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**TECHNOLOGY DEVELOPMENT FOR IRON  
FISCHER-TROPSCH CATALYSIS**

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## Abstract

The goal of the proposed work is the development of iron-based Fischer-Tropsch catalysts that combined high activity, selectivity and life with physical robustness for slurry phase reactors that will produce either low-alpha or high-alpha products. The catalyst that is developed will be suitable for testing at the Advanced Fuels Development Facility at LaPorte, Texas or similar sized plant. Previous work by the offeror has produced a catalyst formulation that is 1.5 times as active as the "standard-catalyst" developed by German workers for slurry phase synthesis. The proposed work will optimize the catalyst composition and pretreatment operation for this low-alpha catalyst. In parallel, work will be conducted to design a high-alpha iron catalyst that is suitable for slurry phase synthesis. Studies will be conducted to define the chemical phases present at various stages of the pretreatment and synthesis stages and to define the course of these changes. The oxidation/reduction cycles that are anticipated to occur in large, commercial reactors will be studied at the laboratory scale. Catalyst performance will be determined for catalysts synthesized in this program for activity, selectivity and aging characteristics.

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## **1.0 Executive Summary**

A number of runs were made in the CSTR systems to provide a comparison of silica base high-alpha catalysts at 230°C and 250°C and a comparison of a reactor start-up solvents.

Two series of runs using five catalysts at synthesis temperatures of 250°C and 230°C were performed in the CSTR systems using C-30 oil and a 5.0 wt.% catalyst loading. The catalysts were prepared to provide a Si/Si+Fe atomic ratio 4.4% and were impregnated with Cu (relative to Fe) at 3 wt.%. Each of the five catalysts were impregnated with different amounts of K (0 wt.%, 2.5 wt.%, 5.0 wt.%, 7.5 wt.% and 10 wt.%) relative to Fe. The results showed, in general, based on % CO conversions for these catalysts, that:

$$T_{\text{syn}} = 250^{\circ}\text{C} > T_{\text{syn}} = 230^{\circ}\text{C} \text{ and}$$

$$5.0 \text{ wt.\%K} = 2.5 \text{ wt.\% K} \approx 7.5 \text{ wt.\% K} > 10.0 \text{ wt.\% K} > 0.0 \text{ wt.\% K}$$

## **2.0 Introduction**

The objective of this research project is to develop the technology for the production of physically robust iron-based Fischer-Tropsch catalysts that have suitable activity, selectivity and stability to be used in the slurry phase synthesis reactor development. The catalysts that are developed shall be suitable for testing in the Advanced Fuels Development Facility at LaPorte, Texas, to produce either low- or high-alpha product distributions. Previous work by the offeror has produced a catalyst formulation that is 1.5 times as active as the "standard-catalyst" developed by German workers for slurry phase synthesis. The proposed work will optimize the catalyst composition and pretreatment operation for this low-alpha catalyst. In parallel, work will

be conducted to design a high-alpha iron catalyst this is suitable for slurry phase synthesis. Studies will be conducted to define the chemical phases present at various stages of the pretreatment and synthesis stages and to define the course of these changes. The oxidation/reduction cycles that are anticipated to occur in large, commercial reactors will be studied at the laboratory scale. Catalyst performance will be determined for catalysts synthesized in this program for activity, selectivity and aging characteristics.

The research is divided into four major topical areas: (a) catalyst preparation and characterization, (b) product characterization, (c) reactor operations, and (d) data assessment.

To accomplish the objectives of the project, these topics have been organized into the following technical tasks:

**a. Task 1.0 Development of Optimum Promoter Levels for Low- and High-Alpha Catalysts**

The goal of this task is to identify and optimize procedure for the preparation of iron-based catalysts that combine high activity selectivity and life with physical robustness. Each of the subtasks address an area of considerable uncertainty in the synthesis of catalysts.

**1.1 Determine Optimized Synthesis Procedure for High-Alpha Iron-Based Fischer-Tropsch Catalysts**

- Role of precursor particle size on activity.
- Role of Cu in precipitated catalysts.
- Define attrition resistance.

1.2 Prepare Catalysts that can be Used to Determine the Role of Promoters for Low- and High-Alpha Catalysts

- Define optimum  $\text{SiO}_2$ .
- Define optimum  $\text{Al}_2\text{O}_3$ .

1.3 Prepare Catalysts that can be Used to Quantify the Role of K on Product Selectivity in both Low- and High-Alpha Catalysts.

1.4 Complete the Optimization of the Two Best Low-Alpha, Iron-Based Fischer-Tropsch Catalysts Developed during the Previous Contract.

**b. Task 2.0 Definition of Preferred Pretreatment for both Low- and High-Alpha Fischer-Tropsch Catalysts.**

The goals of this task are to define the preferred treatment, to define the role of Cu and K during the pretreatment on activity and selectivity and to define the chemical and physical changes which occur during the preferred pretreatment. The subtasks address each of these goals.

2.1 Determine the Role of Cu in the Activation of Precipitated Low- and High-Alpha, Iron-Based Fischer-Tropsch Catalysts.

2.2 Determine the Effect of K Content on Activation Procedures and Determine if the Method of Addition has any Effect on Catalyst Activity and Life.

2.3 Determine the Physical and Chemical Changes that Occur during Catalyst Pretreatment and Use and Determine how these Changes Effect the Strength of the Catalysts.



- 2.4 Evaluate the Effect of Carbon Deposition during Catalyst Activation on Activity, Selectivity and Aging Characteristics.

c. Task 3.0 Catalyst Structure and Characterization.

The goal of this task is to provide basic analyses (surface area, XRD) of all catalyst prepared and to provide additional techniques as required (Mössbauer, SEM, XPS, etc.) to answer specific questions or to provide basic required characterization data for the catalysts.

d. Task 4.0 Catalyst Testing.

The goals of this task are to operate the eight CSTR reactors, measure catalyst performance, determine the stable phases that exist during synthesis at low and high conversions and to determine the rates of interconversion of iron oxide and carbide.

- 4.1 Verify the Quality of Data Obtained from the CSTR's.
- 4.2 Measure Catalyst Performance.
- 4.3 Determine the Stable Phases that Exist during Synthesis at Low and High CO Conversion Levels.
- 4.4 Obtain Data on the Rates Involved in the Interconversion of Iron Oxide and Iron Carbide.

**Comparison of Silica Based Hi-Alpha Catalyst at 230°C and 250°C With C-30 oil at a 5.0wt% Catalyst Loading**

Two series of runs using five catalysts at synthesis temperatures of 250°C and 230°C were performed in the one liter continuously stirred tank reactors (CSTR). When Ethylflo C30 decene trimer was used as the start-up oil, a 5 wt.% catalyst slurry containing 15.3 g and 290 g of oil was used. When PW3000 wax was used, the initial

slurry was 3 wt.% catalyst and contained 9.6 g of catalyst and 310 g of wax. For all the runs, the reactor solvent was C-30 oil with a catalyst loading of 5.0wt%. The iron-based catalysts used in these tests had been co-precipitated so that the atomic ratio of silicon to silicon + iron, i.e.,  $[Si] / [Si+Fe]$ , was at 0.044, or 4.4atomic(or mole)%. All the catalyst had been impregnated with copper such that the weight percentage of copper (relative to Fe) was at 3.0wt%Cu. Each of the five catalysts had a different amount of potassium present, specifically, 0.0wt%K, 2.5wt%K, 5.0wt%K, 7.5wt%K, and 10.0wt%K. As was the case for the copper, the potassium wt%'s are also relative to Fe. The list below shows the five catalysts tested and designates the atomic(mole) ratios of Si, Cu, and K, based on 100 atoms(moles) of Fe.

RJO228 (0.0wt%K) 100Fe:4.60Si/2.72Cu/0.00K

RJO229 (2.5wt%K) 100Fe:4.60Si/2.72Cu/3.66K

RJO230 (5.0wt%K) 100Fe:4.60Si/2.72Cu/7.52K

RJO231 (7.5wt%K) 100Fe:4.60Si/2.72Cu/11.58K

RJO232 (10.0wt%K) 100Fe:4.60Si/2.72Cu/15.87K

The first five runs performed were at 250°C and designated LGX236(0.0wt%K), LGX239(2.5wt%K), LGX240(5.0wt%K), LGX241(7.5wt%K), and LGX242(10.0wt%K). A comparison of the %CO conversion versus days on stream is shown in Figure 1. The second series of runs, specifically LGX235(0.0wt%K), LGX244(2.5wt%K), LGX245(5.0wt%K), LGX246(7.5wt%K), and LGX247(10.0wt%K), was performed at the synthesis temperature of 230°C and the %CO conversion versus days on stream is given in Figure 2.

In general, the catalysts performed better in regards to CO conversion at the synthesis temperature of 250°C. At both temperatures, the catalyst run with the 5.0wt%K loading (RJO230) had the best CO conversion, while also for both temperatures, the 0.0wt%K loaded catalyst (RJO228) runs produced the poorest CO conversions. Again, for both temperatures, the catalysts at 2.5wt%K and 7.5wt%K (RJO229 and RJO231, respectively) produced comparable CO conversions, slightly lower than the CO conversion exhibited by the 5.0wt%K (RJO230) loaded catalyst runs, and the catalyst runs with the 10.0wt%K loadings were the fourth best with respect to the CO conversions, these also at both synthesis temperatures.

Note that for the 230°C synthesis conditions (Figure 2), the CO conversions for the 2.5, 5.0, 7.5, and 10.0wt%K loaded catalysts all fell within a 20% band at the start of the run and improved to a band of 10% or less by the end of the run. This band of CO conversions was also observed for the runs performed at 250°C, but only for the 2.5, 5.0, and 7.5wt%K loaded catalysts. The CO conversions were at ~80% for the 2.5, 5.0, and 7.5wt%K catalysts, while the CO conversion for the 10.0wt%K catalyst had a starting value of only ~50%. This justified another run using the 10.0wt%K catalyst, RJO232, at the synthesis temperature of 250°C. Run LGX250 was performed and the results of the CO conversion are given in Figure 3 and it can be seen that the %CO conversion did improve to values greater than 70%, with the exception in the drop of conversion starting at run hour 168 and reaching a minimum at ~run hour 264, which was found to be due to a faulty inert gas valve. After corrective action was taken in regards to the valve, it can be seen the CO conversion did rebound and if these results were plotted with the 2.5, 5.0, and 7.5wt%K data, they would all fall into a band even

tighter than that found with the 230°C CO conversions (i.e., bandwidth of ~10% CO conversion for the 250°C synthesis conditions).

Thus, in general, based on %CO conversions for these catalysts,

$$T_{\text{syn}} = 250^{\circ}\text{C} > T_{\text{syn}} = 230^{\circ}\text{C}$$

$$5.0\text{wt}\%K > 2.5\text{wt}\%K \cong 7.5\text{wt}\%K > 10.0\text{wt}\%K > 0.0\text{wt}\%K.$$

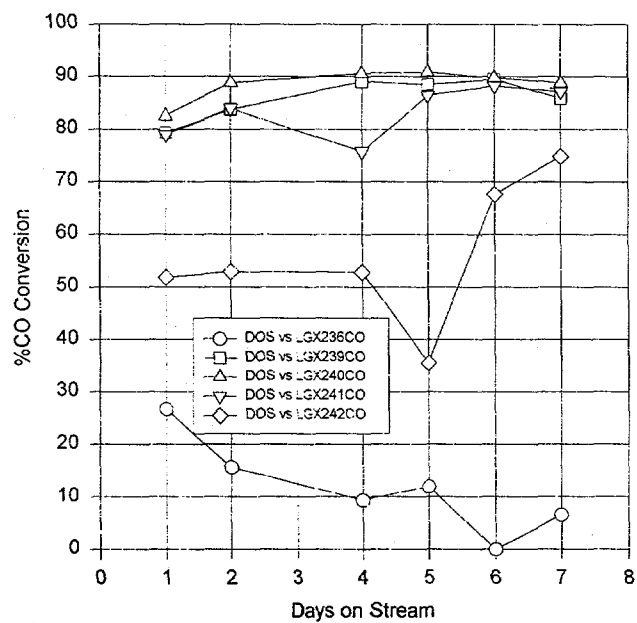


Figure 1. %CO Conversion vs Days on Stream for Runs LGX239-242 @ 250°C.

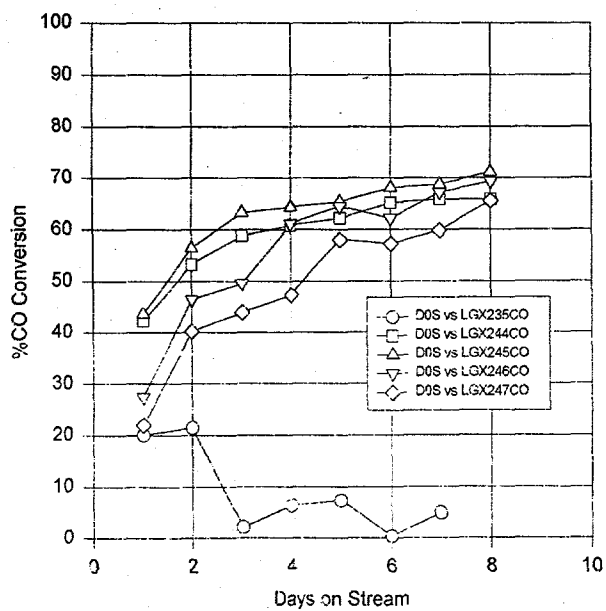


Figure 2. %CO Conversion vs Days on Stream for Runs LGX244-247 @ 230°C.

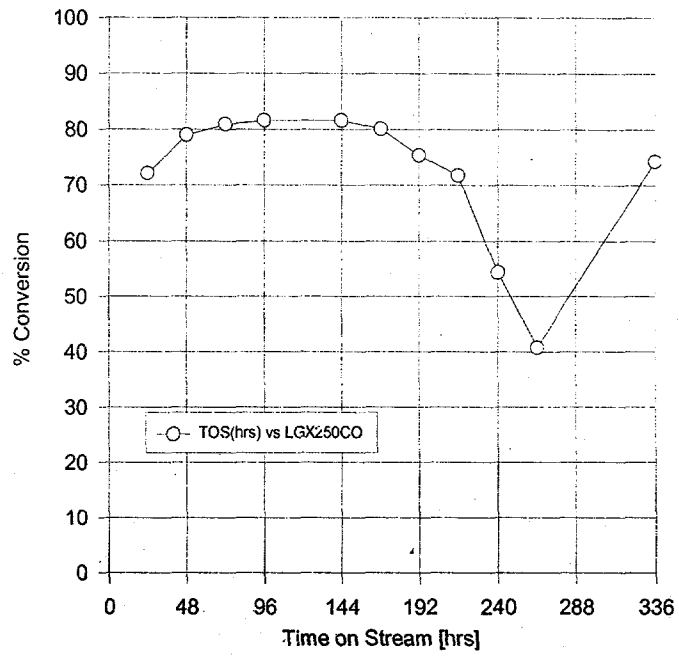


Figure 3. %CO Conversion vs Time on Stream for Run LGX250<sub>R7</sub> with T<sub>syn</sub> @ 250°C.

### Comparison of Reactor Solvents (C-30 oil vs PW<sub>R</sub>3000 Wax)

This series of runs involves comparing the performance of a high molecular weight polyethylene wax, Polywax PW<sub>R</sub>3000, for use as a reactor solvent, to that of the typically used C-30 oil. For this comparison, the well studied 4.4Si150 cyclone catalyst was used (4.4atomic%Si and 1.0atomic%K, both relative to Fe, i.e.,  $[\text{Si}(\text{or K})]/[\text{Si}(\text{or K}) + \text{Fe}]$ ). 32.22g of the catalyst was used in all of the runs, and for the C-30 oil application the catalyst loading was at 10.0wt%, while for the PW<sub>R</sub>3000 wax a 11.1wt% catalyst loading was used. This difference in weight% loadings stemmed from attempts to establish equivalent volumes of solvent during the initial loading of the continuously stirred tank reactors (CSTR). These runs were modeled after previous runs that used the C-30 oil as a solvent, which were normally loaded at a 10.0wt% catalyst loading, specifically 32.22g of catalyst along with 290.0g of C-30 start up oil/solvent. With the density of the C-30 oil at  $\sim 0.80\text{g/cm}^3$ , this yielded a start up solvent volume of  $362.5\text{cm}^3$ , thus the target volume for the PW<sub>R</sub>3000 wax was  $362.5\text{cm}^3$ . As the PW<sub>R</sub>3000 wax is a solid at ambient temperatures, it was heated until it melted, i.e., at  $\sim 130^\circ\text{C}$ , at which point the density was determined to be  $0.71\text{g/cm}^3$ . Thus at  $130^\circ\text{C}$ , it requires 257.4g of PW<sub>R</sub>3000 wax to obtain a volume of  $362.5\text{cm}^3$ . Note that the density of the C-30 oil should have been determined at a temperature of  $130^\circ\text{C}$ , instead of at ambient temperature (at a later date the densities and specific volumes( $\text{cm}^3/\text{g}$ ) of the PW<sub>R</sub>3000 and C-30 oil were determined up to  $210^\circ\text{C}$ , as well as the densities and specific volumes for the C-28 (octacosane) and the PW<sub>R</sub>2000 high molecular weight polyethylene wax, and that algorithms were then developed for the densities and specific volumes as a function of temperature from ambient through  $210^\circ\text{C}$ ).

Run LGX248 was performed as the baseline case with the C-30 oil and the %CO conversion results are given in Figure 1. The %CO conversion results for the PW<sub>R</sub>3000 run, LGX249, are shown in Figure 2. Both reactor solvents produced CO conversions of 80-90%, until gas feed tube pluggages occurred (at ~run hour 550 for the C-30 oil and at ~run hour 460 for the PW<sub>R</sub>3000 solvent). These two runs showed the feasibility of using the PW<sub>R</sub>3000 polyethylene wax as a reactor solvent. It was then decided to repeat the PW<sub>R</sub>3000 run to confirm the reproducibility of the results obtained in run LGX249. Run LGX251 was started and it was observed that the pretreatment pressure had climbed to ~40psig (pretreatment is to be carried out for 24 hours at 0psig), but aborted after two days at synthesis conditions. Thus run LGX252 was initiated, but it too was aborted after three days at synthesis conditions, due to a pressure of ~100psig during the pretreatment period. It was discovered that the reason for the elevated pressures during the pretreatment period was caused by the restriction of the gas out and due to blinding off and/or plugging in the 7 $\mu$ -wax filter and the wax line out of the reactor, which functions as a continuous line out for the gas products produced during the FTS reaction. It was found that the restrictions were caused by the condensing and solidifying of the PW<sub>R</sub>3000 polywax (melting point at ~130°C) which possibly had been entrained in the gas out of the reactor via the wax line out. To rectify this problem, the wax filter was fitted with a thermocouple and an additional heat tape was installed on the wax line, as well as increasing the amount of insulation on the wax line out (this was also done for the rewax line out to allow for the removal of the reactor liquid products). This allowed for the monitoring and adjustment, if necessary, of the temperature of the 7 $\mu$ -wax filter and wax line. After these modifications, run LGX253 was started and the



pretreatment period was successfully completed at the desired pressure of 0psig. Figure 3 gives the %CO conversions for runs LGX251, LGX252, and LGX253 and shows an inverse relationship with %CO conversion and pretreatment pressures. Note that the %CO conversion for run LGX253 agrees rather well to that of the %CO conversion for run LGX249. That is, for run LGX253 the CO conversion starts at ~90% and is maintained at ~85% or greater up through run hour 500. It was thus shown that the PW<sub>R</sub>3000 polyethylene wax could be used as a suitable reactor solvent for the FTS synthesis.

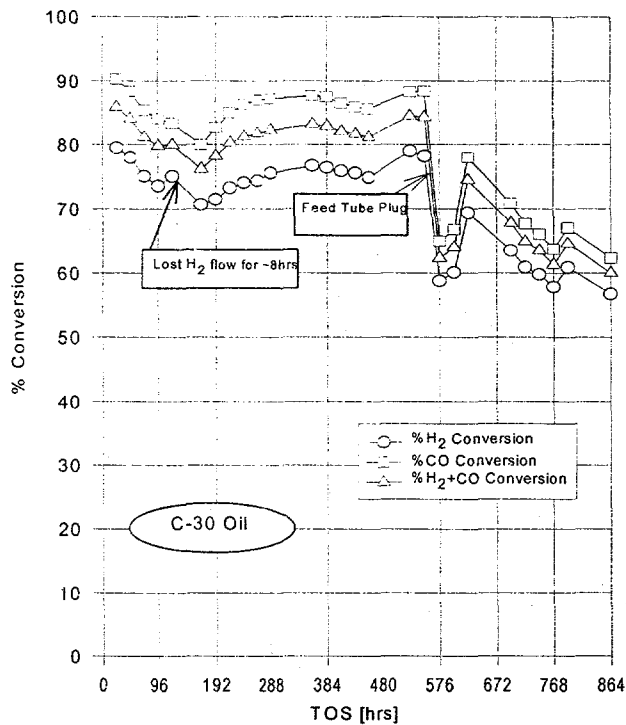


Figure 1. %CO Conversion vs Time on Stream [TOS] for Run LGX248<sub>R1</sub>.

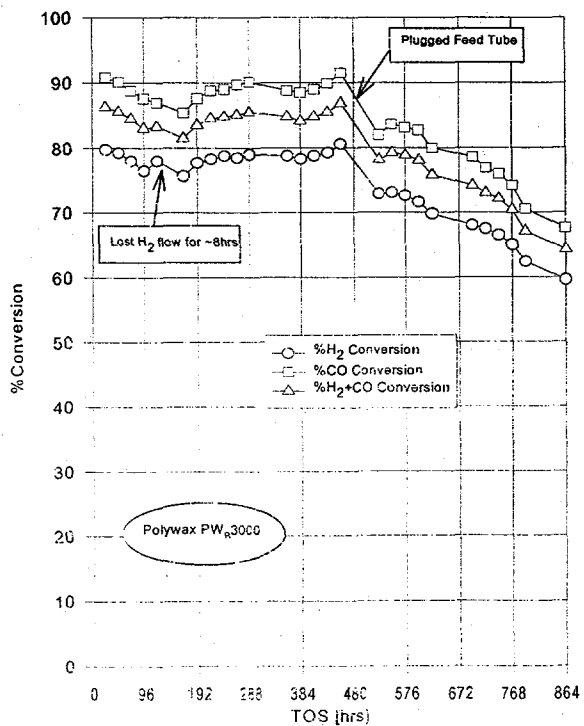


Figure 2. %CO Conversion vs Time on Stream for LGX249<sub>R2</sub>.

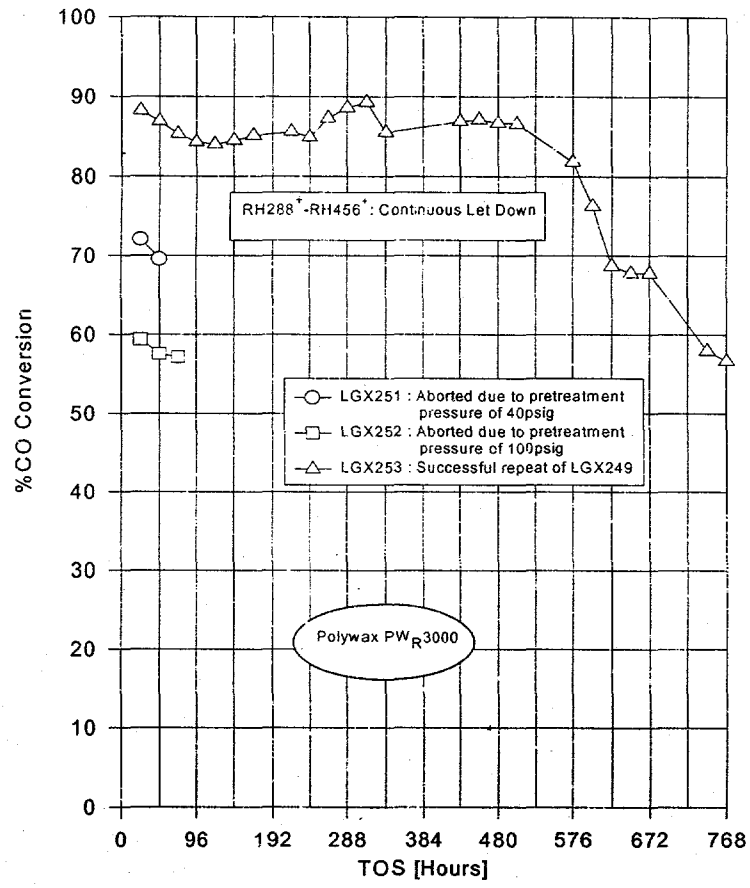


Figure 3. %CO Conversion vs Time on Stream for Runs LGX251-253.