

Determination of the Effect of Coal/Biomass-Derived Syngas Contaminants on the Performance of Fischer-Tropsch and Water-Gas-Shift Catalysts

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Acronyms

α	alpha and represents the probability of chain growth
Al ₂ O ₃	Alumina
NH ₄	Ammonia
Sb	Antimony
Ar	Argon
As	Arsenic
AsH ₃	Arsine
C ₁	Molecular species with 1 carbon atom
C ₇	Molecular species with 7 carbon atoms
C _{frac,i}	Weight fraction of product with i carbon atoms
Cd	Cadmium
CO	Carbon monoxide
CO ₂	Carbon dioxide
COS	Carbonyl sulfide
°C	Degrees Celsius
Cr ₂ O ₃	Chromium oxide
CB	Coal/biomass
CBTL	coal/biomass-to-liquids
Co	Cobalt
Co-FT	Cobalt-based Fischer-Tropsch
CuO	Copper oxide
Cc	cubic centimeters
ΔG_{rxn}	Gibbs free energy of reaction
DOE	Department of Energy
Eq	Equation
FT	Fischer-Tropsch
GC	Gas chromatograph
HTS	High temperature shift
H ₂	Hydrogen
HCl	Hydrogen chloride
H ₂ Se	Hydrogen selenide
H ₂ S	Hydrogen sulfide
In.	Inches
ID	Internal diameter
Fe	Iron
Fe-FT	Iron-based Fischer-Tropsch
Fe ₂ O ₃	Iron oxide
K	Constant in Anderson-Schulz-Flory probability distribution equation
kJ/mol	kilojoules per mole
LTS	Low temperature shift
MgO	Magnesium oxide
μm	microns
mg C ₅₊ /h/g catalyst	Mg of molecular species with 5 or more carbon atoms per hour per gram of catalyst
Hg	Mercury
CH ₄	Methane

MoO ₃	Molybdenum oxide
N _i	Number of carbon atoms
NETL	National Energy Technology Laboratory
ND	Not detected
N/A	Not available
NO _x	Oxides of nitrogen
Ppmv	Parts per million by volume
Ppbv	Parts per billion by volume
Pptv	Parts per trillion by volume
P	Phosphorus
PH ₃	Phosphine
K	Potassium
K ₂ CO ₃	Potassium carbonate
KCl	Potassium chloride
R&D	Research and development
RuO	Ruthenium oxide
Se	Selenium
SiO ₂	Silicon dioxide
Na	Sodium
NaCl	Sodium chloride
SGS	Sour gas shift
SO _x	Oxides of sulfur
SPB-1	Trademark name for GC column manufactured by Sigma Aldrich
SNG	Substitute natural gas
SCI	Süd-Chemie, Inc.
24/7	24 hours a day and 7 days a week
U.S.	United States of America
WGS	Water gas shift
ZnO	Zinc oxide

Abstract

Today, nearly all liquid fuels and commodity chemicals are produced from non-renewable resources such as crude oil and natural gas. Because of increasing scrutiny of carbon dioxide (CO₂) emissions produced using traditional fossil-fuel resources, the utilization of alternative feedstocks for the production of power, hydrogen, value-added chemicals, and high-quality hydrocarbon fuels such as diesel and substitute natural gas (SNG) is critical to meeting the rapidly growing energy needs of modern society. Coal and biomass are particularly attractive as alternative feedstocks because of the abundant reserves of these resources worldwide. The strategy of co-gasification of coal/biomass (CB) mixtures to produce syngas for synthesis of Fischer-Tropsch (FT) fuels offers distinct advantages over gasification of either coal or biomass alone. Co-feeding coal with biomass offers the opportunity to exploit economies of scale that are difficult to achieve in biomass gasification, while the addition of biomass to the coal gasifier feed leverages proven coal gasification technology and allows CO₂ credit benefits.

Syngas generated from CB mixtures will have a unique contaminant composition because coal and biomass possess different concentrations and types of contaminants, and the final syngas composition is also strongly influenced by the gasification technology used. Syngas cleanup for gasification of CB mixtures will need to address this unique contaminant composition to support downstream processing and equipment.

To investigate the impact of CB gasification on the production of transportation fuels by FT synthesis, RTI International conducted thermodynamic studies to identify trace contaminants that will react with water-gas-shift and FT catalysts and built several automated microreactor systems to investigate the effect of single components and the synergistic effects of multiple contaminants on water-gas-shift and FT catalyst performance. The contaminants investigated were sodium chloride (NaCl), potassium chloride (KCl), hydrogen sulfide (H₂S), carbonyl sulfide (COS), ammonia (NH₃), and combinations thereof. This report details the thermodynamic studies and the individual and multi-contaminant results from this testing program.

Executive Summary

The overall objective of this project was to quantify the effects of syngas contaminants generated during entrained-flow gasification of coal/biomass (CB) mixtures on commercial water-gas-shift (WGS) and Fischer-Tropsch (FT) catalysts.

The project approach was to test actual commercial WGS and FT catalysts with simulated syngas containing contaminants specific to CB-derived syngas to quantify

- Changes in catalyst activity and selectivity
- Changes in catalyst physical/chemical properties
- Catalyst changes resulting from simultaneous interaction with multiple contaminants
- Effects of contaminant concentration on catalyst changes

Commercial samples of high-temperature-shift (HTS) catalyst, low-temperature-shift (LTS) catalyst, sour-gas-shift (SGS) catalyst, and cobalt (Co)- and iron (Fe)-based FT catalysts provided by Süd-Chemie Inc. (SCI) were evaluated in the studies.

To determine which trace contaminants present in CB-derived syngas could potentially react with the catalysts, a series of thermodynamic analyses in which the catalysts were represented by their chemical components (active catalyst, binder, support, etc.) were completed. These analyses showed that catalyst components could potentially react with a host of trace contaminants, in particular, with arsenic (As), phosphorous (P), and selenium (Se) identified as the contaminants having the most favored potential for reaction. Based on the thermodynamic analysis results, the contaminants recommended for experimental testing included sulfur (hydrogen sulfide (H₂S) and carbonyl sulfide (COS), ammonia (NH₃), alkalis, hydrogen chloride (HCl), arsine (AsH₃), hydrogen selenide (H₂Se), phosphine (PH₃), and mercury (Hg). In this project, the commercial WGS and FT catalysts were tested with only a subset of these contaminants, specifically H₂S, COS, NH₃, sodium chloride (NaCl), and potassium chloride (KCl), and combinations of these contaminants. Selection of these contaminants and the range of contaminant concentrations used during the test were based on most accurately representing syngas produced by gasification of CB mixtures and potential for catalyst poisoning.

To efficiently evaluate performance of the commercial catalysts, a series of automated microreactor systems were designed, fabricated, and operated to effectively expose each catalyst to simulated CB-derived syngas containing known amounts of contaminants for up to 1,000 continuous hours of testing. The catalyst testing was performed at temperature and pressure conditions typically used in commercial catalyst operation. During testing, the effluent products (gas and waxes) were analyzed by gas chromatograph (GC) to monitor catalyst performance (catalyst activity and selectivity).

The baseline performance for each catalyst was established by conducting an initial trial in which the catalyst was exposed to a simulated CB syngas mixture containing no contaminants. After stable catalyst performance was achieved, introduction of the contaminants was started. The exposure trials for the WGS catalysts focused on multi-contaminant exposure. For the FT catalysts, the exposure trials focused on initial testing with single contaminants followed by testing with multiple contaminants. A summary of these exposure trial results is provided in Table ES-1. In general, the most significant adverse effect on catalyst performance was seen with the sulfur species (H₂S and COS). H₂S was also observed to be a stronger catalyst poison than COS. The catalyst most sensitive to contaminants was the Co-FT catalyst.

Table ES-1. Summary of Changes in Catalyst Performance during Contaminant Exposure Trials

Catalyst	Exposure trial	
	Individual contaminants ¹	Multiple contaminants
LTS		<ul style="list-style-type: none"> No impact observed up to 1,000 parts per million by volume (ppbv) of NH₃ and H₂S
HTS		<ul style="list-style-type: none"> Decline in carbon monoxide (CO) conversion demonstrated for combinations of ≥150 ppbv H₂S and 1,000 ppbv of NH₃ with alkali vapors Alkali vapors did not result in CO conversion decline and potentially resulted in recovery of lost CO conversion after exposure to 1,000 ppbv H₂S
SGS ²		<ul style="list-style-type: none"> No impact observed up to 1,000 ppbv NH₃
Fe-FT	<ul style="list-style-type: none"> H₂S: Performance loss at >150 ppbv COS: Performance loss at >175 ppbv NaCl vapor: No impact KCl vapor: No impact NH₃: No impact 	<ul style="list-style-type: none"> Most significant decrease in CO conversion observed with NaCl, KCl, and 100 ppbv H₂S
Co-FT	<ul style="list-style-type: none"> H₂S: Performance loss at 10 ppbv COS: Performance loss at >100 ppbv NaCl vapor: No impact NH₃: Performance loss at >1,000 ppbv 	<ul style="list-style-type: none"> Statistically significant decrease in CO conversion observed with NaCl, KCl, 10 ppbv H₂S, and 100 ppbv NH₃

¹ Hatched regions indicate that individual contaminant exposure trials were not conducted with WGS catalysts.

² Multi-contaminant exposure trials were focused on alkali vapors and NH₃.

The results discussed in this report are an invaluable contribution to a comprehensive database documenting catalyst performance during operation with contaminant-laden syngas. Such a database will eventually be used to establish syngas contaminant specifications for WGS and FT applications.

1. Introduction

Today, nearly all liquid fuels and commodity chemicals are produced from non-renewable resources such as crude oil and natural gas. Because of increasing scrutiny of carbon dioxide (CO₂) emissions produced using traditional fossil-fuel resources, the utilization of alternative feedstocks for the production of power, hydrogen, value-added chemicals, and high-quality hydrocarbon fuels such as diesel and substitute natural gas (SNG) is critical to meeting the rapidly growing energy needs of modern society. Coal and biomass are particularly attractive as alternative feedstocks because the United States has abundant domestic reserves of these resources available. Research and development (R&D) of technologies focused on the production of liquid fuels and SNG from coal/biomass (CB) mixtures via gasification was supported by the “Alternate Production Pathway” under the Hydrogen and Clean Fuels Program sponsored by the U.S. Department of Energy’s (DOE’s) National Energy Technology Laboratory (NETL). This R&D program is particularly timely for:

- Providing a means to reduce the U.S. dependence on imported oil by using domestic coal and biomass energy resources;
- Reducing the CO₂ footprint of fuel and chemical production by using coal/biomass-to-liquids (CBTL) processes that, when integrated with carbon capture or reuse, have lower CO₂ emissions than conventional petroleum-fuel-based processes;
- Creating a near-zero footprint for other emissions, including SO_x, NO_x, and mercury;
- Increasing energy sustainability by optimizing the integration of renewable biomass utilization in fuel production; and
- Facilitating commercial deployment of the most effective gasification technologies available.

Economic projections indicate that coal-biomass-to-liquid (CBTL) processes should be cost-competitive at oil prices significantly below the current price of \$80 per barrel of crude oil. However, the process assumptions used to generate these economic projections need to be validated and/or optimized for realistic operating conditions. One important assumption pertains to the performance and lifetime of commercial catalysts to be used in the water-gas-shift (WGS) and Fischer-Tropsch (FT) synthesis processes in CBTL production. Because commercial WGS and FT catalysts are very sensitive to poisoning by trace contaminants present in the process gas streams, the economic projections are based on critical assumptions about the catalyst replacement cost and the capital cost for syngas cleaning processes needed to achieve a target catalyst life expectancy. An optimal balance of these two costs is required to provide the most cost-competitive CBTL process, and determination of this optimal cost balance requires

- Identification of the CB-derived syngas contaminants that are poisons for WGS and FT catalysts; and
- Knowledge of the effect of contaminant concentrations on the rates of catalyst degradation and deactivation.

For syngas generated from conventional commercial feedstocks such as natural gas, poisons for WGS and FT catalysts have been identified. Moreover, these conventional feedstocks are not used in their raw (“dirty”) material state because they typically undergo multiple refining operations before being introduced into WGS and FT processes. As a result, the “refined” feedstocks usually have only one or two contaminants that could act as catalyst poisons.

In contrast, a significantly larger number of contaminants, especially at low or trace concentrations, are found in syngas generated from alternative feedstocks such as coal, biomass, or mixtures of coal and

biomass. Thus, there is an increase in the probability of catalyst poisoning not only by single contaminants but also by simultaneous, synergistic interactions of multiple contaminants. In addition to catalyst deactivation through activity loss, the contaminants could adversely affect catalyst support and binder components, leading to undesirable physical changes that further shorten catalyst lifetime. This report provides results from studies evaluating long-term catalyst performance impacts for hydrogen sulfide (H₂S), carbonyl sulfide (COS), ammonia (NH₃), potassium chloride (KCl), and sodium chloride (NaCl) in syngas, with the goal of increasing the knowledge base to be eventually used in defining/establishing contaminant specifications for WGS and FT catalysts and syngas cleanup processes.

1.1 Approach

The approach for this project was to test commercial WGS and FT catalysts with simulated syngas containing contaminants specific to CB-derived syngas to quantify

- Changes in catalyst activity and selectivity;
- Changes in catalyst physical/chemical properties;
- Catalyst changes resulting from simultaneous interaction with multiple contaminants; and
- Effects of contaminant concentration on catalyst changes.

Commercial samples of high-temperature-shift (HTS), low-temperature-shift (LTS), sour-gas-shift (SGS), cobalt-based FT (Co-FT), and iron-based FT (Fe-FT) catalysts were provided by Süd-Chemie Inc. (SCI). The specific contaminants evaluated in this project were H₂S, COS, NH₃, NaCl, and KCl. Catalyst testing was performed at temperature and pressure conditions typically used in commercial catalyst operation. Microreactor systems designed to operate 24/7 with limited supervision were used to expose each catalyst to simulated CB-derived syngas containing known amounts of contaminants for up to 1,000 continuous hours of testing. During testing, the effluent products (gas and waxes) were analyzed by gas chromatograph (GC) to monitor catalyst performance (catalyst activity and selectivity). The length of the tests was sufficient to establish catalyst changes resulting from contaminants.

1.2 Project Objectives

The project objective was to quantify the effects of syngas contaminants generated during entrained-flow gasification of CB mixtures on commercial WGS and FT catalysts. The specific contaminant effects quantified were

- Changes in catalyst activity and selectivity;
- Changes in catalyst physical/chemical properties;
- Catalyst changes resulting from simultaneous interaction with multiple contaminants; and
- Effects of contaminant concentration on catalyst changes.

The scope of the project work involved thermodynamic evaluation of potential interactions between catalyst components (active catalyst, binder, support, etc.) and CB-derived syngas contaminants, development of specialized automated testing systems, and evaluation of commercial WGS and FT catalyst performance with simulated CB-derived syngas containing specific contaminants.

2. Thermodynamic Investigations

2.1 Methodology

To supplement the catalyst testing in this project, a thermodynamic study was used to evaluate potential interactions between contaminants present in CB-derived syngas and commercial FT and WGS catalysts at typical operating conditions. The study results provided educated guidance for selecting suitable contaminant testing levels by helping identify potential reaction mechanisms for changes in catalyst physical properties and performance associated with specific contaminants.

The thermo-chemistry software package HSC Chemistry (v. 5.1) was used to calculate the concentration of different species present at thermodynamic equilibrium conditions. The roster of contaminant species present in CB-derived syngas was developed from U.S. Department of Energy reports, as well as published data on syngas compositions associated with different entrained-flow gasification systems. This contaminant list included antimony (Sb), arsine (AsH₃), hydrogen chloride (HCl), cadmium (Cd), COS, H₂S, mercury (Hg), phosphine (PH₃), selenium (Se), potassium (K), and sodium (Na). The specific chemical components/species in the commercial HTS, LTS, HTS, SGS, Fe-FT, and Co-FT catalyst formulations investigated were obtained from available technical/marketing information in SCI's and Haldor Topsoe's marketing brochures and websites.

2.2 Results

Potential interactions between trace contaminants and catalyst components (active catalyst, binder, support, etc.) were determined by their thermodynamic probability to form a chemical compound with each other based on a Gibbs Free Energy analysis. This thermodynamic probability was divided into three categories: (i) not favored ($\Delta G_{\text{rxn}} > 0$ kJ/mol), (ii) slightly favored (-100 kJ/mol $< \Delta G_{\text{rxn}} < 0$ kJ/mol), and (iii) strongly favored ($\Delta G_{\text{rxn}} < -100$ kJ/mol). Tables 2-1 and 2-2 summarize the thermodynamic probability results for the WGS and FT catalysts, respectively. The rows in these tables show the thermodynamic reaction probability for contaminants, and the columns present the thermodynamic reaction probability for catalyst components. Hence, the intersection of a particular row and column provides the thermodynamic probability of forming a stable chemical compound between the indicated specific contaminant and catalyst component.

As indicated in Tables 2-1 and 2-2, several contaminants are strongly favored thermodynamically to react with WGS and FT catalyst components. The contaminants with the most favored potential for interactions are arsenic (As), phosphorus (P), and Se. Although little reactivity is predicted for Hg, amalgam formation was not included in this thermodynamic analysis. Based on the thermodynamic study, the contaminants recommended for experimental testing included sulfur (H₂S and COS), alkalis, HCl, AsH₃, H₂Se, PH₃, and Hg. In this project, however, only a subset of these contaminants, specifically H₂S, COS, NH₃, NaCl, and KCl, was selected for testing the commercial WGS and FT catalysts. The specific subset of contaminants chosen were based the results from the thermodynamic studies, the unique contaminant mixtures resulting from gasification of CB mixtures, and DOE's programmatic goals.

Table 2-1. Potential Interactions between WGS Catalyst Components and Trace Species Present in CB-Derived Syngas

		Catalyst System											
		HTS			LTS				SGS				
		Fe ₃ O ₄	CuO	Cr ₂ O ₃	Cu	MnO	Cr ₂ O ₃	ZnO	Al ₂ O ₃	CoS	MoS ₂	MgS	Al ₂ O ₃
Contaminants	AsH ₃												
	HCl												
	Sb												
	Cd												
	Hg												
	Se												
	PH ₃												
	Na												
	K												
	H ₂ S												
	COS												

$\Delta G_{rxn} < 100 \text{ kJ/mol}$
 $-100 \text{ kJ/mol} < \Delta G_{rxn} < 0 \text{ kJ/mol}$
 $\Delta G_{rxn} > 0 \text{ kJ/mol}$

Table 2-2. Potential Interactions between FT Catalyst Components and Trace Species Present in CB-Derived Syngas

		Catalyst System										
		Fe-FT					Co-FT					
		Fe ₃ C	K	Mn	Cu	SiO ₂	Al ₂ O ₃	Co	Ru	SiO ₂	Al ₂ O ₃	
Contaminants	AsH ₃											
	HCl											
	Sb											
	Cd											
	Hg											
	Se											
	PH ₃											
	Na											
	K											
	H ₂ S											
	COS											

$\Delta G_{rxn} < 100 \text{ kJ/mol}$
 $-100 \text{ kJ/mol} < \Delta G_{rxn} < 0 \text{ kJ/mol}$
 $\Delta G_{rxn} > 0 \text{ kJ/mol}$

3. Experimental Methodologies

3.1 Catalysts

To provide industrially relevant information to WGS and FT end users, RTI International partnered with SCI, a commercial manufacturer and provider of WGS and FT catalysts. For the tests in this project, SCI supplied commercially available WGS and Co-FT catalysts and a commercially prepared standard Fe-FT catalyst. The formulations of these WGS and FT catalysts are given in Table 3-1.

Table 3-1. WGS and FT Catalyst Formulations

Catalyst	Trade Name	Composition [wt%]
LTS (Low-temperature-shift)	ShiftMax 240 [®]	59.0% CuO 30.5% ZnO 10.5% Al ₂ O ₃
HTS (High-temperature-shift)	ShiftMax 120 [®]	89.5% Fe ₂ O ₃ 8.5% Cr ₂ O ₃ 2.0% CuO
SGS (Sour-gas-shift)	ShiftMax 820 [®]	10.0% MoO ₃ 4.0% CoO 18.0% MgO 68.0% Al ₂ O ₃
Fe-FT (Iron-based Fischer-Tropsch)	RTI-6	84.3% Fe ₂ O ₃ 3.7% CuO 2.0% K ₂ CO ₃ 10.0% SiO ₂
Co-FT (Cobalt-based Fischer-Tropsch)	FTMAX [®]	24.10% CoO 0.16% RuO 75.74% Al ₂ O ₃

Except for the Fe-FT catalyst, which was supplied as a powder, all catalysts supplied by SCI were in pelletized form. To prepare for testing, the pelletized catalysts were first crushed using a mortar and pestle and then sieved to collect particles in the size range of 53 to 104 μm . This particle size range was chosen to minimize gas channeling in the interparticle spaces within the catalyst bed and to allow for effective separation of catalyst from the inert α -alumina diluent in post-trial catalyst characterization. The particle size of the α -alumina used in the trials was larger than 125 μm .

3.2 Reactor Systems and Product Analyses

The performance of the WGS and FT catalysts was determined in laboratory-scale microreactor systems. A dedicated laboratory-scale microreactor system was constructed for each of the five catalysts tested. A schematic for the FT test system is shown in Figure 3-1. Photos of the microreactor systems are shown in Figure 3-2. The downflow fixed-bed reactor in these test systems consisted of a 0.37 in. ID stainless steel tube that contained a nominal 2 cc of catalyst diluted 3:1 by volume with α -alumina to dissipate exothermic heat of reaction during testing. The reactor was heated with band heaters (Watlow) controlled by a thermocouple placed inside a thermowell in the catalyst bed. Mass flow controllers (Brooks 5850i)

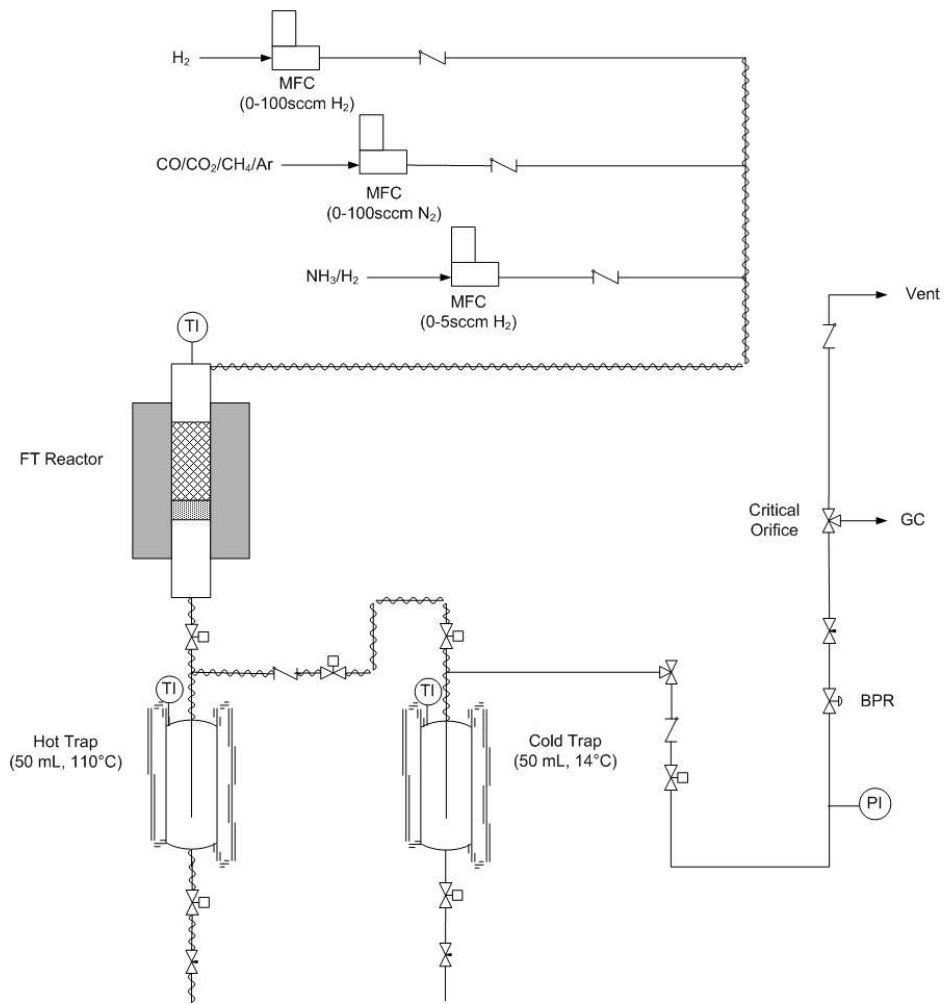


Figure 3-1. Schematic of FT test system.

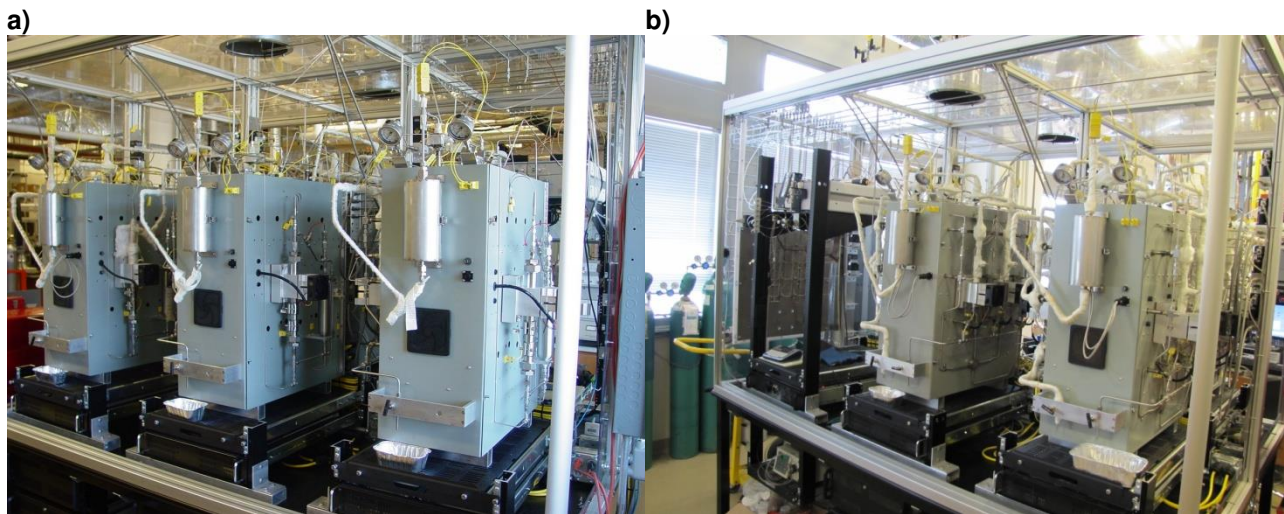


Figure 3-2. Laboratory-scale microreactor systems a) WGS and b) FT.

regulated delivery of the reaction gases from compressed gas cylinders to the system. Argon (Ar) was included in the gas stream fed to the reactor as an internal standard used in product analysis. The WGS and FT catalysts were pretreated per manufacturer specifications before testing. After pretreatment, carbon monoxide (CO), CO₂, methane (CH₄), and hydrogen (H₂) were slowly added to reach the baseline syngas composition.

Because of the reactivity of NH₃, special precautions were implemented to ensure that the NH₃ concentration in the syngas seen by the catalysts was equivalent to the NH₃ concentration in the syngas feed. In the presence of NH₃, CO₂, and H₂O and at low temperatures, chemical reactions produce ammonium carbamate and/or ammonium bicarbonate. To inhibit conversion of NH₃ in the syngas to carbamate and/or bicarbonate products, the syngas feed lines were heat-traced to maintain a temperature of 180 °C, which is significantly higher than the decomposition temperature of these compounds. To mitigate reduction of NH₃ concentration resulting from adsorption on the stainless steel tubing in the contaminant injection lines and equipment, all these tubing runs were passivated by exposure to NH₃ for at least 48 hours prior to NH₃ testing.

Reactant and product gases, including C₁-C₇ hydrocarbons, were analyzed by a Micro GC refinery gas analyzer (Agilent 3000). Condensed liquid samples, which included waxes, light hydrocarbons, and water, were collected every 48 to 72 hours in two sets of temperature-controlled traps. Waxes were collected in a trap held at 120 °C. Light hydrocarbons and water were collected in a trap maintained at 10 to 15 °C. For the WGS trials, only a cold trap (10 to 15°C) was necessary to collect any condensed water. For wax analysis, samples were manually injected into an Agilent 6890 GC equipped with a cool-on-column inlet, SPB-1 column, and flame ionization detector. Wax samples were prepared for GC analysis by dissolving in a small aliquot of 1 ml carbon disulfide. FT wax α values for each sample were calculated using the Anderson-Schulz-Flory probability distribution equation:

$$\log\left(\frac{C_{frac,i}}{N_i}\right) = (\log \alpha)N_i + K \quad (1)$$

where $C_{frac,i}$ is the weight fraction of product with carbon number N_i , α is a parameter indicating the probability of chain growth, and K is a constant. Calibrations of analytical equipment were performed using calibration mixtures from Scott Specialty Gases.

3.3 Experimental Conditions

The specific temperature, pressure and baseline syngas compositions were selected that are representative of commercial operations for each catalyst and are presented in Table 3-2. To establish the typical performance of each catalyst, a baseline test was conducted in which the catalyst was exposed to the baseline syngas composition without any contaminants. This baseline test was continued until the catalyst performance had stabilized. The results from this baseline testing were used to set the initial baseline period during contaminant testing.

After loading the catalyst, a typical contaminant test consisted of a baseline period (without contaminants), which could range from 100 hours to 500 hours in duration followed by a maximum 1,000-h period with contaminants. For the multi-contaminant tests with KCl and/or NaCl, the initial baseline period included the alkali contaminants because these contaminants were generated by vaporization of alkali salts upstream of the catalyst bed and loaded during the loading of the catalyst. During contaminant testing, the product composition was used to evaluate contaminant effect on catalyst performance. The conversion of CO resulting from the WGS reaction (Eq. 2) was used to monitor WGS catalyst performance.



A potential competing reaction to the WGS reaction is the methanation reaction, $3\text{H}_2 + \text{CO} = \text{H}_2\text{O} + \text{CH}_4$. Thus, selectivity for methane was also used to monitor the performance of WGS catalysts.

For FT synthesis, the primary reactions are FT reaction (Eq. 3) and WGS reaction (Eq. 2). Therefore for the FT catalysts, the CO conversion, rate of hydrocarbon and wax production, and distribution of hydrocarbons produced from the FT catalysts were used to monitor and evaluate catalyst performance.

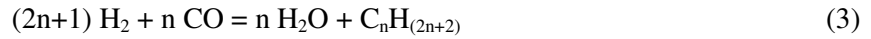


Table 3-2. Baseline WGS and FT System Test Parameters

Component [vol%]	Catalyst system				
	LTS	HTS	SGS	Fe-FT	Co-FT
H ₂	36.1	17.7	21.3	41.3	42.7
CO	4.6	23.0	27.7	24.3	21.3
CO ₂	29	10.6	12.8	29.9	31.6
CH ₄	2.8	2.8	3.4	4.5	4.4
H ₂ O	27.5	45.9	34.9	0	0
H ₂ S	0	0	100 ppmv	0	0
Temperature [°C]	200	375	250	250	210
Pressure [psig]	500	500	500	350	350
Space velocity at STP [h ⁻¹]	10,000	10,000	10,000	3,000	3,000

4. Experimental Results

4.1 Test Plan

The test plan established with NETL included only multi-contaminant testing for the WGS catalysts but included a significant amount of individual contaminant testing for the FT catalysts. Table 4-1 summarizes the specific testing that was completed with each catalyst in this project. Because a large amount of information exists on individual contaminants for the different water gas shift catalyst, testing of these catalysts focused on potential synergistic effects from combinations of these contaminants.

Table 4-1. Project Test Matrix

Catalyst	Baseline	H ₂ S	COS	NH ₃	NaCl	KCl	MC ¹
LTS		Not tested	Not tested	Not tested	Not tested	Not tested	
HTS		Not tested	Not tested	Not tested	Not tested	Not tested	
SGS		Not tested	Not tested	Not tested	Not tested	Not tested	
Fe-FT							
Co-FT						Not tested	

¹ MC (Multi-contaminant): Tests completed with NaCl and KCl vapors, H₂S, and NH₃.

4.2 LTS Catalyst Results

4.2.1 Baseline Testing

As shown in Figure 4-1, 500 hours of testing were completed for the baseline trial on the LTS catalyst. The test conditions used for this trial were provided in Table 3-2. The predicted equilibrium conversion for the WGS reaction at these test conditions is 94.7%. The actual CO conversion for this LTS catalyst in simulated clean CB-derived syngas stabilized at 86.6% with no CH₄ selectivity.

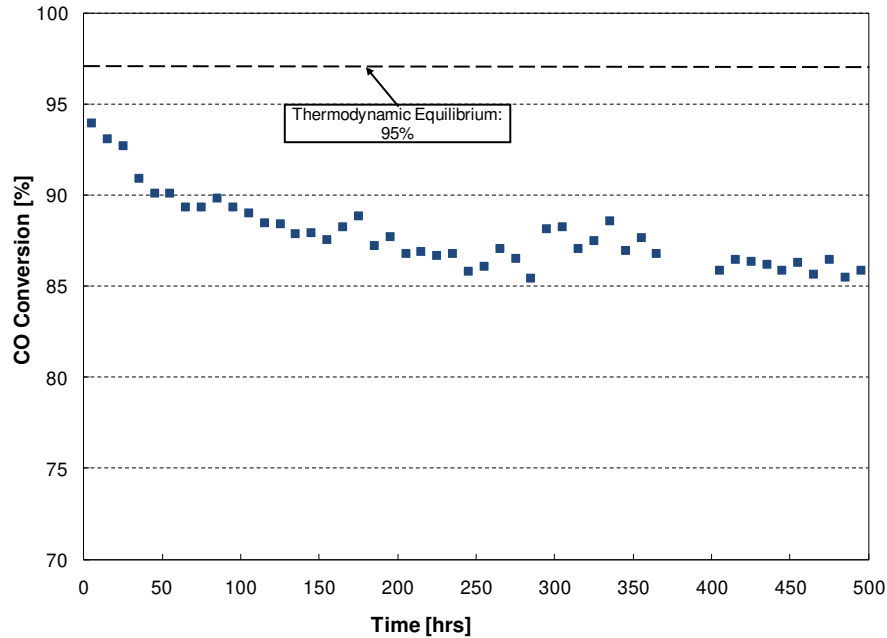


Figure 4-1. Baseline test results for the LTS catalyst.

4.2.2 Multi-contaminant Exposure

The primary objective of the multi-contaminant trial was to evaluate catalyst performance with a more realistic syngas mixture containing contaminants at precisely controlled concentrations to identify specific synergistic effects. The catalyst was sequentially exposed to different groups of contaminants so that changes in catalyst performance could be correlated with a specific group of contaminants. For this test, the LTS catalyst was exposed to a simulated CB-derived syngas containing NaCl, KCl, H₂S, and NH₃. The alkali vapors were generated by vaporization of an alkali salt bed immediately upstream of the catalyst bed. Therefore, NaCl and KCl vapors were constantly present throughout this exposure trial. The specific concentrations of NaCl and KCl vapors present in the syngas were estimated based on the alkali vapor pressures at the specific testing conditions. This approach for estimating the alkali vapor concentrations was demonstrated during initial testing of alkali vapor generation. The estimated alkali concentrations for the test conditions given in Table 3-2 are provided in Table 4-2. The H₂S and NH₃ were added as gas-phase contaminants to the simulated CB-derived syngas. Targeted concentrations were 250, 500, and 1,000 parts per billion by volume (ppbv) for NH₃ and 1,000 ppbv for H₂S.

Table 4-2. Concentrations of Alkali Vapors during Testing with Simulated CB-Derived Syngas

Catalyst	Alkali vapor concentration (pptv)	
	NaCl	KCl
LTS	2.5×10^{-4}	2×10^{-7}
HTS	30.6	1.6
SGS	1.6×10^{-2}	5.6×10^{-5}
Fe-FT	2.2×10^{-2}	7.9×10^{-5}
Co-FT	8.6×10^{-4}	9.7×10^{-7}

CO conversion in the multi-contaminant trial on the LTS catalyst is shown in Figure 4-2. Additional analysis of LTS catalyst performance is provided in Table 4-3. Compared with the baseline trial, the LTS catalyst performance stabilized at a slightly lower CO conversion in the presence of alkali vapors (80% vs. 87%). However, this lower performance cannot be solely attributed to alkali vapors because it may be a result of variability in catalyst samples and/or catalyst activation. Little effect was seen between combinations of alkali vapors with NH₃ and H₂S. The multi-contaminant trial results also indicate that no decline in CO conversion is observed in NH₃ and H₂S concentrations as high as 1,000 ppbv after 1,100 hours of operation.

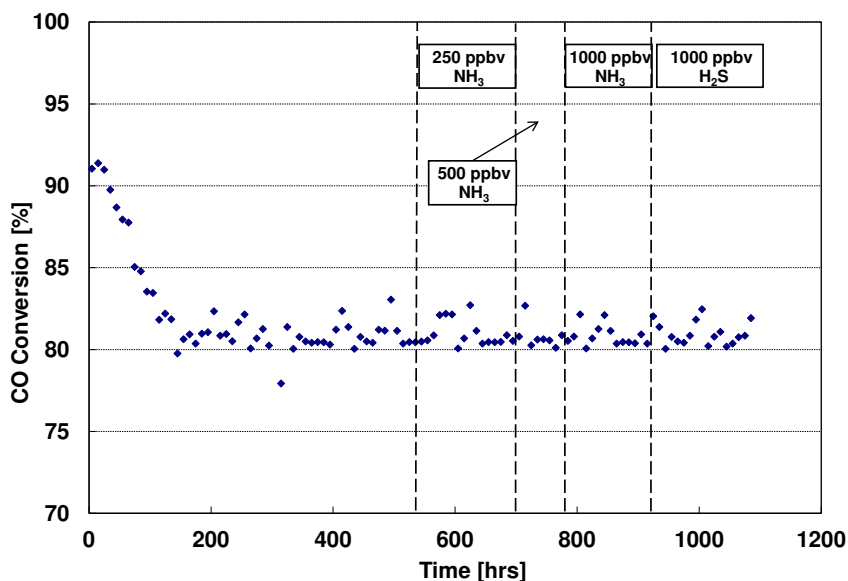


Figure 4-2. Multi-contaminant exposure results for the LTS catalyst.

Table 4-3. LTS Catalyst Performance during Multi-contaminant Testing

Performance parameter	Contaminants				
	Alkali ¹	Alkali ¹ + 250 ppbv NH ₃	Alkali ¹ + 500 ppbv NH ₃	Alkali ¹ + 1,000 ppbv NH ₃	Alkali ¹ + 1,000 ppbv H ₂ S
Exposure time [h]	570	130	90	110	130
CO conversion [%]	80.4	80.4	80.6	80.4	80.2
CH ₄ selectivity [%]	ND ²	ND ²	ND ²	ND ²	ND ²

¹ Alkali = NaCl and KCl vapors (with concentrations given in Table 4-2)

² ND = No selectivity for CH₄ was detected.

4.3 HTS Catalyst Results

4.3.1 Baseline Testing

For the baseline trial on the HTS catalyst, the microreactor system was operated for a total of 500 hours. The experimental results are shown in Figure 4-3. The predicted equilibrium conversion for the WGS reaction on the HTS catalyst at the test conditions given in Table 3-2 is 87.5%. The actual CO conversion determined for this HTS catalyst in simulated clean CB-derived syngas stabilized at 78.3%.

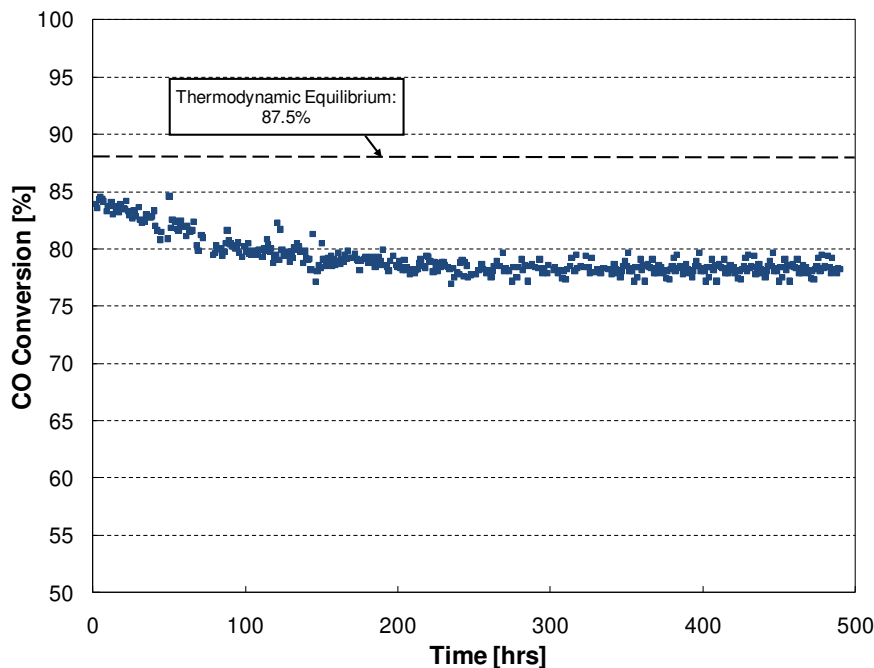


Figure 4-3. Baseline test results for the HTS catalyst.

4.3.2 Multi-contaminant Exposure

Figure 4-4 illustrates how the HTS catalyst performance, as measured by CO conversion, changed during the multi-contaminant exposure trial (blue data symbols) and compares it with the baseline test data (red data symbols). Table 4-4 shows the averaged CO conversion and CH₄ selectivity values for different groups of contaminant exposure. The most visible effect during this multi-contaminant testing was the significant decrease in CO conversion observed during exposure to NaCl, KCl, and 1 parts per million by volume (ppmv) H₂S. Interestingly, upon removal of 1 ppmv H₂S, CO conversion increased and returned to approximately the same conversion before the addition of H₂S. The difference in CO conversion during the baseline period from the multi-contaminant test and the baseline test suggest that exposure to alkali vapors could improve CO conversion. Although the commercial HTS catalyst used in this study does not contain an alkali promoter, alkali promoters are commonly used in many commercial Fe-based catalysts and could potentially explain the enhanced performance seen during exposure to the alkali vapors in this test.

When the HTS catalyst was exposed to simulated syngas containing H₂S, NH₃, or combinations of these two contaminants in addition to alkali vapors, the CO conversion was observed to steadily decline. To evaluate any subtle changes that were not identified by visual inspection, statistical analysis was used to compare changes in the rate of CO conversion for these different contaminant groups. Based on this analysis, the lowest statistically significant decline in CO conversion was observed with the combination of 1 ppmv NH₃, 150 ppbv H₂S, and alkali vapors, demonstrating the compounding effect of multiple contaminants.

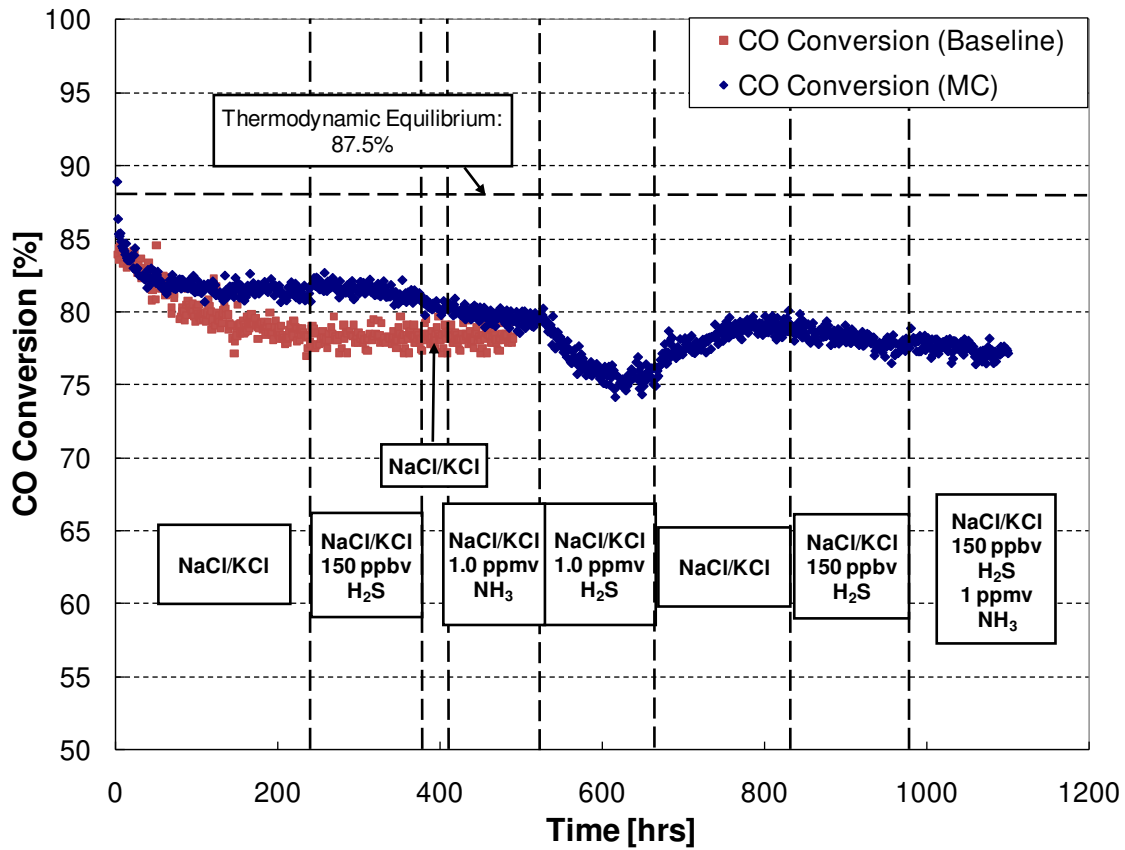


Figure 4-4. CO conversion of the HTS catalyst in the presence of syngas containing multiple contaminants.

Table 4-4. HTS Catalyst Performance during Multi-contaminant Testing

Performance parameter	Contaminants							
	Alkali ¹	Alkali ¹ + 150 ppbv H ₂ S	Alkali ¹	Alkali ¹ + 1,000 ppbv NH ₃	Alkali ¹ + 1,000 ppbv H ₂ S	Alkali ¹	Alkali ¹ + 150 ppbv H ₂ S	Alkali ¹ + 1,000 ppbv NH ₃ + 150 ppbv H ₂ S
Exposure time [h]	90	125	30	110	150	165	100	160
CO conversion [%]	81	81	80	79	76	79	78	77
CH ₄ selectivity [%]	ND ²	ND ²	ND ²	ND ²	ND ²	ND ²	ND ²	ND ²

¹ Alkali = NaCl and KCl vapors (with concentrations given in Table 4-2)

² ND = No selectivity for CH₄ was detected.

4.4 SGS Catalyst Results

4.4.1 Baseline Testing

A total of 500 hours of operation was completed for the baseline test on the SGS catalyst. The predicted equilibrium conversion for the WGS reaction on the SGS catalyst under the test conditions given in Table 3-2 is 92.2%. As shown in Figure 4-5, the actual CO conversion for this SGS catalyst in the micro-reactor system using simulated clean CB-derived syngas stabilized at 78.3%.

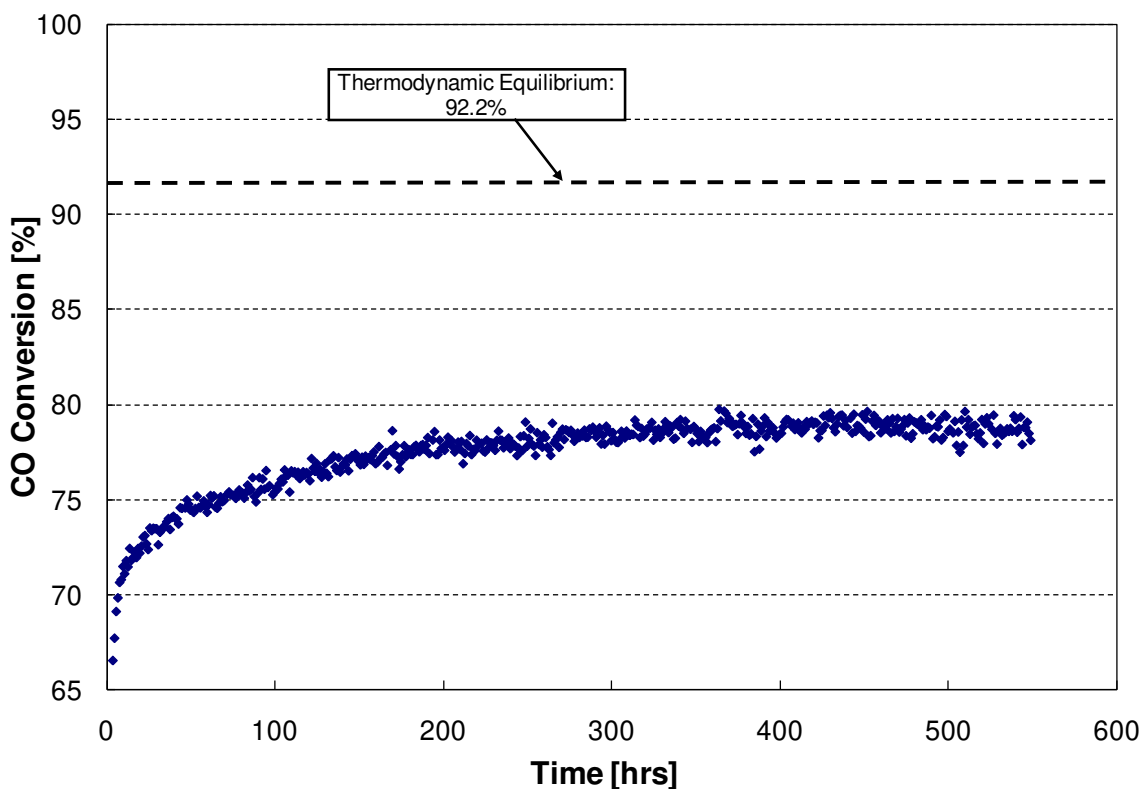


Figure 4-5. Baseline test results for the SGS catalyst.

4.4.2 Multi-contaminant Exposure

For the SGS catalyst multi-contaminant trial, the catalyst was exposed to a simulated CB-derived syngas containing NaCl, KCl, and NH₃ (concentrations for alkali species provided in Table 4-2). Although H₂S is present in the baseline syngas mixture for this catalyst, the H₂S is not considered a contaminant as the H₂S concentration in the baseline syngas mixture is necessary for maintaining the active sulfide species for the WGS reaction and is the reason SGS catalyst are suitable for syngas applications with high H₂S concentrations. The CO conversion for this test is compared with that measured in the baseline test in Figure 4-6, and averaged values for CO conversion and CH₄ selectivity for the different contaminant groups are provided in Table 4-5. Because no significant visible differences were observed, statistical analysis, which consisted of a t-test with null hypothesis that the rate of change are identical, was used to assess changes in the rate of CO conversion during exposure to the different contaminants. This analysis found no statistical difference in CO conversion rates for simulated CB-derived syngas mixtures with alkali only and with alkali plus 1 ppmv NH₃ compared with simulated clean CB-derived syngas.

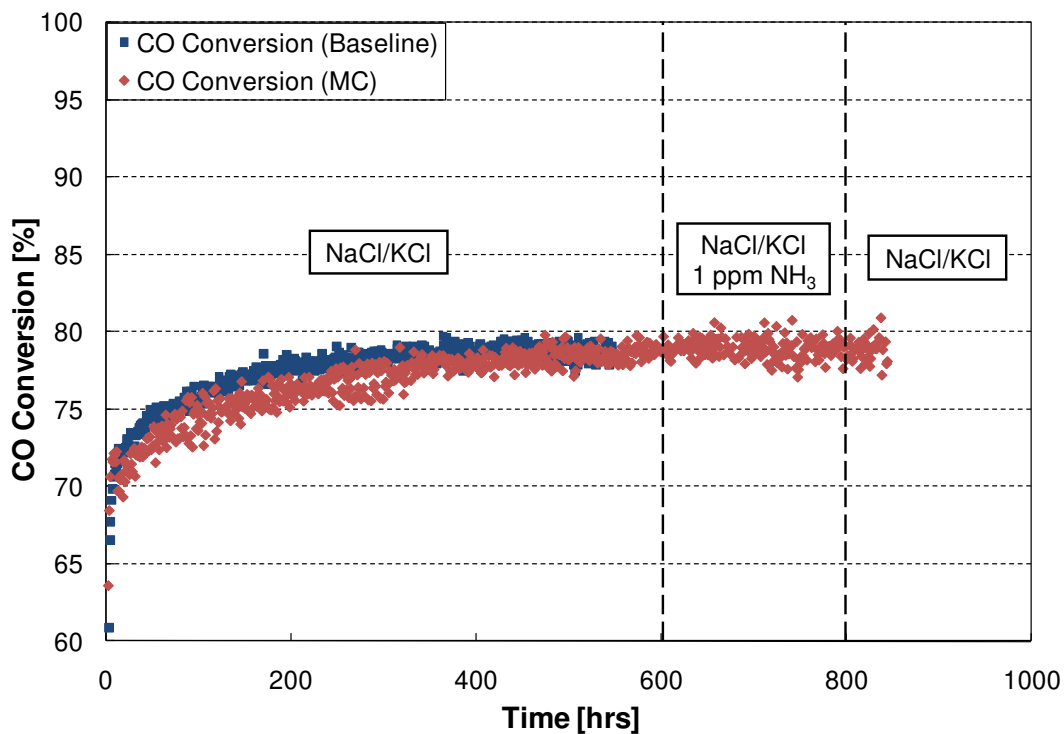


Figure 4-6. CO conversion of the SGS catalyst in multi-contaminant exposure testing.

Table 4-5. SGS Catalyst Performance during Multi-contaminant Testing

Performance parameter	Contaminants		
	Alkali ¹	Alkali ¹ + 1 ppmv NH ₃	Alkali ¹
Exposure time [h]	600	700	840
CO conversion [%]	78.8	78.9	78.8
CH ₄ selectivity [%]	ND ²	ND ²	ND ²

¹ Alkali = NaCl and KCl vapors (with concentrations given in Table 4-2)

² ND = No selectivity for CH₄ was detected.

4.5 Fe-FT Catalyst Test Results

4.5.1 Baseline Testing

Figure 4-7 presents CO conversion for the Fe-FT catalyst in the baseline syngas. Although some changes in the Fe-FT catalyst performance were seen during the first 150 minutes of baseline syngas exposure (i.e., there was a period of increased CO conversion followed by decline or break-in period as seen in other testing), its performance during the next 350 minutes was very consistent and stable. Table 4-6 provides the ranges of CH₄ and CO₂ selectivities, catalyst productivity, and FT wax α (Eq. 1) during this 350-min period of stable operation. Based on these results, subsequent Fe-FT catalyst testing was conducted in clean syngas for at least 150 hours to stabilize the catalyst activity before contaminant exposure was initiated.

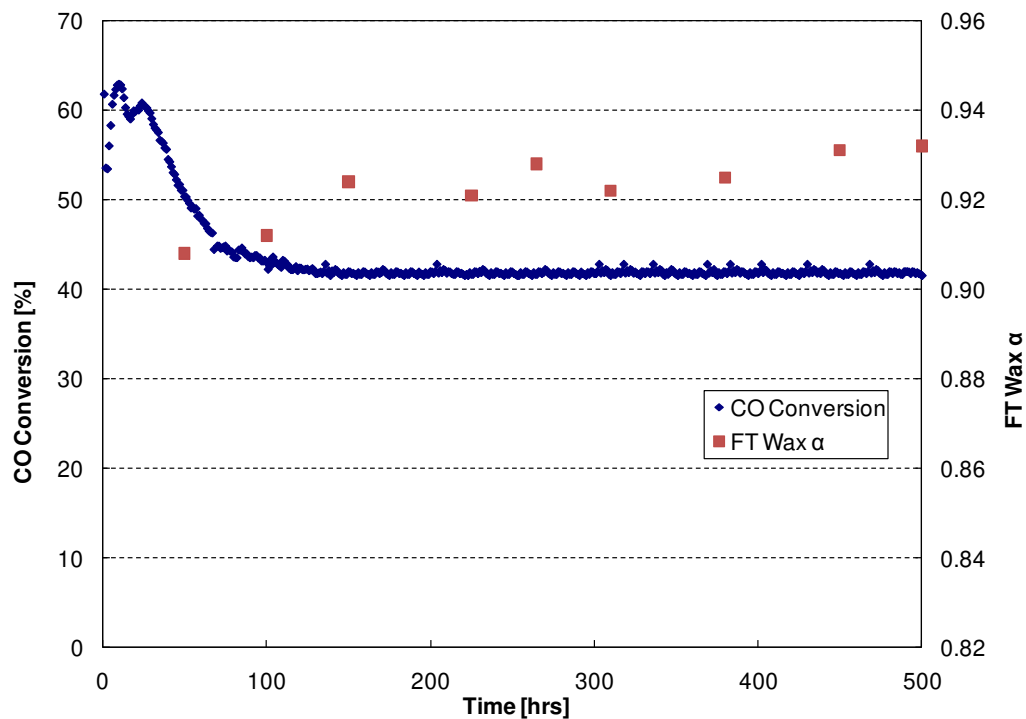


Figure 4-7. Baseline test results for the Fe-FT catalyst.

Table 4-6. Baseline Fe-FT Catalyst Performance and Selectivities

Performance parameter	Value for Fe-FT catalyst
Average CO conversion [%]	41–42
Catalyst productivity [mg C ₅₊ /h/g catalyst]	168–172
CH ₄ selectivity [%]	1–2
CO ₂ selectivity [%]	30–36
FT wax α	0.90–0.93

4.5.2 Exposure to H₂S

To establish its tolerance to H₂S, the Fe-FT catalyst was exposed to H₂S over the concentration range of 100 to 200 ppbv. The unexplained initial increase in CO conversion within the first several hours of testing was again observed, followed by decline and stabilization. The CO conversion and FT wax α profiles for these trials are shown in Figures 4-8 and 4-9, and Table 4-7 provides the average values of catalyst productivity, CO conversion, and CH₄ and CO₂ selectivities. Results after 200 hours of 100 ppbv H₂S exposure showed no measurable impact on catalyst performance between clean syngas and syngas with 100 ppbv of H₂S. With syngas containing 150 ppbv H₂S, the CO conversion and catalyst productivity of the Fe-FT slowly decreased. When the H₂S concentration was increased to 175 ppbv, the rates of decrease in CO conversion and catalyst productivity increased. Additional testing in a second trial with syngas containing 200 ppbv H₂S demonstrated further performance degradation. These results indicate that the H₂S tolerance of this commercial Fe-FT catalyst was about 100 ppbv.

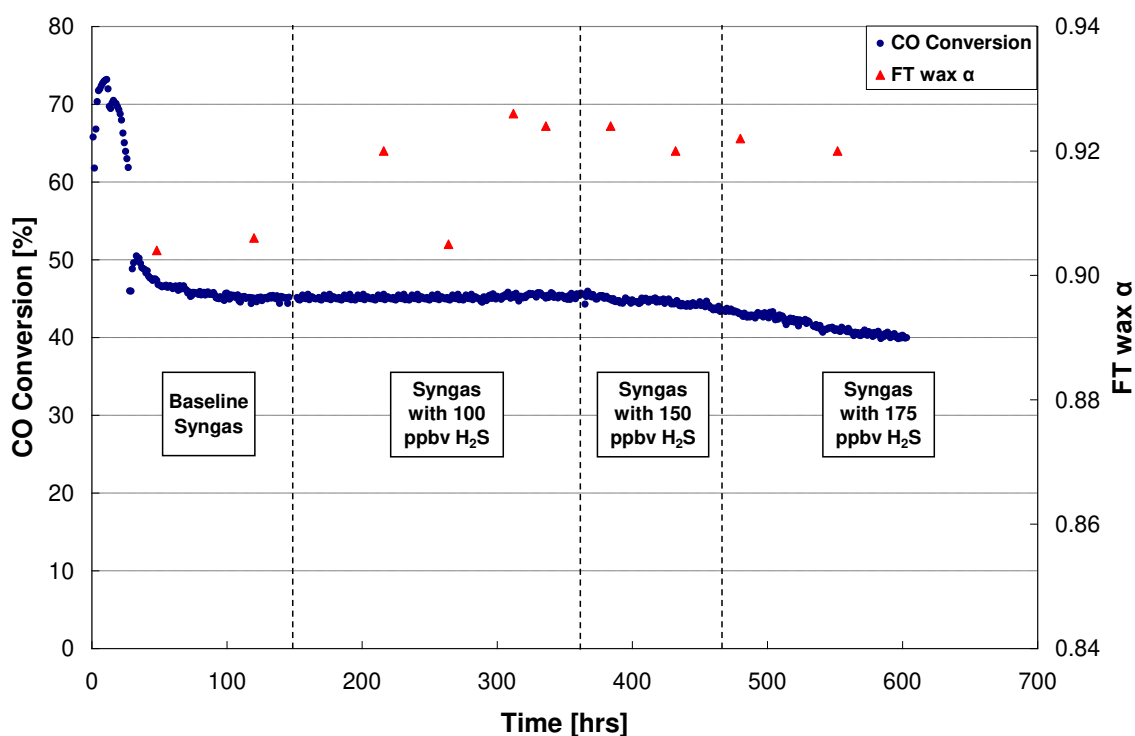


Figure 4-8. Fe-FT catalyst performance with 100, 150, and 175 ppbv H₂S.

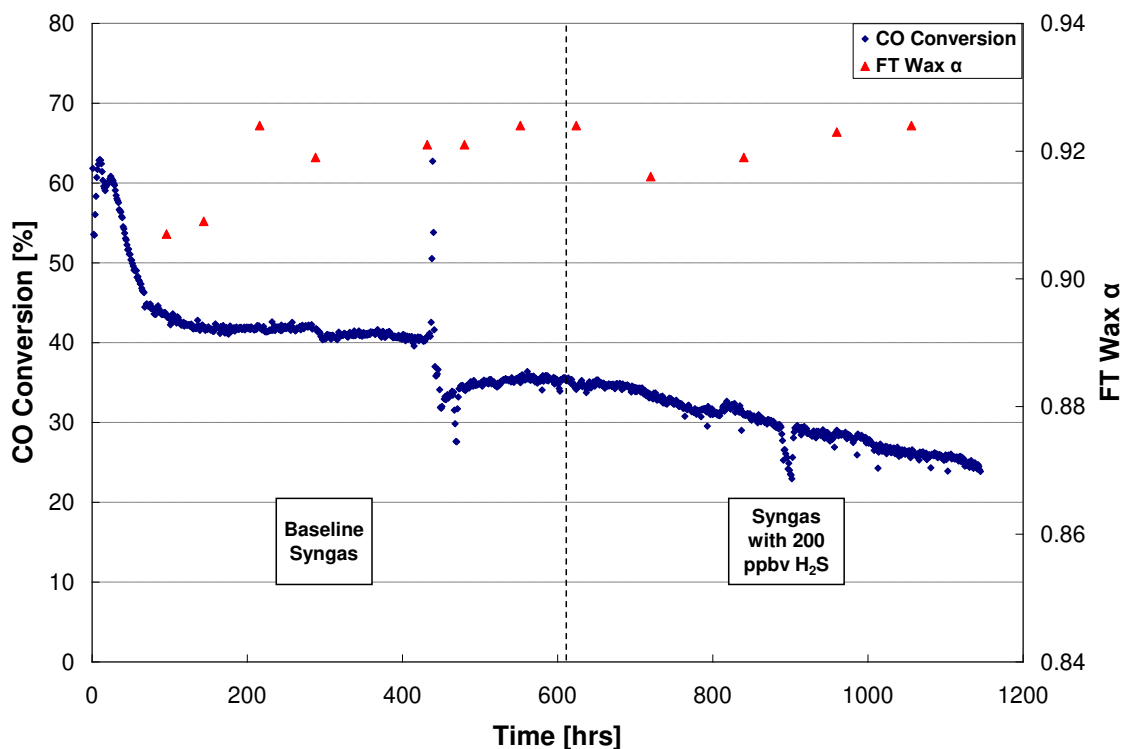


Figure 4-9. Fe-FT catalyst performance with 200 ppbv H₂S.

Table 4-7. Effect of H₂S Concentration on Fe-FT Catalyst Performance

Performance parameter	H ₂ S contaminant concentration (ppbv)				
	0	100	150	175	200
Exposure time [h]	150	110	100	130	550
CO conversion [%]	45.6	45.6	44.5	42.5	24.9
Catalyst productivity [mg C ₅₊ /h/g catalyst]	208	208	200	186	103
CH ₄ selectivity [%]	1.2	1.2	1.2	NA ¹	1.2
CO ₂ selectivity [%]	29	29	29	29	29
FT wax α	0.90–0.92	0.90–0.92	0.90–0.92	0.90–0.92	0.90–0.92

¹ NA Not available

4.5.3 Exposure to COS

To determine the effect of COS on the Fe-FT catalyst performance, tests were performed with syngas containing four different COS concentrations (125, 150, 175, and 200 ppbv). The CO conversion and FT wax α profiles for these tests are shown in Figures 4-10 and 4-11, and Table 4-8 provides the average values of catalyst productivity, CO conversion, and CH₄ and CO₂ selectivities. Up to concentrations of 150 ppbv, COS had little impact on the Fe-FT catalyst performance. However, a noticeable decrease in catalyst productivity and CO conversion was observed when this Fe-FT catalyst was exposed to syngas with 175 ppbv COS. During exposure to 200 ppbv COS, the degradation of CO conversion and catalyst productivity was even more pronounced. In the second test trial, the Fe-FT catalyst was re-evaluated with clean syngas after 300 hours of COS exposure to determine if the sulfur poisoning was permanent. After

65 hours in clean syngas, no improvement in CO conversion or catalyst productivity was observed, thereby demonstrating that the decline in catalyst activity was irreversible.

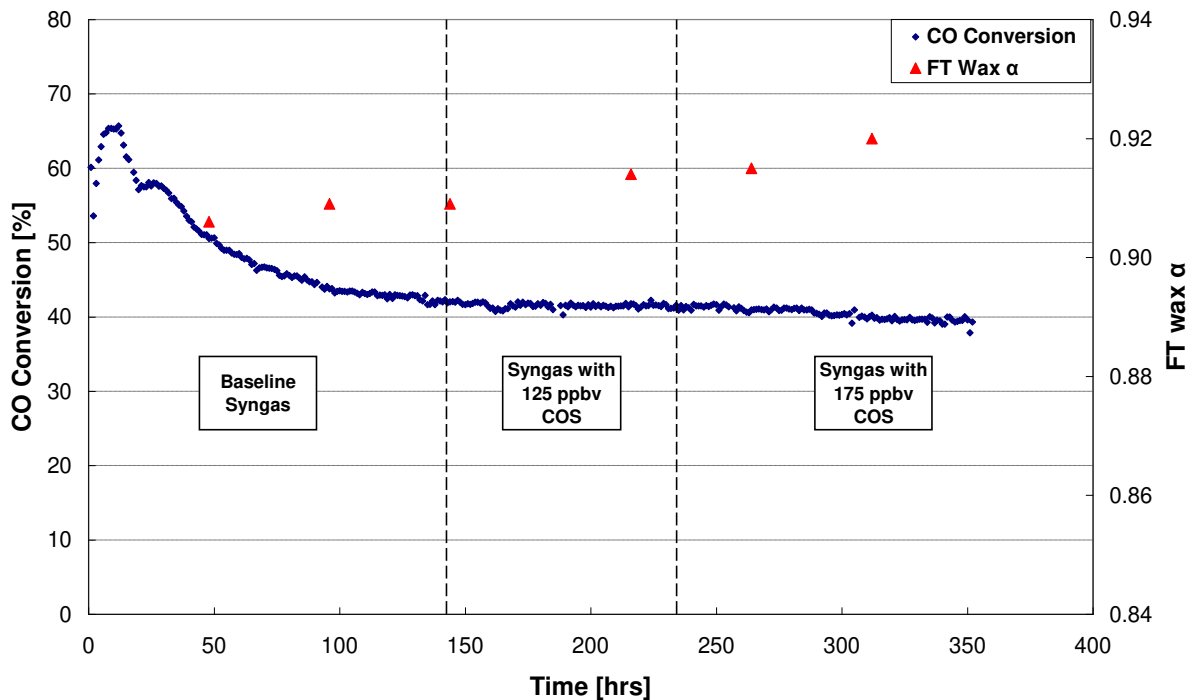


Figure 4-10. Fe-FT catalyst performance with 125 and 175 ppbv COS in syngas.

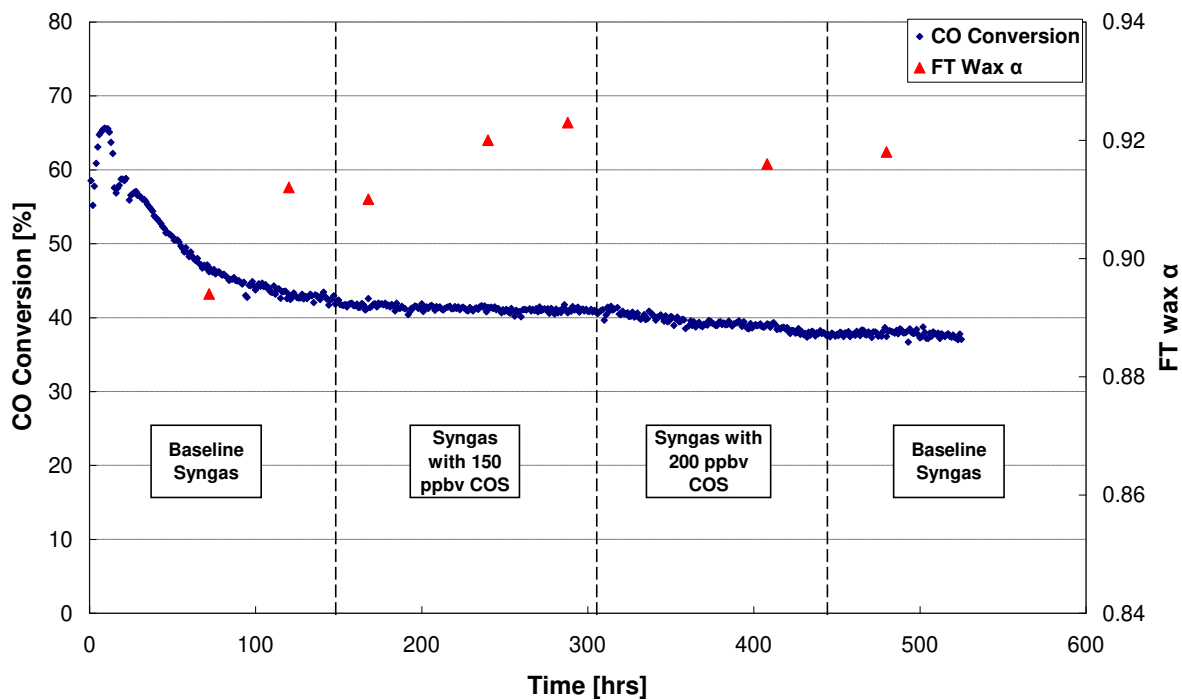


Figure 4-11. Fe-FT catalyst performance with 150 and 200 ppbv COS.

Table 4-8. Effect of COS Concentration on Fe-FT Catalyst Performance

Performance parameter	COS contaminant concentration (ppbv)				
	0	125	150	175	200
Exposure time [h]	140	110	155	170	125
CO conversion [%]	42.3	42.3	39.4	39.4	36.5
Catalyst productivity [mg C ₅₊ /h/g catalyst]	208	210	208	208	196
CH ₄ selectivity [%]	1.9	1.9	1.9	1.9	1.9
CO ₂ selectivity [%]	32	32	32	32	32
FT wax α	0.90–0.92	0.90–0.92	0.90–0.92	0.90–0.92	0.90–0.92

The sulfur contaminant test results on the Fe-FT catalyst clearly show that, at the same concentration, H₂S degraded the catalyst performance more rapidly than COS. At sulfur concentrations above 150 ppbv for either H₂S or COS, the Fe-FT catalyst performance began to decrease. At sulfur concentrations below 100 ppbv for either H₂S or COS, no or only minimal decrease in catalyst performance was observed.

4.5.4 Exposure to NH₃

The effect of 0.1 to 1.0 ppmv of NH₃ in syngas on the Fe-FT catalyst performance was evaluated in a single trial. NH₃ was introduced by metering a certified H₂/NH₃ mixture into the syngas feed with a mass flow controller. Specific precautions to avoid a reduction in NH₃ concentration in the syngas due to undesired reactions and adsorption during catalyst exposure were discussed in Section 3.2. The CO conversion and FT wax α profiles for this test are shown in Figure 4-12. Average values for other catalyst performance parameters during the exposure to syngas with different NH₃ concentrations are provided in Table 4-9. From the NH₃ exposure trial results, NH₃ concentrations below 1 ppmv do not have a measurable impact on the Fe-FT catalyst performance.

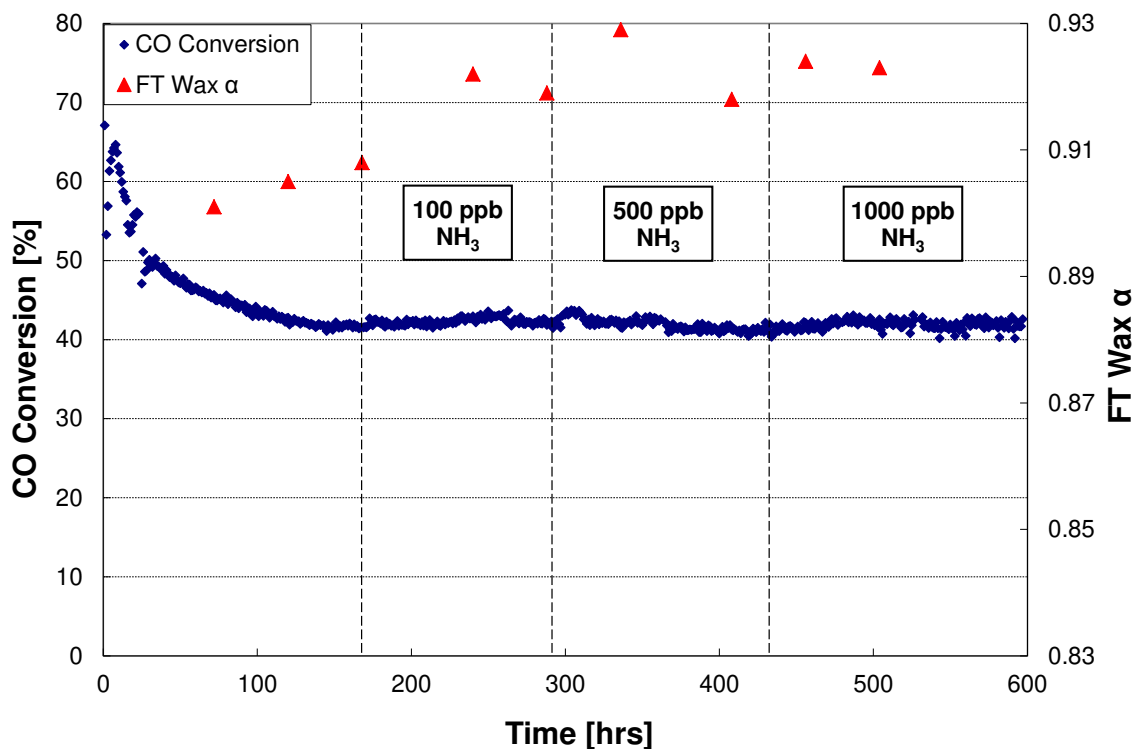


Figure 4-12. Fe-FT catalyst performance with 100, 500, and 1,000 ppbv NH₃.

Table 4-9. Effect of NH₃ Concentration on Fe-FT Catalyst Performance

Performance parameter	NH ₃ contaminant concentration (ppbv)			
	0	100	500	1,000
Exposure time [h]	175	125	150	150
CO conversion [%]	42	42	42	42
Catalyst productivity [mg C ₅₊ /h/g catalyst]	168	164	160	160
CH ₄ selectivity [%]	2	2	2	2
CO ₂ selectivity [%]	33	34	36	36
FT wax α	0.91–0.93	0.91–0.93	0.91–0.93	0.91–0.93

4.5.5 Exposure to NaCl Vapor

The effect of syngas containing NaCl vapor on the Fe-FT catalyst performance was evaluated for 400 hours. Figure 4-13 shows CO conversion and FT wax α profiles for this trial, and Table 4-10 provides the average values for CO conversion, catalyst productivity, and CH₄ and CO₂ selectivities for the baseline syngas case and syngas with NaCl vapor. Comparison of the Fe-FT catalyst performance in the presence of NaCl vapor with baseline syngas conditions shows that the overall catalyst performance was similar in both these reaction environments. The stabilized CO conversion and catalyst productivity with NaCl vapor was slightly higher, but this could be attributed to variability in catalyst samples tested

and/or catalyst activation. In general, it can be concluded from these contaminant test results that NaCl vapor does not adversely affect the Fe-FT catalyst performance.

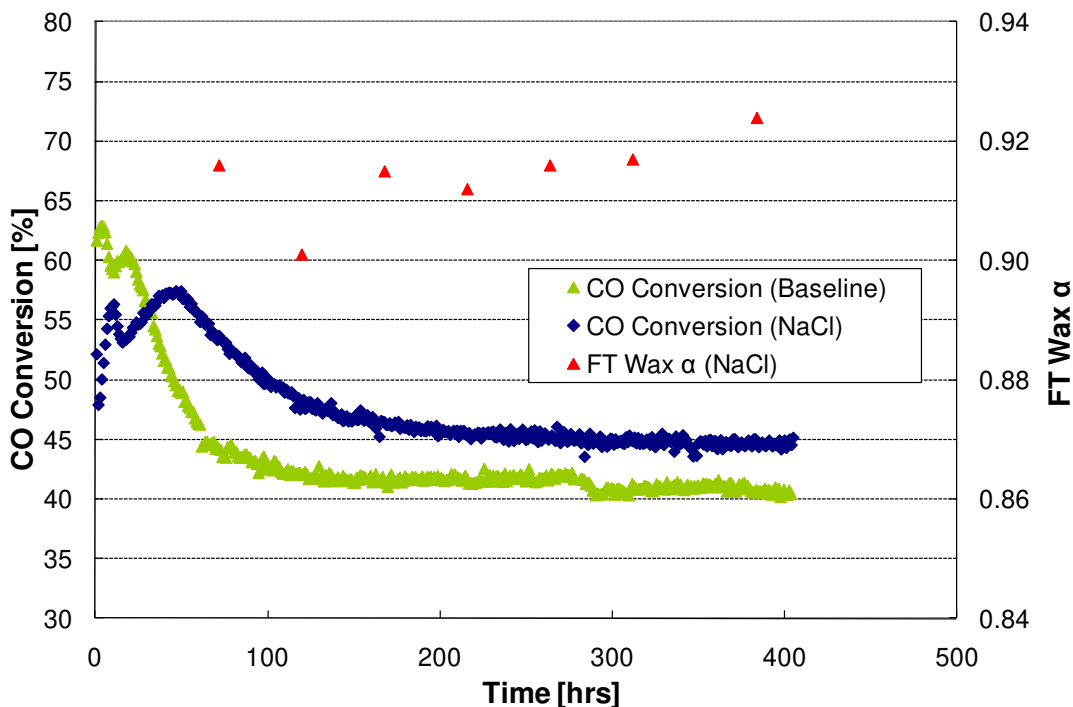


Figure 4-13. Effect of NaCl vapor on Fe-FT catalyst performance.

Table 4-10. Fe-FT Catalyst Performance Results in the Presence of NaCl Vapor

Performance parameter	NaCl vapor concentration (pptv)	
	0	2.2×10^{-2}
Exposure time [h]	400	400
CO conversion [%]	41.6	44.2
Catalyst productivity [mg C ₅₊ /h/g catalyst]	158	162
CH ₄ selectivity [%]	2	2
CO ₂ selectivity [%]	33	33
FT wax α	0.90–0.93	0.90–0.93

4.5.6 Exposure to KCl Vapor

The CO conversion and FT wax α profiles for the Fe-FT catalyst exposed to syngas with KCl vapor are shown in Figure 4-14, and the average values for CO conversion, catalyst productivity, and CH₄ and CO₂ selectivities for the baseline syngas trial and syngas with KCl vapor contaminant are compared in Table 4-11. From these results, the Fe-FT catalyst performance is very similar in reaction conditions with and

without KCl vapor. It can thus be concluded that KCl vapor does not adversely affect the Fe-FT catalyst performance.

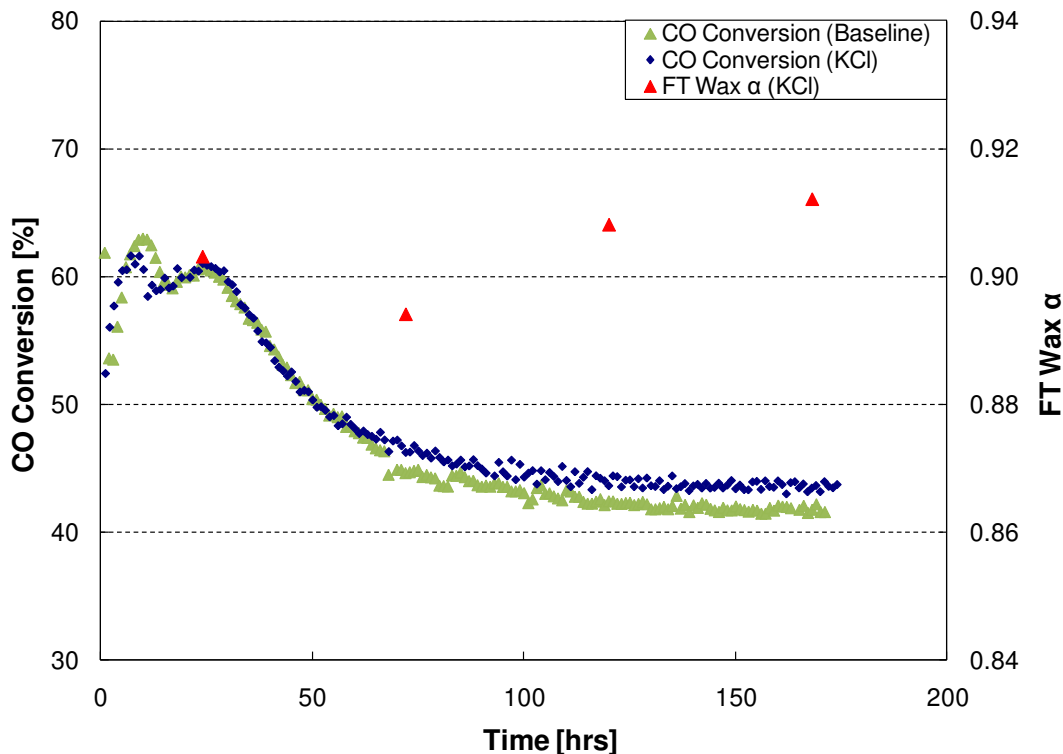


Figure 4-14. CO conversion and FT wax α of the Fe-FT catalyst with syngas containing KCl vapor.

Table 4-11. Fe-FT Catalyst Performance Results in the Presence of KCl Vapor

Performance parameter	KCl vapor concentration (pptv)	
	0	7.9×10^{-5}
Exposure time [h]	150	150
CO conversion [%]	42	44
Catalyst productivity [mg C ₅₊ /h/g catalyst]	162	164
CH ₄ selectivity [%]	2	2
CO ₂ selectivity [%]	33	33
FT wax α	0.90–0.93	0.90–0.93

4.5.7 Multi-contaminant Exposure

In the multi-contaminant exposure study, the Fe-FT catalyst was tested with simulated CB-derived syngas mixtures containing NaCl, KCl, NH₃, and H₂S. The CO conversion and FT wax α profiles measured in the multi-contaminant study are compared with that obtained in the baseline syngas test in Figure 4-15. The average CO conversion, catalyst productivity, and CH₄ and CO₂ selectivities for each portion of the

test trial are summarized in Table 4-12. A comparison of the rates of decline in CO conversion for the different contaminant combinations shows that this rate was statistically greatest for the ternary contaminant group containing NaCl, KCl, and 100 ppbv H₂S, even when compared with that for the combination having all four contaminants (NaCl, KCl, NH₃, and H₂S).

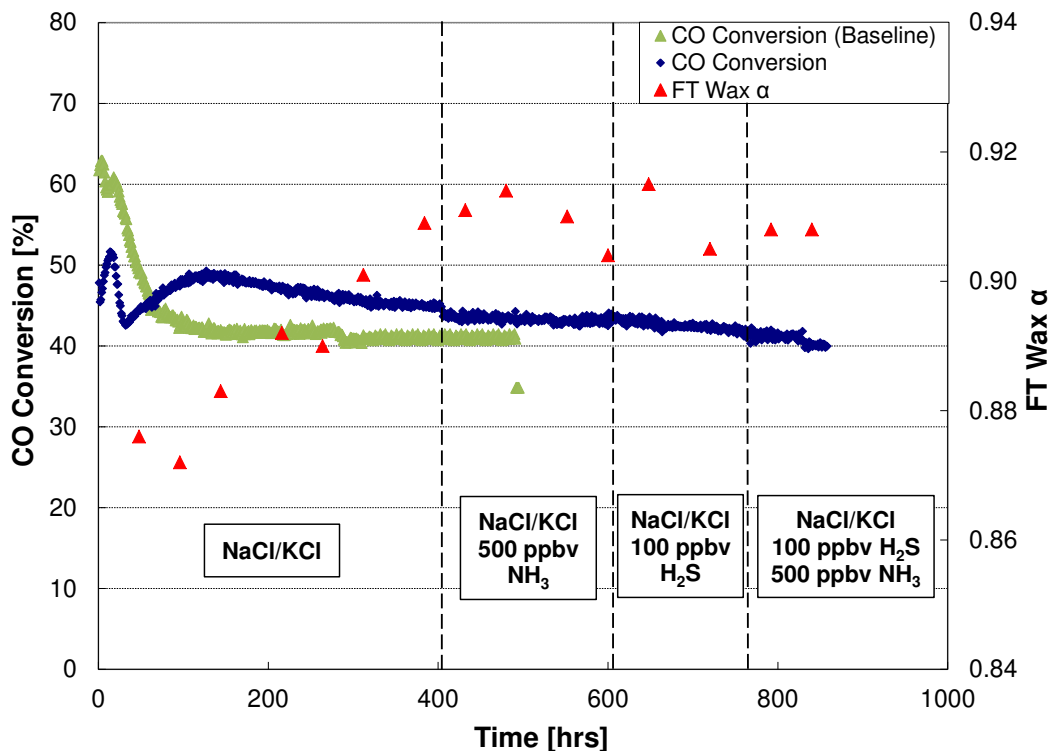


Figure 4-15. CO conversion and FT wax α of the Fe-FT catalyst with syngas containing multiple trace components.

Table 4-12. Fe-FT Catalyst Performance during Multi-contaminant Testing

Performance parameter	Contaminant combination			
	NaCl + KCl	NaCl + KCl + 500 ppbv NH ₃	NaCl+ KCl + 100 ppbv H ₂ S	NaCl + KCl + 500 ppbv NH ₃ + 100 ppbv H ₂ S
Exposure time [h]	250	200	160	80
CO conversion [%]	45	44	42	41
Catalyst productivity [mg C ₅₊ /h/g catalyst]	182	178	173	171
CH ₄ selectivity [%]	3	3	3	3
CO ₂ selectivity [%]	30	30	30	30
FT wax α	0.90–0.93	0.90–0.93	0.90–0.93	0.90–0.93

Note: Alkali vapor concentration = 2.2×10^{-2} pptv for NaCl and 7.9×10^{-5} pptv for KCl (see Table 4-2)

4.6 Co-FT Catalyst Test Results

4.6.1 Baseline Testing

The CO conversion and FT wax α of the commercial Co-FT catalyst in baseline syngas is shown in Figure 4-16. After an initial period of decline, the CO conversion stabilized after 400 hours of operation. Based on these results, subsequent test trials were conducted by exposing the Co-FT catalyst to clean syngas for at least 400 hours to stabilize the catalyst activity before contaminant exposure was initiated.

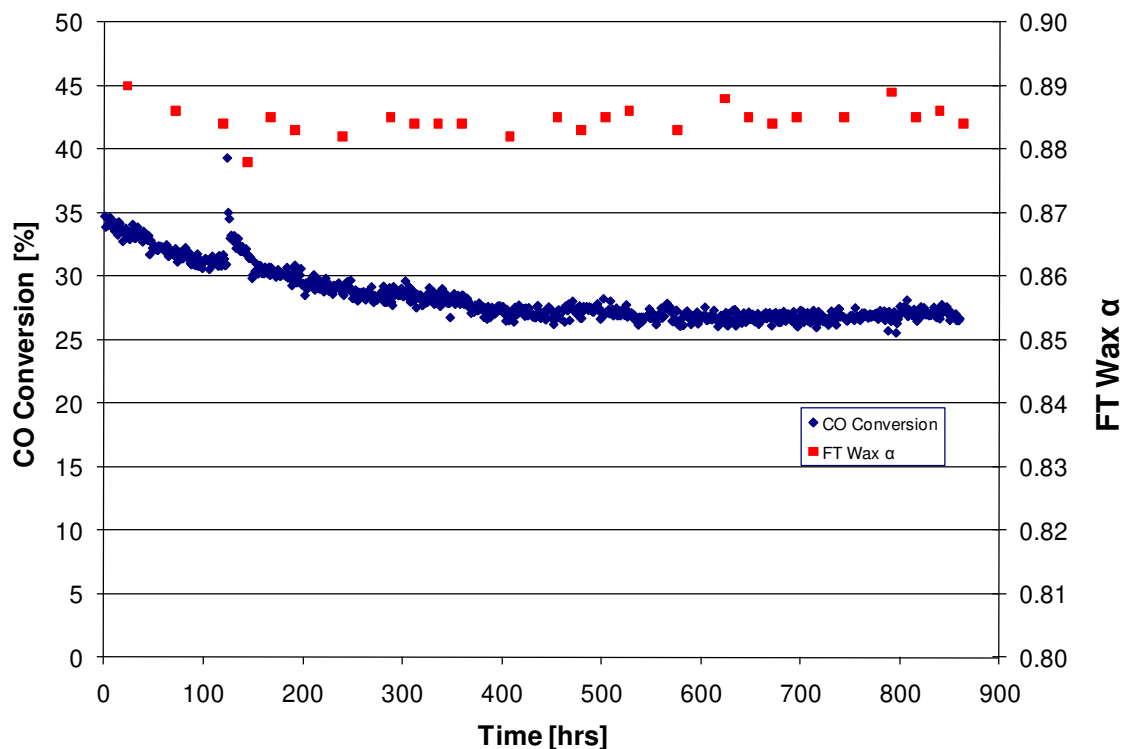


Figure 4-16. Baseline performance of the commercial Co-FT catalyst.

4.6.2 Exposure to H₂S

After stabilizing its activity in clean syngas for 400 h, the Co-FT catalyst was exposed to syngas having 10 ppbv H₂S. The CO conversion and FT wax α profiles for this test are shown in Figure 4-17. After 400 h, the CO conversion for the catalyst continued to steadily decline in the presence of H₂S. This continual performance decline is more clearly seen when it is compared with the CO conversion profile obtained under baseline syngas conditions, which is also shown in Figure 4-17. Results from this trial demonstrate that the commercial Co-FT catalyst is extremely sensitive to even 10 ppbv of H₂S.

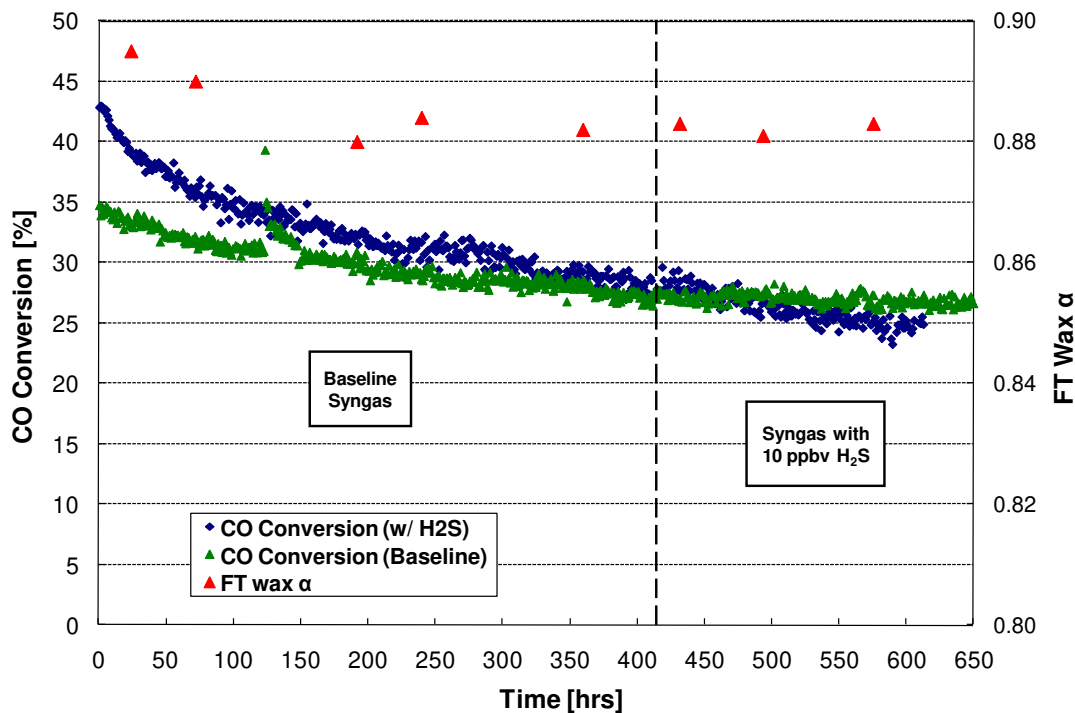


Figure 4-17. Co-FT catalyst performance in syngas with 10 ppbv H₂S.

4.6.3 Exposure to COS

To evaluate the sensitivity of the Co-FT catalyst to COS, a single trial was completed with COS concentrations ranging from 10 to 100 ppbv. Figure 4-18 shows the CO conversion and FT wax α profiles for this trial, and Table 4-13 provides the average CO conversion, catalyst productivity, and CH₄ and CO₂ selectivities. Statistical comparison of the rate of change of CO conversion and catalyst productivity at COS concentrations of 10 and 40 ppbv shows no significant difference relative to that observed in baseline syngas conditions. In contrast, exposure to 100 ppbv COS significantly increased the rate of decrease in CO conversion and catalyst productivity. These data demonstrate that the Co-FT catalyst can perhaps tolerate COS concentrations below 40 ppbv but experiences a decline in CO conversion and catalyst productivity at COS concentrations above 100 ppbv. Furthermore, comparison of these exposure test results with those in Section 4.6.2 above clearly shows that H₂S is a stronger catalyst poison than COS.

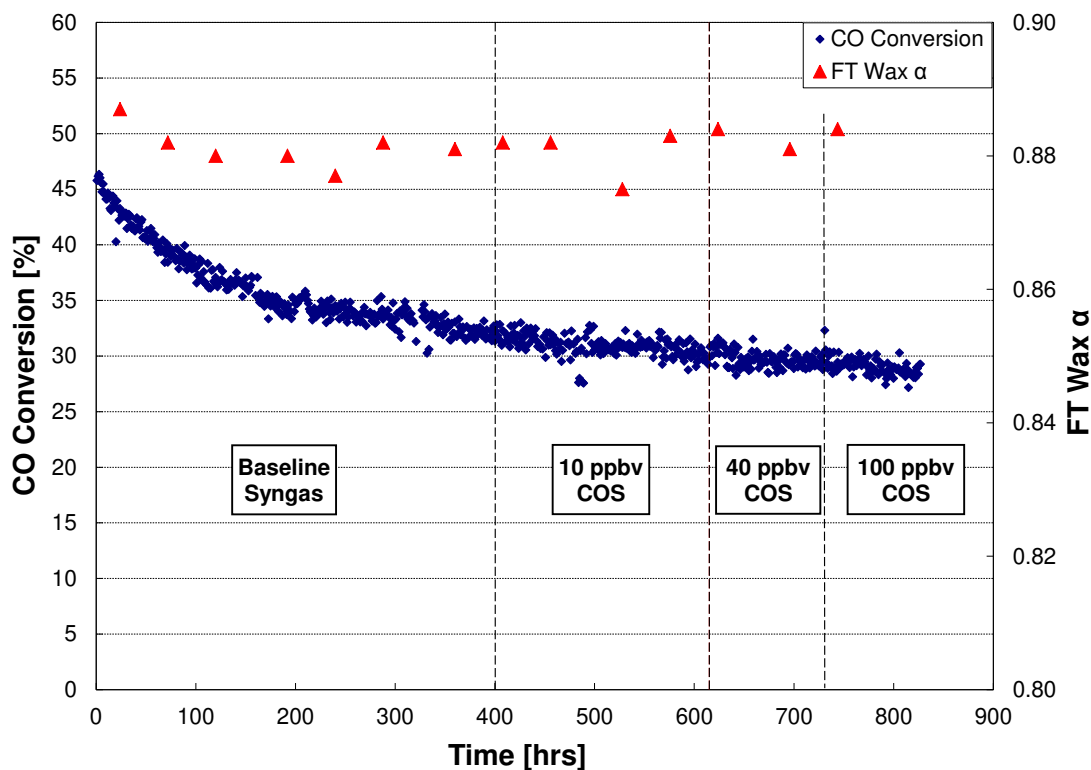


Figure 4-18. Co-FT catalyst performance with 10, 40, and 100 ppbv COS in syngas.

Table 4-13. Effect of COS Concentration on Co-FT Catalyst Performance

Performance parameter	COS contaminant concentration (ppbv)			
	0	10	40	100
Exposure time [h]	400	200	100	100
CO conversion [%]	32	30	30	28
Catalyst productivity [mg C ₅₊ /h/g catalyst]	120	113	110	103
CH ₄ selectivity [%]	13	14	14	14
CO ₂ selectivity [%]	1	1	1	1
FT wax α	0.87–0.89	0.87–0.89	0.87–0.89	0.87–0.89

4.6.4 Exposure to NH₃

The effect of 100 to 1,000 ppbv of NH₃ on the Co-FT catalyst performance was evaluated in a single trial. The CO conversion and FT wax α profiles for this trial are shown in Figure 4-19, and average values of CO conversion, catalyst productivity, and CH₄ and CO₂ selectivities are provided in Table 4-14. A comparison of catalyst performance at the different NH₃ concentrations indicates a decrease in catalyst productivity and CO conversion. Statistical analysis of the rate of change in CO conversion and catalyst productivity shows a significant change in the syngas test with 500 ppbv NH₃. When the Co-FT catalyst

was exposed to 1,000 ppbv NH₃ in the syngas, the catalyst productivity and CO conversion degraded even further by more than 20% relative to the baseline performance values.

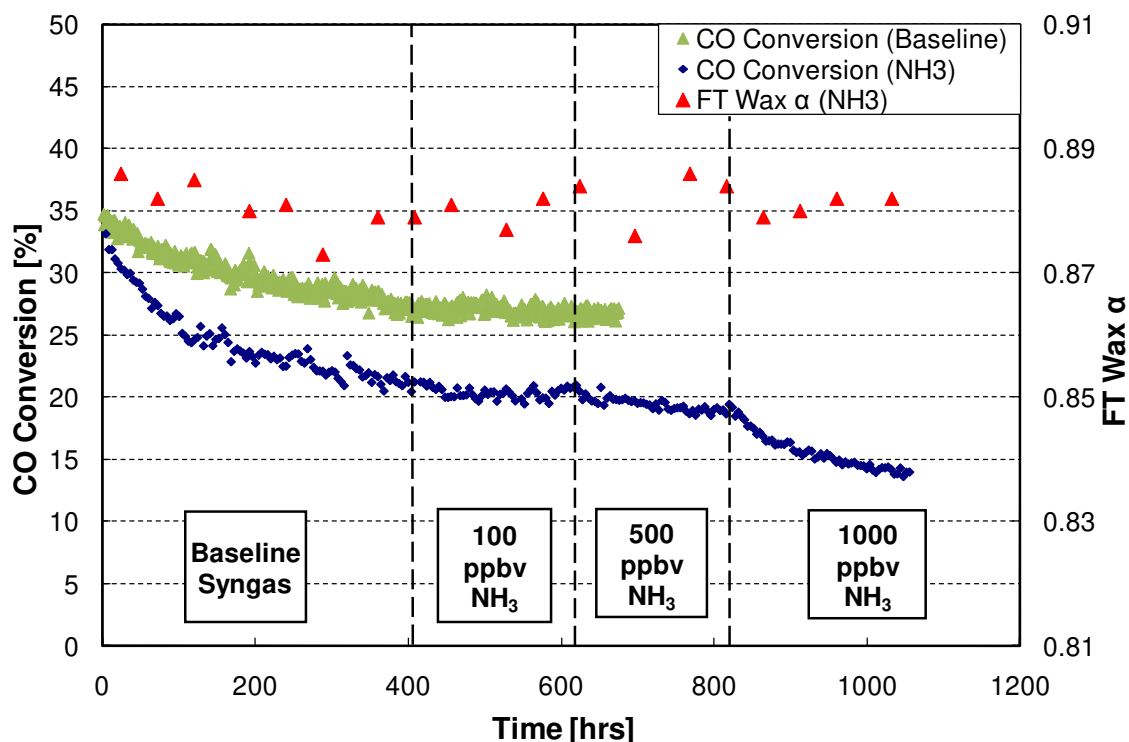


Figure 4-19. CO conversion and FT wax α for the Co-FT catalyst with syngas containing varying NH₃ concentrations.

Table 4-14. Effect of NH₃ Concentration on Co-FT Catalyst Performance

Performance parameter	NH ₃ contaminant concentration (ppbv)			
	0	100	500	1,000
Exposure time [h]	400	225	175	250
CO conversion [%]	21	21	19	14
Catalyst productivity [mg C ₅₊ /h/g catalyst]	68	67	60	44
CH ₄ selectivity [%]	19	19	20	23
CO ₂ selectivity [%]	1	1	1	1
FT wax α	0.87–0.89	0.87–0.89	0.87–0.89	0.87–0.89

4.6.5 Exposure to NaCl Vapor

The effect of NaCl vapor in syngas on the Co-FT catalyst performance was investigated for 500 hours. The CO conversion and FT wax α profiles for the catalyst in the presence of NaCl vapor are compared with that obtained in the baseline syngas test in Figure 4-20, and the average values for CO conversion,

catalyst productivity, and CH₄ and CO₂ selectivities are presented in Table 4-15. From these results, the catalyst performances with and without the NaCl vapor contaminant are very similar. However, analysis of the rate of change in the CO conversion between the two trials demonstrates a statistically significant acceleration in the rate of decline in CO conversion for the case of syngas containing NaCl vapor.

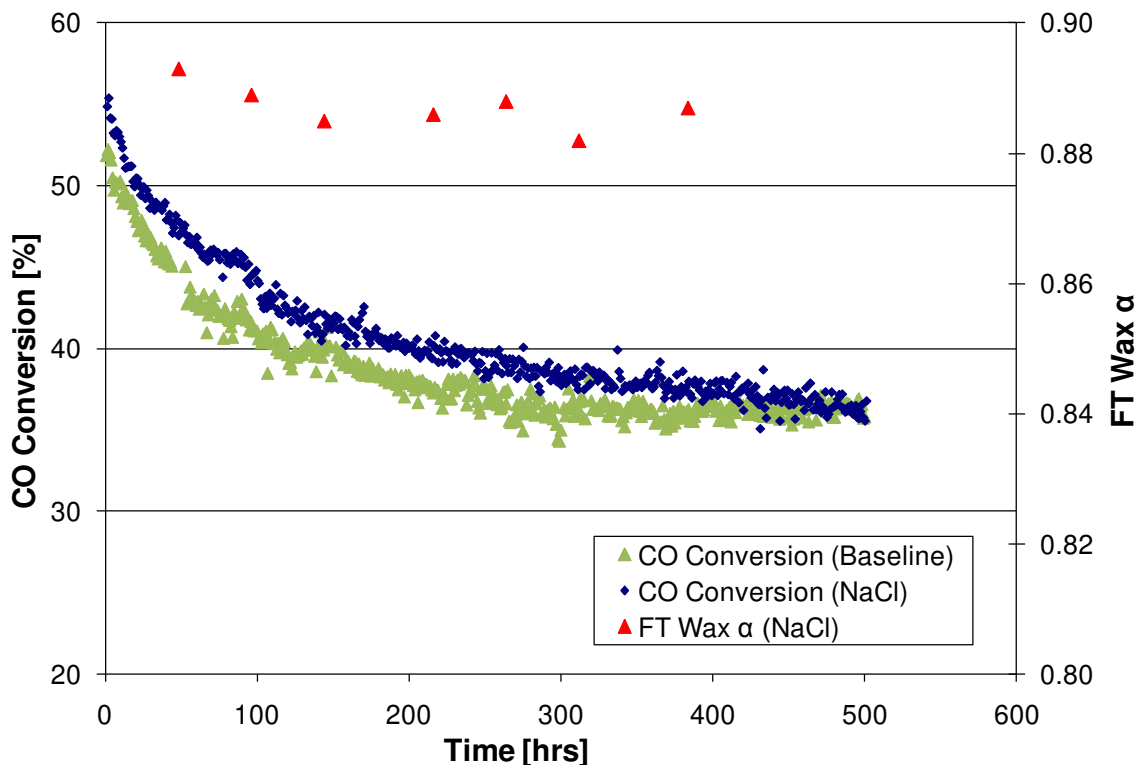


Figure 4-20. Effect of NaCl vapor in syngas on CO conversion and FT wax α of the Co-FT catalyst.

Table 4-15. Co-FT Catalyst Performance Results in the Presence of NaCl Vapor

Performance parameter	NaCl vapor concentration (pptv)	
	0	8.6×10^{-4}
Exposure time [h]	500	500
CO conversion [%]	36	36
Catalyst productivity [mg C ₅₊ /h/g catalyst]	143	144
CH ₄ selectivity [%]	11	11
CO ₂ selectivity [%]	1	1
FT wax α	0.87–0.89	0.87–0.89

4.6.6 Multi-contaminant Exposure

In the multi-contaminant exposure study, the commercial Co-FT catalyst was exposed to simulated CB-derived syngas mixtures containing NaCl, KCl, NH₃, and H₂S. The measured CO conversion and FT

wax α profiles are compared with that obtained in the baseline syngas test in Figure 4-21. The average CO conversion, catalyst productivity, and CH₄ and CO₂ selectivities for the different multi-contaminant combinations are provided in Table 4-16. The rate of decline in CO conversion at the completion of the initial exposure to both NaCl and KCl vapors was statistically similar to that previously seen for syngas containing only NaCl vapor, indicating that KCl vapor does not significantly affect the Co-FT catalyst performance. A comparison of the rates of decline in CO conversion for the different contaminant combinations shows that this rate was statistically greatest for the four-contaminant group consisting of NaCl, KCl, 10 ppbv H₂S, and 100 ppbv NH₃.

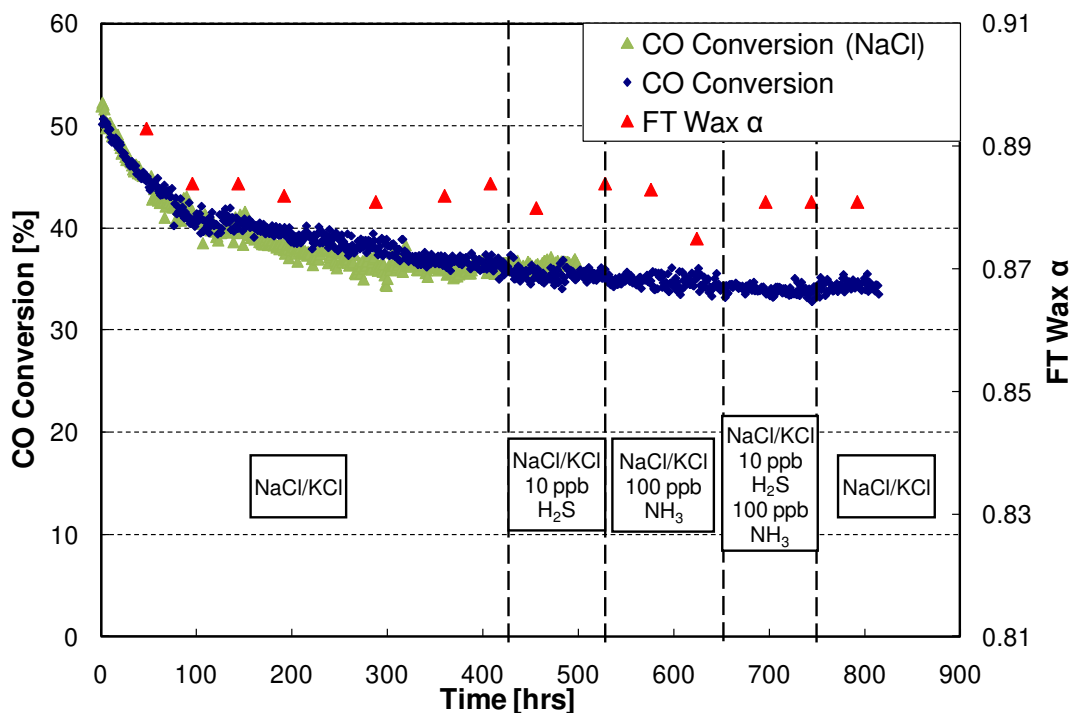


Figure 4-21. CO conversion and FT wax α of the Co-FT catalyst with syngas containing multi-contaminants.

Table 4-16. Co-FT Catalyst Performance during Multi-contaminant Testing

Performance parameter	Contaminant combination				
	NaCl +KCl	NaCl + KCl + 10 ppbv H ₂ S	NaCl + KCl + 100 ppbv NH ₃	NaCl + KCl + 100 ppbv NH ₃ + 10 ppbv H ₂ S	NaCl + KCl
Exposure time [h]	30	100	120	100	65
CO conversion [%]	36	35	35	34	34
Catalyst productivity [mg C ₅₊ /h/g catalyst]	144	141	138	135	136
CH ₄ selectivity [%]	11	11	11	11	11
CO ₂ selectivity [%]	0-1	0-1	0-1	0-1	0-1
FT wax α	0.87–0.89	0.87–0.89	0.87–0.89	0.87–0.89	0.87–0.89

Note: Alkali vapor concentration = 8.6×10^{-4} pptv for NaCl and 9.7×10^{-7} pptv for KCl (see Table 4-2)

5. Conclusions and Recommendations

Significant accomplishments and major conclusions from the WGS and FT catalyst performance studies performed in this project are the following:

- Conducted a series of thermodynamic studies to determine potential of trace contaminants found in CB-derived syngas to react with commercial WGS and FT catalysts
- Designed, fabricated, and operated five highly automated, laboratory-scale microreactor systems to quickly and effectively acquire catalyst performance information
- Completed over 25,000 hours of cumulative operation in evaluating the effects of individual and multi-contaminant effects on commercial WGS and FT catalysts in simulated CB-derived syngas

The results from these exposure trials are summarized in Table 5-1.

Table 5-1. Summary of Results from Contaminant Exposure Trials

Catalyst	Exposure trial	
	Individual contaminants ¹	Multiple contaminants
LTS (Low-temperature-shift)		<ul style="list-style-type: none"> • No impact observed up to 1,000 ppbv of NH₃ and H₂S
HTS (High-temperature-shift)		<ul style="list-style-type: none"> • Decline in CO conversion demonstrated for combinations of ≥150 ppbv H₂S and 1,000 ppbv of NH₃ with alkali vapors • Alkali vapors did not result in CO conversion decline and potentially resulted in recovery of lost CO conversion after exposure to 1,000 ppbv H₂S
SGS² (Sour-gas-shift)		<ul style="list-style-type: none"> • No impact observed up to 1,000 ppbv NH₃
Fe-FT (Iron-based Fischer-Tropsch)	<ul style="list-style-type: none"> • H₂S: Performance loss at >150 ppbv • COS: Performance loss at >175 ppbv • NaCl vapor: No impact • KCl vapor: No impact • NH₃: No impact 	<ul style="list-style-type: none"> • Most significant decrease in CO conversion observed with NaCl, KCl, and 100 ppbv H₂S
Co-FT (Cobalt-based Fischer-Tropsch)	<ul style="list-style-type: none"> • H₂S: Performance loss at 10 ppbv • COS: Performance loss at >100 ppbv • NaCl vapor: No impact • NH₃: Performance loss at >1,000 ppbv 	<ul style="list-style-type: none"> • Statistically significant decrease in CO conversion observed with NaCl, KCl, 10 ppbv H₂S, and 100 ppbv NH₃

¹ Hatched regions indicate that individual contaminant exposure trials were not conducted with WGS catalysts.

² Multi-contaminant exposure trials were focused on alkali vapors and NH₃.

At this time, no further exposure trials are planned. However, based on the thermodynamic analyses, individual and multi-contaminant exposure trials for HCl, AsH₃, H₂Se, PH₃, and Hg are recommended for all WGS and FT catalysts.