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Project Title: Novel Attrition-Resistant Fischer Tropsch Catalyst

Performed by: RBR@Vision and Gas Technology Institute

THERE IS NO PROPRIETARY INFORMATION IN THIS REPORT

Project Director: Dr. Robert B. Rosenberg
RBR@Vision
28 Lake Ridge Club Dr.
Burr Ridge, IL 60527

Principal Investigator: Dr. Chun Choi
Gas Technology Institute
1700 S. Mount Prospect Rd.
Des Plaines, IL 60018-1804

Authors: Logan E. Weast, Gas Technology Institute
Dr. William R. Staats, RBR@Vision

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Executive Summary

There is a strong national interest in the Fischer-Tropsch synthesis process because it offers the possibility of making liquid hydrocarbon fuels from reformed natural gas or coal and biomass gasification products. This project explored a new approach that had been developed to produce active, attrition-resistant Fischer-Tropsch catalysts that are based on glass-ceramic materials and technology. This novel approach represented a promising solution to the problem of reducing or eliminating catalyst attrition and maximizing catalytic activity, thus reducing costs.

The technical objective of the Phase I work was to demonstrate that glass-ceramic based catalytic materials for Fischer-Tropsch synthesis have resistance to catalytic deactivation and reduction of particle size superior to traditional supported Fischer-Tropsch catalyst materials. Additionally, these novel glass-ceramic-based materials were expected to exhibit catalytic activity similar to the traditional materials. If successfully developed, the attrition-resistant Fischer-Tropsch catalyst materials would be expected to result in significant technical, economic, and social benefits for both producers and public consumers of Fischer-Tropsch products such as liquid fuels from coal or biomass gasification.

This program demonstrated the anticipated high attrition resistance of the glass-ceramic materials. However, the observed catalytic activity of the materials was not sufficient to justify further development at this time. Additional testing documented that a lack of pore volume in the glass-ceramic materials limited the amount of surface area available for catalysis and consequently limited catalytic activity. However, previous work on glass-ceramic catalysts to promote other reactions demonstrated that commercial levels of activity can be achieved, at least for those reactions. Therefore, we recommend that glass-ceramic materials be considered again as potential Fischer-Tropsch catalysts if it can be demonstrated that materials with adequate pore volume can be produced.

During the attrition resistance tests, it was learned that the glass-ceramic materials are very abrasive. Attention should be paid in any further developmental efforts to the potential for these hard, abrasive materials to damage reactors.

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Introduction

Current efforts to develop processes for converting coal and biomass to liquid fuels face many challenges, including high cost. An essential element of most such processes is the catalytic Fischer-Tropsch reaction, which reacts carbon monoxide and hydrogen to form hydrocarbons.

The most cost-effective Fischer-Tropsch reactors use slurry- bed reactors, which, although less costly than fixed-bed reactors, cause the catalyst to physically break down through inter-particle collisions. This catalyst attrition causes changes in operating conditions, decreases conversion and output, fouls process filters and equipment, and contaminates product streams. For Fischer-Tropsch plants to become economically competitive, catalyst materials must be developed that resist attrition in slurry-bed reactors, are highly active catalysts, and are cost-effective to produce.

The goal of this Phase I STTR project, a joint effort by RBR@Vision and Gas Technology Institute (GTI), was to test the technical feasibility of a new type of material that promised to be intrinsically more durable than typical alumina- and silica-supported catalysts currently used.

The project was to measure the attrition resistance and catalytic activity of a conventional Fischer-Tropsch catalyst and samples of the new catalyst material and compare them. If the new material met certain specified performance goals, a Phase II grant would be sought to develop it further.

Proposed Concept

Research is being done by others on methods for treating conventional Fischer-Tropsch catalysts to harden the particles and increase their attrition resistance. However, GTI developed and is patenting a novel approach to producing active, attrition-resistant Fischer-Tropsch catalysts, based on glass-ceramic materials and technology.

Glass-ceramic materials are initially melted from a batch mixture of glass cullet, minerals, and oxide components to form an amorphous glass using conventional glass melting technology and practices. The formed glass particles are then subjected to a controlled heat-treatment process during which crystal nuclei are formed, followed by growth of crystalline grains around the nuclei. The final material may be anywhere from 50-99% crystalline, and the interstitial area between ceramic grains is filled with residual glass. By selecting glass composition and controlling the heating parameters used during the nucleation and growth steps, a wide variety of micro-structured materials can be engineered and tailored to specific uses. Glass-ceramics are a relatively new class of materials, only having been discovered in the 1950s, and their use for slurry-bed reactor catalyst supports is unexplored.

Due to their randomly oriented ceramic grains and composite structure, many glass-ceramic materials such as lithium-aluminosilicate (beta-spodumene) and magnesium-aluminosilicate (cordierite) have mechanical and structural properties that recommend them as highly suitable for use in slurry-bed systems. Several properties of interest for these glass-ceramic materials are shown in Table 1, along with those of some traditional support materials. Lower density is a positive characteristic of the glass and glass-ceramic materials because lower density allows for better fluidization within the Fischer-Tropsch reactor without sinking to the reactor bottom. Many glass-ceramics have exceptionally low coefficients of thermal expansion, and this will help prevent thermally induced stresses from developing within the particles and fracturing them. Glass-ceramic materials are harder and have significantly better fracture toughness (resistance to crack formation and elongation) than amorphous catalyst supports.

Table 1 – Properties of Commercial Glass-Ceramic and Traditional Catalyst Support Materials[1]

	Corning 9608	***Corning 9606***	***Schott ZERODUR®***	**Al_2O_3**	**Pyrex Glass**
Primary Crystalline Phase	*beta-spodumene*	*cordierite*	*beta-quartz*	alumina	amorphous
Density (g/cm^3)	*2.5*	*2.6*	*2.5*	3.9	2.5
Thermal Exp. Coefficient (10^{-6}/K)	*1.5*	*4.8*	*0.03*	7.2	4.6
Hardness (Knoop, GPa)	*5.9*	*6.6*	*9.5*	10-20	5
Fracture Toughness (MPa*m$^{1/2}$)	*2.4*	*2.1*	*2.2*	2.7	0.75
Elastic Modulus (GPa)	*88*	*120*	*84*	380	70

Although solid crystalline alumina may have greater hardness and elasticity than most glass-ceramics, the properties of alumina also depend on which crystalline form is used as a catalyst support and the degree to which crystalline alumina particles are sintered. Alumina-based supports, with their higher porosity, are more susceptible to attrition.

Catalyst materials created by integrating active metals with glass-ceramic supports also have a distinct advantage because they can be recycled easily and repeatedly. With these materials, there is no need to separate the catalyst metal from the bulk material during reprocessing. Instead, the metals and bulk glass-ceramic may be remelted at high temperatures, which will oxidize the metals and burn off impurities. During the subsequent recrystallization, the metals are concentrated in secondary phases from which they can be reduced back to the active metallic form.

Value of Proposed Concept

Summary

Durable glass-ceramic catalysts could significantly decrease the cost of gas-to-liquid-fuels plants and coal-to-liquid-fuels plants. The Fischer-Tropsch process, which converts synthesis gas to liquid fuels, is a considerable contributor to the cost of these plants. As described in Appendix A, traditional <u>fixed-bed</u> Fischer-Tropsch reactors cost nearly twice as much to build as newer

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[1] *Engineered Materials Handbook Volume 4 – Ceramics and Glasses*. Edited by S. J. Schneider, ASM International, 1991.

fluidized-bed or slurry-bed reactors. Because the lower-cost slurry-bed reactors only contribute 20% to the investment cost of a gas-to-liquid-fuels plant, the adoption of slurry-bed reactors could reduce the overall capital cost of new gas-to-liquid-fuels plants by about 10%.

Unfortunately, slurry-bed reactors have high catalyst replacement costs because operation of those reactors physically damages the catalyst. If catalyst replacement time could be extended to one year – consistent with the current replacement time for older fixed-bed reactors – the operating cost of a slurry-bed Fischer-Tropsch plant could decrease by more than 20%.

These potential cost reductions have encouraged research aimed at making Fischer-Tropsch catalysts more durable. Most of the research is directed at modifying traditional catalyst support materials to harden them, but the effort by RBR@Vision and GTI is based on a new, proprietary concept for catalyst supports that are intrinsically more durable: glass-ceramic materials. As the demand for gas-to-liquid-fuels and coal-to-liquid-fuels plants increases, there should be a considerable market for these more durable catalysts.

Glass-ceramic catalysts should provide a business advantage to catalyst manufacturers that adopt them. The new catalyst would offer Fischer-Tropsch process operators very significant operating cost savings (estimated at 20%) due to longer catalyst life in slurry-bed reactors.

Potential Technical Advantages

If the glass-ceramic catalyst were to meet its performance goals, it would provide the following advantages over existing catalyst formulations:

1. The inherent hardness of the glass-ceramic substrate would provide very high resistance to attrition of particles. This is especially valuable for Fischer-Tropsch processes that use fluidized-bed or slurry-bubble-column reactors. Low attrition means that catalyst will have a longer life in the reactor and will produce smaller amounts of fine particles that can generate process problems. The glass-ceramic materials that are being evaluated also have high thermal shock resistance, which adds to their attrition resistance.
2. Transition metal catalysts can be incorporated throughout the body of support particles. Thus, catalytic activity is expected to be maintained when the particles do fracture because that fracturing would expose fresh catalyst on the fracture surfaces. Although the cobalt oxide, for example, thus exposed will not be reduced to cobalt metal catalyst at Fischer-Tropsch reactor temperatures, it is believed that the addition of promoters would enable that automatic in-situ reduction. Preliminary experiments have indicated that peak temperatures required to reduce the transition metals in Fischer-Tropsch environments is 700–900ºC, which is significantly higher than Fischer-Tropsch reactor temperatures. The use of promoters to decrease the necessary reduction temperature would be investigated in Phase II.
3. Having catalyst distributed throughout the particle would also reduce the problem of a decrease in catalyst-activity due to catalyst migration from the surface to the interior of the particle.
4. Glass-ceramic catalysts could also be produced with the transition metal thermally impregnated into particle surfaces to reduce the amount of transition metal required. A

related improvement would be to impregnate the surface and also incorporate a lower amount of transition metal into the body of the catalyst to reduce diffusion of catalyst from the surface to the interior of particles. These two approaches would be investigated in Phase II.

5. Fabrication of glass-ceramic-based catalysts will be simpler than catalysts prepared by conventional incipient wetness impregnation techniques. The catalyst can be dry-mixed with the glass-ceramic batch without requiring a separate impregnation step.
6. Reprocessing of fine particles produced by attrition would be inexpensive. The transition metal does not have to be separated from the substrate material; the mixture is merely melted, crystallized, ground, and reduced. By contrast, to reprocess catalysts produced by incipient wetness impregnation, the catalyst must be leached from the substrate, chemically converted to a nitrate salt, and impregnated onto fresh substrate particles. If the glass-ceramic catalyst becomes deactivated by poisoning, it can be remelted and reformed at temperatures lower than the original melting temperature.

Project Goals

The project was proposed to test the feasibility of glass-ceramic catalysts in two areas – attrition resistance and catalytic activity. As described in the proposal, specific performance goals were:

- A fines loss of 15 wt % or less after 12 hours on-stream in the fluidized bed test apparatus would be considered the threshold to proceed to Phase II, with an ideal target value of 10 wt % or less, and 5 wt % or less considered exceptional. For the same test conditions, a net change in volume moment of 15% or less will be considered the minimum to proceed, with an ideal target value of 8% considered ideal, and 4% or less considered exceptional. The fines loss and volume moment of the new catalysts will also have to exceed the performance of a typical Fischer-Tropsch catalyst substantially.
- The activity profile of the new catalyst will also have to be at least as good as a typical Fischer-Tropsch catalyst. Exceptional activity for the new catalysts cannot be expected until its formulation is optimized in Phase II.

Experimental Plan

The catalyst structures tested were:

1. A lithium-aluminosilicate glass-ceramic (Corning 9608 recipe) with 20 wt % cobalt (as cobalt oxide) catalyst integrally distributed throughout the support (designated RBR-1A).
2. A magnesium-aluminosilicate glass-ceramic (Corning 9606 recipe) with 20 wt % cobalt (as cobalt oxide) catalyst integrally distributed throughout the support (designated RBR-2A).
3. A commercial glass-ceramic (Corning Ware®) with cobalt catalyst fused into its surface by a process called thermal impregnation (designated RBR-3A). Based on previous experiments with similar materials, the cobalt oxide loading is estimated to be 5-10 wt %.

4. A conventional type Fischer-Tropsch catalyst fabricated by GTI of alumina with cobalt catalyst added by incipient wetness impregnation (designated RBR-4A). A mass balance calculation indicated an actual loading of 18.3 wt % cobalt oxide.

All materials were crushed and sieved and particles of 150-300 microns were retained for attrition and catalytic activity testing.

It was planned to first test their catalytic activity, then expose them to attrition testing, and then test the post-attrition catalytic activity of the attrited samples.

It should be noted that the proposal for this project only envisioned testing one glass-ceramic catalyst and one traditional (incipient-wetness-impregnated alumina) catalyst. GTI decided to add the other two materials to improve the likelihood of success.

Materials Preparation Techniques

Glass-Ceramic Materials

A description of the general technique for preparing glass-ceramic materials is contained in a recent GTI patent application.[2] The desired material qualities are primarily physical attrition resistance, followed by reasonable surface area and thermal resistance.

Creating a glass-ceramic material follows four basic steps: batching, melting, nucleation, and crystallization. Selecting the composition of the glass-ceramic material must take all of these steps into consideration. First, the composition must be selected so that the batch materials will form a homogenous melt at reasonable temperatures and cool to an amorphous glass state without spontaneously crystallizing.

Next, the composition must either contain a component that will heterogeneously nucleate crystals on subsequent heat treatment or must be of such a nature that crystal nuclei will homogeneously form from the glass during heating. The choice of nucleating agents and components will determine the final primary crystalline phase(s) present in the finished material.

Batching

The glass batch was comprised of high-quality chemically pure components. Calculations were done to formulate a glass batch with a specific composition while accounting for any portions that will react or otherwise be lost from the melt. Table 2 and Table 3 show the compositions and raw materials used to prepare experimental compositions RBR-1A and RBR-2A. The total weight of the raw materials was greater than the desired 200-gram target because the raw carbonates and boric acid release CO_2 or H_2O when the batch is melted.

A laboratory balance was used to weigh the individual chemical components as closely as possible to the desired values from the batch calculation. Plastic containers and utensils were used to avoid contamination of the batch with additional metal elements. The components were sealed in a plastic jar and dry-mixed by tumbling.

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[2] Felix, Larry G.; Rue, David M.; Seward, Thomas P, III; and Weast, Logan E.; “Method for Producing Catalytically-Active Glass-Ceramic Materials, and Glass-Ceramics Produced Thereby,” U.S. Patent Application 2009/0011925 A1, filed July 6, 2007, published January 8, 2009.

The mixed batch was placed in a crucible and melted. Because some of the batch components (e.g. carbonates) will decompose to release gases, the volume of initial charge in the crucible did not exceed ¾ of the crucible volume to avoid overflowing if the melting material foamed. To ensure homogeneous mixing, the batch for a given sample was measured, mixed, and melted without dividing between containers or crucibles. Prior to loading the crucibles, their weights were recorded to allow for later calculation of the glass yield and to check for volatilization losses.

Table 2 – Batch Composition for Catalyst Material RBR-1A

Desired Glass Mass = 200g				
Glass Component	**Raw Material**	**Desired Component wt %**	**Desired Component mol %**	**Measured Raw Material, grams**
SiO_2	SiO_2	50.8	55.5	101.60
CaO	$CaCO_3$	1.6	1.9	5.70
Li_2O	Li_2CO_3	2.8	6.2	13.83
CoO	CoO	20.0	17.5	40.00
Al_2O_3	Al_2O_3	16.0	10.3	32.00
B_2O_3	H_3BO_3	2.2	2.1	7.83
MgO	MgO	1.4	2.3	2.88
TiO_2	TiO_2	3.4	2.8	6.80
ZnO	ZnO	1.8	1.4	3.52

Table 3 – Batch Composition for Catalyst Material RBR-2A

Desired Glass Mass = 200g				
Glass Component	**Raw Material**	**Desired Component wt %**	**Desired Component mol %**	**Measured Raw Material, grams**
SiO_2	SiO_2	45.6	48.5	91.20
CoO	CoO	20.0	17.071	40.00
Al_2O_3	Al_2O_3	16.0	10.0	32.00
B_2O_3	H_3BO_3	1.6	1.5	5.70
MgO	MgO	12.0	19.0	24.00
TiO_2	TiO_2	4.8	3.8	9.60

Melting

The mixed glass batches were melted in an MHI high-temperature box furnace.

Because materials RBR-1A and RBR-2A contain high levels of cobalt, which is both IR-adsorptive and network-modifying in the glass structure, these glasses tend to reach a low viscosity at a temperature close to the glass transition temperature. Thus, it was not necessary to increase the temperature drastically to pour the melts.

Some species will volatilize from the melt more easily and may need a little extra added to the batch to compensate for expected losses. No compensating materials were added for these glass-ceramic materials, and a mass balance over the crucible and product glass showed a volatilization loss of only 1.6 and 1.9% respectively. This loss was probably almost entirely from the volatilization of boron, whose primary function was to flux the batch during the initial stages of melting, and whose loss would have negligible effect on the final product.

For melting the aluminosilicate glasses in this project, each glass batch was placed in the furnace at room temperature, heated to 1500°C at a rate of 5–8°C/min, held at 1500°C for 60 minutes, stepped to 1550°C, held for 90 minutes, removed from the furnace, and poured into a quench bucket.

The final part of the melting process was to remove the sample from the furnace and cool it. Viscosity may change drastically with small changes in temperature, so pouring must be done quickly. Because the intended product of this investigation was catalyst particles of 150-300 microns, it was not necessary to pour the molten glass to a single solid ingot or to anneal the glass after it was poured. Therefore, these glass batches were removed from the hot furnace and immediately quenched by pouring them directly from the crucible into a metal bucket filled with ice water to maximize the rate of cooling from the melt and minimize uncontrolled nucleation or crystallization.

Nucleation and Crystallization

The nucleation and crystallization steps transform the material from a quenched glass into a fine-grained glass-ceramic material. The key to creating a fine-grained glass-ceramic material is to generate a large number of crystal nuclei at a lower temperature and then allow the crystal phase to grow on these nuclei at a higher temperature (but stop growing once the crystals impinge on each other). Nucleation occurs at lower temperatures than crystal growth, but nucleation and crystal growth can also occur simultaneously, as shown in Figure 1. In this figure, the curves represent nucleation and crystal growth rates (not necessarily to scale).

Figure 1 illustrates that the ideal temperature for nucleation of a glass-ceramic is somewhat above the glass transition temperature, T_g, but below the temperature of maximum crystal growth. For most experimental glass-ceramic compositions, these values cannot be determined without completing a series of differential scanning calorimeter experiments. However, one approximation is to start at the T_g value for a known glass with similar composition and add 20-40ºC. For crystallization, a temperature corresponding to the maximum growth rate of the desired crystal phase should be selected.

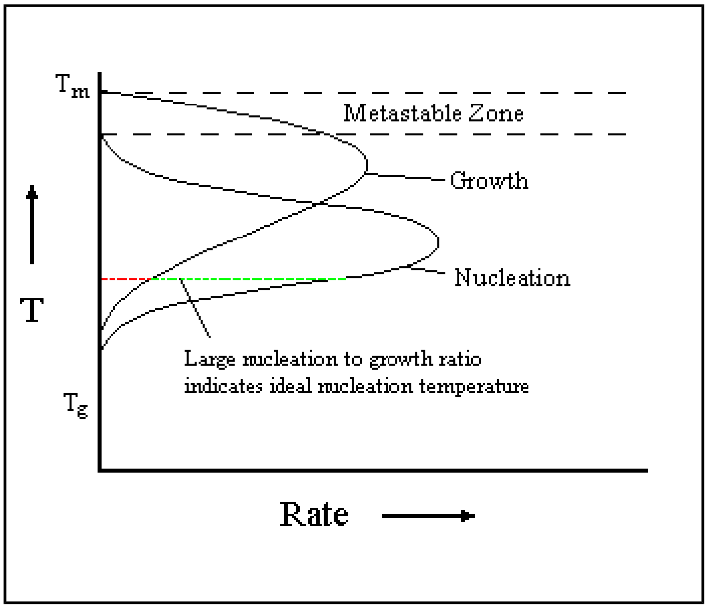

Figure 1 – Nucleation and Growth Curves for an Arbitrary Glass-Ceramic Material

Based on experience with the nucleation and crystallization of similar materials previously produced at GTI, the following heat-treatment schedule was used for sample RBR-1A:

- Heat from room temperature to 750ºC at 15ºC/min.
- Dwell at 750ºC for 120 minutes.
- Heat from 750ºC to 1000ºC at 10ºC/min.
- Dwell at 1000ºC for 60 minutes.
- Power off and cool at furnace rate to room temperature.

Similarly, a second heat-treatment schedule was used for sample RBR-2A:

- Heat from room temperature to 800ºC at 5ºC/min.
- Dwell at 800ºC for 240 minutes.
- Heat from 800ºC to 1180ºC at 2ºC/minute.
- Dwell at 1180ºC for 60 minute.
- Power off and cool at furnace rate to room temperature.

These schedules produced fine-grained glass-ceramics, as evidenced by both a change in color (from black glass to dark green or blue ceramic) and texture (glossy smooth fracture face to “flat” matte fracture face). Previous analyses of similar materials indicated that the primary crystal phases formed in this heat treatment are beta-spodumene for sample RBR-1A and a cordierite solid solution for sample RBR-2A.

After heat-treating, the cerammed samples were crushed by hand with a steel mortar and pestle, sieved to retain particles of the preferred size using brass test sieves and a Ro-Tap® sieve shaker, and then passed over a strong magnet to remove any steel that may have been abraded in the crushing process.

Qualitative observation of the crushing process showed that material RBR-2A is highly attrition-resistant (as expected), requiring much physical effort and multiple passes through the mortar and pestle to fully break the batch of ceramic down to particles small enough for sizing.

One concern with glass ceramic materials produced for catalytic applications is that glass-ceramics have inherently low surface area. Because of this, glass-ceramics may not be a reasonable substitute for traditional supported catalysts in every situation. However, as shown in Figure 2 and Figure 3, examination of SEM images from before and after crystallization of materials previously produced at GTI show that a smooth metal-rich glass material can substantially increase in surface area upon crystallization. Additionally, once the metals are reduced, the surface area is further increased by the formation of metallic particles on the catalyst surface. For small particles with a high ratio of surface area to volume, this increase in surface may be enough for the glass-ceramics to be considered for applications where catalytic activity is an added bonus or in applications, such as Fischer-Tropsch synthesis, where a lower level of catalytic activity helps prevent runaway reaction and overheating.

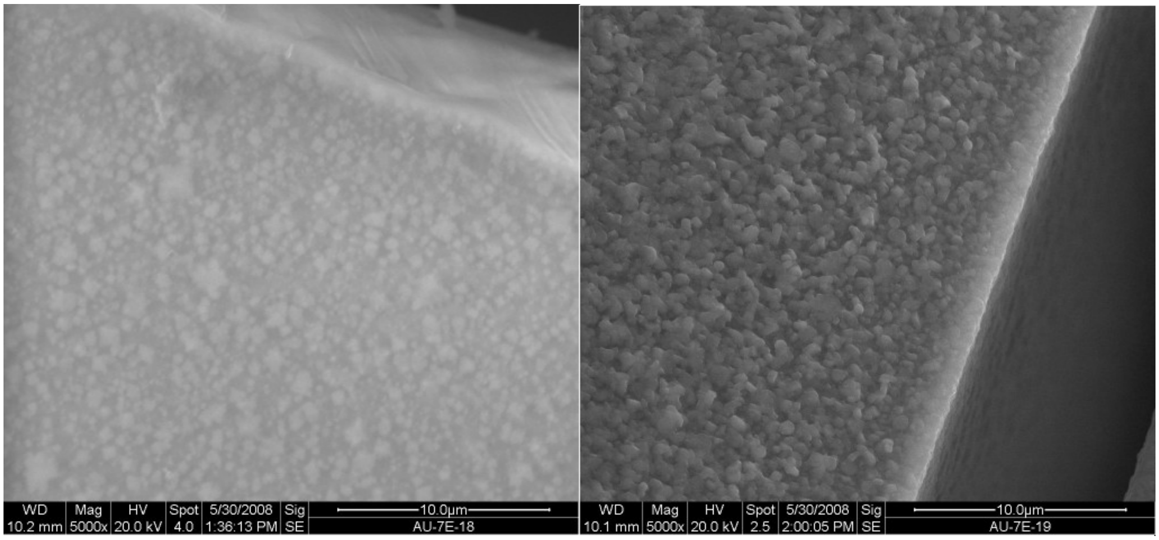

Figure 2 – Change in Surface upon Crystallization of Ni-Mg-Aluminosilicate Glass-Ceramic

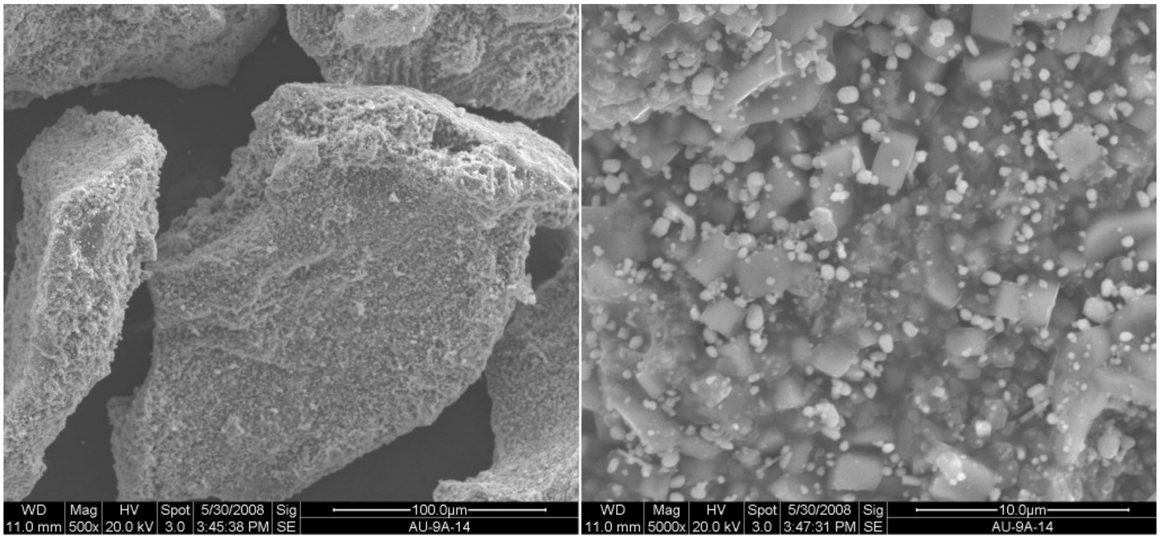

Figure 3 – Surface Detail of Reduced Ni-Mg-Aluminosilicate Glass-Ceramic

Thermally Impregnated Glass-Ceramic Material

Invented in 2005, thermal impregnation is a method for preparing catalytic materials in which heat is used as a driving force to incorporate a catalytically active material into the outer layer of a support material. Prior work at GTI focused on incorporating nickel metal, nickel oxide, and nickel silicate into olivine mineral (iron-magnesium silicate) [3] and lithium-aluminosilicate glass-ceramic support materials.[4] There is some debate as to the precise mechanism by which the catalytic materials integrate with the support. Observations from our experiments support the view that, when a mixture of catalyst and support particles are heated to slightly below the melting point of the support, the catalyst particles induce the formation of a lower-melting eutectic localized at the surface of the support particle. This localized melting allows the catalytically active material to partially diffuse into and strongly attach to the support.

The overall process steps for thermal impregnation are:

- Select appropriate materials.
- Thoroughly mix the finely divided catalyst and sized support materials.
- Heat the mixture for an appropriate time to a temperature that will soften the support and allow the catalyst to bond with the support.
- Reduce the resulting composite to the desired catalyst particle sizes.

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[3] Felix, L.; Choi, C.; Slimane, R. *et al*, "Thermally Impregnated Ni-Olivine Catalysts for Decomposing Tar in Biomass Gasification," Paper OB5.3 presented at the 16th European Biomass Conference and Exhibition, June 2-6, 2008, Valencia, Spain.

[4] Felix, Larry G.; Rue, David M.; and Slimane, Rachid B.; "Method for Producing Catalytically-Active Materials," U.S. Patent Application 20080305948 A1, filed August 13, 2008, published December 11, 2008.

The thermally impregnated sample material was prepared using crushed Corning Ware® (a lithium-aluminosilicate glass-ceramic) as the support material (T_m ~ 1200°C), and cobalt oxide (T_m ~ 1900°C) as the catalyst precursor.

The support was crushed and sieved to obtain the 150–300 μm particles desired for the final product. The catalytically active material was powdered and screened to obtain particles substantially smaller than the support material to allow for separation from the product particles after impregnation. The crushed support material was dry-mixed with enough of the powdered catalyst compound to thoroughly coat and surround the support particles. We used a mixture of 100 grams Corning Ware® with 150 grams CoO (~400-mesh powder from Alfa Aesar®) to fabricate material RBR-3A catalyst.

Mixing of the small batches used in this project was done by placing them in a jar and shaking it by hand for several minutes. When the support and powdered catalyst were observed to be well mixed, the sample was transferred to a crucible for heat treatment.

For heat-treating, the mixed powders were placed in an alumina crucible and heated at 5ºC/min to 1180ºC in a large muffle furnace. The sample was then held at 1180ºC for two hours before cooling to room temperature at the furnace’s natural (powered off) cooling rate. Analysis of several materials previously prepared in this manner at GTI indicated that a single thermal impregnation step might incorporate up to 20 wt % metal oxides into a typical glass-ceramic support. The RBR-3A sample that was prepared contained about 18 wt % CoO.

After impregnation, the resulting product must be checked for proper particle size and, if necessary, comminuted to the appropriate size for use. Because the RBR-3A sample had compacted, it was crushed to form properly sized particles in a mortar and pestle. After re-sieving the mixture, the even coloration of the final product indicated an even dispersion and adhesion of catalyst powder to the granular support

Conventional Incipient-Wetness-Impregnated Alumina Catalyst

Although catalysts have long been prepared via wet impregnation and incipient wetness impregnation (IWI), definitive instructions detailing how these methods are carried out are not readily available or accessible. Thus, the preparation of a traditional type supported cobalt catalyst for this project was completed using a synthesis procedure that incorporated information from published studies, patent documents, and advice from GTI staff experienced in the preparation of catalysts. The IWI catalyst produced for this project was intended to be similar to a high-α cobalt-on-alumina material referenced in the same RTI study on which our Fischer-Tropsch reactor design was based.[5]

While our intent in preparing the catalyst was to make a material as close as possible to a commercial product, due to the complexity of catalyst preparation, our best attempts were only an approximation of proprietary commercial formulations. Much of the uncertainty in our preparation stemmed from the many factors involved in wet impregnation such as starting

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[5] Nikolopoulos, A.A. and Gangwal, S.K, “Chain-Limiting Operation of Fischer-Tropsch Reactor,” Final Report for DOE Project DE-FG26-99FT40680, June 2003.

materials, degree of wetting, solution pH, diffusion rates, drying/calcining rates, and previous impregnations or processing. Some factors, such as degree of wetting, are easily determined, since incipient wetness impregnation is, by definition, the use of precisely enough catalyst solution to fill the available pore space. However, the remaining factors may all affect the final distribution profile of the catalyst particles within the product material. For these factors, no indication could be found in literature for what parameters are typically used, which makes our material an approximation of a commercial catalyst.

The first step in preparing a supported catalyst via IWI is selection and preparation of the support material. The material characterized in the RTI report was prepared by a third party, and exact details were not revealed in that report. However, it was described as having a Brunauer-Emmett-Teller (BET) surface area of 156 m^2/g and a nominal CoO loading of 20 wt %. Based on this, a medium-surface-area alumina catalyst support was purchased (Alfa Aesar #32168) and the as-received pellets were crushed and sieved to obtain 150–300 µm particles. After the particles were sieved, the pore volume was approximated by taking a 10.0-gram sample and adding small amounts of distilled water from a graduated cylinder until the sample was thoroughly moistened, but not dripping water. By this method, the pore volume for the alumina support was found to be approximately 1.1 mL/g.

Once the approximate pore volume was known, the next task was to calculate and mix the catalyst precursor solution. From patent literature (U.S. patent 4,499,209, referenced by RTI), it was determined that cobalt nitrate would be an acceptable catalyst precursor. Cobalt nitrate was obtained in the form of cobalt nitrate hexahydrate, $Co(NO_3)_2{\cdot}6H_2O$ (Alfa Aesar #11341). Assuming that only CoO will remain after drying and calcination, this calculates to 3.88 grams of cobalt nitrate hexahydrate per gram of CoO desired in the dried product. For the initial batch of catalyst material prepared, 33.1 grams of properly sized alumina was used, so, to achieve incipient wetness impregnation to 20 wt % CoO required 36.4 mL of nitrate solution. Because of the large amount of water trapped in the hydrated crystals and the decrease in volume upon dissolution, the solution was prepared by slowly adding distilled water to 32.1 grams of nitrate crystals in a graduated cylinder, mixing and gently heating with each addition, until the crystals were fully dissolved and the required volume was achieved. This actually took very little additional water beyond that contained in the hydrated crystals, indicating that IWI preparation of catalysts with more than 20 wt % CoO may require a different source of cobalt.

After the cobalt solution was prepared, the alumina support was placed in a large beaker and the cobalt solution introduced, a small addition at a time, thoroughly mixing and allowing the nitrate solution to be adsorbed onto the alumina. By the last additions, the mixture was relatively thick and difficult to stir. If the mixture stirred too easily or quickly settled to a flat surface in the beaker, it would have indicated that too much solution was used. Once mixed, the beaker was placed in a drying oven at 120ºC, with periodic stirring of the wet mixture as it dried to help speed the process. After drying overnight, the mixture’s color was bright magenta instead of the rusty red of the initial cobalt nitrate solution. There also appeared to be some clumping of the catalyst and some small crystals at the very top of the beaker, probably from residual nitrate solution.

After stirring again to break up the clumps and residual cobalt nitrate, the mixture was transferred to an alumina crucible and placed in a furnace for calcining. The furnace was programmed to heat at 15ºC/min to 500ºC and hold that temperature for 6 hours before switching off and cooling at the natural furnace rate. After the sample was cooled, it was easily poured from the crucible and was a rich blue-black color like that of cobalt oxide powder, indicating that the calcination process had driven the nitrate from the material as desired. Finally, the sample was placed in a ceramic mortar and gently crushed by hand to break up any remaining agglomerations from the drying and calcination process. After weighing this final sample, it was determined that the material was approximately 18 wt % CoO.

Catalyst Attrition

Attrition Test Method

GTI contracted with PSRI (Particulate Solid Research, Inc., psrichicago.com) to perform the attrition testing of the project materials. PSRI's jet cup attrition unit is based on the well-known Davison jet cup design, but constructed on a much larger scale. Because of its larger scale, the PSRI jet cup requires a sample of approximately 100 grams rather than the 5 grams called for in the Davison jet cup. While this larger sample requirement is more difficult to meet when producing many specialized experimental catalyst materials, the larger sample mass enables greater repeatability and accuracy of measurement and a smaller overall percentage of fine materials lost from the system. A diagram of the PSRI jet cup is shown in Figure 4.

One note on the design is that past testing at PSRI revealed that a conical bottom cup gives more accurate attrition measurements than a cylindrical bottom cup. The conical cup design allows the jet vortex to involve all of the sample material in the attrition process, while a cylindrical design may have a "dead zone" pocket below the vortex that accumulates material that does not participate in the attrition. However, PSRI's fabrication process for the conical design resulted in thinner walls for the cup. Extremely abrasive materials, such as those created in this project, will abrade the inside of the jet cup and eventually create a pinhole leak, allowing significant loss of sample material from the system. Due to this loss issue, testing for this project was completed using the older, but thicker, cylindrical jet cups.

To prepare samples for attrition testing, the experimental materials were first sieved to obtain particles from 150–300 microns. Ideally, 200–210 grams of sized material would be prepared so a second test sample could be on hand as a backup. After screening for proper size, the materials were placed in a 220–250ºC drying oven overnight. After drying, the samples were sealed in sample bottles. If enough material was available for two or more samples, the material was riffled to distribute the particles evenly, sealed in sample bottles, and delivered to PSRI.

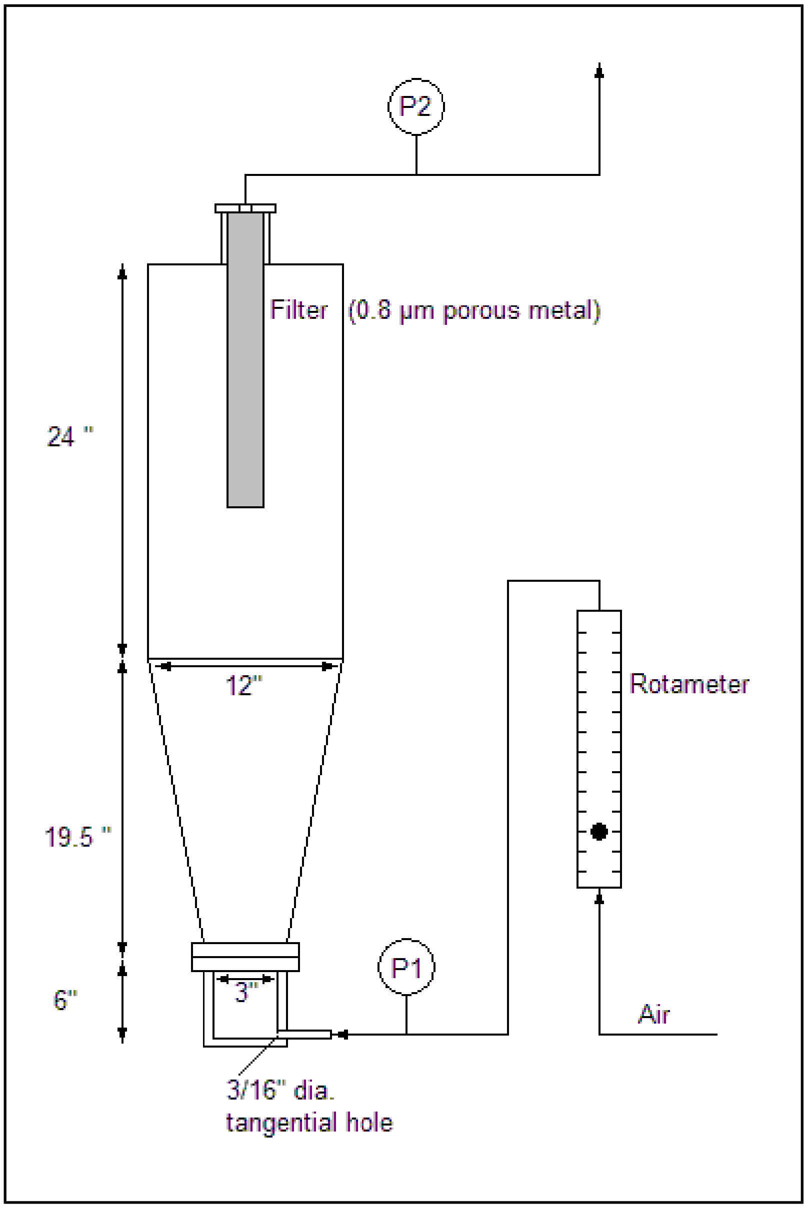


Figure 4 – PSRI Jet Cup Attrition Unit

Testing of the sample began by performing an initial particle size distribution using a MicroTrac S3000 particle size analyzer. After the initial particle size distribution measurement, the remaining sample was weighed and transferred to the jet cup. At this time, the unit's filter was also weighed and recorded. Once the system was loaded, air flow was opened to the jet cup and flow was adjusted to the appropriate velocity. Typical flow velocities will range from 250 to 600 feet/sec depending on the hardness and size of materials, as well as the degree of attrition expected. For the sample materials in this project, an air flow rate of 450 feet/sec was chosen, based on previous observations of similar materials in GTI's ASTM attrition test unit. Ideally, a flow rate should be chosen that would result in approximately 20% of the material becoming attritted over the course of the test. It is also important to choose a flow rate at which the primary mode of attrition is particle surface abrasion, not particle fracture. When particles undergo fracture, the rate of fines generation sharply increases. If time and materials were available, this point between abrasion and fracture regimes could be found experimentally by testing a series of identical samples at increasing flow rates and observing the rate of fines accumulation.

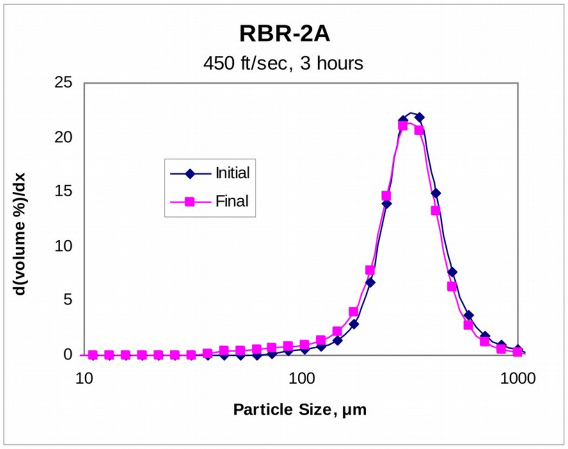
Once gas flow was started, the unit was checked periodically – typically one-hour intervals – to note the gas flow rate and pressure drop across the unit. Readings were recorded at each periodic check, and, after the appropriate time had passed (three hours for our materials), the flow was stopped. The filter assembly was removed from the unit and the fine material was carefully brushed from the filter and collected. Then the filter and collected material were weighed and their final weights recorded. Next, the interior walls of the unit were carefully brushed to knock all remaining material into the bottom cup. The cup was removed from the unit and the recovered sample was weighed.

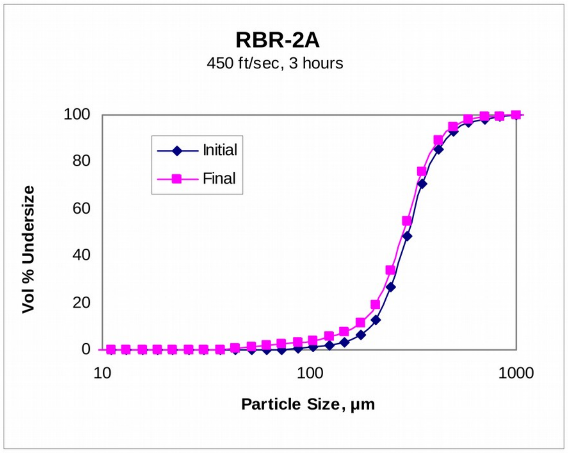
Finally, post-test particle size distributions for the filter sample and the recovered sample were each measured. The final overall particle size distribution was calculated by multiplying the cup particle size distribution by the cup mass fraction and adding it to the filter particle size distribution multiplied by the filter mass fraction. From this final particle size distribution, the percentage of generated fines can be calculated by weight % (or volume %, depending on instrument output) of the particles that are smaller than a specified size, and the volume mean moment particle diameter can be calculated from the distribution of material across the particle size intervals.

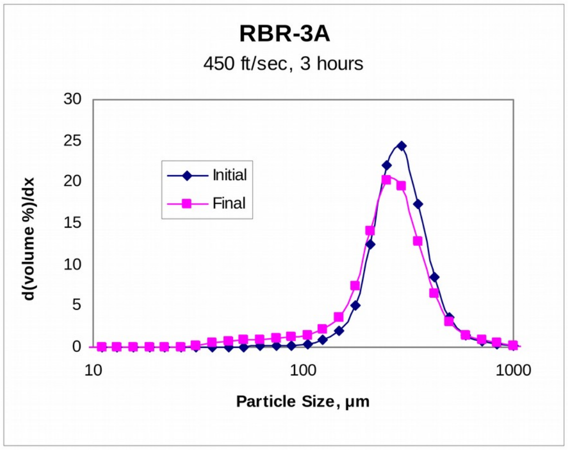
Attrition Test Results

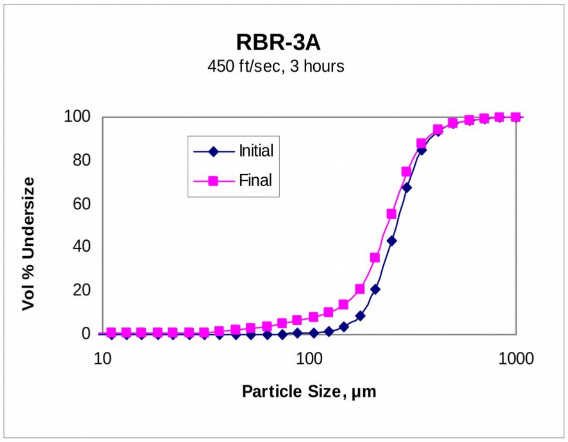
Three samples of catalyst were tested for three hours at a jet velocity of 450 feet per second. Particle size distributions are shown in Figure 5. It is clear that the two glass-ceramic samples, RBR-2A and RBR-3A, did not undergo nearly as much attrition as the traditional catalyst, RBR-4A.

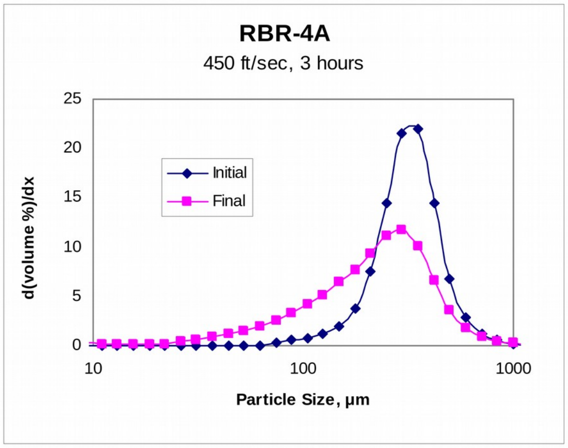
Several interesting trends may be observed from the particle size distributions shown in Figure 5. In the plots of d(volume %)/dx, the change in peak height, width, and location indicate the extent and method of attrition that the particles underwent. First, for all three materials, the peak particle size is roughly the same and does not shift significantly with attrition. This indicates that, for a bulk sample, most of the volume still consists of particles around 300 μm.


RBR-2A
450 ft/sec, 3 hours
d(volume %)/dx
25
20
15
10
5
0
10
100
1000
Particle Size, µm
Initial
Final


RBR-2A
450 ft/sec, 3 hours
Vol % Undersize
100
80
60
40
20
0
10
100
1000
Particle Size, µm
Initial
Final


RBR-3A
450 ft/sec, 3 hours
d(volume %)/dx
30
25
20
15
10
5
0
10
100
1000
Particle Size, µm
Initial
Final


RBR-3A
450 ft/sec, 3 hours
Vol % Undersize
100
80
60
40
20
0
10
100
1000
Particle Size, µm
Initial
Final


RBR-4A
450 ft/sec, 3 hours
d(volume %)/dx
25
20
15
10
5
0
10
100
1000
Particle Size, µm
Initial
Final

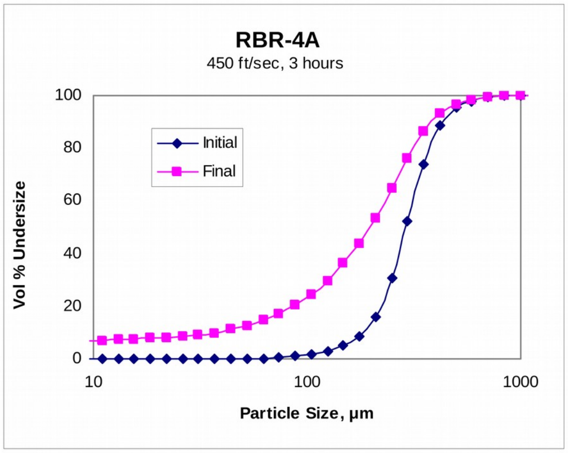

RBR-4A
450 ft/sec, 3 hours
Vol % Undersize
100
80
60
40
20
0
10
100
1000
Particle Size, µm
Initial
Final

Figure 5 – Measured Particle Size Distributions

Of greater interest are the peak height and peak shape. The significant change in peak height for material RBR-4A shows that, while 300 µm is still the most populated volume fraction, at least half of the initial particles of that size were significantly reduced during the attrition test.

Finally, the shape of the peaks tells us about the mode of attrition that the samples underwent. For glass-ceramic samples RBR-2A and RBR-3A, the full width at half maximum (FWHM) was constant or even decreased, indicating that the relative distribution of particle sizes did not change much. This, combined with the growth of a small “plateau” from 30-100 µm, indicates that the primary mode of attrition was abrasion of small chips and fines from particle surfaces. In contrast, the traditional catalyst, RBR-4A, showed significant increase in the FWHM, indicating the generation of many particles across a very wide range of sizes and thus more of a fracture mechanism of attrition. The plots of volume % undersize vs. particle size also echo these conclusions by the change in location and slope of the distribution curve inflection points.

The volume moment mean particle diameters (VMM) of the initial and final distributions were calculated using the following formula:

$$D[4,3] = \Sigma n_i d_i^4 / \Sigma n_i d_i^3$$

Where n_i = the number of particles in the ith size interval, and d_i = the mean diameter within the ith interval.

The percentage fines loss was calculated in two ways.

The first way was to follow Adeyiga[6] and Zhao,[7] who defined fines loss as mass of elutriated material divided by the total recovered mass.

The second way was to count the volume (equivalent to mass) of all particles smaller than a specific size. For our testing, this second method is preferred, because the internal filter of the PSRI jet cup appears to have trapped many larger particles that would not be elutriated into the external filter of the Davison cup used in the aforementioned studies. Zhao had noted that all fines elutriated in his jet cup tests were smaller than 30 µm.[8] We noted that none of our tests started with particles smaller than 52.23 µm, so we used that size as the cutoff point and counted all particles in the final particle size distribution smaller than 52.33 µm as fines.

Table 4 summarizes the results of these calculations and shows that the glass-ceramic materials performed very well. Using any of the three attrition measures, the glass-ceramic materials show exceptionally good performance relative to that of the traditional catalyst formulation. These results are compared to the project’s performance targets in the *Conclusions* section, later in this report.

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[6] Adeyiga, Adeyinka A, “Development of Attrition Resistant Iron-Based Fischer-Tropsch Catalysts,” Final Report on Work Performed Under DOE Grant No.: DE-FG26-99FT40619, p. 16, 38, December 2003.

[7] Zhao, R.; Goodwin, J.G., Jr.; and Oukaci, R.; “Attrition Assessment for Slurry Bubble Column Reactor Catalysts,” *Applied Catalysis A: General, 189* p. 99–116, especially, p. 105, Elsevier, 1999.

[8] *Ibid*. p. 108.

Table 4 – Attrition Resistance Performance

Sample	Material	Fines loss, wt %	Vol % < 52.33 µm	Initial VMM	Final VMM	VMM Decrease
RBR-2A	CoO in Mg-Aluminosilicate	2.5	1.1%	320.9	296.1	7.7%
RBR-3A	CoO on Corning Ware®	5.0	3.0%	278.1	249.9	10.2%
RBR-4A	CoO on Al_2O_3	5.8	12.6%	304.7	211.0	30.8%

Catalyst Activity

Activity Test Method

The design and operation of the Fischer-Tropsch reactor system for this project was modeled primarily on one built and operated by Research Triangle Institute (RTI)[9]. As shown in Figure 6, the reactor train consisted of a gas feed section, a fixed-bed reactor, a condensation section, and product gas analysis instruments. The system was designed to operate at up to 500ºC and 600 psig. At ambient pressure, the reactor could be operated at higher temperatures for the in-situ reduction of catalyst materials. Up to 18 cm^3 of catalyst could be loaded in the reactor tube (.375-inch o.d., .315-inch i.d.) for testing. Gas products were analyzed by two on-line gas chromatographs. Analysis of the collected wax and liquid products was to be completed using an off-line gas chromatograph.

The first stage of the reactor system was the gas feed section. Pure CO, H_2, and N_2 were metered from pressurized cylinders by Brooks mass flow controllers, heated and mixed in-line, and delivered to the pressurized reactor. The mass flow controllers were calibrated at 400 psi. During typical tests, the mass flow controllers were operated at set points of 45–80% of their maximum flow.

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[9] Nikolopoulos, A.A. and Gangwal, S.K, “Chain-Limiting Operation of Fischer-Tropsch Reactor,” Final Report for DOE Project DE-FG26-99FT40680, June 2003. (http://www.osti.gov/bridge/servlets/purl/825370-Ve0VYZ/native/825370.PDF)

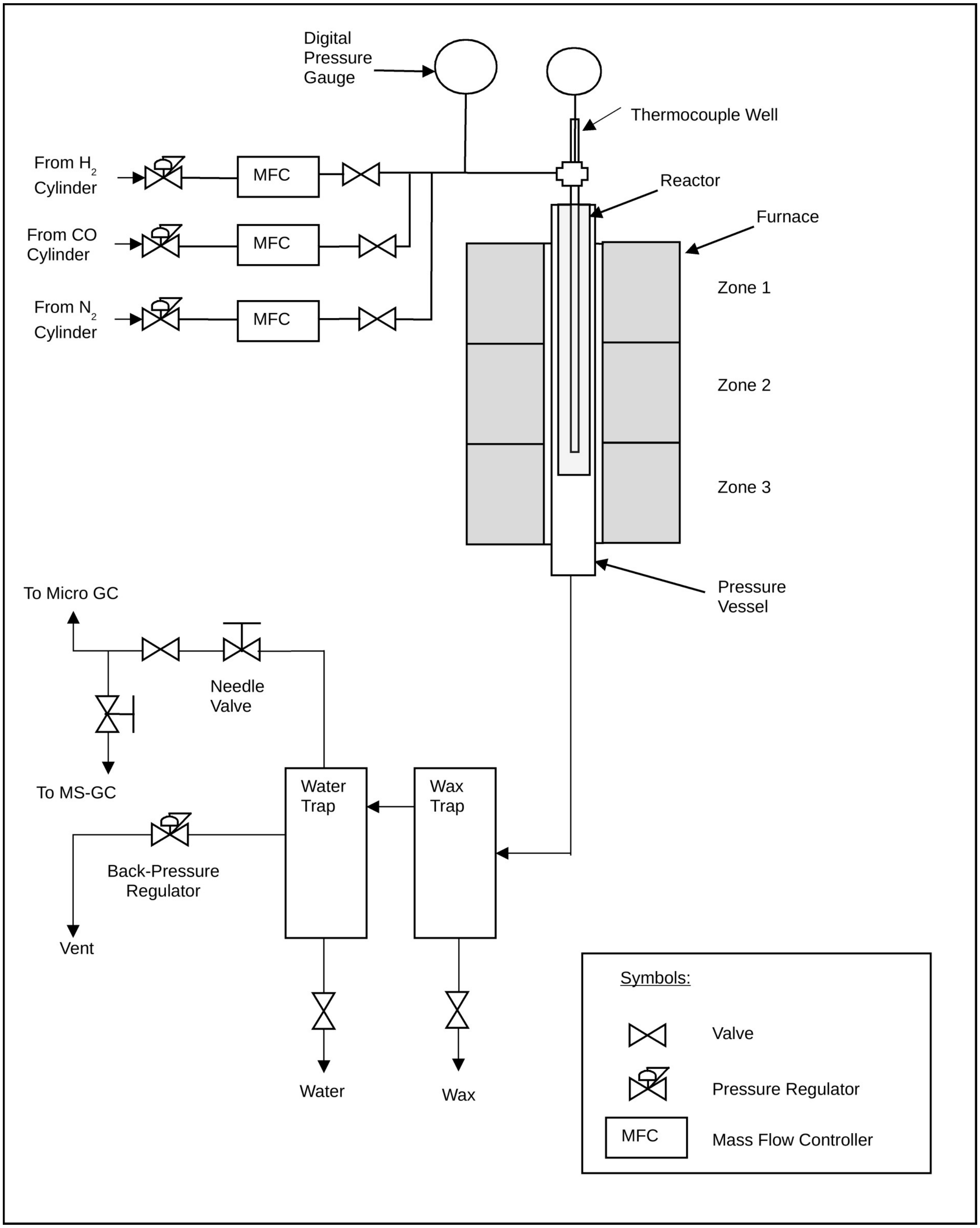

Figure 6 – Catalytic Activity Test Apparatus

The pre-heated gas then entered the reactor section, which consisted of two annular tubes. The outer tube was 1-inch o.d. stainless steel to maintain system pressure. The 3/8-inch stainless steel inner reactor tube was fitted to seal against the outer tube at the top. A 90-µm sintered stainless steel frit was welded to the bottom of the inner reactor tube to support the catalyst bed while allowing reaction products to flow downward and exit. Inside the inner reactor tube, a 1/8-inch o.d. thermowell and multi-point thermocouple set at six inches from the sintered bottom support frit measured the reactor temperature at 6.5, 9.0, 12.0, and 13.5 inches from the frit. The reactor assembly was enclosed in a programmable three-zone tubular furnace.

From the reactor, the reaction products and unreacted feed gas passed through the condensing section. The product was partially cooled as it passed through a wax trap maintained at 140ºC to collect the heavy hydrocarbons. After the wax trap, a portion of the product stream passed through a pair of needle valves (acting as orifices to drop the pressure) and went to the on-line analysis instruments while the remainder of the product stream passed through a water trap to condense the water product and lighter hydrocarbon oils. The water trap was externally cooled by an ice bath that was periodically replaced during the testing. After the water trap, a back-pressure regulator maintained the system pressure at 300 psig during testing. The back-pressure regulator and transport lines were all maintained at 200ºC to prevent condensation and plugging.

From the condensing section, a heated line transported the low-pressure product stream to the on-line gas chromatographs. The first instrument was a HP6890 gas chromatographs operating in mass-spectrometer mode (GCMS) for measuring C_7-C_{20} hydrocarbon species. Since a standard hydrocarbon sample was not available for calibration, primary hydrocarbon species were identified from library data during the initial traditional catalyst test. For subsequent catalyst materials, observed peaks in the data were identified by comparing them to the initial sample’s identification. While this was not the ideal method for identifying product species in general, the measurements did allow a relative comparison of the traditional and experimental materials’ Fischer-Tropsch activity. The second online gas chromatograph was a Varian Micro-GC. Due to the delicate nature and mode of operation of the columns installed in this instrument, the product stream was passed through a chilled impinger at 5ºC to remove any water and condensable hydrocarbons before analysis. After the condensable species were removed, the Micro-GC analyzed the concentrations of N_2, CO, H_2, CO_2, and CH_4 in the product stream. The Micro-GC was calibrated using a set of bottled syn-gas mixtures of known composition.

Except for deviations noted in the test results, the catalytic tests were carried out using the following procedure. The bottom of the reactor were filled with 2.46 grams of alumina to form a three-inch-deep base support, the next 10.5 inches (12 cc) were filled with a mixture of alumina and catalyst as detailed in Table 5, and the top two inches were filled with 1.38g of alumina to form a preheat zone. For each material, the packed density was determined by measuring the mass and volume in a graduated cylinder after tapping on the laboratory bench for several minutes. Using the packed density values, each section of material was weighed on a balance, dry mixed by hand if needed for the center zone, and added to the reactor, tapping the reactor between additions to settle the particles.

Table 5 : Loading of Reactor Center Zone

Test Sample	Alumina Density (g/cc)	Catalyst Density (g/cc)	Alumina Mass (g)	Catalyst Mass (g)	Alumina Volume (cc)	Catalyst Volume (cc)
Alumina Blank	0.64	0.64	7.63	0.00	11.92	0.00
RBR-1A	0.64	1.46	3.81	8.77	5.95	6.00
RBR-2A	0.64	1.64	2.88	12.32	4.50	7.50
RBR-3A	0.64	1.33	3.81	7.91	5.95	5.96
RBR-4A	0.64	0.85	3.81	5.07	5.95	5.95
Alumina Retest	0.64	0.64	7.63	0.00	11.92	0.00
RBR-1A Retest	0.64	1.46	0.00	17.54	0.00	12.00
RBR-2A Retest	0.64	1.64	2.88	12.32	4.50	7.50
RBR-4A Retest	0.64	0.85	3.81	5.07	5.95	5.95

After the reactor was loaded and reassembled in the testing apparatus, the catalyst material was reduced in-situ with hydrogen gas at ambient pressure. Based on the aforementioned RTI report the RBR-4A (traditional type IWI catalyst) material was reduced overnight at 350ºC. However, from previous testing at GTI, it was known that the glass-ceramic materials, as formulated, require a much higher reduction temperature, so they were reduced overnight at 850ºC. Once the material was reduced, the reactor was cooled to room temperature under a nitrogen atmosphere and pressurized to 300 psig for a leak-test.

After the leak test, the CO and H_2 mass flow controllers were started and the reactor was brought to steady-state flow at room temperature. For typical testing, the mass flow controllers were set at 300 scc/min N_2, 200 scc/min H_2, and 100 scc/min CO. These flow conditions give a 2:1 H_2:CO ratio and a catalyst space velocity of 6000 hr^{-1} (based on the inlet flow rate of the gas mixture at standard temperature and pressure). For the first test of material RBR-2A, the catalyst volume was increased to 7.5 cc and feed rates were increased to 375 scc/min N_2, 250 scc/min H_2 and 125 scc/min CO to maintain a space velocity of 6000 hr^{-1}. Then, RBR-2A was retested at the “typical” feed rate, where the larger amount of catalyst corresponded to a reduced space velocity of 4800 hr^{-1}. For the retest of material RBR-1A, the reactor was loaded with 12.0 cc of catalyst to achieve a space velocity of 3000 hr^{-1}.

After steady feed gas flow was achieved, the gas chromatographs were started. Once they were verified to be in working order, the reactor was heated at 2.0ºC/min until the reactor reached 10 to 20 degrees below the desired experiment temperature, at which time the heating rate was slowed to 5 to 10ºC/hour, depending on the reactivity of the test material. For very reactive materials, heating the material quickly could (and for one test did) result in severe temperature overshoot and runaway reaction rates.

After reaching steady state feed and reactor temperature, catalyst activity was confirmed by observing a series of evenly spaced peaks in the GCMS spectra and a corresponding rise in temperature across the reactor bed. Once activity was observed, the reactor was allowed to run at steady operation for up to 48 hours. For some sample materials, the catalytic activity significantly diminished after several hours. At that time, the gas flow was decreased or the temperature increased in an attempt to restore the catalyst to measurable activity levels. Finally, after running the reactor long enough to observe the catalyst activity (or lack thereof), the reactor was purged with nitrogen, depressurized, and cooled to room temperature. After cooling, the wax and water traps were opened and any material found within was collected, weighed, and saved for later analysis in an offline gas chromatograph. However, because several of the materials not producing any measurable amount of wax or oil product, this additional analysis was not completed.

Activity Test Results

Tests of the catalytic activity of the glass-ceramic materials showed little catalytic activity. This result was surprising because of previous work at GTI that will be discussed below.

In this program, the following catalyst samples were tested for activity:

- RBR-1A – Lithium-based glass-ceramic.
- RBR-2A – Magnesium-based-based glass-ceramic.
- RBR-3A – Thermally impregnated Corning Ware®.
- RBR-4a – Traditional incipient wetness impregnated alumina.

Alumina without catalyst was also tested to verify that there was no catalytic activity from the reactor itself.

A critical analysis of the data showed that there were irresolvable analytical issues that made it impossible to produce acceptable material balances. As a result, only qualitative results are being reported. Based on the measurements of the relative amounts of hydrocarbons produced in the activity tests, the following can be concluded:

- Sample RBR-1A initially had an order of magnitude lower catalytic activity than sample RBR-4A and deactivated completely after 3 hours.
- Sample RBR-2A also initially had an order of magnitude lower catalytic activity than sample RBR-4A and deactivated completely after 3 hours.
- Sample RBR-3A initially had catalytic activity comparable to sample RBR-2A, but it deactivated completely after 5.5 hours.

It is apparent from these observations that the catalysts did not meet the proposed catalytic activity targets. To better understand the reasons for low catalytic activity, the available surface area of RBR-4A and a nickel-based glass-ceramic were measured by the BET (Brunauer-Emmett-Teller) method, which indicated that RBR-4A (the traditional catalyst) had a surface area of 87 square meters per gram, while the glass-ceramic has an area of only 0.065 square meters per gram. This indicates that the glass-ceramic does not have internal pore spaces that are necessary to provide the large surface areas needed for high catalytic activity. This observation is surprising because of previous work at GTI, which showed good activity of nickel catalyst on a glass-ceramic support.

Under an earlier DOE Cooperative Agreement, DE-FG36-04GO14314, GTI had evaluated some glass-ceramic based catalyst materials for use in other reaction systems. To date, that work has focused on developing a nickel-based catalyst for decomposing tars and methane in a fluidized-bed gasification reactor. Using facilities available at GTI and partner organizations, such as Alfred University and Ohio State University, researchers have been able to create lithium-aluminosilicate-based catalysts that incorporate up to 30 wt % nickel oxide. When these materials were subjected to a reducing atmosphere, the nickel oxide was reduced to sub-micron nickel metal particles, evenly dispersed across the material surface. Comparing the surface of this novel catalyst with that of a commercial material shows remarkable similarity in metal dispersion, suggesting high catalytic activity. Subsequent testing of tar decomposition activity in GTI's catalyst test facility confirmed that engineered glass-ceramics can have high catalytic activity.

While the DOE-sponsored research has focused on nickel-based tar-decomposing catalysts, continuing internally-funded GTI research is investigating the creation of cobalt- and iron-based glass-ceramic Fischer-Tropsch catalysts. Small quantities of candidate materials with up to 40 wt % CoO have been created in both the lithium-aluminosilicate and magnesium-aluminosilicate glass-ceramic families. Preliminary observations indicate that these materials have catalytic activities similar to the nickel-based catalysts already tested. However, testing of these materials in a laboratory Fischer-Tropsch reactor has not yet been completed.

It was not possible to reconcile the differences in observed catalytic activity in this project. However, the greater activity observed in the other DOE tests suggests that there may be a way to enhance the activity of the subject Fischer-Tropsch catalysts to take advantage of their demonstrated attrition resistance.

Products of This Project

The project did not produce any publications, Internet site descriptions, new techniques, inventions, licenses, computer models, computer programs, or other tangible products.

Preexisting Patents and Technology Transfer

GTI has one patent[10] and two patent applications[11,12]covering the glass-ceramic catalyst concept. Both predate the current grant, and no additional invention occurred during this project.

This patent protection made it feasible to commercialize the concept by licensing to established manufacturers, and this approach was envisioned.

During the early stages of this project, RBR@Vision developed a commercialization plan for the glass-ceramic catalysts. A list of catalyst manufacturers and Fischer-Tropsch catalyst users was

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[10] Felix, Larry G.; Rue, David M.; and Slimane, Rachid B.; "Method for Producing Catalytically-Active Materials," U.S. Patent 7,449,424 B2, filed March 8, 2005, issued November 11, 2008.

[11] Felix, Larry G.; Rue, David M.; and Slimane, Rachid B.; "Method for Producing Catalytically-Active Materials," U.S. Patent Application 20080305948 A1, filed August 13, 2008, published December 11, 2008.

[12] Felix, Larry G.; Rue, David M.; Seward, Thomas P, III; and Weast, Logan E.; "Method for Producing Catalytically-Active Glass-Ceramic Materials, and Glass-Ceramics Produced Thereby," U.S. Patent Application 2009/0011925 A1, filed July 6, 2007, published January 8, 2009.

prepared and preliminary screenings of company data were done to determine the best contact points. A draft letter was prepared, which described the glass-ceramic catalyst concept and the commercial benefits that would accrue if this Phase I project met its technical targets. Comparisons with traditional Fischer-Tropsch catalysts were made, based on available literature data, and potential economic benefits were calculated where possible. The goal of the commercialization effort was to obtain company involvement during the Phase I project to help guide technical developments that would lead to both technical and economic participation in a Phase II effort.

It was agreed with GTI that the letter would not be sent to the target companies until the Phase I project produced some initial results that established the likelihood of achieving the proposed benefits. As was discussed in the section on catalytic activity, problems with analytical measurements and the subsequent inability of the materials as prepared to demonstrate significant catalytic activity resulted in the cancellation of further commercialization efforts.

Conclusions

The glass-ceramic materials met or exceeded the targeted attrition resistance. The proposed targets were expressed in terms of maximum fines loss during testing and maximum change in volume moment mean diameter changes during testing, as follows:

- Fines loss of 15 wt % or less – minimum threshold to proceed to Phase II.
- Fines loss of 10 wt % or less – ideal target value.
- Fines loss of 5 wt % or less – exceptional performance.
- Net change in volume moment mean diameter of 15% or less – minimum to proceed to Phase II.
- Net change in volume moment mean diameter of 8% or less – ideal target value.
- Net change in volume moment mean diameter of 2% or less – exceptional performance.

Table 4 shows that the glass-ceramic materials performed very well. They had lower fines loss than the traditional catalyst and achieved a level of exceptional performance for that parameter. They also achieved the ideal target value for change in volume moment mean diameter, with value of less than one-third the change for the traditional catalyst.

In attrition testing, the glass-ceramic materials eroded the jet cup test equipment, which indicates that they might cause similar problems in Fischer-Tropsch reactors.

Unfortunately, the glass-ceramic catalysts did not have adequate reactivity to justify an application for a Phase II grant at this time. Additional research is needed to achieve formulations that produce substantially greater porosity to increase the internal surface area.

Recommendations

Because the project did not achieve its performance goals with respect to catalytic activity, RBR@Vision will not submit a Phase II proposal. However, the concept still has merit and potential commercial importance. If GTI resolves its activity measurement discrepancies and shows evidence that the particle surface area of glass-ceramic particles can be significantly increased through reformulation, the feasibility of the concept should be explored again.

At the outset of this project, it was believed that the change in surface area from the crystallization and metal reduction steps (Figure 2 and Figure 3) would present sufficient surface area to make a reasonable catalyst. However, the testing revealed that these materials still have substantially less surface area and reactivity, so the next step is to consider methods for manipulating the glass-ceramic surfaces by thermal, mechanical, or chemical means to increase the overall porosity while still keeping most of the observed material strength. Some options include:

- Formation of micro-bubbles in the melt by mechanical agitation or chemical addition.
- Additional reduction of the secondary crystal phase after ceramic formation.
- Manipulation of composition to encourage liquid/liquid phase separation within the glass during heat treatment.
- Chemical etching of the surface to remove one glass or crystalline phase.

Appendix A – Potential Cost Advantages of Glass-Ceramic Catalysts

This appendix explains and documents the capital and operating cost advantages cited in the section entitled *Value of Proposed Concept*.

Process Capital Costs

For Fischer-Tropsch synthesis, it is recognized that slurry-phase bubble-column reactors have many advantages over other reactor types, especially for reactors that produce high-boiling liquids.[13] The advantages include:

- Simple design and construction.
- Ease of addition and removal of catalyst.
- Good heat transfer and temperature control.
- Good selectivity control.
- Low pressure drop.
- Potentially high capacity.
- Construction costs about 45% lower than tubular fixed-bed reactors.

The construction cost advantage is considerable, because, even using the lower-cost slurry reactors, nearly 20% of the capital cost of a coal-to-liquids plant is attributable to the Fischer-Tropsch synthesis step.[14]

A report by Bechtel, Inc., published in 1990 indicated that using slurry-bed rather than fixed-bed Fischer-Tropsch reactors in a coal-to-liquids plant would reduce overall plant investment costs by 8.5%.[15]

The temperature control advantage is also very important. Removal of the heat of reaction (about 25% of the calorific value of the syn-gas feed) is a major issue in Fischer-Tropsch reactor design.[16]

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[13] P. Samuel, "Gas-to-Liquid Fuels Technology - Challenges and Opportunities in Catalysis," *Bulletin of the Catalysis Society of India*, *2*, 82-99, (2003). (See page 92.) The article is available at http://203.199.213.48/183/1/254_P._Samuel.pdf

[14] Lawrence Van Bibber, *et al.*, "Baseline Technical and Economic Assessment of a Commercial Scale Fischer-Tropsch Liquids Facility," DOE/NETL-2007/1260, Final Report, April 9, 2007. (See page 5.) The report is available at http://www.netl.doe.gov/energy-analyses/pubs/Baseline%20Technical%20and%20Economic%20Assessment%20of%20a%20Commercial%20S.pdf

[15] J.M. Fox, et al., "Slurry Reactor Design Studies, Slurry vs. Fixed-Bed Reactors for Fischer-Tropsch and Methanol: Final Report," Report on Work Performed under DOE contract AC22-89PC89857, NTIS accession code DE1005752. June 1990. (See pages 63-69.) The report is available at http://www.fischer-tropsch.org/DOE/DOE_reports/91005752/de91005752_toc.htm

[16] P. Samuel, "Gas-to-Liquid Fuels Technology - Challenges and Opportunities in Catalysis," *Bulletin of the Catalysis Society of India*, *2*, 82-99, (2003). (See page 94.) The article is available at

Fischer-Tropsch Operating Costs

Unfortunately, slurry-phase bubble-column reactors have an operating cost disadvantage. High rates of catalyst replacement are needed because of damage to catalyst particles as they collide and grind together; and catalyst replacement costs are a large component of Fischer-Tropsch process operating costs.

The Bechtel reportError: Reference source not found can also be used to estimate the effect of catalyst durability on process operating costs. Table 6 shows the report's comparison of variable operating costs for using slurry-bed Fischer-Tropsch reactors to those of comparable fixed-bed reactors.

Table 6 – Comparison of Variable Operating Costs of Fischer-Tropsch Reactors

Variable Cost Component	**Slurry Reactor, $MM/year**	**Fluid-Bed Reactor, $MM/year**
Fuel gas	12.44	17.58
Raw water	0.25	0.30
Catalysts and chemicals	14.04	8.20
Total variable costs	**26.73**	**26.08**

The data in the table indicate a slight cost disadvantage for the slurry reactor, but the report also indicated an advantage for the slurry-bed reactors in fixed operating costs (maintenance). Maintenance for the slurry-bed reactors would cost 10.66 $MM/year, while for the fixed-bed reactors, it would cost 13.27 $MM/year. Therefore, the use of slurry-bed reactors would save a net amount of 1.96 $MM/year, about 7% of the Fischer-Tropsch operating cost.

However, the important point is that the Bechtel study assumed that the catalyst in the slurry-bed reactors would have to be replaced every two months, while the catalyst in the fixed-bed reactors would only have to be replaced once a year. Bechtel estimated that, if the catalyst life in the slurry reactors could be increased to one year, the operating cost advantage of the slurry-bed reactor would increase to 9.06 $MM/year, more than 20% of the Fischer-Tropsch operating cost.

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