Fischer Tropsch Catalyst Test on Coal-Derived Synthesis Gas

Introduction

Coal represents a major energy source that can be transformed into transportation fuels and chemical feedstocks. The United States has the world's largest coal reserves with an estimated 270 billion recoverable tons[1]. Converting 5 percent of the U.S. coal reserves to Fischer-Tropsch (FT) fuels would equal the existing U.S. crude reserves of 22 billion barrels.[2,3,4] It is possible to essentially double the nation's domestic motor fuel supply through the application of coal-to-liquids (CTL) technology.

Although CTL has been practiced on a commercial scale in South Africa since the 1950's, most of the recent advances in reactor and catalyst technology have been for gas to liquids (GTL) processes. The most significant of these are the new generation of cobalt catalysts and the slurry reactor technology. Cobalt catalysts maximize yield of premium diesel and have been used for all GTL projects since the mid-1990's. Slurry reactor technology allows use of high activity/selectivity small catalyst particles while providing an efficient means of reactor heat removal and temperature control.

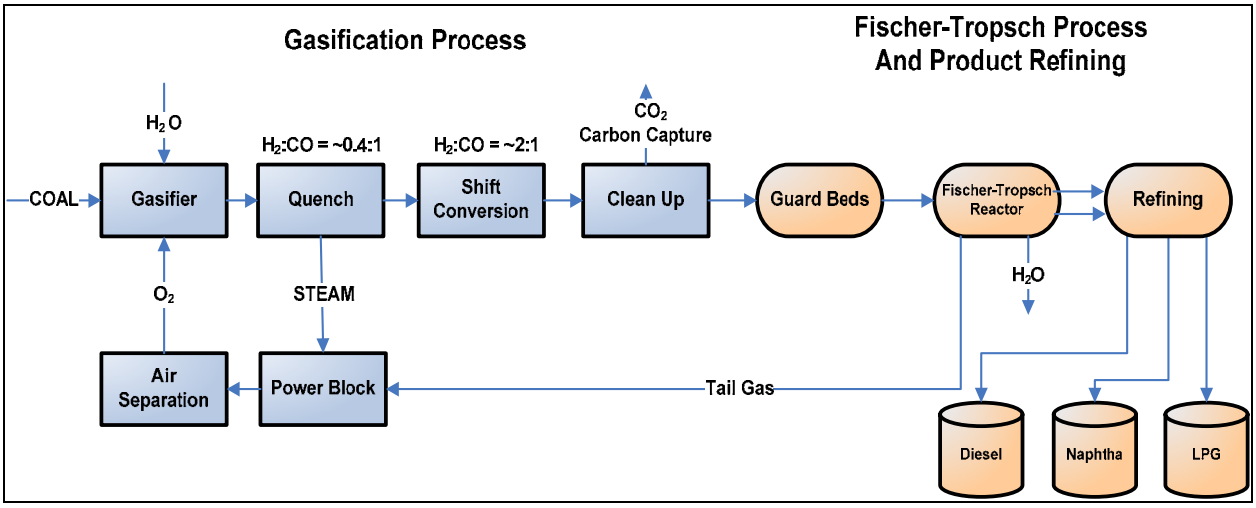
In November 2005, Syntroleum Corporation and Eastman Chemical Company entered into an agreement to conduct bench-scale demonstration of Syntroleum's cobalt FT slurry catalyst with coal-derived synthesis gas (syngas). Syntroleum conducted the testing program with Eastman Chemical Company in order to demonstrate the effectiveness of the Syntroleum FT catalyst with coal gasification and synthesis gas clean-up processes proven by Eastman. The testing program began in December 2006 and concluded in the 3rd quarter of 2007. Capitalizing on the experience of both companies, a 100 day stable run demonstrated excellent performance of Syntroleum's cobalt FT catalyst on live syngas from Eastman's Coal Gasification Facility.

CTL Process Overview

Eastman Chemical Company's coal gasification and syngas cleanup experience combined with Syntroleum FT technology has demonstrated that coal conversion to transportation fuels can be achieved with cobalt slurry FT catalyst.

Figure 1 shows the two major process steps in a CTL plant. The first major step is Gasification. The gasification process produces ratio-adjusted clean syngas from coal (see shift conversion subsection below). The second major step is Liquids Production. Liquids Production includes the Fischer-Tropsch process and product refining. The Syntroleum demonstration unit at Kingsport Tennessee was designed to collect data and product from the Syntroleum FT reactor system (proprietary cobalt slurry catalyst) with coal-derived syngas from Eastman's process. Product refining was not in the scope of the demonstration as it is well established that CTL FT products will refine in a similar manner to GTL FT products.

Figure 1. Typical Coal-to-Liquids Process Scheme



Gasification Technology

A gasifier converts coal feedstock into gaseous components by applying heat and pressure to the coal in the presence of steam and oxygen. A gasifier differs from a combustor in that the amount of oxygen inside the gasifier is carefully controlled such that only a relatively small portion of the fuel burns completely, minimizing the formation of carbon dioxide. The combustion and gasification reactions are shown in Eq 1 and Eqs 2-4 respectively. The reaction of Eq 2 is termed partial oxidation. Rather than burning, most of the carbon-containing feedstock is chemically broken apart by the gasifier's heat and pressure producing syngas. Water introduced into the gasifier also takes part in the chemical decomposition of coal, producing carbon oxides and hydrogen as in Eq 3-4.

Chemical Equation	Description	Equation #
$C + O_2 \rightarrow CO_2$	Combustion	Equation (1)
$C + ½\ O_2 \leftrightarrow CO$	Partial Oxidation	Equation (2)
$C + H_2O \leftrightarrow CO + H_2$	Hydrolysis Reaction	Equation (3)
$CO + H_2O \leftrightarrow CO_2 + H_2$	Water Gas Shift Reaction	Equation (4)

The produced syngas is primarily hydrogen and carbon monoxide with other gaseous components. The actual composition depends on the conditions in the gasifier and the type of feedstock. Typical coal syngas H_2:CO ratios are in the 0.4:1 to 0.9:1 range.

For FT conversion, the desired ratio is 2.1:1. "Ratio adjustment" via the water-gas shift reaction of Eq 4 is thus required to convert syngas to FT hydrocarbons. This may be done in the gasifier, a catalytic shift converter, or the FT reactor itself by using catalysts with water-gas shift selectivity (e.g. iron). For optimum operation of the gasifier and the FT reactor, the preferred option is the catalytic shift converter. This has the added advantage of eliminating CO_2 from FT reactor tail gas and simplifying carbon capture. (All CO_2 is captured after water-gas shift as part of syngas cleanup.)

Other major gaseous components found in the syngas stream are derived from the sulfur and nitrogen containing compounds found in coal. In addition to the sulfur and nitrogen components the syngas may contain metals, e.g. mercury and arsenic. The metals, sulfur and reactive nitrogen compounds are removed from the gasifier effluent to provide clean syngas for further processing. Non-combustible components e.g. calcium and silicon, typically leave the bottom of the gasifier as slag.

Fischer-Tropsch Conversion

The FT process uses a catalyst to convert syngas to hydrocarbon products according to the general chemical pathway given by Eq 5.

Chemical Equation	Description	Equation #
$n\ CO + 2n\ H_2 \rightarrow (–CH_2–)_n + H_2O$	Fischer-Tropsch Reaction	Equation (5)

There is a distribution of intermediate feedstocks generated during this FT chemical process including unreacted gases, short and long chain paraffins, olefins and alcohols. The type of catalyst and operating conditions impact the distribution of the intermediate feedstocks generated.

Standard refinery hydroprocessing and fractionation is used to convert the raw chemicals generated into commercial products, primarily transportation fuels. The unconverted syngas and light gas products in the reactor tail gas are used for internal power generation as shown in Figure 1.

Coupling the Technologies

Eastman Chemical Company and Syntroleum Corporation have developed their respective technologies and expertise independently. The companies combined their experience to demonstrate that coal can be effectively converted to liquid hydrocarbons with a cobalt based FT catalyst.

FT catalysts have historically been based on iron or cobalt. While iron catalyst requires a lower initial investment, cobalt has numerous performance advantages such as higher activity, higher diesel yields, longer life, and lower water gas shift activity resulting in lower overall operating cost.[5] The higher activity and longer life of cobalt catalyst offsets the initial higher cost.

By not causing water-gas shift in the FT reactor, cobalt catalysts localize carbon capture (CO_2 sequestering) to the shift reactor syngas product. The CO_2-concentrated syngas may effectively be scrubbed as part of the cleanup process shown in Figure 1.

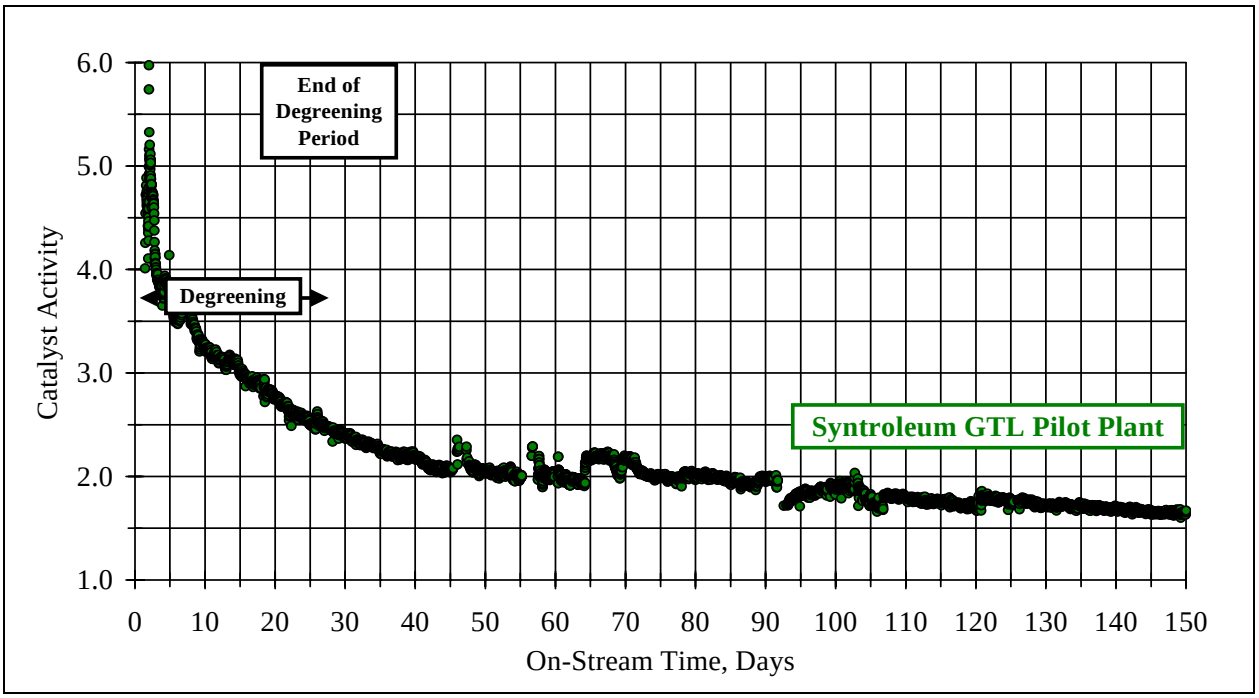
Exposure to contaminants increases with the longer life of the cobalt catalyst resulting in increased potential for catalyst deactivation. Therefore cobalt catalyst must be designed consistent with commercially available syngas cleanup processes.

Syntroleum has invested over one million hours of run time in bench scale FT catalyst tests, much of it in Continuous Stirred Tank Reactors (CSTR) like those used in the present study. These tests include extensive studies on trace levels of various contaminants and a patented regeneration process. Syntroleum's regeneration process separates the catalyst from the wax matrix returning it to the original oxide form. The catalyst is then re-reduced, slurried and returned to the reactor. This procedure has been demonstrated at lab, pilot, and demonstration scale, restoring catalyst activity from a wide range of deactivation mechanisms. With this background, Syntroleum was able to establish a maximum target level of contaminants in the syngas and designed guard beds through which syngas produced at the Eastman facility was processed The combined experience of the two companies was essential in the success of the demonstration program.

Demonstration of Performance

Based on Syntroleum's extensive FT catalyst experience, the objective of the testing program was to complete a 100 day run on live syngas while maintaining commercial catalyst activity. The key measurable indicators were the deactivation rate of the FT catalyst and initial activity after regeneration. After a fresh start-up, FT catalysts go through a degreening period followed by steady state operations. Figure 2 shows the typical catalyst deactivation profile. The degreening period for the run in Figure 2 lasted for 26 days. Following the degreening period the catalyst activity stabilizes and deactivates at a reduced rate relative to the degreening period.

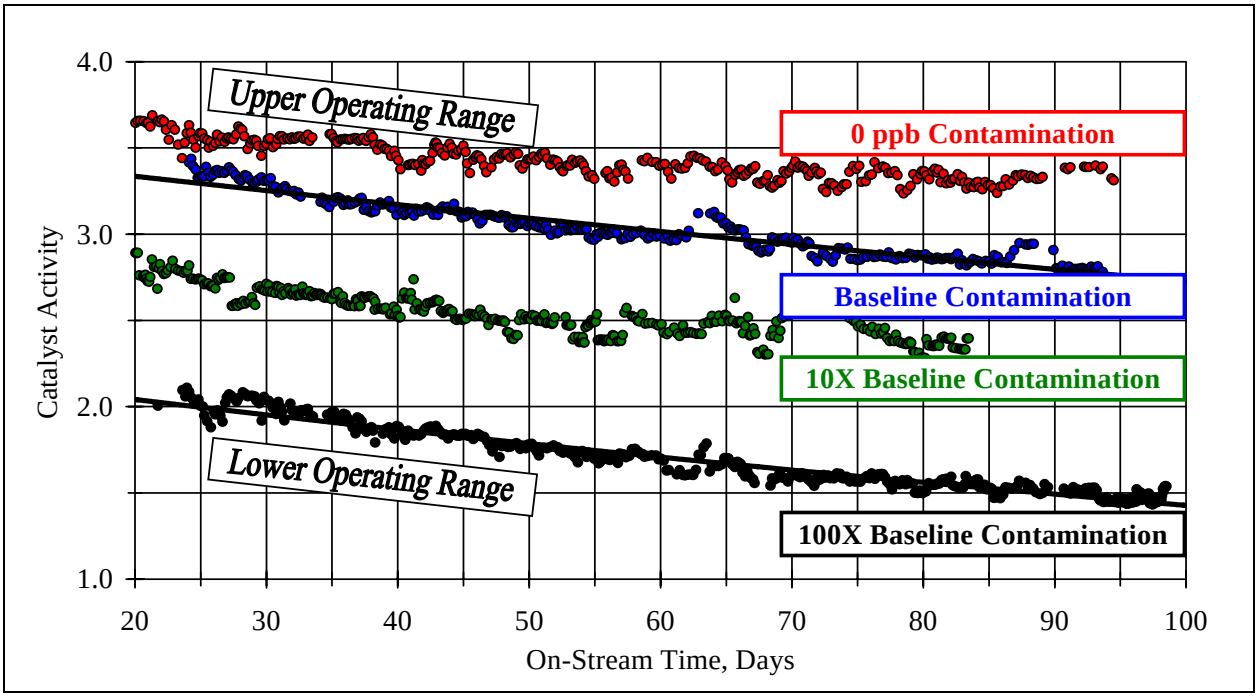
Figure 2. Typical Catalyst Deactivation Profile



The steady state rate of catalyst deactivation must be relatively low to get acceptable economic life from the catalyst. Figure 3 shows a grid of four lines; representing four separate lab runs at carefully controlled conditions with varying levels of a known contaminant at part per billion

levels. For clarity, the degreening period (first 20 days) is not shown. The contaminant concentrations are zero, Baseline Contamination (BC), ten times Baseline Contamination (10xBC) and one hundred times Baseline Contamination (100xBC). Clearly small amounts of contaminant cause an offset in activity but after the initial loss of activity, the steady state rate of deactivation is similar. Increasing levels of contaminants, 10xBC and 100xBC, cause a larger offset of activity loss but again only until the catalyst equilibrates to a stable rate of deactivation. The commercially acceptable range of operations is delineated by the black lines labeled Upper Operating Range and Lower Operating Range in Figure 3.

Figure 3. Laboratory Contaminant Study



The testing program was conducted exclusively with CSTR's because they accurately represent a three phase slurry system, and Syntroleum has a database of operations which are used to correlate catalyst performance between CSTR, pilot scale and demonstration scale reactors.

Testing at Eastman's facility employed two CSTR's operating in parallel. The Eastman Live CTL CSTR operated with coal-derived syngas taken from the process line feeding commercial operations within the Eastman plant. The H_2:CO ratio of the live syngas during the tests is presented in Figure 4. The live CSTR was thus exposed to the typical composition swings observed in a commercial coal gasifier.

The Eastman Reference CSTR was operated with high-purity synthesis gas that was cryogenically separated and cleaned. The reference CSTR helps to gage the differences in performance due to contaminants in the commercial coal-derived syngas. The reference CSTR is also used to ascertain that the Eastman CSTR's have comparable performance to Syntroleum laboratory CSTR's.

Figure 4. Coal Syngas Composition Trend During Tests

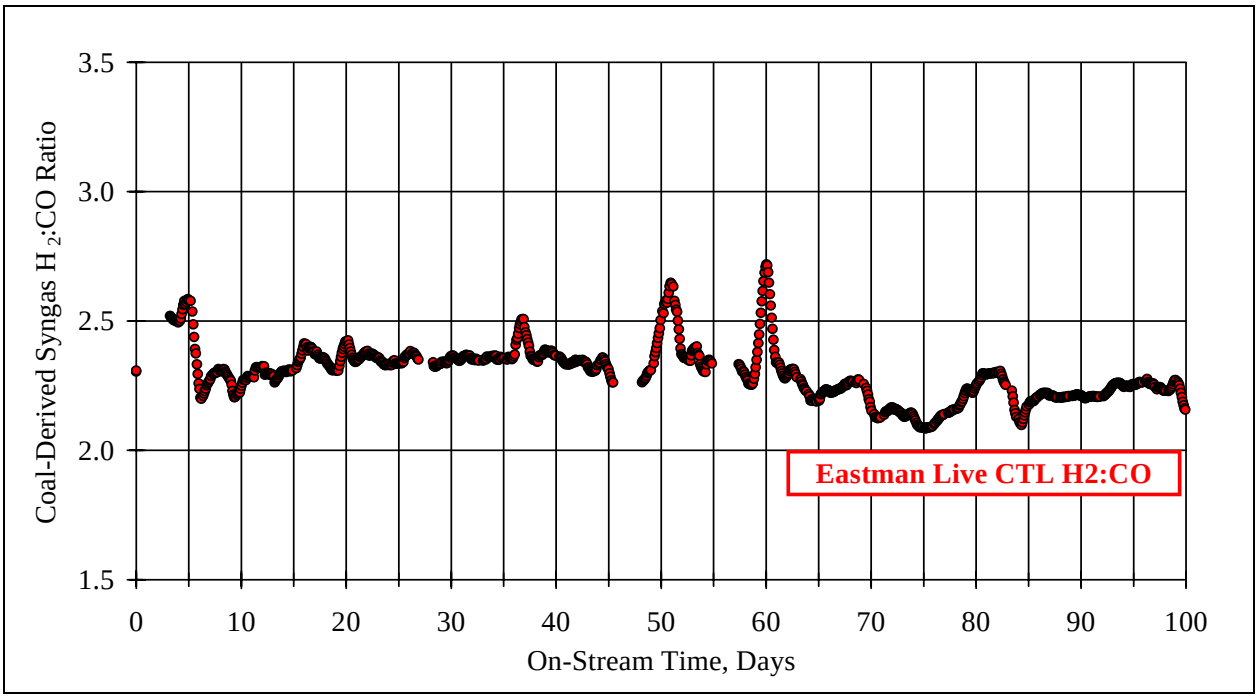


Figure 5 shows the results of the reactor operations at Eastman Chemical. CSTR runs of 100 days are shown. Data represented by the symbol "x" correspond to the CSTR that operated on live syngas, while the circles are data from the CSTR on reference gas. There is an offset of activity between the reference CSTR and the live CTL CSTR; however both catalyst activity and deactivation rates are within the commercially anticipated range. The commercially anticipated range is delineated by the black lines. In addition to meeting the target conversion performance criteria, the catalyst showed no signs of physical degradation (attrition) for the term of the run.

Figure 6 shows the Eastman Live CTL CSTR run (symbol "x") and a run conducted at Syntroleum's GTL pilot plant (circles) for the same catalyst based on syngas generated from natural gas. This run demonstrates very good agreement with results from the live coal derived syngas of Eastman Chemical.

As previously stated, Syntroleum has patented a cobalt catalyst regeneration process that restores activity attributed to a broad range of deactivation mechanisms. Figure 7 shows the run curve for the Eastman Live CTL CSTR run (symbol "x") and the Eastman Reference CSTR run (circles) and the results from catalyst regeneration. After the 100 day run at Eastman the catalyst was returned to Syntroleum to evaluate the effectiveness of Syntroleum's catalyst regeneration technology on catalyst operated with coal-derived syngas. The catalyst from both runs were regenerated and run at Syntroleum's lab. Figure 7 shows that Syntroleum's catalyst regeneration technology is able to fully restore activity of both the live coal syngas and the reference catalysts. The activity of the regenerated catalysts is restored and undergoes the same deactivation profile as fresh catalysts (rapid degreening period, followed by slow deactivation thereafter).

Figure 5. Eastman CSTR Data

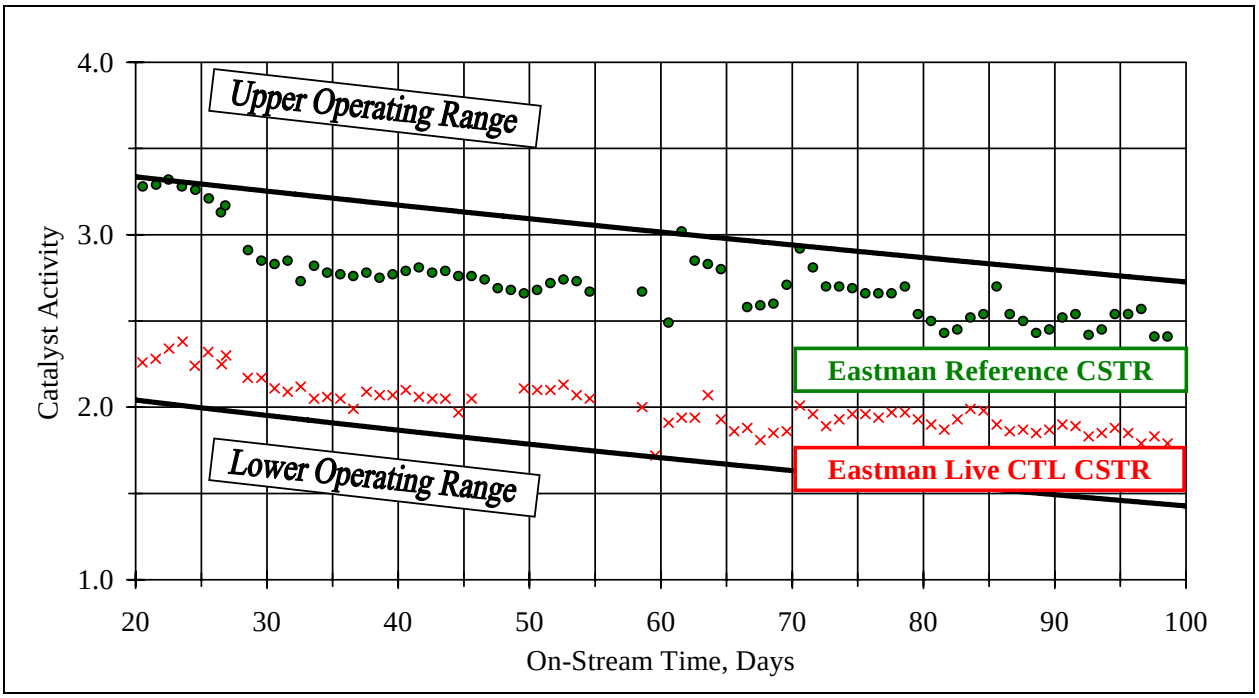


Figure 6. Eastman CSTR Data and Syntroleum Pilot Plant Data

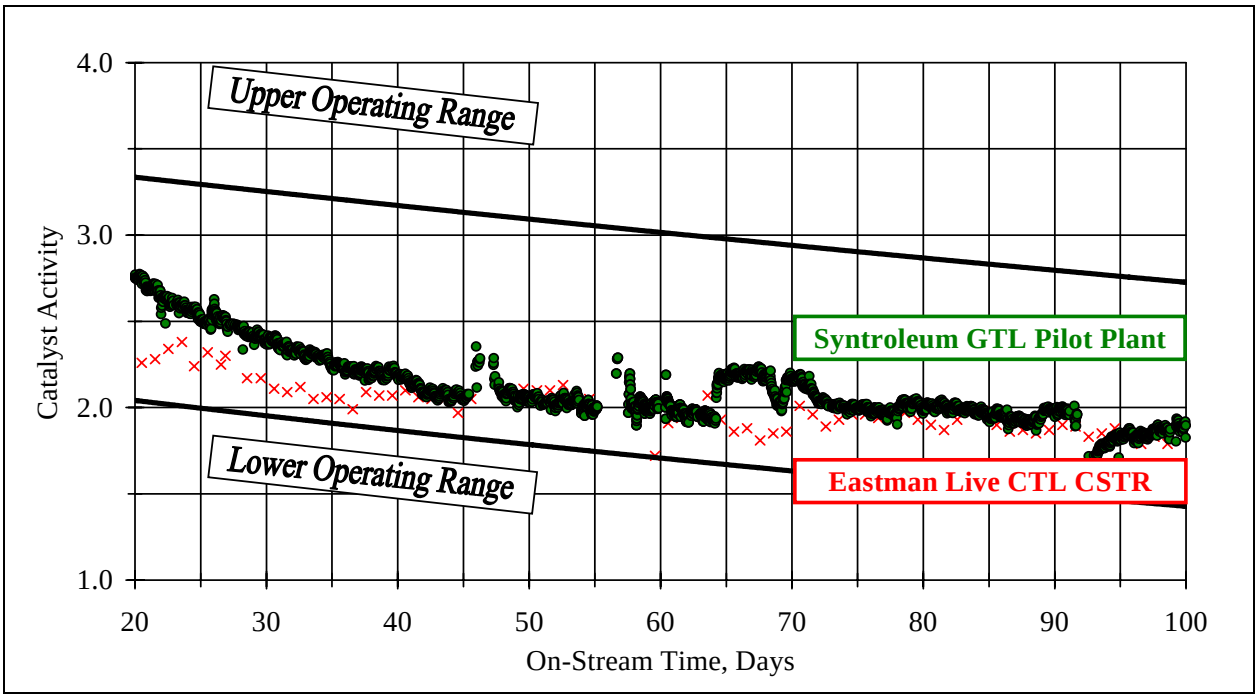
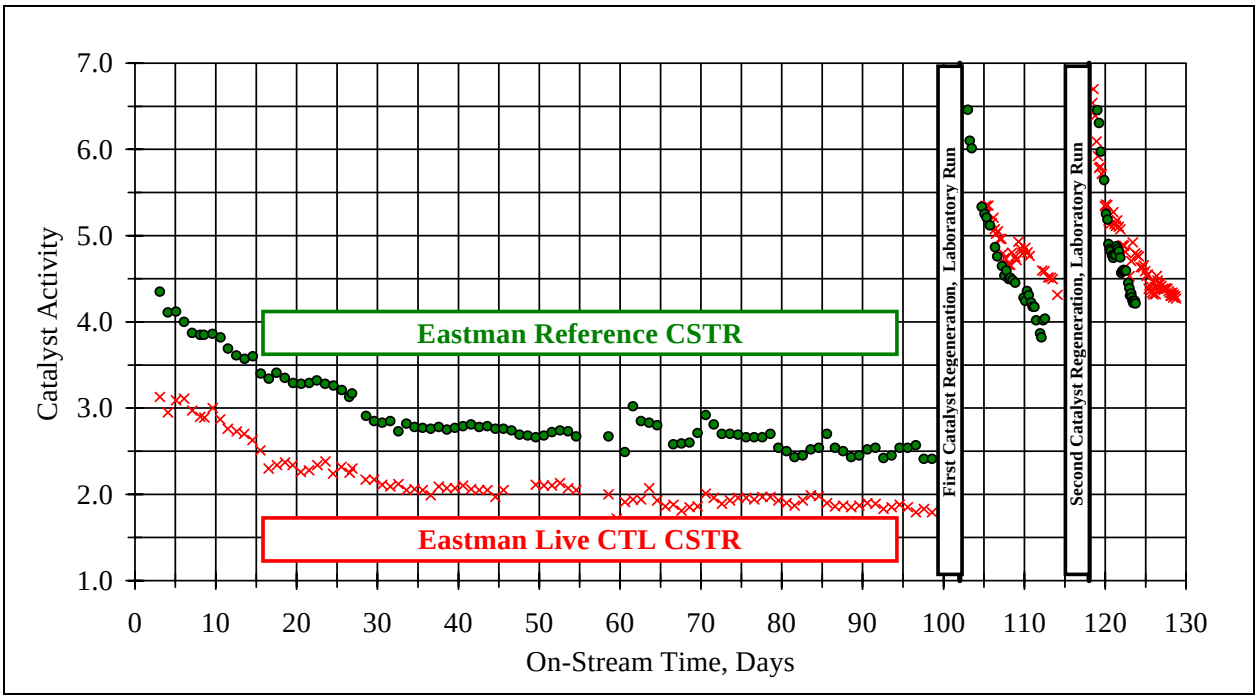


Figure 7. Syntroleum FT Catalyst from Eastman CTL Run Before and After Regeneration



**Note second regeneration run is ongoing*

Product Yield Comparison

FT reactor products are characterized by the Anderson-Schulz-Flory distribution.[6] The distribution is defined by a hydrocarbon chain growth probability constant, also referred to as the "alpha" value. Alpha value of 0.87 corresponds to maximum C12-C18 yield (diesel).[7] The crude FT product from the live coal syngas and the reference reactor were measured to have average alpha values of 0.86 and 0.87 respectively. The GTL pilot plant average alpha value at comparable operating temperatures is 0.88.

Another measure of FT liquids yield is C5+ hydrocarbon selectivity. This was measured as 82% and 81% for the live coal syngas and the reference reactors respectively. The GTL pilot plant average C5+ selectivity at comparable temperatures is 80%.

These differences may be explained by the fluctuations in syngas H_2:CO ratio (Figure 4) and are within experimental error. The cobalt catalyst therefore achieved its characteristic high diesel yield performance in coal syngas service.

Summary

The combination of a long stable bench scale run on coal-derived synthesis gas coupled with on-line clean up operations and a characteristic deactivation rate provides confidence in the commerciality of using cobalt based catalyst in a coal derived syngas operation. The successful demonstration of Syntroleum's patented regeneration technology adds an additional level of assurance to the commerciality of cobalt based FT slurry catalyst for production of fuels from coal derived syngas. The key findings of the study are highlighted below.

- Cobalt catalyst perform the same in coal and natural gas syngas conversion service;

- Guard beds perform as designed;
- Cobalt catalyst performance was not impacted by operational variations in H_2:CO ratio;
- Catalyst regeneration performed the same under coal or natural gas syngas;
- Wax production (alpha value) was the same for CTL and GTL FT waxes;
- C5+ hydrocarbon selectivity was the same for coal or natural gas syngas; and
- Variations in H_2:CO ratios typically seen in commercial operations did not affect catalyst performance

Syntroleum has shown that coal gasification coupled with a cobalt based FT process is a viable technology for generating an alternative source of transportation fuels and chemical feedstocks.

References

1. "International Data: Coal"; Energy Information Agency, Washington, DC; 2007. (http://www.eia.doe.gov/pub/international/iea2003/table82.xls)

2. "Petroleum: Reserves, Reserve Changes, and Production"; Energy Information Agency, Washington, DC; 2007. (http://www.eia.doe.gov/emeu/international/reserves.html)

3. Assuming a conversion factor of 1.75 bbl FT distillate per ton coal, 22 billion barrels = 12.6 billion tons or 4.7% of 270 billion ton reserves.

4. Landrum, Mark; Warzel, Jon; "High Quality Competitive Distillate Fuels from Coal-to-Liquids Processing"; Baker & O'Brien Inc., presented at NPRA Annual Meeting, March 2007. (http://www.bakerobrien.com/images/uploads/NPRA%20CTL%20Presentation.pdf)

5. Dry, M. E. In *Fischer-Tropsch Technology*; Stenberg, A. P.; Dry, M. E. Ed.; Studies in Surface Science and Catalysis 152; Elsevier: New York, 2004; pp 593-596.

6. Claeys, M.; van Steen, E. In *Fischer-Tropsch Technology*; Steynberg, A. P.; Dry, M. E. Ed.; Studies in Surface Science and Catalysis 152; Elsevier: New York, 2004; pp 624-628.

7. Steynberg, A. P.; Dry, M. E.; Daves, B. H.; Breman, B. B. In *Fischer-Tropsch Technology*; Steynberg, A. P.; Dry, M. E. Ed.; Studies in Surface Science and Catalysis 152; Elsevier: New York, 2004; p 65.