technology.

SUMMARY AND PLAN

Under the Wyoming funding, Ceramatec and WRI have demonstrated that the reactor design addresses many of the thermal control issues that have been the limiting feature of the conventional FT reactors. Ceramatec's syngas generation and compression system allowed demonstration of syngas to liquid hydrocarbon fuel conversion for extended periods of operation. WRI demonstrated conversion of coal syngas to synthetic methane using Ceramatec's reactor. The project identified additional modifications to the cooling strategy that are needed. Future work will incorporate a liquid coolant to the FT reactor to improve uniformity of temperature in the catalyst bed which will also allow increasing the size of reactor tubes. The increased reactor tube size will reduce the parts count in an FT plant which in turn will improve the economic viability of coal to liquid conversion.