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Impact of Contaminants Present in Coal-Biomass Derived Synthesis Gas on Water-gas Shift and Fischer-Tropsch Synthesis Catalysts

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Abstract

Co-gasification of biomass and coal in large-scale, Integrated Gasification Combined Cycle (IGCC) plants increases the efficiency and reduces the environmental impact of making synthesis gas ("syngas") that can be used in Coal-Biomass-to-Liquids (CBTL) processes for producing transportation fuels. However, the water-gas shift (WGS) and Fischer-Tropsch synthesis (FTS) catalysts used in these processes may be poisoned by multiple contaminants found in coal-biomass derived syngas; sulfur species, trace toxic metals, halides, nitrogen species, the vapors of alkali metals and their salts (e.g., KCl and NaCl), ammonia, and phosphorous. Thus, it is essential to develop a fundamental understanding of poisoning/inhibition mechanisms before investing in the development of any costly mitigation technologies.

We therefore investigated the impact of potential contaminants (H_2S , NH_3 , HCN , AsH_3 , PH_3 , HCl , NaCl , KCl , AS_3 , NH_4NO_3 , NH_4OH , KNO_3 , HBr , HF , and HNO_3) on the performance and lifetime of commercially available and generic (prepared in-house) WGS and FT catalysts; ferrochrome-based high-temperature WGS catalyst (HT-WGS, Shiftmax 120™, Süd-Chemie), low-temperature Cu/ZnO-based WGS catalyst (LT-WGS, Shiftmax 230™, Süd-Chemie), and iron- and cobalt-based Fischer-Tropsch synthesis catalysts (Fe-FT & Co-FT, UK-CAER). In this project, TDA Research, Inc. collaborated with a team at the University of Kentucky Center for Applied Energy Research (UK-CAER) led by Dr. Burt Davis.

We first conducted a detailed thermodynamic analysis. The three primary mechanisms whereby the contaminants may deactivate the catalyst are condensation, deposition, and reaction. AsH_3 , PH_3 , H_2S , HCl , NH_3 and HCN were found to have a major impact on the Fe-FT catalyst by producing reaction products, while NaCl , KCl and PH_3 produce trace amounts of deposition products.

The impact of the contaminants on the activity, selectivity, and deactivation rates (lifetime) of the catalysts was determined in bench-scale tests. Most of the contaminants appeared to adsorb onto (or react with) the HT- and LT-WGS catalysts were they were co-fed with the syngas:

- 4.5 ppmv AsH_3 or 1 ppmv PH_3 in the syngas impacted the selectivity and CO conversion of both catalysts
- H_2S slowly degraded both WGS catalysts
 - A binary mixture of H_2S (60 ppmv) and NH_3 (38 ppmv) impacted the activity of the LT-WGS catalyst, but not the HT-WGS catalyst
- Moderate levels of NH_3 (100 ppmv) or HCN (10 ppmv) had no impact
- NaCl or KCl had essentially no effect on the HT-WGS catalyst, but the activity of the LT-WGS catalyst decreased very slowly

Long-term experiments on the Co-FT catalyst at 260 and 270 °C showed that all of the contaminants impacted it to some extent with the exception of NaCl and HF . Irrespective of its source (e.g., NH_3 , KNO_3 , or HNO_3), ammonia suppressed the activity of the Co-FT catalyst to a moderate degree. There was essentially no impact the Fe-FT catalyst when up to 100 ppmw halide compounds (NaCl and KCl), or up to 40 ppmw alkali bicarbonates (NaHCO_3 and KHCO_3).

After testing, BET analysis showed that the surface areas, and pore volumes and diameters of both WGS catalysts decreased during both single and binary H_2S and NH_3 tests, which was attributed to sintering and pore filling by the impurities. The HT-WGS catalyst was evaluated with XRD after testing in syngas that contained 1 ppmv PH_3 , or 2 ppmv H_2S , or both H_2S (60

ppmv) and NH_3 (38 ppmv). The peaks became sharper during testing, which was indicative of crystal growth and sintering, but no new phases were detected. After LT-WGS tests (3-33 ppmv NH_3 and/or 0-88 ppmv H_2S) there were a few new phases that appeared, including sulfides. The fresh Fe-FT catalyst was nanocrystalline and amorphous.

ICP-AA spectroscopy and other methods (e.g., chromatography) were used to analyze for Fe, Cu, S, K, Na, P, As, Cl, C, H, and N on both the fresh and tested catalysts. The HT-WGS catalyst displayed higher concentrations of impurities from H_2S , NaCl, PH_3 , KCl, and AsH_3 on its surface, but no measurable increases in the concentrations of N, H, and C. The LT-WGS catalyst also contained higher concentrations of impurities from H_2S , NaCl, $\text{NH}_3+\text{H}_2\text{S}$, and AsH_3 , but no measurable increase in N, H, P, and C. The WGS catalysts exposed to the alkali contaminants (i.e., Na^+ , K^+ and Cl^-) showed much higher levels of these metals since they were mixed directly with the catalyst. The Fe-FT catalyst tested in 40 ppmw NaHCO_3 or KHCO_3 had 300-400 ppmw Na^+ or K^+ while testing in KCl resulted in 800 and 111 ppmw K^+ or Cl^- , but these small amounts had no impact.

A techno-economic trade-off analysis was carried out that evaluated the cost of cleaning up the syngas versus the added costs of premature catalyst replacement due to poisoning. Using the experimentally determined rates of catalyst deactivation, we estimated catalyst lifetimes to identify the critical deactivation rates that would require a syngas cleanup system to protect the catalysts. We found that in most cases a cleanup system would be economically justified.

This project enabled us to determine the sensitivity of the WGS and FT catalysts used in CBTL processes to the contaminants in coal-biomass derived syngas, provided information on their service lifetimes, and will enable DOE and FTS technology developers to assess the risk of catalyst deactivation if these contaminants slip through syngas clean-up systems. We developed a fundamental understanding of the catalyst degradation mechanisms, which can help guide follow-on research on potential catalyst improvements and/or process modifications needed to reduce the capital and operating expenses of producing drop-in liquid fuels in CBTL plants. The commercialization of CBTL technologies depends on the development of syngas clean-up systems that can virtually eliminate these contaminants from syngas to protect the catalysts from deactivation.

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Executive Summary

Gasification technologies convert coal and biomass into synthesis gas ("syngas") feed streams that can be used as a chemical feedstock for Coal-Biomass-to-Liquids (CBTL) processes (Leckel and Phillips 2011). The CBTL system uses renewable domestic feedstocks, has a smaller greenhouse gas footprint than conventional petroleum fuels, and is projected to be economical at a world oil price significantly below existing levels of roughly \$100 per barrel (Gray, White et al. 2007). However, in order to meet the aggressive production goals that have been set for alternative methods of conversion to liquid transportation fuels, biomass is best utilized as a partial feed (co-feed) to large-scale, coal-fed gasification technologies that were originally developed over the past 30 years for Integrated Gasification Combined Cycle (IGCC) applications (Gray, Plunkett et al. 2009; Maxim, Cormos et al. 2011). This technological approach avoids the key problems with small biomass-only gasification plants (e.g., high specific cost, low efficiency, tar and oil formation in the raw syngas, and risk of shutdown if there is a biomass shortage). Co-gasification, mainly oxy-co-gasification with steam, improves the increased efficiency and reduces the environmental impact in a variety of gasifier types.

For grid-scale power generation and refinery applications (>50 MWe), the gasification field is dominated by plants based on pressurized, oxygen-blown, entrained-flow gasification. Recent successful tests with crop and waste biomass indicate that these types of gasifiers are reasonably well-suited to co-gasify biomass with coal, and critically, they eliminate tar formation and are apparently not greatly impacted by ash contents that differ from coal. However, the syngas generated by coal and biomass co-gasification contains multiple contaminants that may poison the water-gas shift (WGS) and Fischer-Tropsch synthesis (FTS) catalysts used in coal-to-liquids (CTL) and gas-to-liquid (GTL) chemical conversion processes. The commercialization of CBTL technologies depends on the development of clean-up and purification processes that can virtually eliminate these contaminants from the syngas feedstock to protect the catalysts from poisoning and deactivation.

Thus, it is essential to investigate the effects of a long list of potential coal and biomass contaminants on WGS and FT catalyst lifetime and performance (both activity and selectivity) and to develop a fundamental understanding of potential poisoning/inhibition mechanisms. This new understanding could lead to catalyst/process modifications that would prevent poisoning. In addition, before investing in the development of any costly mitigation technologies, a trade-off analysis must be carried out as a logical first step in an effort to prioritize the list of contaminants to be targeted for removal and to determine the threshold impurity concentrations and the associated deactivation rates that will require installation of a syngas clean-up system upstream of the catalytic processes.

The poisoning effects of heteroatoms (e.g., sulfur, nitrogen and oxygen) as well as halides and trace metals are well-documented for these catalysts. In the co-gasification of coal and biomass, it is anticipated that the quantities and concentrations of ash, sulfur species, trace toxic metals, halides, and nitrogen species will be lower than in the syngas generated by coal alone. Nevertheless, the impact of these contaminants must be re-evaluated at the reduced concentrations predicted for coal-biomass gasification for the production of liquid fuels. In addition, biomass feedstocks introduce a different spectrum of contaminants, which includes the vapors of alkali metals (such as sodium and potassium compounds) and their respective salts (e.g., KCl and NaCl), ammonia, and phosphorous that could render the WGS and FT catalysts inactive for the CBTL chemical conversion processes.

The main objective of this project was to investigate the effects of coal and biomass contaminants in coal-biomass derived syngas on the performance and lifetime of the most commonly used WGS and FT catalysts. We therefore investigated the impact of a long list of potential contaminants on commercially available and generic (prepared in-house) WGS and FT catalysts. Altogether we evaluated four different catalysts; commercial ferrochrome high-temperature WGS catalyst (HT-WGS, Shiftmax 120™, Süd-Chemie), low-temperature copper/zinc-oxide WGS catalyst (LT-WGS, Shiftmax 230™, Süd-Chemie), and in-house iron- and cobalt-based Fischer-Tropsch synthesis catalysts (Fe-FT & Co-FT, UK-CAER). We first evaluated the interaction of these catalysts with fifteen different contaminants present in coal-biomass derived syngas (H_2S , NH_3 , HCN , AsH_3 , PH_3 , HCl , NaCl , KCl , As_2S_3 , NH_4NO_3 , NH_4OH , KNO_3 , HBr , HF , and HNO_3) in a thermodynamic analysis, and then determined the effect of each of these contaminants on the long-term performance of the catalysts at their typical industrial operating conditions in bench-scale experiments that typically lasted for >100 h. Some of the contaminants adsorbed on the catalysts or reacted with them, which caused a reduction in their performance during testing. The physical and chemical interactions of the contaminants with each tested catalyst were subsequently examined using various analytical tools (e.g., BET, XRD, ICP/AA).

In this project, TDA Research, Inc. collaborated with a team at the University of Kentucky Center for Applied Energy Research (UK-CAER) led by Dr. Burt Davis. The experiments on the impact of contaminants on low- and high-temperature WGS catalysts were carried out at TDA Research and the cobalt- and iron-based FTS catalyst studies primarily took place at UK-CAER. The UK-CAER team also conducted the bulk of the post-testing catalyst characterization work, which provided insight into the poisoning/inhibition mechanisms.

This project consisted of five primary tasks that were also the subject of separate interim Topical Reports (except for Task 1). First, a project management plan was developed in Task 1. Applied thermodynamic modeling tools were used in Task 2 to identify contaminants that will react with the active phases and promoters in the WGS and FT catalysts (Table 1 and Table 2). In Task 3 we then carried out long-term catalyst-contaminant experiments that utilized both commercial and generic (synthesized in-house) catalysts to measure changes in activity and selectivity due to exposure to contaminant species in syngas under representative reaction conditions. We then characterized both fresh (as-prepared) and tested catalysts in Task 4 using physical and chemical analytical tools to understand the poisoning/inhibition mechanisms (if any). Finally, we performed a trade-off analysis in Task 5 to determine the threshold deactivation rates that would require the installation of a gas clean-up and purification system to protect the catalysts from unacceptable losses in activity and/or selectivity.

In Task 2 of this project, we conducted a detailed thermodynamic analysis. We found that there are three primary mechanisms by which the contaminant may deactivate the catalyst:

- Condensation: The contaminant itself or its decomposition product(s) that form adsorb on the surface of the catalyst.
- Deposition: Products of the reaction of the contaminant with components of the syngas mixture deposit onto the catalyst surface.
- Reaction: The contaminant forms inactive reaction products with the catalyst active phase.

The results of the thermodynamic contaminant impact study carried out for the four different catalysts are summarized in Table 1. We observed that each of the contaminants considered in the study could potentially impact every one of the catalysts. However, in practice the condensation and deposition products will be formed upstream and deposit in the heat

Table 1. Summary of the impact of contaminants on WGS and FT catalysts from the results of a thermodynamic assessment.

	HT-WGS		LT-WGS		Fe-FT	Co-FT
	Fe	Cr	Cu	Zn	Fe	Co
AsH ₃	C, R	C	C, R	C, R _t	R	C _t , R
H ₂ S	R	C _t , R _t	R	R	R	R
NH ₃	D _t , R _t	D _t	D _t	D _t	R	D _t , R _t
NaCl	C, D, R _t	C, D, R _t	C, D, R	C, D, R _t	C, D _t , R _t	C, D _t , R _t
KCl	C, D, R _t	R	C, D, R	C, D _t , R _t	C, D _t , R _t	C, D _t , R _t
HCl	R	R	R	R	R	R
PH ₃	D _t , R	D	R	R	D _t , R	D, R _t
HCN	D _t , R _t	D _t	D _t	D _t	R	D _t , R _t

C - Condensation mechanism

D - Deposition mechanism

R - Reaction mechanism

subscript "t" indicates trace amounts

exchangers and process pipelines rather than on the catalyst, since the catalyst does not take part in these specific deactivation mechanisms. If we eliminated these condensation and deposition mechanisms then we could categorize the contaminants into groups depending on their potential to cause major or minor impact derived from the results of the thermodynamic study as shown in Table 2. For example, AsH₃, PH₃, H₂S, HCl, NH₃ and HCN were found to have a major impact on the Fe active phase in the Fe-FT catalyst by producing reaction products, while NaCl, KCl and PH₃ also produce trace amounts of deposition products.

An extensive experimental campaign was undertaken in Task 3 to evaluate the impact of anticipated contaminants in the synthesis gas generated by coal and biomass co-gasification on the components (e.g., the active phases, promoters, and supports) and activity, selectivity, and lifetime of water-gas shift (WGS) and Fischer-Tropsch synthesis (FTS) catalysts. We evaluated the interaction of the fifteen different contaminants (H₂S, NH₃, HCN, AsH₃, PH₃, HCl, NaCl, KCl, AS₃, NH₄NO₃, NH₄OH, KNO₃, HBr, HF, and HNO₃) with the four different catalysts in long-term (typically >100 h) bench-scale experiments at the relevant industrial reaction conditions. These long-term bench-scale experiments were conducted in flow-through catalyst beds to determine

Table 2. Contaminants categorized based on thermodynamic study.

Catalyst	Major Contaminants	Minor Contaminants	No Impact
HT-WGS	AsH ₃ , H ₂ S, HCl, KCl, PH ₃	NaCl, NH ₃ , HCN	
LT-WGS	AsH ₃ , H ₂ S, HCl, NaCl, KCl, PH ₃		NH ₃ , HCN
Fe-FT	AsH ₃ , H ₂ S, HCl, NH ₃ , HCN, PH ₃	NaCl, KCl	
Co-FT	AsH ₃ , H ₂ S, HCl	NaCl, KCl, NH ₃ , HCN, PH ₃	

the impact of these contaminants on each catalyst and to quantify the rates of catalyst deactivation under representative reaction conditions. These tests were generally long enough to establish measurable deactivation rates even though the catalysts were exposed to low levels of these contaminants.

Most of the contaminants included in the HT- and LT-WGS catalyst experimental studies appeared to adsorb onto these catalysts because they were not detected downstream of the catalyst beds during testing. However, it is possible that some of the contaminants (such as NH_3) were removed in the steam condenser prior to the analysis point.

The results of the LT- and HT-WGS catalyst-contaminant tests can be summarized as follows:

- Syngas that contained 4.5 ppmv AsH_3 impacted the selectivity and conversion of the HT-WGS catalyst because it adsorbed onto it.
 - AsH_3 had an even greater impact on the LT-WGS catalyst.
- H_2S slowly degraded both the LT- and HT-WGS catalysts over time.
 - The CO conversion remained stable over the LT-WGS catalyst after the introduction of 10 ppm H_2S .
- A mixture of H_2S (60 ppmv) and NH_3 (38 ppmv) did not impact the performance of the HT-WGS but did impact the activity of the LT-WGS catalyst
- PH_3 appreciably impacted the performance of the WGS catalysts.
- Moderate levels of NH_3 did not impact the performance of either of the WGS catalyst and the CO conversion remained stable after the introduction of up to 100 ppmv NH_3 .
- No change in performance for either of the catalysts was observed following a long induction period after the introduction of 10 ppmv HCN .
- In tests run with alkali salts (NaCl or KCl) directly intermixed with the catalysts, virtually no effect was observed on the HT-WGS catalyst, but the activity of the LT-WGS catalyst decreased very slowly.

In binary contaminant tests, the effect of introducing mixtures of H_2S and NH_3 into the syngas on the catalytic activity of the commercial LT- and HT-WGS catalysts was evaluated. We observed a decrease in the performance of the LT-WGS catalyst following a short induction period after introducing a combination of NH_3 (38 ppmv) and H_2S (60 ppmv) into the syngas feed. H_2S conclusively adsorbed onto the HT-WGS catalyst during the single-contaminant test, and it also noticeably adsorbed when it was co-fed with ammonia. The combination of NH_3 and H_2S (38 and 60 ppmv) in the syngas feed resulted in H_2S uptake by the HT-WGS catalyst until it appeared to saturate the bed, as evidenced by H_2S breakthrough after only a few hours on-stream. Interestingly, very little decrease in CO conversion activity was observed during the test, even after more than half of the feed concentration of H_2S was detected in the WGS product stream.

The results of the bench-scale contaminant impact study carried out on the UK-CAER Co-FT catalyst showed that all of the contaminants impacted FTS over this catalyst to some extent with the exception of NaCl and HF . An aqueous solution of each compound, including chloride salts and bicarbonates, was injected into the reactor as the source of contaminant ions in syngas. The results of the contaminant experiments clearly established that poisoning of Co-FT synthesis catalysts is very complex and depends upon a number of factors. This makes it a demanding task to define experiments that focus on a specific feature of catalyst poisoning. It also appeared that, irrespective of its source (e.g., NH_3 , KNO_3 , or HNO_3), ammonia tended to suppress Co-FT catalyst activity to a moderate degree at all of the concentration levels examined. Neither the mode of deactivation nor the strength of the poisoning effect (e.g.,

reversibility) is known at this time. For example, the impact of the nitrate ion appeared to be influenced by its ability to undergo hydrogenation to water and ammonia, and that its impact was in fact due to the effect of ammonia. Furthermore, the loss of activity of the Co-FT catalyst in clean syngas (no contaminants) due to the accumulation of FTS reaction products made it difficult to know when to begin the poisoning study and how to differentiate between the impact of the contaminants on CO conversion and the normal rate of decline in activity.

The effect of NaCl, KCl, NaHCO₃ and KHCO₃ (0.1- 100 ppmw) contaminants co-fed with syngas on the performance of the UK-CAER high-alpha Fe-FT catalyst was studied at 260 and 270 °C. These contaminants had no significant impact on the Fe-FT catalyst and its activity. The hydrocarbon selectivities of the catalyst also did not significantly change while Na⁺, K⁺, Cl⁻ ions were continuously fed during tests that lasted between 72-144 h. The activity and selectivity results for the FTS reaction indicated that there was essentially no impact on the Fe-FT catalyst activity and selectivity when up to 100 ppmw halide compounds (NaCl and KCl), or up to 40 ppmw alkali bicarbonates (NaHCO₃ and KHCO₃) were co-fed with the syngas feed at both 260 °C and 270 °C. This suggests that neither the alkali ions (i.e., Na⁺ or K⁺) nor chloride ion (i.e., Cl⁻) adsorbed strongly enough on the catalyst surface to deactivate it during the FTS reaction in the CSTR, (if they are assumed to physically block the Fe active sites or change the electronic character of the Fe-FT catalyst).

The long-term experimental contaminant tests were supported with extensive characterization of the catalyst samples in Task 4 to identify the physical and chemical changes that occurred due to the catalyst-contaminant interactions. The results of the thermodynamic analysis, bench-scale experiments and catalyst characterization studies helped us to develop a fundamental understanding of the degradation mechanisms induced by these contaminants.

BET analysis showed that the surface areas, pore volumes, and pore diameters of both the LT- and HT-WGS catalysts all decreased during both single and combined H₂S and NH₃ contaminant tests. These reductions were probably due to sintering and pore filling by the impurity, especially in the case of sulfur.

The Fe-based HT-WGS catalyst was evaluated with XRD after testing in syngas that contained 1 ppmv PH₃, or 2 ppmv H₂S, or both H₂S (60 ppmv) and NH₃ (38 ppmv). The peaks became sharper during testing, which was indicative of crystal growth and sintering. However, the concentration of any new phases that may have formed were too low to detect. After testing the copper/zinc-oxide-based LT-WGS catalyst (Shiftmax 230) in syngas that contained either 3-33 ppmv NH₃ or 0-88 ppmv H₂S there were a few unidentified new phases that appeared, with significant differences apparent between the catalyst tested in NH₃ versus H₂S. The broad semi-amorphous peaks between 35-40° 2θ for the fresh catalyst almost disappeared for the catalyst tested in H₂S. In contrast, for the catalyst tested in NH₃, these peaks became more resolved and crystalline.

The XRD patterns for two different LT-WGS tests in syngas containing binary H₂S (60 ppmv or 500 ppmv) and NH₃ (38 ppmv) contaminant mixtures showed several new sulfide peaks compared to the XRD pattern for the fresh catalyst. The patterns for the tested catalysts showed several distinct new peaks compared to the XRD pattern for the fresh catalyst. The additional small peaks at ~30° and between 45-50° 2θ on the catalysts exposed to H₂S were most likely sulfides, and as previously noted the large semi-amorphous peaks between 35-40° 2θ for the fresh catalyst were almost gone in the tested samples. There were also some subtle differences in the peak shapes and the phases that formed between the catalysts tested at low or high H₂S concentrations and those tested in single (H₂S or NH₃) versus binary contaminant mixtures (H₂S

and NH_3). Broad, low-intensity peaks indicated that the Fe-FT catalyst was primarily nanocrystalline and amorphous prior to testing.

ICP-AA spectroscopy and other methods (e.g., chromatography) were used to analyze for all of the elements of interest (i.e., Fe, Cu, S, K, Na, P, As, Cl, C, H, and N) on both the fresh WGS and FT catalysts and the catalyst samples that were exposed to contaminants during the long-term tests. For the HT-WGS catalyst, the catalysts that were subjected to testing in syngas with co-fed contaminants displayed higher concentrations of the elements that composed that contaminant relative to the composition of the fresh catalyst in the cases of H_2S (484 ppm sulfur compared to 132 ppm sulfur in the fresh catalyst), NaCl (9.51% sodium compared to 488 ppm and 9.65% chlorine compared to 0.13%), PH_3 (0.44% phosphorus compared to 196 ppm), KCl (8.67% potassium compared to 52 ppm and 6.05% chlorine compared to 0.13%), and AsH_3 (1819 ppm arsenic compared to 11 ppm). For the other elements (i.e., N, H, and C), the results indicated either no measurable increase in the concentration of the contaminant in question, or a decrease in its concentration (e.g., C with HCN) within the limits of experimental error for the analysis technique.

For the Cu-based LT-WGS catalyst, the samples of catalyst that were subjected to contaminant exposure tests also contained higher concentrations of the elements that compose the contaminant of interest relative to the fresh catalyst in the cases of H_2S (2.37% sulfur relative to 84 ppm in the fresh catalyst), NaCl (8.83% sodium relative to 397 ppm and 15.6% chlorine relative to 0.08%), $\text{NH}_3 + \text{H}_2\text{S}$ (3.02% sulfur relative to 84 ppm), and AsH_3 (259 ppm arsenic relative to 9 ppm). For the other elements (i.e., N, H, P, and C), the results indicated no measurable increase in the concentration of the contaminant in question within the limits of experimental error for the analysis technique.

ICP and chromatographic analyses of the HT- and LT-WGS catalysts exposed to the alkali contaminants (i.e., Na^+ , K^+ and Cl^-) showed much higher levels of these residual metals after testing compared to the other contaminants since each of the alkalis was introduced by mixing its crystalline powder directly with the catalyst rather than feeding it into the catalyst bed in the gas phase. For the Fe-FT catalyst, the results of the elemental analyses indicated that only small quantities of these contaminant ions adsorbed onto the surface of the catalyst during testing. However, the concentrations of contaminants on the Fe-FT catalyst could have theoretically reached 0.4-1.5 wt.% if the entire quantity fed was adsorbed and retained by the catalyst during testing. This explains why essentially no changes in catalyst activity or selectivity were observed during the Fe-FT catalyst experiments that were conducted in the presence of these contaminants.

After the long-term FTS runs that examined the impact of 0-40 ppmw NaHCO_3 or KHCO_3 on the Fe-FT catalyst, 300-400 ppmw Na^+ or K^+ ions were present on the Fe-FT catalyst surface, which is only 2.6% (Na^+) and 7.6% (K^+) of the maximum theoretical values. The concentrations of K^+ and Cl^- in the Fe-FT catalyst after FTS testing in the presence of KCl were also low (800 and 111 ppm), respectively, which are just 1.5% (Na^+) and 10% (K^+) of the calculated maximum theoretical values. These results clearly indicate that the uptake of these contaminants by the Fe-FT catalyst under FTS conditions was very low, which explains why they did not affect FTS during the long-term tests.

ICP analysis of the alkali contaminant ion (e.g., Na^+ , K^+ or Cl^-) concentrations in the FTS products (i.e., water, oil and wax) from the four different contaminant test runs on the Fe-FT catalyst detected Na^+ , K^+ or Cl^- ions in all phases of the FTS products. However, most of the contaminant ions were retained in the wax slurry in the reactor (>90% in most cases), with the

remaining (<10%) distributed between the oil- and aqueous-phases. This further suggests that the contaminant ions injected on-line into the CSTR reactor in the aqueous solution did not strongly adsorb onto the Fe-FT catalyst surface under slurry FTS conditions, and that their impact on catalyst behavior could differ compared to the addition of trace amounts of these contaminants directly onto the catalyst or co-fed with the syngas.

A techno-economic study was carried out for Task 5 that evaluated the cost trade-off between cleaning up the coal-biomass derived syngas versus the added costs of catalyst replacement due to poisoning. Using the experimentally determined rates of catalyst deactivation from the long-term syngas-contaminant tests performed in Task 3, we carried out a system analysis to identify the critical deactivation rates that would trigger the requirement to install a warm-gas cleanup system downstream of the gasifier and upstream of the CBTL process. Anticipated catalyst lifetimes during exposure to the various contaminants were determined from the results of the long-term syngas-contaminant tests. This trade-off analysis showed that the use of a contaminant removal system would be economically justified in many cases to reduce the cost of premature catalyst replacement due to poisoning.

The results of this project enabled us to determine the sensitivity of the WGS and FT catalysts used in CBTL processes to the contaminants in coal-biomass derived syngas, provided information on the long-term cumulative degradation and service life for these catalysts, and will enable DOE and FT technology developers to assess the risk of catastrophic damage if higher than planned levels of these contaminants slip through syngas clean-up systems. The results of this work can help guide follow-on research to investigate potential catalyst improvements and/or process modifications needed to ultimately reduce the capital and operating expenses associated with producing drop-in liquid transportation fuels from coal-biomass derived syngas mixtures. The findings of this investigation will also be critical in establishing failure mode and effect criteria for co-gasified coal-biomass clean-up systems that operate in FTS plants.

1. Introduction

In this project, TDA Research, Inc. collaborated with the University of Kentucky Center for Applied Energy Research (UK-CAER) to evaluate the effects of contaminants in coal-biomass syngas on water-gas shift (WGS) and Fischer-Tropsch (FT) synthesis catalysts. Both a comprehensive thermodynamic analysis and an extensive experimental campaign were carried out to evaluate the impact of potential contaminants in the syngas generated by coal and biomass co-gasification on catalyst activity, selectivity, and lifetime. Altogether we evaluated four catalyst systems; iron- and copper-zinc-oxide based high- and low-temperature water-gas shift catalysts (HT-WGS and LT-WGS), and iron- and cobalt-based Fischer-Tropsch synthesis catalysts (Fe-FT and Co-FT). We evaluated the interaction of these catalysts with fifteen different contaminants (H_2S , NH_3 , HCN , AsH_3 , PH_3 , HCl , NaCl , KCl , As_3 , NH_4NO_3 , NH_4OH , KNO_3 , HBr , HF , and HNO_3), and determined the effect of each of these contaminants on the long-term (>100 h) performance of the catalysts at their typical operating conditions. We also carried out a trade-off analysis to determine the threshold deactivation rates that would require the installation of a gas clean-up and purification system to protect the catalysts from unacceptable losses in activity and/or selectivity.

1.1. Background

Coal and biomass mixtures can be co-gasified and converted into a syngas feed stream that can then be transformed into liquid hydrocarbon fuels. Synthesis gas (syngas) is a mixture of hydrogen and carbon monoxide that is used as a feedstock in coal-to-liquids (CTL) or gas-to-liquids (GTL) routes to produce methanol, ammonia or synthetic fuels *via* catalytic processes such as Fischer-Tropsch synthesis. Specifically, the Coal-Biomass-to-Liquids (CBTL) process uses domestic feed stocks, has a smaller greenhouse gas footprint than conventional fossil fuels, and is projected to be economically competitive at a world oil price significantly below \$100 per barrel. However, to meet the aggressive liquid transportation fuel production goals and minimize the potential for biomass supply disruptions, biomass is best utilized as a partial feed (co-feed) in large-scale, coal-based gasification facilities. This approach avoids the key problems of small biomass-only type gasifiers (e.g., high specific cost, low efficiency, tar and oil formation in the raw syngas, and interruptions due to biomass shortages).

Depending on the oxygen source for gasification, the H_2/CO ratio derived from biomass varies in the range of 1.0 to 1.5 for air-blown gasification, and 1.5 to 2.2 for gasification using pure O_2 . Pressurized, entrained-flow oxy-co-gasification with steam in large units (>50 MWe) allows increased efficiency and reduced environmental impact. Recent successful tests with crop and waste biomass indicate that these gasifiers are reasonably well-suited to co-gasify biomass with coal; tar formation is eliminated and ash content has not been a problem. However, the syngas generated by coal and biomass co-gasification contains myriad contaminants such as sulfur compounds (H_2S , COS), traces of metals mercury (Hg) and lead (Pb), halide compounds (NaCl and KCl), nitrogen-containing chemicals (NH_3 and HCN) and other compounds (e.g., NaHCO_3 , KHCO_3 , HCl , HF , and HBr) in addition to ash and tars that may poison the water-gas-shift (WGS) and Fischer-Tropsch (FT) catalysts used downstream in CBTL processes (Anderson, Karn et al. 1965).

The effect of coal contaminants on both WGS and FT catalysts has been studied, however, more thorough investigations are still needed to fully evaluate the effects of biomass derived contaminants on catalyst lifetime and performance (both activity and selectivity) (Mondal, Dang et al. 2011). So far, there are few data in the open literature to define the acceptable levels of these potential catalyst poisons and even less is known about how they impact WGS and FT catalyst behavior over extended periods of time. The identification of the most potent poisons as

well as a fundamental understanding of potential poisoning/inhibition mechanisms could lead to modifications in catalyst formulations, the process, or to the development of cleanup systems that prevent these contaminants from reaching the catalysts. In addition, before investing in the development of costly mitigation technologies, a logical first step is to prioritize the list of contaminants to be targeted for removal, and determine the threshold deactivation rates that will require implementation of a syngas clean-up system to protect the catalyst from deactivation.

1.1.1. Identification of Potential Poisons for FT and WGS Catalysts

The most common low-temperature (190-220 °C) WGS catalysts are varieties of copper/zinc-oxides supported on alumina substrates (Cu/ZnO/Al₂O₃). Ferrochrome (Fe-Cr) oxide based formulations are the most commonly used high-temperature (320-450 °C) WGS catalyst. Cobalt/molybdenum (CoMo)-based shift catalysts are also widely used for syngas streams that contain very high levels of sulfur. In particular, these so-called "sour-shift" catalysts are preferred by plants that use low-temperature bulk desulfurization systems, where the shift catalyst must operate upstream of the gas cleanup system in the presence of up to percent levels of sulfur. For example, Eastman Chemical's coal-to-chemicals plant at Kingsport, Tennessee uses the low temperature Rectisol process for bulk desulfurization of the syngas downstream of the sulfur-tolerant CoMo shift catalyst that adjusts the H₂:CO ratio of the feedstock. The FT catalysts used in the coal-to-liquids (CTL) or coal-biomass-to-liquids (CBTL) processes utilize transition metals, such as cobalt or iron in two-phase slurry column and gas phase fixed-bed reactors.

A common requirement for all of these catalysts (with the partial exception of the sour-shift catalysts) is a reasonably pure, contaminant-free syngas feedstock to ensure stable long-term operation. The transition metal catalysts used in these processes can lose their activity through various mechanisms including:

- 1) conversion of the active metal site into a stable inactive oxide
- 2) sintering (agglomeration of catalytic sites into less active larger clusters with lower surface area)
- 3) loss of active area by carbon deposition
- 4) chemical poisoning

The most recent advanced catalyst designs address these issues. For instance, carbon deposition during FT synthesis can be reduced by adding promoters such as potassium (K) to facilitate the gasification of carbon deposits and prevent them from blocking surface catalytic sites. Similarly, catalyst oxidation can be minimized with the use of bimetallic catalysts. It has also been shown that the addition of small amounts of precious metals such as platinum (Pt) helps to maintain cobalt in the reduced metallic state that is active for FT synthesis. The use of rhenium (Re) and other metal and metal oxide stabilizers prevents sintering and agglomeration of the Co particles. These added compounds form physical barriers and eliminate metal migration through surface diffusion or Ostwald ripening (Twigg and Spencer 2001).

One of the most prominent catalyst deactivation mechanisms (but also one of the more controllable modes) is the loss of activity due to chemical poisoning. It is well documented that both Co- and Fe-based FT catalysts can be easily poisoned by heteroatom contaminants (such as sulfur, nitrogen and oxygen) and halides (chlorine and fluorine) in the syngas. The Cu/ZnO/Al₂O₃ catalysts are even more sensitive to heteroatom and halide impurities due to the highly reactive nature of copper and zinc oxides in these formulations (Twigg and Spencer 2001).

In addition to these commonly known contaminants, syngas generated by coal gasification also contains trace levels of metal impurities. The literature on the impact of trace metal impurities (e.g., arsenic, mercury) on catalytic performance is limited to only a few industrial examples. One of the best sources of information comes from the Liquid Phase Methanol Process (LPMEOH™), a joint venture between the DOE, Air Products and Chemicals and Eastman Chemicals (Quinn, Dahl et al. 2004). In this application, it was observed that even ppb levels of arsenic vapor and arsenic hydride (referred to as arsine: AsH₃) in the syngas could rapidly deactivate the Cu/ZnO/Al₂O₃ methanol synthesis catalyst, and this composition is very similar to that of the LT-WGS catalyst. Eastman Chemicals has also reported deactivation of sour shift catalyst by arsenic poisoning at the Kingsport plant (Gardner, Gupta et al. 2012).

Our thermodynamic analysis also showed that AsH₃ could be a potent poison for FT catalysts because the formation of Fe and Co arsenides (e.g., FeAs, Co₂As₃, CoAs, CoAs₂) is favorable at the FT synthesis conditions. The poisoning mechanism of arsenic and other volatile metals such as selenium (Se) and cadmium (Cd) on the transition metal catalysts is two-fold: (1) the strong affinity between arsenic and metal leads to its irreversible chemisorption on the active sites, blocking these sites and rendering the catalyst inactive and (2) the metal arsenides or selenides and the metal amalgams (e.g., CuHg, CuCd, CoCd) form a solid-solution with the remaining metal sites at the operating temperatures of interest, which increases the mobility of the metal crystallites. These “micro-fluxes” promote the rapid sintering of the metals and substantially reduce their catalytic activity. As a result of their higher concentrations in some coals and their highly reactive nature, arsenic, selenium and their hydrides should be of particular concern. Mercury could potentially form amalgams with the transition metals and promote a similar sintering effect. At the Eastman Chemical coal-to-chemicals plant in Kingsport, Tennessee, the mercury concentration of the syngas feed is reduced to sub-ppb levels using ambient temperature activated carbon beds downstream of the Rectisol unit before it contacts the catalyst in the slurry column methanol synthesis reactor.

1.1.2. Gas Cleanliness Requirements

Due to the complex nature of raw syngas and the many molecular forms in which these contaminants are present, it is difficult to formulate a FT or WGS catalyst that is resistant to them all. Therefore, the common approach is to treat the syngas feed prior to the synthesis process, insuring that the impurity levels are acceptable for the long-term stable operation of the process.

By far the most abundant, important and the most studied FT catalyst poison is sulfur (S). Sulfur compounds rapidly deactivate Cu, Fe and Co catalysts, presumably by forming surface metal sulfides that do not have catalytic activity (Anderson, Karn et al. 1965). There is really no safe sulfur level for the WGS or FT synthesis catalysts; ideally, there should be no sulfur in the syngas. In practice the level of gas cleaning is based on economic considerations; namely, how long the catalyst remains active versus the investment in the gas cleanup system. A maximum sulfur content of 0.2 ppmv (parts-per-million by volume) is recommended based on commercial experience in the SASOL plants (Dry 1988). Strong sulfur adsorption (and in

Table 3. Syngas impurities and tolerances.

Impurity	Tolerance Level	Source
Sulfur	0.2 ppm 1 ppmv 60 ppb	Dry, 1981 Boerrigter, <i>et al</i> , 2002 Turk, <i>et al</i> , 2001
Halides	10 ppb	Boerrigter, <i>et al</i> , 2002
Nitrogen	10 ppmv NH ₃ 0.2 ppmv NO _x 10 ppb HCN	Turk, <i>et al</i> , 2001

extreme cases formation of a metal sulfide phase *via* covalent bonding) diminishes the number of active sites available for the reaction (Bhatt, 1990). Several more recent references cite even lower sulfur tolerances for the FT catalysts. Turk and coworkers claimed that the total sulfur content should be lower than 60 ppbv, with cobalt catalysts indicated as being more sensitive to sulfur poisoning than iron catalysts (Turk, Merkel et al. 2001).

Other syngas impurities such as halides, nitrogen species and volatile metals also poison FT catalysts. Table 3 summarizes the syngas impurities the tolerance of FT catalyst for them (Espinoza, 2000). Halide levels in syngas should be <10 ppbv and referenced nitrogen levels are 10 ppmv NH_3 , 0.1 ppmv NO_x and 10 ppbv HCN (Hamelinck, Faaij et al. 2004). Similarly, sulfur poisoning effects are well documented for WGS catalysts; commercial licensors of methanol plants (that commonly use LT-WGS catalyst to adjust the $\text{CO}:\text{H}_2$ molar ratio in addition to the methanol synthesis catalyst) design processes for feedstock that contains <50 ppbv of these common poisons (Twigg and Spencer 2001).

In the co-gasification of coal and biomass, it is anticipated that the concentrations ash, sulfur species, trace toxic metals, halides, and nitrogen species will be lower than in the syngas generated by coal alone. Nevertheless, the impact of these contaminants on WGS and FT catalysts must be re-evaluated at the reduced concentrations predicted for coal-biomass co-gasification systems.

1.1.3. Biomass-based Contaminants in Coal-biomass Synthesis Gas

In addition to the relatively well-known and studied coal contaminants, biomass feedstocks will introduce a different spectrum of impurities from coal including the vapors of alkali metals (such as sodium and potassium compounds) and their respective salts (e.g., KCl and NaCl), ammonia (NH_3) and phosphorous (in the form of phosphine, PH_3) that could render the WGS and FT catalysts inactive.

The herbaceous types of biomass contain elevated levels of potassium, chlorine and sulfur species. Sulfur is largely incorporated into the organic structure of the plant, while chlorine and potassium are mainly present as free ions in the cellular fluids together with other organic and inorganic ions. Chlorine and potassium are also associated with charged groups in minor amounts in the organic matrix. The concentration of these elements in annual biomass typically ranges from 0.1-1% (by mass) for chlorine, 0.5-2% for potassium, and 0.05-0.3% for sulfur with parameters such as growth conditions, weathering and how the biomass is stored before use influences the mineral content.

The problematic behavior of the Cl-K-S system is linked to the volatile nature of their salts, KCl and K_2SO_4 . These elements are partly released into the gas phase during gasification. In addition to catalyst poisoning, the these volatile salts may also lead to heavy deposits on heat transfer surfaces, which results in reduced heat transfer and enhanced corrosion rates. Furthermore, high mass loads of aerosols are generated along with relatively high emission levels of HCl and H_2S .

In order to mitigate the harmful effects of these species, kaolinite-based additives are commonly added to biomass-fired grate boilers to capture potassium and sodium salt vapors to prevent damage to heat exchanger surfaces and eliminate their emissions. It is likely that the ash content of the coal also removes some of these alkalis, however it is probable that a fair amount of these potassium and sodium salts partition into the vapor phase and remain entrained in the syngas.

Other major contaminants in biomass are silica (Si) and phosphorous (P). These species can be found at high concentrations in the soil and the dirt that inevitably comes along with the biomass. These contaminants should also be of concern because of their volatile nature. At elevated gasification temperatures and in the presence of high partial pressures of water vapor, silica reacts with water to form silicon hydroxide $[\text{Si}(\text{OH})_2]$, which has a vapor pressure of 120 torr at 800 °C (Hildebrand et al., 1998). As the gas temperature drops, silica could deposit onto the surface of the catalyst and block its active sites.

Biomass-based phosphorous is converted into phosphine inside the gasifier, another highly reactive and corrosive species. A recent analysis by SRI showed that after arsenic, phosphorous is the worst poison for the nickel-based electrocatalysts and nickel-cobalt based interconnect materials used in solid-oxide fuel cells.

1.2. Project Objectives

The primary objective of this project was to determine the effects of major coal and biomass contaminants on the performance and lifetime of commonly used WGS and FT catalysts. The impact of a long list of potential contaminants on commercially available and generic (prepared in-house based on scientific and patent literature) WGS and FT catalysts was investigated. The overall contaminant test matrix is provided in Table 5. For the WGS catalysts, we primarily evaluated the copper/zinc oxide/alumina ($\text{Cu/ZnO/Al}_2\text{O}_3$) based formulations that are widely used for low-temperature WGS and the ferrochrome ($\text{Fe}_2\text{O}_3/\text{Cr}_2\text{O}_3$) based catalyst used for high-temperature WGS. For FT synthesis we evaluated both the iron and cobalt-based catalyst formulations that are used in gas-phase and liquid-phase processes.

Bench-scale experiments were conducted to determine the impact of these contaminants on each catalyst for a minimum of 100 h and to quantify the rates of catalyst deactivation under representative reaction conditions. The duration of these tests was long enough to establish measurable deactivation even though the catalysts were exposed to low levels of these contaminants. The tests were supported with extensive characterization of the catalyst samples to identify the physical and chemical changes that occurred due to the catalyst-contaminant interaction. The experiments and characterization results helped us to develop a fundamental understanding of the degradation mechanisms induced by these contaminants. From these experimental results, we carried out a system analysis to identify the critical deactivation rates that would trigger the requirement to install a warm-gas cleanup system downstream of the gasifier and upstream of the CBTL process. The economic trade-off study was based on the cost comparison between investing in syngas cleaning versus tolerating decreased production due to poisoning of the catalyst.

1.3. Catalyst Selection

As the intent of this study was to provide information that is usable in the CBTL field, the catalysts chosen for testing were commercially available or comparable to those used in existing processes. Süd-Chemie (now Clariant) provided samples of their Shiftmax 120™ and Shiftmax 230™, high-temperature and low-temperature WGS catalysts, respectively. The catalysts used in the Fischer-Tropsch synthesis evaluation studies were produced in-house by UK-CAER. The nominal composition of each catalyst used in this study is given in Table 4 (as given in the manufacture's MSDS for Shiftmax 120 and 230). The compositions of the Fe- and Co-FT

catalysts from UK-CAER were given on a molar metals basis, but are shown as the metal oxide equivalent for comparison purposes.

1.4. Contaminant Selection

To establish a general test plan that could be adopted by all of the DOE contractors working simultaneously in this program, we first estimated the potential contaminant concentrations (the highest range) in coal-biomass derived syngas. The expected contaminant concentrations were determined based on worst-case estimations (e.g., no loss of contaminants in the gasifier) using a typical syngas composition for an oxygen-blown entrained-flow gasifier. We estimated that about 10% of the fuel feed to the gasifier will be from biomass; the ratios of carbon feed to oxygen and water were modeled to determine the final concentration of the contaminants in the gas.

The catalyst and contaminant testing matrix is shown in Table 5. Each catalyst was exposed to a contaminant singly, then in a combined test to evaluate for synergistic contaminant effects. The duration of each test was at least 100 h after the addition of the contaminant(s) to establish measurable deactivation rates.

The catalyst and contaminant testing matrix is shown in Table 5. Each catalyst was exposed to a contaminant singly, then in combined tests to evaluate for synergistic contaminant effects. The duration of each test was at least 100 h after the addition of the contaminant(s) to establish measurable deactivation rates. The alkali salts and other contaminants (e.g., NH_4NO_3 , NH_4OH , KNO_3 , HCl , HBr , HF , HNO_3 , KHCO_3 and NaHCO_3) were introduced into the reactors in multiple chemical forms in either the vapor or liquid phase (by co-feeding them with the syngas or injecting them dissolved in water), which enabled us to study the impact of these contaminants on the FTS catalysts. The WGS catalysts were mixed directly with the salt crystals (NaCl or KCl), so that each catalyst was exposed to the equilibrium vapor level at its given reaction condition. KCl has a higher vapor pressure than NaCl and was selected for evaluation with the FTS catalysts. The vapor pressure of KCl at the FTS reaction conditions is still extremely low, which made it difficult to introduce it into the catalyst in the gas phase. However, KCl could be introduced as a solid by mixing it with either the catalyst or the wax, which enabled us to study its impact on the FT catalysts.

1.5. Technical Approach and Work Plan

The R&D effort was divided into five parts. The first requirement was the completion of the management plan in Task 1 (not discussed in this report). In Task 2, a thermodynamic analysis was carried out to assess the impact of coal and biomass contaminants on WGS and FT catalysts for a range of conditions. In Task 3, the impact of the contaminants on catalyst performance was evaluated under representative reaction conditions. In the bench-scale experiments the potential surface-contaminant interactions (e.g., adsorption of contaminants onto the catalysts) was also examined. In Task 4, detailed analytical characterization of the physical and chemical properties of the WGS and FT catalysts exposed to the contaminants was conducted to gain understanding about the poisoning/inhibition mechanisms. In Task 5, an economic trade-off analysis was used to evaluate the threshold contaminant concentrations that would result in catalyst deactivation rates that justify investment in a contaminant control

Table 4. Catalyst compositions.

Sud-Chemie ShiftMax 120	
Fe_2O_3	80.0%
Cr_2O_3	8.5%
CuO	2.0%
Inert	9.5%
Sud-Chemie ShiftMax 230	
CuO	58.0%
ZnO	31.0%
Al_2O_3	11.0%
CAER Co-FT	
CoO	31.8%
Pt	0.5%
Al_2O_3	67.7%
CAER Fe-FT	
Fe_2O_3	92.9%
SiO_2	3.6%
K_2O	1.6%
CuO	1.9%

system. The results for Tasks 2, 3 and 4 are also described in detail in individual Interim Topical Reports that were submitted to the DOE.

1.5.1. Thermodynamic Equilibrium Analysis

Applied thermodynamic modeling tools were used to identify the contaminants that will react with the active phases and promoters in the WGS and FT catalysts. Further details on the methodology and results are given in Section 2 of this report.

1.5.2. Experimental Measurement of the Impact of Contaminants on the Performance of WGS and FT Catalysts

Once the most potent catalyst poisons were identified by thermodynamic analysis, bench-scale experiments were carried out in Task 2 to measure the uptake kinetics of the coal-biomass contaminants on the FT and WGS catalysts, and to quantify the catalyst deactivation rates when exposed to selected contaminants. As the objective was to evaluate the effect of contaminants on catalyst performance and lifetime, the deactivation rates for the catalysts and contaminant levels remaining in the effluent stream were determined in this task. Two approaches have been used to define the sensitivity of FTS catalysts to impurities in syngas. One is to incorporate trace amounts of impurities into the catalyst and then to explore the differences in catalyst performance (activity, selectivity and stability) relative to those of the reference catalyst. Another method is online co-feeding of an impurity-containing solution or gas with syngas and then studying the changes in catalyst performance with time. This approach was used in many sulfur poisoning studies.

Commercially available low-temperature (190-300 °C) Cu/ZnO/Al₂O₃ WGS catalyst and a high-temperature (350 °C) Fe-Cr WGS catalysts were obtained for the bench-scale tests (Shiftmax 230 and Shiftmax 120, Süd-Chemie). Generic formulations of iron and cobalt-based FT synthesis catalysts were prepared in-house by Dr. Davis' group at the UK-CAER. Their material selections and synthesis methods were similar to commercial formulations, thus, confidentiality agreements did not limit the extent of characterization that could be performed. The WGS and the cobalt-based FT catalysts were evaluated in a gas phase bench-scale reactor, while a slurry bubble-column reactor was used to evaluate the sensitivity of the iron- and cobalt-FT catalysts to the contaminants.

Table 5. Catalyst contaminant testing matrix.

Contaminants	HT-WGS	LT-WGS	Co-FT	Fe-FT
H ₂ S	1ppmv	1ppmv	1ppmv	1ppmv
NH ₃	1ppmv	1ppmv	1ppmv	1ppmv
H ₂ S/NH ₃	1ppmv (ea)	1ppmv (ea)	1ppmv (ea)	1ppmv (ea)
KCl	equil	equil	equil	equil
NaCl	equil	equil	equil	equil
Alkali/H ₂ S	equil/1ppmv	equil/1ppmv	equil/1ppmv	equil/1ppmv
Alkali/NH ₃	equil/1ppmv	equil/1ppmv	equil/1ppmv	equil/1ppmv
Alkali/NH ₃ /H ₂ S	equil/1ppmv (ea)	equil/1ppmv (ea)	equil/1ppmv (ea)	equil/1ppmv (ea)
AsH ₃	1ppmv	1ppmv		
PH ₃	1ppmv	1ppmv		
AsH ₃ /PH ₃	1ppmv (ea)	1ppmv (ea)		

At the start of the project, TDA Research already had in place the infrastructure to safely store, handle, blend and analyze the trace contaminants at the concentration levels of interest (i.e. 1-100 ppmv), most of which requires special manifolding and containment due to their reactive, toxic and hazardous nature. As a result, the effect of all coal and biomass contaminants of interest on the LT- and HT-WGS catalysts were evaluated in existing bench-scale testing units at TDA's facilities dedicated to handling and analyzing these trace contaminants, as shown in Figure 1 and Figure 2. As these tests required long-term operation of the system and catalyst in the presence of the contaminants, the gaseous species had to be supplied at high concentrations and metered down to the concentrations specified for testing.

TDA's test units housed a variety of the analytical tools that allowed us to continuously monitor the trace contaminant concentrations at sub ppm levels. As the objective was to evaluate the effect of contaminants on catalyst performance and life, deactivation rates for the catalysts and contaminant levels remaining in the effluent stream were determined. Gas chromatographs (GC) were used to evaluate contaminant levels. Non-dispersive infrared (NDIR) and thermal conductivity detectors (TCD) analyzers were used for monitoring gas compositions and real-time catalyst performance, while mass spectroscopy (MS) was used for evaluation of FT synthesis liquid products.

The CO and H₂ conversion rates were measured in the bench-scale catalyst evaluation experiments to determine the WGS and FTS activity of the catalysts in the presence and absence of the contaminants. The CO, H₂, CO₂ and hydrocarbon concentrations in the feed and effluent streams were monitored continuously with on-line analyzers and gas chromatographs (for liquid and gas phase sampling). First, stable baseline conditions were established for the HT-WGS reaction using a clean (no contaminants) syngas feed that contained 32.7% H₂, 42.5% CO, 19.6% CO₂, and 5.2% CH₄ (or N₂) on a dry molar basis. Excess water was provided as steam (37% of the total feed flow rate). We chose 20 h as the minimum duration for collecting the baseline (or until steady-state operation was observed), 100 h for determining the impact of the contaminant(s) and to measure the deactivation rate, and an additional 20 h of testing in clean syngas after exposure to the contaminant(s) to assess their impact.

Figure 1. Catalyst testing rigs used for gas-phase WGS-contaminant testing at TDA Research.

Baseline tests were conducted first to measure the catalyst performance in the absence of any contaminants and this performance data was used as a benchmark to assess the effects of potential poisons. The optimal gas hourly space velocity (GHSV) was also determined as part of the baseline testing for each catalyst. The ideal space velocity was one that resulted in the best performance (i.e., to achieve the level of conversion predicted by thermodynamic equilibrium), while operating at the edge of the catalyst's capabilities. Since the real-time metric was the water-gas shift performance, for example, operating at these conditions (maximum utilization of the catalyst) provided immediate feedback on the contaminant's effect – i.e., any reduction in available active catalyst phase caused a measurable decrease in the catalyst performance. The conditions used for the WGS catalyst tests are shown in Table 6.

If no change in the CO and H₂ conversion was observed during testing, this was indicative of the relative inertness of the catalyst towards a particular impurity, although catalytic activity alone was not the sole indicator used to determine the impact of a specific contaminant because detection of some of the deactivation processes could have taken a much longer duration than the exposure times. If we observed that the selected contaminant was readily removed from the feed mixture by the catalyst (which indicated its corrosive nature), we extended the duration of the test to better understand the poisoning mechanism. Once we fully examined one contaminant, we tested the next one using a fresh catalyst. Some of these tests were repeated using more than one contaminant to identify any potential synergistic adsorption or inhibition effects.

While WGS testing used a baseline feed composition derived from the anticipated industrial coal-biomass gasifier syngas composition, the FT catalyst testing only used a mixture of

hydrogen and carbon monoxide. As industrial applications are expected to use a Selexol or Rectisol clean-up process prior to the FT reactor, levels of carbon dioxide and methane will already be low; the expected compositions are shown later in Table 7. The lack of diluents also greatly simplified measurements of catalyst activity and tracking the carbon balance through the system. Polywax 3000 was used as the startup surrogate wax in the CSTR.

Initial gas-phase tests were conducted in TDA's Fischer-Tropsch synthesis test system shown in Figure 2, using the Co-FT catalyst provided by UK-CAER. The test rig had a control and datalogging system (Labview, National Instruments), automatic pressure control valve (Badger) and a wet test meter. However, in these preliminary scoping tests the catalyst exhibited very high activity, but low selectivity for FT liquids and high methane production.

Table 6. Summary of baseline catalyst test conditions.

	HT-WGS	LT-WGS	Co-FT	Fe-FT
H ₂	20.6%	43.2%	67.7%	41.2%
CO	26.8%	4.5%	32.3%	58.8%
CO ₂	12.3%	34.4%	0%	0%
CH ₄	3.3%	2.9%	0%	0%
H ₂ O	37.0%	15.0%	0%	0%
H ₂ :CO	0.8	9.6	2.1	0.7
Temperature (C°)	350	240	220	240
Pressure (psig)	400	400	300	300
GHSV (h ⁻¹)	TBD	6000	TBD	TBD

1.5.2.1 Impurity Analysis

For the analysis of common gas-phase contaminants we used a continuous emission single-point monitor (SPM, Honeywell) that measured the AsH_3 , PH_3 , and HCN concentrations at ppb concentrations in the reactor effluent or in the feed when the reactor was bypassed (Figure 4). The analyzer uses a reactive tape that changes color upon contacting the targeted contaminant; the color intensity is correlated to the concentration. For the detection of sulfur species including H_2S , COS , CS_2 and thiophene, we used a Sulfur Chemiluminescence Detector with a 1 ppbv lower detection limit. For HCl and Cl_2 analysis we used an on-line analyzer (Thermo Scientific), as shown in Figure 3.

1.5.2.2 Design of the experiment to assess the impact of low concentrations of H_2S , PH_3 and AsH_3

Since in the actual process the catalyst is exposed to only low concentrations of the contaminants (but for thousands of hours), an accelerated test was designed so that the impact of the contaminants at low concentrations could be studied in a shorter time frame of about 100 h. In our contaminant evaluation study we established a GHSV of $12,000 \text{ h}^{-1}$ as standard baseline condition so that the catalyst had high WGS activity, which made it easier to observe any change in catalyst activity due to presence of contaminants. Also, in order to see the impact of the contaminant in the 100 h test window, we had to increase the concentration of the contaminants to higher levels so that catalyst could be loaded with enough of the contaminants to influence the WGS activity.

Figure 2. TDA's CSTR Fischer-Tropsch synthesis system.

The experimental design involved an initial ~20 hour test at the designated GHSV of $12,000 \text{ h}^{-1}$ to evaluate baseline catalyst performance. Then the catalyst was exposed to low contaminant concentrations at high GHSV until it was detected at the reactor outlet i.e., a low contaminant concentration was maintained at all times until the catalyst was fully loaded with the contaminant at the low concentration. Finally, after the contaminant testing, the catalyst performance was evaluated again at the designated GHSV of $12,000 \text{ h}^{-1}$ in clean syngas. The contaminant capacities and rates of performance decline were subsequently used to estimate the real-world catalyst lifetimes.

1.5.2.3 Evaluation of Cobalt- and Iron Fischer-Tropsch Catalysts by UK-CAER

UK-CAER investigated the impact of syngas contaminants on the performance (activity and selectivity) and life of both Co- and Fe-FT catalysts. UK-CAER prepared their own Co and Fe-based FT catalysts for this subtask and evaluated them in the presence of 13 different contaminants; As_2S_3 , NH_3 , NH_4NO_3 , NH_4OH , NaCl , KNO_3 , KCl , HCl , HBr , HF , HNO_3 , KHCO_3 and NaHCO_3 .

All of the contaminant co-feeding tests were made in a 1 L CSTR with approximately 10 g of activated Pt promoted Co/ γ - Al_2O_3 catalyst (0.5%Pt-25%Co/ γ - Al_2O_3 , identification number GJ456). Each CSTR was equipped with a magnetically driven stirrer fitted with a turbine impeller, a gas-inlet line, and a vapor outlet line with a stainless steel (SS) fritted filter. A tube fitted with a SS fritted filter (2 μm particle cut-off grade media) extended below the liquid level of the reactor for withdrawing reactor wax in order to maintain a nearly constant liquid level in the reactor. Mass flow controllers were used to control the feed flow rates of hydrogen and carbon monoxide. The gases were premixed in a vessel before entering the reactor. Carbon monoxide was passed through a vessel containing lead-oxide/alumina to remove traces of iron carbonyl. The mixed gases entered the CSTR below the stirrer, which was operated at 750 rpm. The reactor slurry temperature was maintained ($\pm 1^\circ\text{C}$) by a temperature controller.

The gaseous reaction products were continuously removed from the vapor phase of the reactor and passed through two traps maintained at different temperatures – a warm trap maintained at 100°C and a cold trap held at 0°C . The uncondensed vapor stream was reduced to atmospheric pressure through a pressure letdown valve. The gas flow was measured using a wet test meter and analyzed by an online GC. The accumulated reactor liquid

Figure 4. Single-point monitor (SPM) used to measure ppb concentrations of impurities.

Table 7. Syngas feed compositions for Fischer-Tropsch synthesis.

	Co-FT	Fe-FT
H_2	65.4%	42.8%
CO	31.9%	55.6%
CO_2	2.4%	1.3%
CH_4	0.3%	0.3%
H_2O	0.0%	0.0%
$\text{H}_2:\text{CO}$	2.1	0.8

Figure 3. Sulfur analysis instrument.

products were removed every 24 h by draining them through a 2 μm sintered SS frit filter located below the liquid level in the CSTR. Conversion of CO was obtained by gas-chromatography analysis (i.e., using a micro-GC equipped with thermal conductivity detectors) of the reactor exit gas mixture. The products were separated into different fractions (rewax, wax, oil and aqueous) for quantification. However, the oil and wax fractions were mixed prior to GC analysis. The desired contaminant compound was introduced as an aqueous solution (except gaseous compounds such as NH_3) along with syngas at the rate of 1.0 ml/h via a high performance syringe pump (Isco). Each contaminant compound was introduced into the CSTR after steady-state CO conversion was achieved in the baseline test. To isolate the effect of the contaminant during cobalt-catalyzed FT synthesis, deionized water was introduced before and after the poison test (1.0 ml/h) in order to subtract out the effect of co-fed water on the deactivation rate.

For the Co and Fe FT catalyst evaluations, UK-CAER first conducted baseline tests to measure the catalyst performance in the absence of any contaminant and use this performance as a benchmark to assess the impact of potential poisons. The optimal GHSV was determined as part of the baseline testing. As industrial applications are expected to use a Selexol or Rectisol clean-up process prior to the FT reactor, the levels of carbon dioxide and methane will already be low, with the expected compositions as shown in Table 7. However, our FT catalyst tests used a mixture of only hydrogen and carbon monoxide.

2. Summary of the Thermodynamic Equilibrium Analysis to Determine the Impact of Contaminants on Water-gas Shift and Fischer-Tropsch Synthesis Catalysts

In Task 2 of this project we carried out a detailed thermodynamic analysis to evaluate the impact of potential contaminants in the syngas generated by coal and biomass co-gasification on the water-gas shift (WGS) and Fischer-Tropsch (FT) catalyst components (e.g., the active phases, promoters, and supports). Altogether we evaluated four catalyst systems; high-temperature WGS, low-temperature WGS catalysts, and Fe- and Co-based Fischer-Tropsch catalysts. We evaluated the impact of a single contaminant on each of the metal or metal oxide species present in each of the catalysts. We evaluated the interaction of these with eight different contaminants, including H_2S , NH_3 , HCN , AsH_3 , PH_3 , HCl , NaCl , KCl . For this analysis, we applied thermodynamic modeling tools (HSC Chemistry 5.11 Thermodynamic Simulation Software, Outokumpo Research, Oh, Finland).

These thermodynamic-equilibrium calculations were expanded to include a wide range of trace-contaminant species and their interactions with the major components of each catalyst. The thermodynamic calculations did not take the role of chemical kinetics into account, but they bound the problem. This thermodynamic approach provided us with a rapid, low cost and effective tool for identifying the contaminant species that could prove to be most problematic for the WGS and FT catalysts in the CBTL process.

2.1. Technical Approach

We first estimated the most stable structure of the catalyst components at the specified reaction conditions under a clean (no contaminants) syngas composition. This initial calculation provided us with information on the oxidation state of the metal (e.g., to determine if metallic Fe, Fe_2O_3 , Fe_3O_4 or FeO was the dominant iron phase at the operating conditions of interest for the HT-WGS catalyst) and the possibility of forming mixed metal oxides and chemical complexes (e.g., the feasibility of forming aluminates) using the Equilibrium Compositions Module of the HSC Software. The most prevalent forms of iron determined from this analysis were then used in two separate analyses:

1. Gibbs Free Energy Analysis
2. Equilibrium Analysis

In the Gibbs free energy analysis, once again we used the Reaction Equations Module of the HSC to estimate the heat of reaction of the individual contaminants with the catalyst components short-listed earlier. The free energy of formation (i.e., ΔG) showed the lowest energy state and the likelihood for the spontaneous formation of a particular compound (e.g., the more negative the ΔG value, the higher the likelihood for a particular reaction to occur). We used stoichiometric compositions of the selected catalyst component (the most prevalent phase specified in the earlier analysis) and the contaminant species. We acknowledge that this was only a first-order analysis and it was only used to identify the most critical contaminants that needed to be considered in a more comprehensive Equilibrium Analysis.

In the Equilibrium Analysis, we carried out a more detailed evaluation of each catalyst component exposed to a representative gas composition that contained the contaminant. For this analysis, we used a total of 100 mole of the gas phase species (simulated syngas) that contained 1 ppmv of the selected contaminant and 1 mole of catalyst component in the form listed by the catalyst manufacturer (the catalysts typically contained the metals in the highest oxidation state, but due to the presence of ample amounts of reducing gas, the thermodynamic analysis accounted for any potential phase changes and the reduction in the oxidation state at

the operating conditions). We used 3 phases in our calculations; the gas phase (containing the syngas along with the contaminant), the aqueous phase (for water condensation if any) and a solid phase (containing the metal, metal oxides, carbonates, and other contaminant reaction products). We allowed miscibility of different solids for the solid phase. We believe this was a valid assumption for most of the contaminants. For example, any arsenide or sulfide phases are highly miscible in the oxide phases due to their low melting points and very high surface and bulk diffusivity. We varied the temperature to obtain temperature dependent equilibrium compositions, while maintaining the same pressure.

Figure 5. Equilibrium composition of Fe in the HT-WGS catalyst at 400 psig with a starting syngas composition of CO=26.8 mol, H₂=20.6 mol, CO₂=12.3 mol, CH₄=3.3 mol and H₂O=37 mol and a Fe composition of Fe₂O₃=1 mol.

Detailed thermodynamic calculations were carried out to evaluate the propensity for the formation of solid-phase compounds by equilibrium reaction between the contaminant species and common catalyst constituents such as iron, cobalt and copper. An example of one series of such thermodynamic calculations is illustrated in the following analysis where we investigated the corrosive nature of arsine (AsH₃) on the iron component of ferrochrome HT-WGS catalyst. The catalyst composition of commercial catalyst ShiftMax 120 (Süd-Chemie), as provided in the Material Safety Data Sheet (MSDS), was given previously in Table 4. Although the catalyst composition contains chromium and copper phases as promoters as indicated in the MSDS, and our thermodynamic analysis included these other phases, in this example we will only document the approach for the dominant Fe phase in this formulation. The gas composition we used for the Equilibrium Analysis was given previously in Table 6 (these conditions were pre-determined based on DOE guidance at the project outset).

2.1.1. Gibbs Free Energy Analysis

In support of this analysis, we first determined the most prevalent iron oxide phase under the syngas composition provided in Table 6 at 400 psig using the commercial software package HSC Chemistry 5.11. The results of the equilibrium prediction for the potential iron oxide phases are shown in Figure 5. In this analysis we used a starting syngas composition of CO = 26.8 mol, H₂ = 20.6 mol, CO₂ = 12.3 mol, CH₄ = 3.3 mol and H₂O = 37 mol and a Fe composition of Fe₂O₃=1 mol to represent the contaminated syngas feed stream and the FT catalyst. The assumption is that there will be more syngas components will be available than the catalyst (i.e., there is enough reducing components to change the oxidation state of the metal oxide which will be a realistic simulation of the actual application). We observed that Fe is mostly present as magnetite (Fe₃O₄, 0.638 mol) and only small amounts of hematite (Fe₂O₃, 0.042 mol) are present, with additional traces of iron carbonate (FeCO₃) and iron metal (Fe) at 350 °C.

We then evaluated the impact of the contaminant

arsine. Iron may react with arsine to form stable iron arsenide phases, including FeAs, FeAs₂ or Fe₂As. It

is also highly likely that an arsenic phase could dissolve in the Fe metal phase (or a reduced iron oxide phase), which could potentially inhibit the catalytic activity. Finally, arsine could decompose into arsenic metal and hydrogen followed by condensation of arsenic and indiscriminate fouling of the catalytic surface. We first estimated the Gibbs free energy of reactions for these arsenide formations with the different Fe compounds using stoichiometric amounts of each reactant (e.g., iron oxide and arsenic). The results of the Gibbs free energy analysis are reported in Table 8; the Fe_xAs_y/As phases indicate the simultaneous formation of arsenide phases and condensation byproducts. The Gibbs free energy of reaction is reported on the basis of per mole of AsH₃(g) consumed (the estimated free energies of formation were normalized per mole of contaminant species).

Table 8. Gibbs free energy analysis for reactions of arsine with Fe compounds present in HT- WGS catalyst at 350°C.

+ AsH ₃ (g)	FeAs	FeAs ₂	Fe ₂ As	FeAs/As	FeAs ₂ /As	Fe ₂ As/As
Fe ₂ O ₃	-24.27	-23.05	-19.60	-21.75	-21.78	-18.16
Fe ₃ O ₄	-21.71	-21.77	-14.47	-20.46	-21.04	-15.45
FeCO ₃	-31.10	-26.47	-33.27	-22.02	-21.96	-19.72
Fe	-26.15	-23.99	-23.36	-21.43	-21.56	-18.93

In Table 8, we have highlighted the most favorable reactions based on the most negative Gibbs free energy heat of formations. We see that different reactions are favorable depending on the iron compound. The order of preference for the formation of various arsenide compounds with Fe₂O₃ based on the Gibbs free energy is listed below:

For example, when arsine reacts with Fe₂O₃, the formation of FeAs is favored the most, followed by the formation of FeAs₂, FeAs₂/As (i.e., FeAs₂ formation with simultaneous condensation of solid arsenic byproduct), FeAs/As, Fe₂As, and Fe₂As/As.

The order of preference for arsenide formation with other iron compounds based on the Gibbs free energy are listed below:

Although we showed the possible arsenic-iron oxide interactions for each iron oxide-iron metal phase, the previous analysis suggests that Fe₃O₄ is the most predominant iron compound under HT-WGS conditions, and Fe₃O₄ clearly forms a stable iron di-arsenide (FeAs₂) phase. In addition to the most prevalent Fe₃O₄ phase, all other iron phases could react with arsine and form relatively inactive species (i.e., the ΔG for various iron arsenide formations are all negative). Hence, arsine is identified as a potent poison for the active component of the HT-WGS catalyst.

The proposed approach provided valuable information when the analysis was extended to other contaminants. For example, the interaction of Fe₃O₄ with H₂S results in the formation of a stable iron sulfide phase. Based on the free energy calculations we concluded that both AsH₃ and H₂S

are potent contaminants for Fe_3O_4 due to the high free energy of formation for reaction between these contaminants and the catalytic phase, while judging by the higher free energy arsine was identified as a more aggressive contaminant than H_2S .

Figure 6. Equilibrium composition of Fe in the HT-WGS catalyst at 400 psig with a starting syngas composition of $\text{CO}=26.8$ mol, $\text{H}_2=20.1$ mol, $\text{CO}_2=12.3$ mol, $\text{CH}_4=3.3$ mol, $\text{H}_2\text{O}=37$ mol and $\text{AsH}_3(\text{g})=1$ ppmv and Fe composition of $\text{Fe}_2\text{O}_3=1$ mol with miscibility of oxide and arsenide phases.

This first order comparison provided by the free energy calculations allowed us to identify a broad range of contaminants that could potentially poison the catalyst, particularly when the effect of each contaminant is benchmarked against others. However, this analysis does not fully take into consideration the impact of the syngas components on the formation of the phases. For example, it is well known that water inhibits the formation of the sulfides (because it is a reaction product and high concentrations of water shift the reaction to the products side), which suggested that its impact must be carefully assessed during the contaminant-catalyst interaction studies (although for comparison between H_2S and AsH_3 water is present on the product side in both cases; this may not be the case for other contaminants).

2.1.2. Equilibrium Analysis

Following the Gibbs Free Energy analysis, we carried out the Equilibrium Analysis for the most potent contaminants identified from the Gibbs free energy analysis. The equilibrium analysis was based on two separate assumptions allowing the miscibility and non-miscibility of oxide and arsenide phases. The results of the equilibrium analysis for Fe interaction with AsH_3 under HT-WGS conditions with miscible oxide and arsenide phases are shown in Figure 6. In this analysis we used a starting syngas composition that consisted of 1 ppmv AsH_3 in 26.8 mol CO, 20.6 mol H_2 , 12.3 mol CO_2 , 3.3 mol CH_4 , 37 mol H_2O , and 1 mol Fe_2O_3 . We observed that arsenic condensation is the most preferred reaction below 240 °C and FeAs is the most predominant arsenide above 240 °C, followed by FeAs_2 . Almost all of the arsine partitions into the solid phase (at the temperatures of our analysis); it either condenses as arsenic on the catalyst or forms iron arsenides. For the HT-WGS reaction at 350 °C, the arsine present in the syngas is also expected to condense on the catalyst surface as arsenic and also form iron arsenides such as FeAs, and to a lesser extent FeAs_2 . This suggests that arsine is a potent poison for the iron-based HT-WGS catalyst.

The results of the equilibrium analysis for Fe interaction with AsH_3 under HT-WGS condition with non-miscible oxide and arsenide phases are shown in Figure 7. In this analysis we used a starting syngas composition of $\text{CO} = 26.8$ mol, $\text{H}_2 = 20.6$ mol, $\text{CO}_2 = 12.3$ mol, $\text{CH}_4 = 3.3$ mol and $\text{H}_2\text{O} = 37$ mol and Fe composition of $\text{Fe}_2\text{O}_3 = 1$ mol along with 1 ppmv AsH_3 . We observed that arsenic condensation is the most preferred reaction below 260 °C and FeAs_2 is the most predominant arsenide above 260 °C, followed by FeAs . Below 400 °C, almost all of the arsenic partitions into the solid phase by either condensing on the catalyst as arsenic or by forming iron arsenides. For the HT-WGS reaction at 350 °C, the arsine present in the syngas is expected to either condense on the catalyst surface or form iron arsenides such as FeAs_2 and FeAs . Hence, both the miscible and non-miscible analyses suggest that arsine is a potent poison for HT-WGS catalyst.

Figure 7. Equilibrium Composition of Fe in the HT-WGS Catalyst at 400 psig with starting syngas composition of $\text{CO} = 26.8$ mol, $\text{H}_2 = 20.6$ mol, $\text{CO}_2 = 12.3$ mol, $\text{CH}_4 = 3.3$ mol, $\text{H}_2\text{O} = 37$ mol and $\text{AsH}_3(\text{g}) = 1$ ppmv and Fe composition of $\text{Fe}_2\text{O}_3 = 1$ mol with non-miscibility of oxide and arsenide phases.

2.2. Results of the Thermodynamic Equilibrium Analysis

From the results of the thermodynamic study we observed that there are three main mechanisms by which the contaminant may deactivate the catalyst:

- Condensation: The contaminant itself or its decomposition product(s) that form adsorb on the surface of the catalyst.
- Deposition mechanism: Products of the reaction of the contaminant with components of the syngas mixture deposit onto the catalyst surface.
- Reaction: The contaminant forms inactive reaction products with the catalyst active phase.

The results of the thermodynamic contaminant impact study carried out for the four catalysts are summarized in Table 9. We observed that all the contaminants included in the study showed at least some impact on each of the catalysts. However, the condensation and deposition products will be formed upstream in the heat exchangers and process pipelines rather on the catalyst, since the catalyst does not take part in these deactivation mechanisms. Therefore, we eliminated the condensation and deposition mechanisms and categorized the major and minor contaminants based on the results of the thermodynamic study as shown in Table 10. Further details on the thermodynamic study are contained in Interim Topical Report #1, including an extended analysis for each catalyst-contaminant system.

Table 9. Impact of contaminants on the WGS and FT catalysts from a thermodynamic analysis.

	HT-WGS		LT-WGS		Fe-FT	Co-FT
	Fe	Cr	Cu	Zn	Fe	Co
AsH ₃	C, R	C	C, R	C, R _t	R	C _t , R
H ₂ S	R	C _t , R _t	R	R	R	R
NH ₃	D _t , R _t	D _t	D _t	D _t	R	D _t , R _t
NaCl	C, D, R _t	C, D, R _t	C, D, R	C, D, R _t	C, D _t , R _t	C, D _t , R _t
KCl	C, D, R _t	R	C, D, R	C, D _t , R _t	C, D _t , R _t	C, D _t , R _t
HCl	R	R	R	R	R	R
PH ₃	D _t , R	D	R	R	D _t , R	D, R _t
HCN	D _t , R _t	D _t	D _t	D _t	R	D _t , R _t

C - Condensation mechanism

D - Deposition mechanism

R - Reaction mechanism

subscript "t" indicates trace amounts

Table 10. Contaminants categorized based on the thermodynamic study.

Catalyst	Major Contaminants	Minor Contaminants	No Impact
HT-WGS	AsH ₃ , H ₂ S, HCl, KCl, PH ₃	NaCl, NH ₃ , HCN	
LT-WGS	AsH ₃ , H ₂ S, HCl, NaCl, KCl, PH ₃		NH ₃ , HCN
Fe-FT	AsH ₃ , H ₂ S, HCl, NH ₃ , HCN, PH ₃	NaCl, KCl	
Co-FT	AsH ₃ , H ₂ S, HCl	NaCl, KCl, NH ₃ , HCN, PH ₃	

3. Long-term Exposure Tests to Determine the Impact of Contaminants on High-temperature Water-Gas Shift Catalyst

In Task 3 (Subtask 1) of this project, we evaluated the interaction of high-temperature water-gas shift (HT-WGS) catalyst with eight different contaminants; NaCl, KCl, H₂S, HCl, NH₃, HCN, AsH₃, and PH₃. Samples of commercially available ShiftMax 120 HT-WGS catalyst were obtained from Süd-Chemie for the bench-scale catalyst-contaminant evaluations. The nominal catalyst composition as provided in the supplier's Material Safety Data Sheet (MSDS) is shown in Table 11. The catalyst also contains unspecified amounts of chromium and copper phases as promoters, again as indicated in the MSDS. Table 12 shows the gas composition used for the long-term tests (these standard baseline conditions were pre-determined with DOE guidance and are based on the anticipated composition of coal-biomass syngas after warm-gas cleanup).

Table 11. Composition of HT-WGS catalyst (source: MSDS).

Süd-Chemie ShiftMax 120	
Fe ₂ O ₃	80.0%
Cr ₂ O ₃	8.5%
CuO	2.5%
Inert	9.5%

The catalyst was provided in the form of 6×3 mm diameter tablets that were crushed and sieved to a particle size between 325-400 mesh (38-45 μm) prior to loading into a 1/2" (1.27 cm) diameter stainless steel reactor. The pellets were supported by a porous SS VCR frit gasket. The volume of the catalyst bed was 4 cm³ unless otherwise noted. In the proceeding sections, we describe the details of each long-term catalyst test and discuss the results of our assessment of each catalyst-contaminant interaction.

Table 12. Baseline syngas composition used for HT-WGS catalyst tests.

Gas Composition	
CO	26.8%
H ₂	20.6%
CO ₂	12.3%
CH ₄	3.3%
H ₂ O	37.0%
Pressure (psig)	400
Temperature (°C)	350

3.1. Establishment of Baseline HT-WGS Catalyst Testing Conditions

The syngas composition used for testing the HT-WGS catalysts is shown in Table 12. The baseline gas hourly space velocity (GHSV) was determined for the HT-WGS in an initial set of scoping experiments that were conducted at 350 °C with GHSVs of 6,000 h⁻¹, 8,000 h⁻¹, 10,000 h⁻¹, and 14,000 h⁻¹. The results of this experiment are shown in Figure 8 with the CO concentration in the effluent gas (dry basis) and the equilibrium level at the test temperature shown as a reference. As the WGS reaction converted CO (in the presence of steam) to CO₂ and H₂, better conversion resulted in a lower level of CO in the effluent. The catalyst exhibited WGS activity at all the space velocities tested, with a flat curve of activity versus space velocity down to 8,000 h⁻¹ GHSV. Since the conversion at 6,000 h⁻¹

Figure 8. HT-WGS catalyst space velocity test at 350 °C (ShiftMax 120, Süd-Chemie).

Figure 9. Baseline test for HT-WGS catalyst in clean syngas (no contaminants) at 350 °C and 400 psig (ShiftMax 120, Süd-Chemie).

GHSV was better than at the high space velocities (while still above predicted equilibrium), this space velocity was chosen as the minimum value for the remainder of the HT-WGS testing. A baseline test for the catalyst was run at the final test conditions for 120 h, with conversion results shown in Figure 9. The test showed some initial degradation, but the CO concentration leveled off during the remainder of the test.

3.2. Impact of AsH₃ on HT-WGS Catalyst

Catalyst-contaminant testing began with a study to assess the impact of arsine (AsH₃) on the performance of HT-WGS catalyst. Table 12 (on the prior page) shows the nominal composition of the standard baseline syngas composition used in testing. About 4 cc of the crushed and sieved catalyst was packed into the reactor and clean syngas was introduced for ~20 h before introducing the contaminant. The GHSV was 12,000 h⁻¹. Nitrogen was substituted for methane because both are essentially inert at these conditions. The AsH₃ concentrations in the feed and effluent gas streams were challenging to accurately measure. We were able to analyze the reactor outlet gas flow to obtain an accurate assessment of the AsH₃ concentration downstream of the catalyst and observed that most of the AsH₃ was removed by the catalyst bed.

AsH₃ degraded the catalyst performance and the catalyst lost most of its activity during the run, as shown in Figure 10. We also observed that the CO concentration in the exit gas slowly increased indicating a loss in catalytic activity due to absorption of AsH₃. We encountered several power failures during the experimental run, which resulted in shutdowns and restarts between 90 and 170 h although this did not appear to affect the end result. The catalyst removed the AsH₃ completely for awhile and then we observed some breakthrough of AsH₃ through the catalyst bed after around 130 h.

Figure 10. Impact of 4.5 ppmv AsH_3 on HT-WGS catalyst at 350 °C and 400 psig. GHSV = 12,000 h^{-1} . Feed: 26.8% CO, 12.3% CO_2 , 20.6% H_2 , 3.3% N_2 , and 37% H_2O .

3.3. Impact of H_2S on HT-WGS Catalyst

The results of the experiments to assess the impact of hydrogen sulfide (H_2S) on the performance of the HT-WGS catalyst are shown in Figure 11 and Figure 12. About 4 cc of the crushed and sieved catalyst was packed into the reactor and clean syngas was introduced for ~25 h before introducing 2 ppmv H_2S into the syngas feed. The GHSV was 6,000 h^{-1} . Nitrogen was substituted for methane because both are essentially inert at these conditions. The H_2S concentration in the effluent from the catalyst bed was measured using a GC. In Figure 11, the effect of H_2S is apparent in the gradual decrease in CO conversion (increase in concentration) when 2 ppmv H_2S was co-fed. These results were expected because H_2S is a well known catalyst poison. The rate of deactivation (defined as the change in CO percentage conversion over the time-on-stream) calculated from the data was -0.31%/h.

The second H_2S contaminant test was conducted at a GHSV of 15,000 h^{-1} and a H_2S concentration of 85 ppmv to accelerate the rate of H_2S adsorption onto the catalyst, as presented in Figure 12. This was done in order to determine if the effect of H_2S exposure was cumulative, because the decrease in activity during the 100 h test at a GHSV of 6000 h^{-1} was only slight. As illustrated in Figure 12, the catalyst activity did not decrease more rapidly when exposed to 2 ppmv H_2S at the higher space velocity. In fact, the catalyst deactivation rate during this test was -0.075%/h, which is less than the rate of conversion loss during the test at the lower GHSV. The concentration of H_2S in the product stream did increase with time-on-stream (TOS), presumably as the catalyst bed became saturated with the contaminant byproducts. This test confirmed that H_2S reacted with the catalyst and that the accumulation of these reaction products probably caused the decreased WGS activity we observed. Interestingly, the activity of the HT-WGS catalyst was relatively unaffected, even after the bed was apparently saturated with H_2S . If the poisoning effect was simply related to the reversible adsorption of the contaminant on the surface, then the increased contaminant concentration in the feed syngas (85 vs. 2 ppmv) would be expected to influence the rate of activity decrease.

Figure 11. Impact of 2 ppmv H₂S on HT-WGS catalyst (ShiftMax 120, Süd-Chemie) at 350°C and 400 psig. GHSV = 6,000 h⁻¹. Feed: 26.8% CO, 12.3% CO₂, 20.6% H₂, 3.3% N₂, 37% H₂O, and 2 ppmv H₂S.

Figure 12. Impact of 85 ppmv H₂S on HT-WGS catalyst (ShiftMax 120, Süd-Chemie) at 350°C and 400 psig. GHSV = 15,000 h⁻¹. Feed: 26.8% CO, 12.3% CO₂, 20.6% H₂, 3.3% N₂, 37% H₂O, and 85 ppmv H₂S.

3.4. Impact of NH₃ on HT-WGS Catalyst

Catalyst evaluation testing continued with a study on the impact of ammonia (NH₃) on the performance of the HT-WGS catalyst (Shiftmax 120, Süd-Chemie). The syngas composition used in testing is shown in Table 13. About 4 cc of the catalyst was packed into the reactor and clean syngas was introduced for ~10 h before 90 ppmv ammonia was introduced into the feed gas mixture (Figure 13). The GHSV was 12,000 h⁻¹. Nitrogen was substituted for methane for convenience because both are essentially inert at these conditions.

Table 13. Inlet syngas conditions for testing the impact of NH₃ on HT-WGS catalyst.

Gas Composition	HT-WGS
CO ₂	12.3%
CO	26.8%
H ₂	20.6%
CH ₄	3.3%
H ₂ O	37.0%
NH ₃	90 ppmv
Temperature (°C)	350
Pressure (psig)	400

An ammonia concentration of 90 ppm was used throughout the HT-WGS test and ammonia was measured downstream of the reactor using the SPM, shown previously in Figure 1. Ammonia was challenging to measure and it was difficult to obtain an accurate assessment of the ammonia concentration downstream of the catalyst because most of the ammonia was knocked out in the water condenser. However, the concentrations of CO and hydrogen in the reactor effluent were excellent indicators of catalyst activity, and any decrease in hydrogen or increase in CO concentration meant a reduction in catalyst activity, therefore, CO conversion was used as a sensitive performance criterion to assess the impact of the contaminant. However, as evident by the stable CO concentration over a 100 h test, the effect of ammonia on the activity of this catalyst was minimal at these HT-WGS conditions.

Figure 13. Impact of NH₃ on HT-WGS catalyst (ShiftMax 120, Süd-Chemie) at 350 °C and 400 psig. GHSV = 12,000 h⁻¹. Feed: 26.8% CO, 12.3% CO₂, 20.6% H₂, 3.3% N₂, 37% H₂O, and 85 ppmv NH₃.

The SPM indicated that ammonia was present in the effluent during the first ~40 h of testing, and after switching to bypass the catalyst bed, ammonia was detected in the feed gas, but at a concentration of ~45 ppmv instead of 90 ppmv. However, during subsequent testing of the catalyst for another ~60 h in the WGS gas mixture containing 90 ppmv ammonia, no ammonia was detected by the SPM. A Draeger tube placed in the effluent stream did indicate the presence of traces of ammonia, however. In conclusion, no effect due to ammonia on the WGS activity of the catalysts was observed, as determined by the constant CO (reactant) and hydrogen (product) concentrations in the product stream for >100 h.

3.5. Binary H₂S-NH₃ Contaminant Tests on HT-WGS Catalyst

Mixed contaminant tests on the HT-WGS catalyst were conducted using NH₃ and H₂S. The results of these tests are shown in Figure 14. The H₂S concentration downstream of the reactor was measured to within a few ppmv of experimental error using a GC. During a test of the HT-WGS catalyst (Figure 14) that contained 38 ppmv NH₃ and 60 ppmv H₂S in the feed, there was a slow, steady rise in the outlet concentration of H₂S, which suggested that the catalyst was adsorbing less sulfur as the test progressed due to saturation of the catalyst bed with sulfur. However, the calculated decrease in CO conversion over time in this combined NH₃ (38 ppmv) and H₂S (60 ppmv) test was only -0.0038%/h, which indicated that the shift performance was essentially unaffected. About 90 h into the test, the CO₂ ran out for several hours, so the run was aborted. A subsequent WGS test in clean syngas without any contaminants showed no change in performance compared to the original baseline.

Figure 14. Impact of NH₃ + H₂S on HT-WGS catalyst (ShiftMax 120, Süd-Chemie) at 350 °C and 400 psig. GHSV = 12,000 h⁻¹. Feed: 26.8% CO, 12.3% CO₂, 20.6% H₂, 3.3% N₂, 37% H₂O, and 38 ppmv NH₃ and 60 ppmv H₂S.

3.6. Impact of NaCl on HT-WGS Catalyst

Prior to catalyst evaluation, we first measured the salt evaporation rate using thermogravimetric analysis (TGA) as presented in Figure 15 and Figure 16. Crushed Pyrex glass was used to determine the buoyancy of the Pt pan in the apparatus at different temperatures so that this effect could be subtracted. Neither salt had an appreciable vapor pressure at 350 °C, therefore, the salt was mixed directly with the catalyst during the tests.

Figure 15. TGA results for NaCl evaporation at temperatures between 550-675 °C.

NaCl was also evaluated for its intrinsic catalytic activity by mixing it with glass beads to determine if there was any interaction between the syngas mixture and the salt, as shown in Figure 17. The results suggest that the salt itself catalyzes a small amount of WGS reaction, although the activity seemed to degrade with time. The NaCl also caused the formation of some methane (methanation was not observed over the KCl).

The performance of the HT-WGS catalyst was first established at the baseline conditions of 375 °C and 400 psig with the standard syngas composition of 26.8% CO, 12.3% CO₂, 20.6% H₂, 3.3% N₂, and 37% H₂O at a GHSV = 12,000 h⁻¹, as shown in Figure 18. After establishing the baseline conversion in this initial test without the contaminant, we removed the catalyst from the reactor, mixed it with NaCl (crystalline powder), replaced the mixture in the test cell, and resumed the test. There was only a slight decrease in activity after the salt was introduced, however, the activity remained stable for the duration of the 135 h test. Another similar test was conducted for more than 90 h at 350 °C, as shown in Figure 20. The HT-WGS catalyst showed very stable WGS performance even when mixed directly with crystalline NaCl.

Figure 16. NaCl and KCl evaporation rates at temperatures above 500 °C.

Figure 17. NaCl mixed with glass beads tested at 200 psi, 350 °C, 12,000 h⁻¹ with 21.3% H₂O, 12.7 % CO₂, 27.7% CO and 38.3% H₂.

Figure 18. Baseline HT-WGS catalyst (ShiftMax 120, Süd-Chemie:) test at 375 °C and 400 psig. GHSV = 12,000 h⁻¹. Clean syngas feed: 26.8% CO, 12.3% CO₂, 20.6% H₂, 3.3% N₂, and 37% H₂O (no contaminants).

Figure 19. Impact of NaCl on HT-WGS catalyst (ShiftMax 120, Süd-Chemie) at 375 °C and 400 psig. GHSV = 12,000 h⁻¹. Feed: 26.8% CO, 12.3% CO₂, 20.6% H₂, 3.3% N₂, and 37% H₂O, and 10% wt. NaCl mixed with the catalyst.

Figure 20. Impact of NaCl on HT-WGS catalyst (ShiftMax 120, Süd-Chemie) at 350 °C and 400 psig. GHSV = 12,000 h⁻¹. Feed: 26.8% CO, 12.3% CO₂, 20.6% H₂, 3.3% N₂, and 37% H₂O, and 10 wt.% NaCl mixed in with the catalyst.

Figure 21. Impact of KCl on HT-WGS catalyst (ShiftMax 120, Süd-Chemie) at 375 °C and 400 psig. GHSV = 12,000 h⁻¹. Feed: 26.8% CO, 12.3% CO₂, 20.6% H₂, 3.3% N₂, and 37% H₂O, with 0.778 g KCl mixed into the catalyst.

3.7. Impact of KCl on HT-WGS Catalyst

The performance of the HT-WGS catalyst was first established at the baseline conditions of 375 °C and 400 psig with an inlet gas composition of 26.8% CO, 12.3% CO₂, 20.6% H₂, 3.3% N₂, and 37% H₂O at a GHSV = 12,000 h⁻¹ as shown in Figure 21. After this >40 h initial test period without the contaminant, we removed the catalyst from the reactor, mixed it with KCl (crystalline powder), replaced the mixture in the test cell, and resumed the test. There was a slight upward slope in the CO concentration over time indicating a potential decrease in activity, but it was not any steeper than the slope before the KCl was added to the catalyst bed. ShiftMax 120 HT-WGS catalyst showed very stable conversion even when mixed with directly with crystalline KCl.

3.8. Impact of PH₃ on HT-WGS Catalyst

The impact of phosphine (PH₃) on the high-temperature WGS catalyst performance is shown in Figure 22. About 8 cc of the catalyst was loaded into the reactor and clean syngas was fed for 8 h before introducing 1 ppmv PH₃ into the gas mixture. The nitrogen concentration was still decreasing after 8 h, which indicated that at least 24 h was required to establish the baseline and reach steady state. In all of the HT-WGS catalyst tests that followed, a minimum 24 hr baseline was established prior to the 100 h contaminant exposure test, followed by another 24 hour baseline. PH₃ seemed to slightly impact the performance of the catalyst and the CO conversion slowly decreased at a rate of 0.003%/h while PH₃ was co-fed.

Figure 22. Impact of PH_3 on high temperature WGS catalyst (ShiftMax 120, Süd-Chemie) at 350 °C and 400 psig. GHSV = 6,000 h^{-1} . Feed composition: 26.8% CO, 12.3% CO_2 , 20.6% H_2 , 3.3% N_2 , 37% H_2O , and 1 ppmv PH_3 .

Figure 23. Impact of 10 ppmv HCN on HT-WGS catalyst (ShiftMax 120, Süd-Chemie) at 350 °C and 400 psig. GHSV = 12,000 h⁻¹. Feed: 26.8% CO, 12.3% CO₂, 20.6% H₂, 3.3% N₂, 37% H₂O, and 10 ppmv HCN.

3.9. Impact of HCN on HT-WGS Catalyst

The results of a test to assess the impact of hydrogen cyanide (HCN) on the performance of the HT-WGS catalyst are shown in Figure 23. About 4 cc of the catalyst was packed into the reactor and clean syngas was fed for ~30 h before introducing 10 ppmv of the contaminant into the syngas. The GHSV was 12,000 h⁻¹. Nitrogen was substituted for methane because both are essentially inert at these conditions.

Unfortunately, the HCN concentration was challenging to accurately measure, it was difficult to obtain an assessment of the HCN concentration downstream of the catalyst and because most of the HCN was likely knocked out in the water condenser. The higher hydrogen concentration observed between 30 and 55 h was due to higher hydrogen flow into the reactor because of a malfunctioning mass flow controller. After the mass flow controller was fixed, the CO and H₂ concentrations in the product stream remained constant, which indicated that the catalyst exhibited stable activity during the 100 hour exposure test and 10 ppmv of HCN in the syngas feed did not have any impact on the WGS activity. At the end of the test, the catalyst bed was bypassed by the feed gas and HCN was detected on the SPM, which indicated that the analyzer was functioning properly and that HCN was either taken up by the catalyst or removed by the steam condenser during the run.

3.10. Summary of Long-term Experimental Contaminant Studies on HT-WGS Catalyst

The results of the bench-scale contaminant impact experimental study carried out for the ferrochrome HT-WGS catalyst are summarized in Table 14. Most of the contaminants included in the study appeared to adsorb onto the catalyst because they were not detected downstream of the catalyst bed. However, it is possible that some of the contaminants such as NH₃ were removed in the steam condenser prior to the analysis point. Syngas that contained 4.5 ppmv

Table 14. Summary of the impact of contaminants on HT-WGS catalyst.

Contaminant	Concentration (ppmv)	Approx. Test Duration (h)*	Inhibition	Adsorption
Arsine, AsH ₃	4.5	300	Yes	Yes
Hydrogen sulfide, H ₂ S	85	20	Yes	Yes
Ammonia, NH ₃	90	120	No	Yes
Sodium chloride, NaCl	10 wt.% [†]	450	No	No
Potassium chloride, KCl	10 wt.% [†]	120	No	No
Phosphine, PH ₃	1	40	Yes	Yes
Hydrogen cyanide, HCN	10	170	No	Yes
NH ₃ +H ₂ S	38 + 60	100	No	Yes

*cumulative, including baseline tests

[†]gas-phase vapor pressure of the alkali salts at test conditions was very low so they were introduced as a solid mixed directly with the catalyst

AsH₃ impacted the selectivity and conversion of the HT-WGS catalyst because it adsorbed onto it.

The impact of PH₃ on the HT-WGS catalyst seemed to be slight and the rate of the decrease in CO conversion was similar to the rate in clean syngas. In contrast, H₂S had a noticeable effect on the performance of HT-WGS catalyst during the tests, although the rate of decrease in CO conversion was essentially the same for both 2 and 85 ppmv H₂S. It conclusively adsorbed onto the catalyst and its impact was also noticeable when it was co-fed with ammonia. The combination of NH₃ and H₂S (38 and 60 ppmv) in the syngas feed resulted in H₂S uptake by the catalyst until it appeared to saturate the bed, as evidenced by H₂S breakthrough after only a few hours on-stream. Interestingly, very little decrease in CO conversion activity was observed during the test, even after more than half of the feed concentration of H₂S was detected in the WGS product stream.

4. Long-Term Exposure Tests to Determine the Impact of Contaminants on Low-temperature Water-gas Shift Catalyst

In Task 3 (Subtask 2) we evaluated the interaction of the LT-WGS catalyst with eight different contaminants; NaCl, KCl, H₂S, HCl, NH₃, HCN, AsH₃, and PH₃. Samples of commercially available ShiftMax 230 low-temperature water-gas shift (LT-WGS) catalyst were obtained from Süd-Chemie (now Clariant) for the bench-scale catalyst-contaminant evaluations. The nominal catalyst composition as provided in the supplier's Material Safety Data Sheet (MSDS) is shown in Table 15. Table 16 shows the gas composition we used for the long-term catalyst tests (these conditions were predetermined with DOE guidance based on the anticipated composition of coal-biomass derived syngas and the gas composition downstream of a high-temperature WGS catalyst bed). Nitrogen was substituted for methane because both are essentially inert at these conditions.

The catalyst was provided in the form of 6x3 mm diameter tablets that were crushed and sieved to a particle size between 325-400 mesh (38-45 μ m) prior to loading into a 1/2" (1.27 cm) diameter stainless steel reactor. The pellets were supported by a porous SS VCR frit gasket. The volume of the catalyst bed was 4 cm³ unless otherwise noted. In the following sections, we describe the details of each long-term catalyst test and discuss the results of our assessment of each catalyst-contaminant interaction.

Table 15. Composition of LT-WGS catalyst (source: MSDS).

Süd-Chemie Shift-max 230	
CuO	58.0%
ZnO	31.0%
Al ₂ O ₃	11.0%

Table 16. Baseline syngas composition for LT-WGS catalyst tests.

LT-WGS Gas Composition	
CO	4.5%
H ₂	43.2%
CO ₂	34.4%
CH ₄	2.9%
H ₂ O	15.0%
Pressure (psig)	400
Temperature (°C)	240

4.1. Establishment of Baseline LT-WGS Catalyst Testing Conditions

As discussed previously for the HT-WGS catalyst, baseline evaluations were conducted to measure the catalyst performance in the absence of any contaminant(s) to use this performance as a benchmark to assess the impact of potential poisons. The ideal space velocity is one that gives the best performance (i.e., approaches the level of conversion predicted by thermodynamic equilibrium), while operating at the edge of the catalyst's capabilities. Since the real-time metric was water-gas shift performance, operating at these conditions (maximum utilization of the catalyst) provided immediate feedback on the contaminant's effect – i.e., any reduction in available active catalyst phase caused a measurable decrease in the catalyst performance.

The baseline reaction conditions were determined for the LT-WGS test with an initial set of scoping experiments at 200 °C as a lower operating temperature boundary condition for the catalyst, with gas hourly space velocities (GHSVs) of 6,000 h⁻¹, 10,000 h⁻¹, and 15,000 h⁻¹. Results of this experiment are shown in Figure 24. Not unexpectedly, the conversion was substantially lower than that predicted by thermodynamic equilibrium at this temperature, due in part to the high space velocities tested. If the CO level in the effluent gas (dry basis) is compared to the calculated equilibrium level at the test temperature as a reference, as the WGS reaction converts CO (in the presence of steam) to CO₂ and H₂, higher conversion results in a lower level of CO in the product stream.

The same series of tests was conducted on a fresh sample of catalyst at 240 °C at the final conditions determined for the test plan. These results are shown in Figure 25. The conversion approached the calculated equilibrium for CO concentration in the product stream at a GHSV =

Figure 24. LT-WGS catalyst space velocity test at 200 °C (ShiftMax 230, Süd-Chemie).

6000 h⁻¹ – but the CO concentration was still slightly above that determined by thermodynamic equilibrium. Therefore, a space velocity of 12,000 h⁻¹ was chosen as the baseline feed flow rate for LT-WGS testing to ensure that any impurity effects would be noticeable. A baseline test for the catalyst was run at GHSV = 6000 h⁻¹ for 140 h. No change in the performance of the catalyst was observed for the duration of the test in clean syngas, as shown in Figure 26.

Figure 25. LT-WGS catalyst space velocity test at 240 °C (ShiftMax 230, Süd-Chemie).

Figure 26. Baseline test for LT-WGS catalyst (Shiftmax 240, Süd-Chemie).

4.2. Impact of AsH₃ on LT-WGS Catalyst

The LT-WGS catalyst-contaminant testing began with an experiment to assess the impact of arsene (AsH₃) on the performance of the LT-WGS catalyst. About 4 cc of the crushed and sieved catalyst was packed into the reactor and clean syngas was fed for ~25 h before introducing the contaminant. The GHSV was 12,000 h⁻¹. Nitrogen was substituted for methane

Figure 27. Impact of 4.5 ppmv AsH₃ on LT-WGS catalyst (ShiftMax230, Süd-Chemie) at 240 °C and 400 psig. GHSV = 12,000 h⁻¹. Feed: 4.5% CO, 24.4% CO₂, 43.2% H₂, 6% N₂, 15% H₂O, and 4.5 ppmv AsH₃.

Figure 28. Impact of H₂S on low-temperature WGS catalyst (ShiftMax 230, Sud-Chemie) at 240 °C and 400 psig. GHSV = 6,000 h⁻¹. Feed: 4.5% CO, 34.4% CO₂, 43.2% H₂, 2.9% N₂, 15% H₂O, and 2-10 ppm H₂S. Total H₂S loading = 0.58% wt.% deposited on the catalyst by the end of the test as determined by ICP.

because both are essentially inert at these conditions. The AsH₃ concentrations in the feed and effluent gas streams were challenging to accurately measure. We carried out analysis of the outlet gas flow to obtain an accurate assessment of the AsH₃ concentration downstream of the catalyst and observed that most of the AsH₃ was removed by the catalyst bed. At the end of the test, the feed gases were routed past the catalyst bed to validate the analyzer results. However, as was evident from the stable CO concentration over a 100 h test, the presence of AsH₃ did not appreciably affect the catalyst activity during the 100-h test window as shown in Figure 27. Since the AsH₃ was almost completely removed from the feed gas by adsorption onto the catalyst we would expect the catalyst to eventually experience activity loss after AsH₃ adsorption reached a certain saturation level.

4.3. Impact of H₂S on LT-WGS Catalyst

About 8 cc of the catalyst was packed into the reactor and clean syngas was introduced for ~10 h before introduction of 2 ppmv H₂S into the feed gas mixture Figure 28. The GHSV was 6000 h⁻¹. The H₂S concentration downstream of the reactor was measured to within a few ppmv using a GC. We observed that 2 ppmv H₂S did not appreciably affect the performance of the catalyst and the CO concentration in the outlet remained stable even after the introduction of 10 ppm H₂S over the last 50 h of a 100 h test. CO conversion was used as a performance criterion to assess the impact of the contaminants; returning to the baseline shift condition of clean syngas after 100 h confirmed that no activity was lost over the course of the test.

Figure 29. Impact of H₂S on low temperature WGS catalyst (ShiftMax 230, Süd-Chemie) at 240 °C and 400 psig. GHSV = 6,000-16,000 h⁻¹ (see plot). Feed: 4.5% CO, 34.4% CO₂, 43.2% H₂, 2.9% N₂, 15% H₂O, and 0-88 ppm H₂S. Total H₂S (sulfur) loading = 17.1 wt.% as determined by ICP.

Since exposure to low levels of H₂S did not appear have any impact on the LT-WGS catalyst during a 100 h test, another evaluation was performed on a fresh sample of the same catalyst at higher space velocities and greater H₂S concentrations as shown in Figure 29. About 4 cc of the catalyst was packed into a smaller reactor and clean syngas was introduced for ~25 h before adding 12 ppmv H₂S into the feed gas mixture. The GHSV was 12,000 h⁻¹ at the beginning of the test. When no change in performance was observed, the H₂S concentration was successively doubled to 24, 46, and then 88 ppmv. Some degradation in shift activity was observed under 46 ppmv of H₂S, and more significant loss in activity was observed at 88 ppmv. After ~160 h of cumulative testing the GHSV was increased to 16,000 h⁻¹, which corresponded to a H₂S concentration of 75 ppm in the feed. A slow decrease in performance continued to be observed as evidenced by the steadily increasing CO concentration. Furthermore, after about 30 more hours H₂S finally began breaking through the bed. Inductively coupled plasma (ICP) analysis of the catalyst after testing showed it contained a sulfur loading of 17.1 wt.%.

4.4. Impact of NH₃ on LT-WGS Catalyst

Catalyst evaluation testing continued with a study on the impact of ammonia (NH₃) on the performance of the low-LT-WGS catalyst. About 4 cc of the catalyst was packed into the reactor and clean syngas was introduced for ~20 h before 3 ppmv ammonia was introduced into the feed gas mixture as shown in Figure 30. The GHSV was 12,000 h⁻¹.

Table 17. Inlet syngas conditions for testing the impact of NH₃ on LT-WGS catalyst.

Gas Composition	LT-WGS
CO ₂	43.2%
CO	4.5%
H ₂	34.4%
CH ₄	2.9%
H ₂ O	15.0%
NH ₃	3-96 ppmv
Temperature (°C)	240
Pressure (psig)	400

Figure 30. Impact of NH_3 on LT-WGS catalyst (ShiftMax 230, Süd-Chemie) at 240 °C and 400 psig. GHSV = 12,000 h^{-1} . Feed: 4.5% CO, 34.4% CO_2 , 43.2% H_2 , 2.9% N_2 , 15% H_2O , and 3-33 ppm NH_3 . Total theoretical NH_3 (nitrogen) loading = 5.25 wt.%.

Figure 31. Effect of 85 ppmv NH_3 on low-temperature WGS catalyst (ShiftMax 230, Süd-Chemie) at 240 °C and 400 psig. GHSV = 12,000 h^{-1} . Feed: 4.5% CO, 34.4% CO_2 , 43.2% H_2 , 2.9% N_2 , 15% H_2O , and 85 ppmv NH_3 .

Quantification of the ammonia concentration downstream of the catalyst also proved to be difficult because most of it was likely knocked out in the steam condenser. However, CO and hydrogen concentrations are an excellent indicator of catalyst activity and any increase (CO) or decrease (H_2) means a reduction in catalyst activity, therefore, CO conversion was used as a performance criterion to assess the impact of the contaminant. We observed that neither 3 or 33 ppmv ammonia appreciably affected the performance of the catalyst and the CO concentration in the outlet remained stable throughout the >100 h test (Figure 30). Returning to the baseline shift condition by feeding clean syngas after 100 h confirmed that no activity was lost over the course of the test.

Since exposure to low levels of ammonia did not appear have any impact on the LT-WGS catalyst during the 100 h test, another evaluation was performed on the same catalyst at higher ammonia concentration and using a different ammonia analyzer Figure 31. A single point monitor (SPM) was used for ammonia analysis downstream of the catalyst bed. Switching to bypass mode confirmed that the analyzer was detecting ammonia but not at the expected concentration; the analyzer detected only ~6 ppm of the 85 ppm fed. No ammonia was detected by the SPM downstream of the catalyst during water-gas shift testing, so either the catalyst was absorbing all of the ammonia that was fed, or the ammonia was being removed in the steam condenser. Based on the CO and hydrogen concentrations measured in the reactor effluent, no change in shift activity was observed in syngas containing 85 ppm of NH_3 after ~60 h of cumulative testing.

4.5. Binary H_2S - NH_3 Contaminant Tests on LT-WGS Catalyst

For the LT-WGS catalyst, a baseline CO conversion rate without contaminants was established that was fairly constant (Figure 32). After about 50 h on stream the impurities gradually reduced the catalyst activity as determined by the decrease in CO conversion (increase in outlet

Figure 32. Impact of H_2S + NH_3 on LT-WGS catalyst (ShiftMax 230, Süd-Chemie) at 240 °C and 400 psig. GHSV = 12,000 h^{-1} . Feed: 4.5% CO, 34.4% CO_2 , 43.2% H_2 , 2.9% N_2 , 15% H_2O , 38 ppmv NH_3 and 60 ppmv H_2S . Total theoretical H_2S loading = ~12 wt.%.

concentration). The H_2S concentration downstream of the reactor was measured to within a few ppmv using a GC. Finally, after about 75 h H_2S was observed to break through the catalyst bed, which suggested that it had stopped adsorbing or reacting with the catalyst. From the estimated flow rate, we calculated that the catalyst had adsorbed around 12 wt.% sulfur, derived from the total quantity of H_2S fed to the reactor minus the quantity estimated from the concentrations measured by the GC. ICP analysis of this catalyst sample exceeded our estimate with a quantitative result of 18.5 wt.% sulfur.

4.6. Impact of NaCl on LT-WGS Catalyst

The results of alkali salt sublimation tests were described previously. Measurements indicated miniscule evaporation rates (ppb or less) for NaCl (and KCl) at temperatures below 500 °C, which presented a significant challenge for introducing these ubiquitous biomass contaminants into WGS gas streams to study their effect on the LT-WGS catalyst. Neither salt had an appreciable vapor pressure at 240 °C. From the gas flow rate and the vaporization rate, we estimated the salt concentration introduced into the gas flow at approximately ~250 ppbw for NaCl and 800 ppbw for KCl at temperatures above 550 °C. Hence, in a gasifier system these salts can be expected to condense long before getting to the WGS reactors and would likely have minimal impact on the WGS catalysts because of their very low concentrations (in the ppb range).

After establishing the baseline catalyst performance with the salt only experiments (see Figure 17), the LT-WGS catalyst was tested in the presence of crystalline NaCl by mixing the crystalline powder directly with the catalyst. The standard LT-WGS baseline test conditions of 240 °C and 400 psig with an inlet syngas composition of 15% H_2O , 34.4% CO_2 , 4.5% CO and 43.2% H_2 at a GHSV = 12,000 h^{-1} were used again for this test. Figure 33 shows the results of

Figure 33. Impact of NaCl on LT-WGS catalyst (ShiftMax 230, Süd-Chemie) at 240 °C and 400 psig. GHSV = 12,000 h^{-1} . Feed: 4.5% CO, 34.4% CO_2 , 43.2% H_2 , 2.9% N_2 , 15% H_2O , and 10% wt. NaCl mixed with the catalyst.

Figure 34. Impact of KCl on LT-WGS catalyst (ShiftMax 230, Süd-Chemie) at 240 °C and 400 psig. GHSV = 12,000 h⁻¹. Feed: 4.5% CO, 34.4% CO₂, 43.2% H₂, 2.9% N₂, 15% H₂O, and 0.78 g KCl mixed in with the catalyst.

the test; there was only a slight initial decrease in WGS activity, but the catalyst retained almost all of its activity and exhibited slightly reduced conversion throughout the remainder of the ~130 h test.

4.7. Impact of KCl on LT-WGS Catalyst

After an initial ~40 h test period without the contaminant, we removed the LT-WGS catalyst from the reactor and mixed it with KCl, replaced the mixture in the reactor and resumed the test as shown in Figure 34. We observed that ShiftMax 230 exhibited very stable conversion even when mixed directly with KCl powder. There was only a slight initial decrease in activity, and then a very slow decrease in conversion throughout the rest of the test.

4.8. Impact of PH₃ on LT-WGS Catalyst

The impact of phosphine (PH₃) on the performance of high-temperature WGS catalyst is shown in Figure 35. About 8 cc of the catalyst was loaded into the reactor and clean syngas was fed for 24 h before introducing 1 ppmv PH₃ into the gas mixture. The concentration of PH₃ in the product stream was not measured because it could not be detected because it was probably knocked out with steam in the condenser or adsorbed onto the catalyst. PH₃ seemed to slightly impact the performance of the catalyst and the CO conversion slowly decreased while PH₃ was co-fed.

Figure 35. Impact of 1 ppmv PH₃ on LT-WGS catalyst (ShiftMax 230, Süd-Chemie) at 240 °C and 400 psig. GHSV = 6,000 h⁻¹. Feed: 4.5% CO, 34.4% CO₂, 43.2% H₂, 2.9% N₂, 15% H₂O, and 1 ppmv PH₃.

4.9. Impact of HCN on LT-WGS Catalyst

The results of a test to assess the impact of hydrogen cyanide (HCN) on the performance of the LT-WGS catalyst are shown in Figure 36. About 4 cc of the catalyst was packed into the reactor and clean syngas was introduced for ~30 h before introducing 10 ppmv of the contaminant. The GHSV was 12,000 h⁻¹. The slight decrease in H₂ concentration was from a change in the mass flow controller for the H₂ gas stream during HCN introduction. HCN is challenging to accurately measure. Unfortunately, it was difficult to obtain an assessment of the HCN concentration downstream of the catalyst because most of the HCN was likely knocked out in the water condenser or adsorbed onto the catalyst. However, as evident by the stable CO concentration in the product stream throughout the 100 h test, the presence of HCN did not affect the performance of the catalyst.

Figure 36. Impact of 10 ppmv HCN on LT-WGS catalyst (ShiftMax 230, Süd-Chemie) at 240 °C and 400 psig. GHSV = 12,000 h⁻¹. Feed: 4.5% CO, 34.4% CO₂, 43.2% H₂, 2.9% N₂, 15% H₂O, and 10 ppmv HCN.

4.10. Summary of Long-term Experimental Contaminant Studies on LT-WGS Catalyst

The results of the contaminant impact study carried out on the LT-WGS catalyst (Shiftmax 120, Süd-Chemie) are summarized in Table 18. Some of the contaminants included in the study had little or no effect on the LT-WGS catalyst, but the impact of H₂S, AsH₃, and PH₃ was significant. NH₃, H₂S, HCN all seemed to adsorb onto the LT-WGS catalyst, however, these contaminants may have also been knocked out in the steam condenser. The alkali salts were physically mixed in with the catalyst; NaCl had no effect, but KCl seemed to inhibit the WGS reaction slightly. NH₃ and H₂S together also poisoned the catalyst, although it took awhile to saturate the catalyst with adsorbed H₂S.

Table 18. Summary of the impact of contaminants on LT-WGS catalyst.

Contaminant	Concentration (ppmv)	Approx. Test Duration (h)*	Inhibition	Adsorption
Arsine, AsH ₃	4.5	160	Yes	Yes
Hydrogen sulfide, H ₂ S	2-88	365	Yes	Yes
Ammonia, NH ₃	3-85	200	No	Yes
Sodium chloride, NaCl	10 wt.% [†]	130	No	-
Potassium chloride, KCl	10 wt.% [†]	135	Yes (slight)	-
PH ₃	1	170	Yes	No
HCN	10	145	No	Yes
NH ₃ +H ₂ S	38 + 60	85	Yes	Yes

*cumulative, including baseline tests

[†]gas-phase vapor pressure of the alkali salts at test conditions was very low so they were introduced as a solid mixed directly with the catalyst

5. Long-Term Exposure Tests to Determine the Impact of Contaminants on Cobalt-based Fischer-Tropsch Synthesis Catalyst

In Task 3 (Subtask 3) of this project, we evaluated the interaction of cobalt-based Fischer-Tropsch (Co-FT) synthesis catalyst with eleven different contaminants; AS_3 , NH_3 , NH_4NO_3 , NH_4OH , $NaCl$, KNO_3 , KCl , HCl , HBr , HF , and HNO_3 . UK-CAER made the Co-FT catalyst (#GJ-456) that was used for the bench-scale evaluations.

5.1. Preparation of Co-FT Catalyst

The catalyst composition and synthesis method was based on commercial catalyst formulations, but synthesized by UK-CAER. Thus, confidentiality agreements did not limit the extent of characterization that could be performed on the material both before and after testing. The porous gamma alumina support (Catalox Sba-150, $150\text{ m}^2/\text{g}$ $\gamma\text{-Al}_2\text{O}_3$) was procured from Sasol. The support was calcined at $400\text{ }^\circ\text{C}$ for 4 h in a muffle furnace prior to the impregnation step. A slurry was utilized to load the support in three impregnation and drying steps, where enough cobalt nitrate was added to achieve between 2 and 3 kilograms of ~25% Co on Al_2O_3 after calcination. The catalyst was dried by rotary evaporation under vacuum at $\sim 95\text{ }^\circ\text{C}$. Prior to calcination, platinum promoter was added (to ~0.5% by weight) by aqueous incipient wetness impregnation (IWI) of the Co/Al_2O_3 with tetraamminePt(II) nitrate. The resulting 0.5%Pt-25%Co/ Al_2O_3 Fischer-Tropsch synthesis catalyst (identification number GJ456) was calcined at Süd-Chemie, Inc.

5.2. Establishment of Baseline Co-FT Catalyst Testing Conditions

Initial gas-phase tests were conducted in TDA's bench-scale Fischer-Tropsch synthesis system on a sample of the Co-FT catalyst provided by UK-CAER. In these preliminary scoping tests the catalyst exhibited very high activity, but low selectivity for FT liquids and high methane production.

Table 19. FT synthesis feed gas compositions.

	Co-FT	Fe-FT
H_2	65.4%	42.8%
CO	31.9%	55.6%
CO_2	2.4%	1.3%
CH_4	0.3%	0.3%
H_2O	0.0%	0.0%
$H_2:CO$	2.1	0.8

Five criteria were used to assess the performance of the Co-FT catalyst under the impact of the contaminants. These included the extent of CO conversion, the FT liquid rate, the liquid product distribution, and the methane and carbon dioxide concentrations in the gas phase product. The CO conversion was based on the gas phase carbon balance and the CO_2 and CH_4 levels in the effluent gas (dry basis); the calculated thermodynamic equilibrium conversion level at the specific test temperature was used as a performance metric. The CO conversion included the FTS reactions that formed higher hydrocarbons, the methanation reaction, and the water-gas shift reaction that formed CO_2 and H_2 . The CO conversion and FTS rate were calculated as shown below:

$$CO\text{ Conversion (\%)} = \left(\frac{(CO\text{ moles in}) - (CO\text{ moles out})}{(CO\text{ moles in})} \right) \times 100 \quad (5.1)$$

$$CO\text{ Rate (mol/h)} = (CO\text{ feed \{mol/h\}}) \times (CO\text{ Conversion}) \quad (5.2)$$

$$FT\text{ Rate (g HC / g cat / h)} = \left\{ \frac{[CO\text{ Rate (mol/h)}] - [CO_2\text{ in Pdt (mol/h)}]}{[amount\ of\ catalyst\ used\ (g)]} \right\} \times 14.027 \quad (5.3)$$

The CH₄ and C₅₊ selectivities (carbon atom basis), and C₄ olefin selectivity were calculated as follows:

$$CH_4, C_{5+} \text{ selectivity (\%)} = \left(\frac{(CO \text{ moles in}) - (CH_4 \text{ or } C_{5+} \text{ moles out})}{(CO \text{ moles in})} \right) \times 100 \quad (5.4)$$

$$C_4 \text{ olefin selectivity (\%)} = \left(\frac{(C_4 \text{ alkenes out})}{(C_4 \text{ alkenes out}) + (C_4 \text{ alkanes out})} \right) \times 100 \quad (5.5)$$

$$C_{1-4} \text{ olefin selectivity (\%)} = \left(\frac{(C_{1-4} \text{ alkenes out})}{(C_{1-4} \text{ alkenes out})} \right) \times 100 \quad (5.6)$$

5.3. Impact of AsH₃ on Co-FT Catalyst

Arsine gas (AsH₃) was co-fed during FT synthesis over Co-FT catalyst. Figure 37 shows that the percentage of deactivation increased with an increase in the arsine concentration from 50 to 1000 ppbv. The slope of the percentage of CO conversion versus time-on-stream (TOS) curve increased from 0.0164 to 0.0239 for 50 ppbv of arsine in the feed and increased further to 0.064 for 300 ppbv. Figure 38 displays the effect of 500 ppbv and 1 ppmv AsH₃ on the CO conversion; the deactivation rate increased to 0.0573. Arsine did not change the selectivity towards hydrocarbons very much. In this regard, Figure 39 shows that the methane selectivity increased slightly with increasing arsine levels in the feed, while the C₅₊ content in the product concurrently decreased. Figure 40 shows the effect of arsine on olefinic selectivity for C₂, C₃ and C₄ hydrocarbons. It appears that the olefinic selectivity for C₃ and C₄ hydrocarbons dropped slightly while the C₂ product fraction remained more or less the same with increasing arsine concentration. Analogous to sulfur, arsine could act like a permanent poison that depletes the sites of metallic cobalt, which is known to be an active phase for FT synthesis (Khodakov, Chu et al. 2007).

Figure 37. Effect of arsine (50 and 300 ppbv AsH₃) on CO conversion over Co-FT catalyst at 220 °C, 275 psig, H₂/CO = 2.0, and syngas SV = 5.0 slph (H₂+CO).

Figure 38. Effect of arsine (500 ppbv and 1 ppmv AsH₃) on CO conversion over Co-FT catalyst at 220 °C, 275 psig, H₂/CO = 2.0, and syngas SV = 5.0 slph (H₂+CO).

Figure 39. Effect of arsine (50, 300, 500, and 1000 ppb AsH₃) on selectivity for Co-FT synthesis at 220 °C, 275 psig, H₂/CO = 2.0, and syngas SV = 5.0 slph (H₂+CO).

Figure 40. Effect of arsine (50, 300, 500 and 1000 ppbv AsH₃) on C₂, C₃ and C₄ olefinic selectivity for Co-FT synthesis at 220 °C, 275 psig, H₂/CO = 2.0, and syngas SV = 5.0 slph (H₂+CO).

Figure 41. CO conversion versus time on-stream for a 100 ppmv NH₃ (1000 ppmv NH₃ in N₂) contaminant test on the Co-FT GJ456 catalyst (0.5%Pt-25%Co/Al₂O₃). Syngas SV = 4.0 slph/g, H₂/CO = 2.0, T = 220 °C, and P = 275 psig.

5.4. Impact of NH₃ Compounds on Co-FT Catalyst

Figure 41 shows that the CO conversion dropped much more rapidly (42.5% loss) when 100 ppmv of ammonia (1000 ppmv NH₃ in N₂) was introduced along with the syngas than the rate of decrease observed during another separate test in which ammonium nitrate was co-fed (50 ppmv NH₄NO₃ in 1.0 ml/h H₂O), as shown in Figure 42. The Co-FT catalyst deactivated during the first few hours of exposure to 100 ppmv NH₃ (a 26% loss) and additional contaminant addition (50 ppmv NH₄NO₃) did not further impact the activity to a measurable extent. During NH₃ addition the CO conversion leveled off within a few hours of synthesis, although the selectivities for methane and C₅₊ hydrocarbons remained essentially constant, as evident in Figure 43. The methane (9.0 wt.%) and C₅₊ (80 wt.%) selectivity also remained relatively unchanged with NH₄NO₃ addition, as shown in Figure 44. It should be noted that Claeys et al. reported that co-feeding up to 25% NH₃ in the syngas did not significantly affect the Fischer-Tropsch synthesis activity over a cobalt catalyst, and Borg et al. observed no change in activity when ammonia was added at concentrations up to 4.2 ppmv during cobalt-catalyzed FT synthesis (Claeys, van Steen et al. 2010; Borg, Hammer et al. 2011). At the end of our 400 h test, the catalyst did appear to slowly recover from exposure to the contaminant under clean baseline feed conditions.

Figure 42. CO conversion versus TOS for a 50 ppmv NH₄NO₃ contaminant test on the Co-FT catalyst (0.5%Pt-25%Co/Al₂O₃). Syngas SV = 3.0 slph/g, H₂/CO = 2.0, T = 220 °C, and P = 275 psig. H₂O was used to deliver the contaminant into the FT reactor.

Figure 43. Selectivity versus time on-stream for a 100 ppmv NH₃ contaminant test on the Co-FT GJ456 catalyst (0.5%Pt-25%Co/Al₂O₃). Syngas SV = 4.0 slph/g, H₂/CO = 2.0, T = 220 °C, and P = 275 psig.

Figure 44. Selectivity versus time on-stream for a 50 ppmv NH_4NO_3 contaminant test on the Co-FT GJ456 catalyst (0.5%Pt-25%Co/ Al_2O_3). Syngas SV = 3.0 slph/g, H_2/CO = 2.0, $T = 220^\circ\text{C}$, and $P = 275$ psig. H_2O was used to deliver the contaminant into the FT reactor at a rate of 1.0 ml/h.

Unlike for the case of ammonia, the deactivation of Co-FT catalyst was comparatively less (approximately a 16% loss) with the addition of 100 ppmv ammonium hydroxide (NH_4OH), as illustrated in Figure 45. H_2O was used to deliver the contaminant into the FT reactor at a rate of 1.0 ml/h. Also, the rate of deactivation changed with TOS. For example, within the first few hours of contaminant addition, the decrease in CO conversion was 16%, but then the deactivation rate decreased to 3.5%/day with the continued addition of ammonium hydroxide. Figure 46 indicates that the selectivity to methane decreased slightly and the C_{5+} selectivity increased.

To study the effect of ammonium hydroxide concentration on Co-FT catalyzed FTS, we compared the deactivation of cobalt by ammonium hydroxide at two different concentrations (100 and 1200 ppmv). From the results presented in Figure 47, the deactivation of the Co-FT catalyst by ammonia hydroxide did not appear to be concentration dependent. Also, the deactivation rates were very high for first few hours of poison introduction and then they exhibited a smaller slope.

From this study, it appears that ammonia tended to suppress Co-FT synthesis activity to a moderate degree at the concentration levels examined, irrespective of the source. Neither the mode of deactivation nor the strength of the poisoning effect (e.g., reversibility) is known at this time.

Figure 45. CO conversion versus time on-stream for a 100 ppmv NH_4OH contaminant test on the Co-FT GJ456 catalyst ($0.5\%\text{Pt}-25\%\text{Co}/\text{Al}_2\text{O}_3$). Syngas SV = 3.0 slph/g, H_2/CO = 2.0, T = 220 °C, and P = 275 psig. H_2O was used to deliver the contaminant into the FT reactor at a rate of 1.0 ml/h.

Figure 46. Selectivity versus time on-stream for a 100 ppmv NH_4OH test on the Co-FT GJ456 catalyst ($0.5\%\text{Pt}-25\%\text{Co}/\text{Al}_2\text{O}_3$). Syngas SV = 3.0 slph/g, H_2/CO = 2.0, T = 220 °C, and P = 275 psig. H_2O was used to deliver the contaminant into the FT reactor at a rate of 1.0 ml/h.

Figure 47. Selectivity versus time on-stream for 1200 and 100 ppmv NH₄OH contaminant tests on the Co-FT GJ456 catalyst (0.5%Pt-25%Co/Al₂O₃). Syngas SV = 3.0 slph/g, H₂/CO = 2.0, T = 220 °C, and P = 275 psig. H₂O was used to deliver the contaminant into the FT reactor.

5.5. Impact of NaCl on Co-FT Catalyst

After reaching a steady CO conversion level of 37% without the contaminant, as shown in Figure 48, 100 ppmv NaCl was introduced along with syngas. The CO conversion decreased substantially within a few hours and then leveled off. However, a steady decline in CO conversion was observed by adding 1.0 ml/h of an aqueous solution of 400 ppmv NaCl along

Figure 48. CO conversion versus time on-stream for a 100 ppmv and 400 ppmv NaCl contaminant test on the Co-FT GJ456 catalyst (0.5%Pt-25%Co/Al₂O₃). Syngas SV = 4.0 slph/g, H₂/CO = 2.0, T = 220 °C, and P = 275 psig.

Figure 49. Selectivity versus time on-stream for a 100 ppmv and 400 ppmv NaCl contaminant test on the Co-FT GJ456 catalyst (0.5%Pt-25%Co/Al₂O₃). Syngas SV = 4.0 slph/g, H₂/CO = 2.0, T = 220 °C, and P = 275 psig.

with the syngas as shown in Figure 48. The selectivity to methane appears to have increased slightly with NaCl addition (100 ppmv), with a corresponding decrease in C₅₊ hydrocarbons (Figure 49). The selectivity was very similar at 100 and 400 ppmv NaCl.

5.6. Impact of KNO₃ and KCl on Co-FT Catalyst

Potassium was also found to poison the cobalt catalyst under Fischer-Tropsch synthesis conditions. Before the contaminant was introduced, steady-state CO conversion was achieved. Then, 1.0 ml/h of deionized water that contained the contaminant was co-fed along with the syngas (H₂+CO) at a temperature of 220 °C and a pressure of 275 psig. Figure 50 and Figure 51 show that potassium did not display any poisoning effect on cobalt at the 10 and 100 ppmv levels. However, KNO₃ did poison cobalt at higher concentrations. For example, the CO conversion dropped from 38% to 10% within 100 h of co-feeding 500 ppmv of KNO₃ and stabilized, even with further potassium nitrate addition (500 ppmv). This phenomenon was also observed in recent studies (Khodakov, Chu et al. 2007; Borg, Hammer et al. 2011).

Surprisingly, the selectivity to both CO₂ and also CH₄ also increased during the same time period (Figure 52). This showed that potassium promoted the WGS activity to a greater extent and suppressed the FT activity. Potassium also influenced the olefinic selectivity of C₂, C₃ and C₄ hydrocarbons. Figure 53 shows an increasing trend for C₂ olefins and a decreasing trend for C₃ and C₄ olefins, although the reason for this is not clear. The concentrations of potassium (K⁺) and ammonium (NH₄⁺) ions present in the aqueous phase of the FT products was measured, as shown in Figure 54. The potassium levels were well below 0.1 ppm and remained constant during the entire period of FTS with co-fed potassium. However, we found an increase in the concentration of ammonium in the aqueous FT products that suggests that potassium nitrate underwent reduction to form ammonia, which is why an increase in ammonium levels was

Figure 50. Effect of potassium (10 ppmv KNO₃) on CO conversion over Co-FT catalyst at 220 °C, 275 psig, H₂/CO = 2.0, and syngas SV = 3.0 slph (H₂+CO).

observed after the addition of potassium nitrate. Therefore, an estimated quantity of 3.8 g of the added potassium must have adsorbed on the catalyst (the total amount of potassium fed during the entire run was 4.2 g). KCl did not cause any deactivation of the Co-FT catalyst up to the 100 ppmv level, as shown in Figure 55.

Figure 51. Effect of potassium (100 and 500 ppmv KNO₃) on CO conversion over Co-FT catalyst at 220 °C, 275 psig, H₂/CO = 2.0, and syngas SV = 2.0 slph (H₂+CO).

Figure 52. Effect of potassium (100 and 500 ppmv KNO₃) on selectivity for Co-FT synthesis at 220 °C, 275 psig, H₂/CO = 2.0, and syngas SV = 2.0 slph (H₂+CO).

Figure 53. Effect of potassium (100 and 500 ppmv KNO₃) on C₂, C₃ and C₄ olefinic selectivity for Co-FT synthesis at 220 °C, 275 psig, H₂/CO= 2.0 & SV= 2.0 slph (H₂+CO).

Figure 54. The concentrations of ammonia and potassium found in the aqueous phase during co-feeding KNO₃ (100 and 500 ppmv) over Co-FT synthesis catalyst at 220 °C, 275 psig, H₂/CO = 2.0, and syngas SV = 2.0 slph (H₂+CO).

Figure 55. Effect of potassium (50 and 100 ppmv KCl) on CO conversion over Co-FT catalyst at 220 °C, 275 psig, $H_2/CO = 2.0$, and syngas SV = 4.0 slph (H_2+CO).

5.7. Impact of HCl on Co-FT Catalyst

HCl exhibited a moderate poisoning effect over CO conversion during Co-FT synthesis at concentrations of 500 ppbv and 1.0 ppmv in the syngas feed; the CO conversion dropped at a rate of 0.52% per day at 500 ppbv of HCl, and 0.69 % per day for 1.0 ppmv of HCl as displayed in Figure 56. The selectivities to CH_4 and C_{5+} hydrocarbons remained more or less the same during the exposure to 500 ppbv and 1.0 ppmv of HCl in the syngas (Figure 57 and Figure 58). However, the olefinic content in the hydrocarbon products was reduced by the addition of HCl.

Figure 59 shows a slight increase in the concentration of C_2 olefins, but the concentrations of C_3 and C_4 olefins essentially remained constant. As shown in Figure 60, a linear relationship existed between the amount of HCl poison added and the decrease in CO conversion (with negative slope). The amount of chloride anion in the spent catalyst was evaluated by ICP (after the removal of polywax by extraction using o-xylene) and it was determined to be 0.2 wt.%. Based on the amount of catalyst (10 g), a total of 0.02 g of chloride was present in the spent catalyst. We fed nearly 0.5 g of chloride during the experiment. Thus, the majority of the added HCl must have ended up in the oil and wax slurry, hydrocarbons, and aqueous products.

Figure 56. Effect of added HCl (500 ppbv and 1.0 ppmv) on the CO conversion over Co-FT catalyst at 220 °C, 275 psig, H₂/CO = 2.0, and syngas SV = 3.0 slph.

Figure 57. Effect of added HCl (500 ppbv) on methane and C₅₊ hydrocarbon selectivity for Co-FT synthesis at 220 °C, 275 psig, H₂/CO=2.0, and syngas SV = 3.0 slph.

Figure 58. Effect of added HCl (1.0 ppmv) on the CH₄ and C₅₊ hydrocarbon selectivity for Co-FT synthesis at 220 °C, 275 psig, H₂/CO = 2.0, and syngas SV = 3.0 slph.

Figure 59. Effect of added HCl (500 ppbv and 1.0 ppmv) on the selectivity for C₂-C₄ olefins for Co-FT synthesis at 220 °C, 275 psig, H₂/CO = 2.0, and syngas SV = 3.0 slph.

Figure 60. Effect of added HCl (500 ppbv and 1.0 ppmv) on CO conversion rates for Co-FT synthesis at 220 °C, 275 psig, $H_2/CO = 2.0$, and syngas SV = 3.0 slph.

5.8. Impact of HBr on Co-FT Catalyst

The data presented in Figure 61 and Figure 62 show that HBr did not have a poisoning effect on Co-FT synthesis at the 500 ppbv or 1.0 ppmv levels. The percentage of CO selectivity that was lost each day is shown in Figure 63 and increased from 0.80%/d to 0.99%/d for 1.0 ppmv HBr, 1.94%/d for 10 ppmv, and 2.61%/d for 100 ppmv of HBr (co-fed in 1.0 ml/h of deionized water). Also, CH_4 and C_{5+} hydrocarbon selectivities were influenced mainly due to the changes on CO conversion. As presented in Figure 64, Figure 65 and Figure 66, the methane selectivity increased with increasing HBr concentration, as the CO conversion correspondingly decreased. The rate of deactivation of the Co-FT catalyst appeared to increase with increasing HBr concentration from 1.0 to 100 ppmv (Figure 67). The amount of bromide in the spent catalyst was 0.038 g; however, we fed nearly 1.2362 g of bromide during the entire run. Hence, most of the bromide must have accumulated in the reactor slurry and/or liquid hydrocarbons and aqueous products. If we compare the two halides, bromide poisoned cobalt much more potently than chloride at an equal concentration.

Figure 61. Effect of added HBr (500 ppbv, 1.0 and 10 ppmv) on the conversion of CO for Co-FT synthesis at 220 °C, 275 psig, H₂/CO = 2.0, and syngas SV = 5.0 slph.

Figure 62. Effect of added HBr (20 ppmv) on the conversion of CO for Co-FT synthesis at 220 °C, 275 psig, H₂/CO = 2.0, and syngas SV = 3.0 slph.

Figure 63. Effect of added HBr (100 ppmv) on the CO conversion for Co-FT synthesis at 220 °C, 275 psig, H₂/CO = 2.0, and syngas SV = 3.0 slph.

Figure 64. Effect of added HBr (500 ppbv, 1.0 and 10 ppmv) on the selectivity of Co-FT catalyst at 220 °C, 275 psig, H₂/CO = 2.0, and syngas SV = 5.0 slph.

Figure 65. Effect of HBr (20 ppmv) on the selectivity for Co-FT synthesis at 220 °C, 275 psig, H₂/CO = 2.0, and syngas SV = 3.0 slph.

Figure 66. Effect of added HBr (100 ppmv) on the selectivity of Co-FT synthesis catalyst at 220 °C, 275 psig, H₂/CO=2.0, and syngas SV = 3.0 slph.

Figure 67. Effect of added HBr on the CO conversion rates for Co-FT synthesis catalyst at 220 °C, 275 psig, $H_2/CO = 2.0$, and syngas SV = 3.0 or 5.0 slph.

5.9. Impact of HF on Co-FT Catalyst

During cobalt-catalyzed FT synthesis, 250 ppbv HF was introduced into the syngas and no additional deactivation was observed in comparison to the baseline deactivation rate, as shown in Figure 68. As illustrated in Figure 69, the CO conversion also remained relatively unchanged (at a level of approximately 37%) during the addition of 1000 ppbv and 15 ppmv HF, suggesting that HF did not suppress Co-FT activity under the experimental conditions used. Similarly, the methane and C_{5+} selectivities were also relatively unaffected as shown in Figure 70.

Figure 68. Selectivity versus time-on-stream for a 250 ppbv HF contaminant test on the Co-FT GJ456 catalyst (0.5%Pt-25%Co/Al₂O₃). Syngas SV = 4.0 slph/g, H₂/CO = 2.0, T = 220 °C, and P = 275 psig.

Figure 69. CO conversion versus time-on-stream for a 1000 ppbv and 15 ppmv HF contaminant co-feed test on the Co-FT GJ456 catalyst (0.5%Pt-25%Co/Al₂O₃). Syngas SV = 4.0 slph/g, H₂/CO = 2.0, T = 220 °C, and P = 275 psig.

Figure 70. Selectivity versus time-on-stream for a 1000 ppbv and 15 ppmv HF contaminant test on the Co-FT GJ456 catalyst (0.5%Pt-25%Co/Al₂O₃). Syngas SV = 4.0 slph/g, H₂/CO = 2.0, T = 220 °C, and P = 275 psig.

5.10. Impact of HNO₃ on Co-FT Catalyst

Nitric acid (HNO₃) exhibited a poisoning effect (Figure 71 and Figure 72) that was very similar to that of ammonia. The poisoning effect was irreversible. Figure 72 shows a sharp decline in CO conversion only for the first data point after we started feeding HNO₃ at 1.0 ppmv, and thereafter the slope follows a different trend. Hence, this suggests that the added HNO₃ underwent hydrogenation and behaves very similar to the effect of ammonia. The selectivities to methane and C₅₊ hydrocarbons (Figure 73 and Figure 74) were about the same during and after the HNO₃ poisoning test.

Figure 71. Effect of added HNO_3 (500 ppbv) on the CO conversion for Co-FT synthesis catalyst at 220 °C, 275 psig, $\text{H}_2/\text{CO} = 2.0$, and syngas SV = 3.0 slph.

Figure 72. Effect of added HNO_3 (1.0 ppmv) on the conversion of CO over Co-FT synthesis catalyst at 220 °C, 275 psig, $\text{H}_2/\text{CO} = 2.0$, and syngas SV = 3.0 slph.

Figure 73. Effect of added HNO_3 (500 ppbv) on the selectivity of Co-FT synthesis catalyst at 220 °C, 275 psig, $H_2/CO = 2.0$, and syngas SV = 3.0 slph.

Figure 74. Effect of added HNO_3 (1.0 ppmv) on the selectivity of Co-FT synthesis catalyst at 220 °C, 275 psig, $H_2/CO = 2.0$, and syngas SV = 3.0 slph.

Table 20. Summary of the impact of contaminants on Co-FT catalyst.

Contaminant	Concentration (ppbv and ppmv)	Approx. Test Duration (h)*	Inhibition
Arsine, AsH ₃	50, 300, 500 & 1000 ppbv & 1 ppmv	2100 h	Yes
Ammonia, NH ₃	100	500 h	Yes
Ammonium nitrate, NH ₄ NO ₃	50	550 h	Yes
Ammonium hydroxide, NH ₄ OH	100 and 1200 ppmv	2650 h	Yes
Sodium chloride, NaCl	100 and 400 ppmv	600 h	Yes
Potassium nitrate, KNO ₃	10, 100 and 500 ppmv	900 h	only at 500 ppmv
Potassium chloride, KCl	50 and 100 ppmv	400 h	No
Hydrogen chloride, HCl	500 ppbv & 1.0 ppmv	700 h	Yes
Hydrogen bromide, HBr	500 ppbv, 1.0, 10, 20 and 100 ppmv	1400 h	Yes (> 1.0 ppmv)
Hydrofluoric acid, HF	250 and 1000 ppbv and 15 ppmv	500 h	No
Nitric acid, HNO ₃	500 ppbv and 1.0 ppmv		Yes

*cumulative, including baseline tests

5.11. Summary of Long-term Experimental Contaminant Studies on Co-FT Catalyst

The results of the contaminant impact study carried out on the UK-CAER Co-FT catalyst are summarized in Table 20. The results of the bench-scale contaminant experiments clearly established that poisoning of Co-FT synthesis catalysts is very complex and depends upon a number of factors. This makes it a demanding task to define experiments that focus on a specific feature of catalyst poisoning.

It appeared that, irrespective of its source (e.g., NH₃, NH₄OH, NH₄NO₃, KNO₃, or HNO₃), ammonia tended to suppress Co-FT catalyst activity to a moderate degree at all of the concentration levels examined. Neither the mode of deactivation nor the strength of the poisoning effect (e.g., reversibility) is known at this time. For example, the impact of the nitrate ion appeared to be influenced by its ability to undergo hydrogenation to water and ammonia and that its impact was in fact due to the effect of ammonia. Furthermore, the loss of activity of the Co-FT catalyst in clean syngas (no contaminants) due to the accumulation of FTS reaction products made it difficult to know when to begin the poisoning study and how to differentiate between the impact of the contaminants on CO conversion from the normal rate of decline in activity.

6. Long-Term Exposure Tests to Determine the Impact of Contaminants on Iron-based Fischer-Tropsch Synthesis Catalyst

In Task 3 (Subtask 4) of this project, we evaluated the interaction of iron-based Fischer-Tropsch (Fe-FT) synthesis catalysts with several different contaminants; NaCl, KCl, KHCO_3 and NaHCO_3 .

Table 21. Composition of Fischer-Tropsch synthesis catalyst prepared by UK-CAER.

CAER Fe-FT	
Fe_2O_3	92.9%
SiO_2	3.6%
K_2O	1.6%
CuO	1.9%

6.1. Catalyst Preparation and Physical Characterization

A sample of a Fe-FT catalyst made by UK-CAER was used for the bench-scale Fischer-Tropsch synthesis (FTS) contaminant evaluations. The 100Fe:5.1Si:3.0K:2.0Cu catalyst (#GJ-457, UK-CAER high-alpha iron) was prepared by sequential impregnation of iron(III) oxide (Fe_2O_3) with an appropriate amount of solution containing potassium nitrate (KNO_3 , 99.9% purity) and copper nitrate [$\text{Cu}(\text{NO}_3)_2 \cdot 2.5 \text{H}_2\text{O}$, 99.9% purity]. The nominal catalyst composition is provided in Table 21. Further details about the catalyst preparation method can be found elsewhere (Davis, Jacobs et al. 2009). Between each step, the catalyst was dried under vacuum in a rotary evaporator at 80 °C and the temperature was slowly increased to 95 °C. After the second impregnation/drying step, the catalyst was calcined by Süd-Chemie, Inc. researchers under flowing air at 350 °C for 4 h. The BET surface area of the as-prepared catalyst was measured to be 107 m^2/g , and single point pore volume and pore diameter were determined to be 0.15 cm^3/g and 6.0 nm.

6.2. Establishment of Baseline Fe-FT Catalyst Testing Conditions

A 1 liter continuous stirred tank reactor (CSTR) was used to evaluate the FT catalyst. We mixed 13 g of the catalyst with 200 g of melted Polywax 3000 diluent in the CSTR. The stirring speed was set at 750 rpm and the reactor pressure was increased to 300 psig with 40% CO in N_2 at a GHSV of 12 SL/h/g catalyst. The reactor temperature was increased to 280 °C with the bed temperature maintained at 265 °C for 24 h. After this initial catalyst activation period, the catalyst bed temperature was maintained at 240 °C. Table 22 lists the gas composition used for the baseline and contaminant tests (these conditions were predetermined based on DOE

Table 22. Syngas composition used to test Fe-FT catalyst.

Fe-FT Gas Composition	
CO	55.6%
H_2	42.8%
CO_2	1.3%
CH_4	0.3%
H_2O	0%
Pressure (psig)	300
Temperature (°C)	240

guidance) and this composition was approximated in this test by feeding the CSTR with a constant gas flow of H_2 :CO in a 2:1 ratio. The reactor was also equipped with a port for sampling the liquids/wax that contained higher carbon number hydrocarbons. Liquid samples were periodically collected from the condensers, the water (aqueous) and the organic layers were then separated and analyzed in a GC-MS. Liquid samples were collected periodically after steady state was established. The analysis of the gas phase products was accomplished with an IR analyzer (NOVA) capable of detecting H_2 , CO, CO_2 and CH_4 , and a GC equipped with an FID that was capable of detecting C1–C7 hydrocarbons, as illustrated in Figure 75. The liquid-phase FTS products were condensed out of the gaseous effluent into two condensers maintained at different temperatures.

Figure 75. Sample GC results from the baseline Fe-FT catalyst test.

We first conducted baseline evaluations to measure the catalyst performance in the absence of any contaminants to establish a benchmark against which the effects of potential poisons could be assessed. The baseline tests were conducted on the Fe-FT catalyst at 240 °C. The first test reached steady-state after 20 h and the CO conversion leveled off during the remainder of the test, as shown in Figure 76. The FT-liquids product distribution (FT rate = 0.613 g/h or 0.044 mol CH_2/h) for another baseline test (33 h) is shown in Figure 77. Lower levels of CO_2 (< 3%) and CH_4 (< 1%) in the effluent gas indicated that most of the 40% CO that was fed was converted into FT products. Liquid samples were collected periodically at steady-state to analyze the FT product distribution using a GC-MS, as illustrated in Figure 77.

The extended baseline test shown in Figure 78 demonstrated that at least 40 h was needed to reach steady state in the CSTR during FT synthesis. The FT-liquid product distribution (FT rate = 0.57

Figure 76. Baseline Fe-FT catalyst test at 240 °C.

g/h or 0.041 mol CH₂/h) is shown in Figure 79. Hence, the minimum duration for the baseline test was fixed at 40 h, followed by an additional 100 h to assess the impact of the contaminant, then another 40 h without the contaminant to determine its permanent impact as evidenced by any changes in performance. The Fe-FT catalyst attained 49% CO conversion with 3.4% CO₂ and 1.1% CH₄ in the gas phase product. The FT-liquid product distribution for Fe-FT catalyst at 240 °C is shown in Figure 79 (FT rate = 0.57 g/h or 0.041 mol CH₂/h).

6.3. Experimental Protocol for Fe-FT Catalyst-Contaminant Testing

The 100Fe:5.1Si:3.0K:2.0Cu catalyst was activated *in-situ* in a continuously-stirred tank reactor (CSTR) under the conditions of 2.0 NL/g-cat/h CO, 270 °C and 1 atm for 24 h. The FTS reaction was carried out on Fe-FT catalyst at UK-CAER using two sets of conditions: 270 °C, 10.0 NL/g-cat/h, 1.31 MPa, and a H₂/CO ratio of 0.77, or 260 °C, 10.0 NL/g-cat/h, 1.31 MPa, and a H₂/CO ratio of 0.67. An aqueous solution containing a specific concentration of each contaminant was fed into the CSTR using a precision syringe pump (ISCO 500D) after steady state was established, usually between 90 and 120 h on stream depending on the temperature used. We investigated the changes in CO conversion (defined previously, by equations 5.1-5.6).

To determine if any of the contaminant ions (Na⁺, K⁺, and Cl⁻) were retained on the Fe-FT catalyst surface during FTS, some of the slurry from the reactor containing Fe-FT catalyst was washed several times with hot o-xylene to remove slurry residues from the catalyst surface, and then analyzed using ICP. A portion of the water, oil and wax products that accumulated during FTS was periodically collected and analyzed

Figure 77. FT-liquids product distribution for Fe-FT catalyst at 240 °C (FT rate = 0.613 g/h or 0.044 mol CH₂/h).

Figure 78. Baseline Fe-FT catalyst test at 240 °C.

Figure 79. FT liquid product distribution for Fe-FT catalyst at 240 °C; FT rate = 0.57 g/h or 0.041 mol CH₂/h.

by ICP during high-concentration contaminant testing (e.g., in the 20-100 ppm range) to determine if the contaminant was being adsorbed by the catalyst.

6.4. Impact of KCl and NaCl on Fe-FT Catalyst

The sensitivity of the Fe-FT catalyst to 400 ppbw KCl or, in a separate study, 400 ppbw NaCl in the syngas feed, was evaluated at 270 °C. No significant impact on the catalyst behavior was observed for either contaminant. As shown in Figure 80a-d, the CO conversion decreased slightly during exposure to the contaminant containing solutions, but the slopes of the curves following contaminant addition were essentially the same as that of baseline catalyst deactivation rate during the first 120-168 h of baseline testing. The catalyst selectivities to CH₄,

Figure 80. Impact of alkali halides (KCl and NaCl) on Fe-FT catalyst: (a) CO conversion, (b) CH₄ and C₅₊ selectivities (c) CO₂ selectivity, and (d) C₄ olefin selectivity. Test conditions: 270 °C, 1.31 MPa (CO+H₂), H₂/CO = 0.77, SV_{CO+H₂} = 10 NL/g-cat/h.

C₅₊, and C₄ and C₁₋₄ olefins, reported in Figure 80b-d, were nearly identical before and after adding 100 ppbw and 400 ppbw of either contaminant. The CO₂ selectivity (Figure 80c) increased slightly after feeding KCl or NaCl solutions, which was likely due to enhanced WGS activity because of the additional aqueous solution.

The above tests were run under the conditions of 270 °C and 10 NL/g-cat/h and lasted about 400 h before being terminated due to wax accumulation in the reactor. To obtain further information about the sensitivity of the Fe-FT catalyst to KCl or NaCl contaminants, longer tests run at higher concentration levels were required. Consequently, we conducted long-term tests with 100 ppbw and 20 ppmw KCl or 0.1, 0.25-5, 30, and 100 ppmw NaCl at 260 °C, as shown in

Figure 81a-d. The Fe-Ft catalyst reached a stable CO conversion of 59% after about 120 h at 260 °C (Figure 81a). The experiment was continued at steady state which for the next 90 h before 0.1 ppmw KCl was added at 210 h. During 140 h of testing at this concentration, the catalyst activity was very stable, and the selectivities to CH₄ (~2.1%), C₅₊ (86.5%), and C₄ (86.2%) and C₁₋₄ olefins (total C₄ olefins = 87%), were nearly constant (Figure 81b-d), albeit with a slight increase in CO₂ selectivity (46.8 to 47.8%). The test was run for another 100 h after the KCl concentration in the syngas was increased to 20 ppmw, and the catalyst activity and

Figure 81. Effect of alkali halides (KCl and NaCl) on Fe-FT catalyst: (a) CO conversion, (b) CH₄ and C₅₊ selectivities (c) CO₂ selectivity and (d) C₄ olefin selectivity. Test conditions: 260 °C, 1.31 MPa (CO+H₂), H₂/CO = 0.67, SV_{CO+H₂} = 10 NL/g-cat/h.

selectivity essentially remained unchanged. These results are consistent with the results obtained at 270 °C, further indicating that even concentrations as high as 20 ppmw KCl did not significantly deactivate the Fe catalyst, at least during this timeframe.

The sensitivity of the Fe-FT catalyst to NaCl was also studied during a longer test run at 260 °C. Seven different NaCl concentrations in the syngas feed (e.g., 0.1, 0.25, 0.75, 1.5, 5, 30 and 100 ppmw) were examined in an almost 1500-h-long test run, as also presented in Figure 81a-d. The test duration at each concentration was in the range of 72-144 h. The Fe-FT catalyst activity and selectivities did not change during the addition of 0.1 ppmw (during hours 190 to 384) or 0.25 ppmw NaCl (during hours 384 to 456), which is consistent with the results obtained at 270 °C. However, the catalyst displayed a slight, but steady deactivation rate between hours 456 and 578 h when 0.75 ppm NaCl was added, as evidenced by the decrease in CO conversion (the data for 0.25-5.0 ppmw was lumped together in Figure 81a). Since this

deactivation induced by the relatively low contaminant concentration was suspect (as the steady deactivation rate could have originated from other unknown factors such as upsets occurring during the run or variation in the flow rate from the liquid pump) the addition of NaCl solution was suspended between hours 578 and 650 h to establish a new baseline conversion of approximately 46%. A feed concentration of 0.75 ppmw NaCl in the syngas was resumed at hour 650, and the catalyst did not show any measurable catalyst deactivation in terms of both CO conversion and its selectivity to CO₂, CH₄, and C₅₊ and C₄ olefins for the next 144 h.

After 793 h, the NaCl concentration in the syngas feed was increased from 1.5 up to 100 ppmw. Interestingly, the addition of 1.5-30 ppmw NaCl for 530 h (hours 793 to 1323) did not result in any significant change in the activity of the Fe-FT catalyst or its selectivity to CH₄, C₅₊, or C₄ olefins. However, CO₂ selectivity was not stable and fluctuated from 41 to 46% at 790-1200 h; after that, it stabilized at about 46%. With the introduction of 100 ppm NaCl into the syngas at 1323 h, a slow decrease in the rate of CO conversion occurred. Therefore, the results at 260 °C again suggest that the UK-CAER high-alpha Fe catalyst is not sensitive to KCl and NaCl poisons. Only when the concentration in syngas was relatively high (e.g., 100 ppm) was it observed to slowly deactivate the Fe-FT catalyst.

6.5. Impact of KHCO₃ and NaHCO₃ on Fe-FT Catalyst

The sensitivity of the Fe-FT catalyst to up to 40 ppmw KHCO₃ or 40 ppmw NaHCO₃ in the syngas feed was evaluated at 270 °C for about 300 h. Comparing the slopes of CO conversion obtained during contaminant exposure to the conversion during the baseline period of the test (Figure 82a-d), co-feeding either 400 ppbw KHCO₃ or 400 ppbw NaHCO₃ with the syngas feed did not measurably influence the behavior of the catalyst. However, when the concentration was increased to 40 ppmw for either contaminant, the catalyst activity decreased slightly; however, the decreases observed were essentially equivalent to the rate of activity decline prior to feeding the salt solutions. This implies that neither KHCO₃ nor NaHCO₃ added to the feed in concentrations up to 40 ppmw significantly changed or diminished the activity of the Fe-FT catalyst.

The selectivity of the Fe-FT catalyst to CH₄, C₅₊, and C₄ and C₁₋₄ olefins was nearly identical before and after adding concentration levels of either 100 ppbw, 400 ppbw, or 40 ppmw KHCO₃ or NaHCO₃ contaminants, as evident in Figure 82b-d. Slightly higher C₄ olefin selectivity at the end of both runs might have been caused by the accumulation of heavy hydrocarbons in the reactor. Similar to the effects of KCl and NaCl addition discussed previously, the CO₂ selectivity increased slightly after feeding KHCO₃ or NaHCO₃ solutions (Figure 82c), which was again likely due to an enhancement in the WGS activity by added water.

Figure 82. Effect of alkali compounds (KHCO₃ or NaHCO₃) on Fe-FT catalyst: (a) CO conversion, (b) CH₄ and C₅₊ selectivities, (c) CO₂ selectivity, and (d) C₄ olefin selectivity. Test conditions: 270 °C, 1.31MPa (CO+H₂), H₂/CO = 0.77, SV_{CO+H₂} = 10 NL/g-cat/h.

6.6. Summary of Long-term Experimental Contaminant Studies on Fe-FT Catalyst

The effect of NaCl, KCl, NaHCO₃ and KHCO₃ (0.1- 100 ppmw) contaminants co-fed with syngas on the performance of the UK-CAER high- α Fe-FT catalyst was studied at 260 and 270 °C. An aqueous solution of each alkali compound, including chloride salts and bicarbonates, was injected into the reactor as the source of contaminant ions in syngas. The contaminants included in this study had no significant impact on the Fe-FT catalyst. The activity and hydrocarbon selectivities of the catalyst did not significantly change while Na, K, Cl ions were continuously fed during tests that lasted between 72-144 h. The activity and selectivity results for the FTS reaction indicated that there was essentially no effect on the Fe-FT catalyst activity and selectivity when up to 100 ppmw halide compounds (NaCl and KCl), or up to 40 ppmw alkali bicarbonates (NaHCO₃ and KHCO₃) were co-fed with the syngas feed at both 260 °C and 270 °C. This suggests that the neither the alkali ions (i.e., Na⁺ or K⁺) nor chloride ion (Cl⁻) adsorbed strongly on the catalyst surface to deactivate it during the FTS reaction in the CSTR, (if they are assumed to physically block the Fe active sites or change the electronic character of the Fe-FT catalyst). The tested catalysts were subjected to elemental analysis using ICP as described in the following chapter on Catalyst Characterization.

The contaminants could have theoretically reached concentrations of 0.4-1.5 wt% in the catalyst if all of them were retained during testing. However, the ICP results suggested that only small

quantities of the contaminant ions (Na, K or Cl) adsorbed onto the catalyst. This explains why essentially no changes in catalyst activity or selectivity were observed during the FTS experiments that were conducted in the presence of each contaminant.

ICP analysis of FTS products indicated that contaminant ions (Na, K or Cl) were present in all of the FTS product phases (i.e., water, oil and wax). These results differed somewhat from one sample to another, but the results showed that the ions were mainly retained in the reactor in the wax (>90%). The remaining ions were distributed rather equally in the oil- and aqueous-phase FTS products. The CO₂ selectivity of the Fe-FT catalyst increased slightly after injecting the aqueous contaminant solutions, which was likely due to water enhancing the water-gas shift reaction.

7. Catalyst Characterization

In Task 4, the long-term catalyst experiments were supported with extensive characterization of the catalyst samples both before and after testing to identify any physical and chemical changes that occurred due to catalyst-contaminant interactions. These catalyst characterization studies that proceeded after the bench-scale experiments helped us to develop a fundamental understanding of the degradation mechanisms induced by the contaminants. The post experimental analyses also revealed information about the accumulation of impurities on the catalysts and the related changes in the physical properties (e.g., surface area, porosity and mechanical strength) and chemical characteristics (e.g., structure, phases, and composition).

Both TDA Research and UK-CAER carried out analyses of fresh (as-prepared or received) and tested WGS and FT catalyst samples using techniques such as XRD, ICP-AA, chromatography, and BET (i.e., surface area and porosity). After the long-term syngas-contaminant tests, the UK-CAER team conducted an extensive elemental composition characterization study of the contaminants adsorbed on the 15 tested LT- and HT-WGS catalyst samples, which are listed in Table 23. Both of the reference catalysts (Samples #1 and #2 correspond to as-received untested Shiftmax 120 and Shiftmax 230 catalysts) and samples of the used catalysts after the long-term syngas-contaminant tests were examined. Pictures of the fresh and tested (with HCN and AsH₃) LT-WGS catalysts are shown in Figure 83.

7.1. Catalyst Characterization Analytical Tools

The catalyst materials used in the bench-scale tests were extensively characterized using the following analytical methods and instruments so that we could draw conclusions about the deactivation mechanisms and identify the nature of the contaminant-catalyst interactions.

7.1.1. Surface Area and Porosity

The surface areas of both the untested and tested catalysts were measured using the Brunauer-Emmett-Teller (BET) method in a Micromeritics 2300E Gemini FlowSorb instrument. We used nitrogen as an adsorbate at liquid nitrogen temperatures (roughly -196 °C).

Table 23. Description of tested LT- and HT-WGS catalyst samples and elements analyzed by UK-CAER.

#	Sample Description Provided by TDA Research, Inc.	Elements analyzed by UK-CAER
1	Shiftmax 120 catalyst	Fe, Cu, S, K, Na, P, As, Cl, C, H, N
2	Shiftmax 230 catalyst	Fe, Cu, S, K, Na, P, As, Cl, C, H, N
3	Shiftmax 120 + H ₂ S	Fe, Cu, S, K, Na, P, As, C, H, N
4	Shiftmax 120 + NaCl	Fe, Cu, S, K, Na, P, As, Cl
5	Shiftmax 120 + NH ₃	Fe, Cu, S, K, Na, P, As, C, H, N
6	Shiftmax 120 + PH ₃	Fe, Cu, S, K, Na, P, As, C, H, N
7	Shiftmax 120 + HCN	Fe, Cu, S, K, Na, P, As, C, H, N
8	Shiftmax 120 + KCl	Fe, Cu, S, K, Na, P, As, Cl
9	Shiftmax 120 + AsH ₃	Fe, Cu, S, K, Na, P, As, C, H, N
10	Shiftmax 230 + H ₂ S	Fe, Cu, S, K, Na, P, As, C, H, N
11	Shiftmax 230 + NaCl	Fe, Cu, S, K, Na, P, As, Cl
12	Shiftmax 230 + NH ₃ + H ₂ S	Fe, Cu, S, K, Na, P, As, C, H, N
13	Shiftmax 230 + PH ₃	Fe, Cu, S, K, Na, P, As, C, H, N
14	Shiftmax 230 + HCN	Fe, Cu, S, K, Na, P, As, C, H, N
15	Shiftmax 230 + AsH ₃	Fe, Cu, S, K, Na, P, As, C, H, N

Figure 83. Pictures of fresh and tested LT-WGS catalysts (ShiftMax 230, Süd-Chemie).

7.1.2. X-ray Diffraction (XRD)

XRD was used to determine the phases present in both the untested and tested catalysts and to evaluate the changes in composition compared to the untested materials. Bulk formation of chemical structures was also measured by post-test XRD analysis.

7.1.3. Inductively Coupled Plasma Atomic Absorption (ICP-AA) Spectroscopy

ICP-AA spectroscopy was used to determine the bulk chemical composition of both the untested and tested catalysts. Metal and metalloid (Fe, Cu, K, Na, P, and As) contents were determined using a modified ASTM D 6349 procedure. The samples were digested using a combination of acids followed by analysis of the solution using a Varian 720 ICP unit at UK-CAER. Selected samples were also sent to an independent laboratory (Hazen Research, Golden, Colorado) for elemental chemical analysis.

7.1.4. Chlorine Analysis

Where applicable, chlorine content was determined using a modified ASTM D 4208 procedure. The sample was combusted in an oxygen bomb followed by injection into a Dionex Ion Chromatograph.

7.1.5. Carbon, Hydrogen, and Nitrogen Analysis

For appropriate samples, the carbon, hydrogen, and nitrogen contents were determined using ASTM procedure ASTM D 3176 and a Leco CHN 628 unit.

7.2. Catalyst Surface Area and Porosity

Catalyst samples were evaluated with BET surface area and pore size measurements after both single and combined contaminant tests in syngas containing H_2S and NH_3 . Table 24 shows the 42-point BET surface areas, and pore volumes and diameters for fresh LT- and HT-WGS catalysts compared to the results for these catalysts exposed to NH_3 and H_2S , either in single or binary contaminant tests. All of the catalyst-contaminant tests resulted in a substantial decrease in all three parameters; BET surface area, pore volume, and pore diameter. These reductions were probably due to sintering and pore filling by the impurity, especially in the case of sulfur. The BET parameters determined for the fresh Fe-FT catalyst are also listed in Table 24.

Table 24. Physical characteristics of fresh and tested LT-WGS, HT-WGS, and Fe-FT catalysts.

Catalyst Sample	Contaminant	BET Surface Area (m ² /g)	Pore Volume (cm ³ /g)	Pore Diameter (nm)
LT-WGS (Shiftmax 230)	500 ppm H ₂ S	25.25	0.100	15.9
LT-WGS (Shiftmax 230)	H ₂ S & NH ₃ [†]	44.40	0.243	21.9
LT-WGS (Shiftmax 230)	fresh	93.09	2.457	105.6
LT-WGS (Shiftmax 230)	85 ppmv NH ₃	22.91	0.216	37.7
LT-WGS (Shiftmax 230)	85 ppmv H ₂ S	32.49	0.177	21.8
HT-WGS (ShiftMax 120)	fresh	97.2	0.042	1.74
HT-WGS (ShiftMax 120)	10 ppm H ₂ S	79.3	0.324	16.8
Fe-FT (UK-CAER)	fresh	107	0.15	6.0

[†]38 ppmv NH₃ and 60 ppmv H₂S

7.3. X-ray Diffraction

As shown in Figure 84, samples of the HT-WGS catalyst (Shiftmax 120) were evaluated by XRD after testing in syngas that contained 1 ppmv PH₃, or 2 ppmv H₂S, or both H₂S (60 ppmv) and NH₃ (38 ppmv). The XRD pattern for fresh HT-WGS catalyst is shown for comparison. The peaks became sharper and more narrow during testing, which is indicative of sintering and grain growth. The concentration of any new phases that may have formed were too low to detect.

Figure 84. XRD patterns for fresh HT-WGS catalyst (ShiftMax 120, Süd-Chemie), and HT-WGS catalyst tested in syngas that contained 1 ppmv PH₃, or 2 ppmv H₂S, or a mixture of NH₃ (38 ppmv) and H₂S (60 ppmv) at 350 °C and 400 psig. GHSV = 12,000 h⁻¹. Feed: 26.8% CO, 12.3% CO₂, 20.6% H₂, 3.3% N₂, 37% H₂O, and the contaminant(s).

Figure 85. XRD patterns for fresh LT-WGS catalyst (ShiftMax 230, Süd-Chemie) and LT-WGS catalyst tested in syngas that contained 85 ppmv NH₃, or 88 ppmv H₂S, or a mixture of NH₃ (38 ppmv) and H₂S (60 ppmv) at 350 °C and 400 psig. GHSV = 6000-12,000 h⁻¹. Feed: 26.8% CO, 12.3% CO₂, 20.6% H₂, 3.3% N₂, 37% H₂O, and the contaminant(s).

XRD results are shown in Figure 85 for the LT-WGS catalyst (Shiftmax 230) after testing in syngas that contained either 3-33 ppmv NH₃ or 0-88 ppmv H₂S. The XRD pattern for fresh HT-WGS catalyst is shown for comparison. A few unidentified new phases appeared during testing, with significant differences apparent between the catalyst tested in NH₃ versus H₂S. The peaks became sharper and more narrow during testing, which is indicative of grain growth and the large semi-amorphous peaks between 35-40° 2θ for the fresh catalyst almost disappeared for the catalyst tested in H₂S. In contrast, for the catalyst tested in NH₃, the peaks between 35-40° 2θ became more resolved and crystalline.

Figure 86 compares the XRD patterns for two different Shiftmax 230 tests at low (60 ppmv) and high (500 ppmv) H₂S concentrations in a binary H₂S and NH₃ (38 ppmv) syngas-contaminant mixture. The patterns for the tested catalysts show several distinct new peaks compared to the XRD pattern for the fresh catalyst. The additional small peaks at ~30° and between 45-50° 2θ on the catalysts exposed to H₂S are most likely sulfides, and as previously noted the large semi-amorphous peaks between 35-40° 2θ for the fresh catalyst are almost gone in the tested samples. There are also some subtle differences in the peak shapes between catalyst tests at low and high H₂S concentrations.

Figure 87 shows an XRD pattern for the fresh UK-CAER Fe-FT synthesis catalyst. The broad, low-intensity peaks indicate that the material was primarily nanocrystalline and amorphous prior to testing.

Figure 86. XRD patterns for fresh LT-WGS catalyst (ShiftMax 230, Süd-Chemie) and LT-WGS, exposed to H₂S + NH₃ at 240 °C and 400 psig. GHSV = 12,000 h⁻¹. Feed: 4.5% CO, 34.4% CO₂, 43.2% H₂, 2.9% N₂, 15% H₂O, and 38 ppmv NH₃ and 60 or 500 ppmv H₂S.

Figure 87. XRD pattern for fresh Fe-FT catalyst (UK-CAER).

7.4. Elemental Analysis

7.4.1. Fresh and Contaminated WGS Catalysts

The findings from the ICP-AA spectroscopy and other elemental analyses methods (e.g., chromatography) on the WGS catalyst samples that were exposed to contaminants during the long-term tests are reported in Table 25. Samples of fresh (as-prepared) and tested HT- and LT-WGS catalysts were analyzed for all of the elements of interest (i.e., Fe, Cu, S, K, Na, P, As, Cl, C, H, and N) to provide reference levels for comparison with the catalysts subjected to contaminant addition.

For the Fe-based Shiftmax 120 HT-WGS catalyst, the catalysts that were subjected to testing in syngas with co-fed contaminants displayed higher concentrations of the elements that composed that contaminant relative to the baseline catalyst composition in the cases of H₂S (484 ppm sulfur compared to 132 ppm sulfur in the fresh catalyst), NaCl (9.51% sodium compared to 488 ppm and 9.65% chlorine compared to 0.13%), PH₃ (0.44% phosphorus compared to 196 ppm), KCl (8.67% potassium compared to 52 ppm and 6.05% chlorine compared to 0.13%), and AsH₃ (1819 ppm arsenic compared to 11 ppm). However, in the case of NH₃ contaminant testing (0.27% nitrogen compared to 0.32% and 0.63% hydrogen compared to 0.82%) and HCN (4.55% carbon compared to 9.14%, 0.59% hydrogen compared to 0.82%, and 0.28% nitrogen compared to 0.32%) the results indicated either no measurable increase in the concentration of the contaminant in question, or a decrease in concentration (e.g., C with HCN) within the limits of experimental error for the analysis technique.

For the Cu-based LT-WGS catalyst (Shiftmax 230), the samples of catalyst that were subjected to contaminant exposure testing also contained higher concentrations of the elements that compose the contaminant of interest relative to the baseline catalyst in the cases of H₂S (2.37% sulfur relative to 84 ppm in the fresh catalyst), NaCl (8.83% sodium relative to 397 ppm and 15.6% chlorine relative to 0.08%), NH₃+ H₂S (3.02% sulfur relative to 84 ppm), and AsH₃ (259 ppm arsenic relative to 9 ppm). However, in the cases of NH₃ + H₂S addition (0.12% nitrogen relative to 0.28% and 0.17% hydrogen relative to 0.91%), PH₃ addition (phosphorus <1 ppm relative to 196 ppm) and HCN addition (4.82% carbon relative to 5.71%, 0.92% hydrogen relative to 0.91%, and 0.22% nitrogen relative to 0.28%) the results indicated no measurable increase in the concentration of the contaminant in question within the limits of experimental error for the analysis technique.

ICP and chromatographic analyses of the HT- and LT-WGS catalysts exposed to the alkali contaminants (i.e., Na⁺ and K⁺) showed much higher levels of these residual metals after testing compared to the other contaminants since each of the alkalis was introduced by mixing its crystalline powder directly with the catalyst rather than feeding it into the catalyst bed in the gas phase.

Table 25. Elemental analyses of fresh and tested catalyst samples by UK-CAER.

#	Sample Description	Fe (%)	Cu (%)	S (ppm)	K (ppm)	Na (ppm)	P (ppm)	As (ppm)	Cl (%)	C (%)	H (%)	N (%)
1	Shiftmax 120 catalyst	27.17	1.68	132 ppm	52 ppm	488 ppm	196 ppm	11	0.13	9.14	0.82	0.32
2	Shiftmax 230 catalyst	0.7	43.03	84 ppm	53 ppm	397 ppm	<1 ppm	9	0.08	5.71	0.91	0.28
3	Shiftmax 120 + H ₂ S	25.77	1.68	484 ppm	88 ppm	537 ppm	364 ppm	81		19.82	0.74	0.42
4	Shiftmax 120 + NaCl	29.9	1.78	125 ppm	135 ppm	9.51%	136 ppm	19	9.65			
5	Shiftmax 120 + NH ₃	27.99	1.69	484 ppm	104 ppm	345 ppm	429 ppm	624		7.31	0.63	0.27
6	Shiftmax 120 + PH ₃	34.41	1.73	425 ppm	55 ppm	546 ppm	0.44%	11		4.4	0.71	0.2
7	Shiftmax 120 + HCN	27.05	1.69	401 ppm	253 ppm	634 ppm	205 ppm	16		4.55	0.59	0.28
8	Shiftmax 120 + KCl	24.09	1.54	196 ppm	8.67%	562.4 ppm	173 ppm	9	6.05			
9	Shiftmax 120 + AsH ₃	30.85	2.03	349 ppm	73 ppm	219 ppm	254 ppm	1819		6.27	0.1	0.18
10	Shiftmax 230 + H ₂ S	0.4	38.25	2.37%	47 ppm	348 ppm	<1 ppm	11		4.71	0.61	0.19
11	Shiftmax 230 + NaCl	0.56	27.03	77 ppm	66 ppm	8.83%	<1 ppm	6	15.6			
12	Shiftmax 230 + NH ₃ + H ₂ S	0.19	56.1	3.02%	29 ppm	218 ppm	<1 ppm	28		4.61	0.17	0.12
13	Shiftmax 230 + PH ₃	0.44	45.85	156 ppm	49 ppm	383 ppm	<1 ppm	11		5.16	0.69	0.2
14	Shiftmax 230 + HCN	0.93	43.88	499 ppm	252 ppm	478 ppm	<1 ppm	12		4.82	0.92	0.22
15	Shiftmax 230 + AsH ₃	0.59	39.72	334 ppm	69 ppm	330 ppm	<1 ppm	259		6.07	0.81	0.26

Table 26. Concentrations of contaminant ions on the Fe-FT catalyst surface after testing.

Poisons	Theoretical value ^(a) , %			Experimental value ^(b) , ppm		
	Na ⁺	Extra K ⁺	Cl ⁻	Na ⁺	Extra K ⁺	Cl ⁻
0.1-40 ppm NaHCO ₃ (361 h)	0.40			302		
0.1-40 ppm KHCO ₃ (392 h)		1.51			400	
0.1-20 ppm KCl (451 h)		0.80	0.73		800	111
0.1-100 ppm NaCl (1468 h)	5.90		9.10	n/a		n/a

(a) assuming all poisons fed into the CSTR during testing were adsorbed onto or reacted with the Fe-FT catalyst

(b) measured by ICP

Table 27. Concentration of contaminant ions in the Fe-FT synthesis products measured by ICP.

Time, h	Poison concentration in syngas, ppm	Ion concentration by ICP, ppm		
		Water	Oil	Wax accumulated in reactor)
NaCl test run (Na/Cl ions) ⁽¹⁾				
1,295	30.0	2.5/84	37/110	19/30
1,373	100.0	1.8/90	33/176	91/128
KCl test run (K/Cl ions) ⁽¹⁾				
382	20.0	0.3/45	35/34	46/157
429	20.0	0.3/40	22/32	44/117
NaHCO ₃ test run (Na ions) ⁽¹⁾				
361	40.0	0.9	34	62
KHCO ₃ test run (K ions)				
391	40.0	2.1	26	94

(1) A material balance on the Na and K ions fell between the range of 90- 150%.

Table 28. Distribution of contaminant ions in the Fe-FT synthesis products.

Time, h	Na ion in H ₂ O phase, %	Na ion in oil phase, %	Na ion in wax phase, %	K ion in H ₂ O phase, %	K ion in oil phase, %	K ion in wax phase, %	Cl ion in H ₂ O phase, %	Cl ion in oil phase, %	Cl ion in wax phase, %
NaCl test run (0.1-100 ppm in feed)									
1295	0.56	9.24	90.21				9.89	14.56	75.54
1373	0.11	2.23	97.66				3.58	7.68	88.74
KCl test run (0.1-20 ppm in feed)									
382				0.04	7.89	92.07	1.78	2.34	95.88
429				0.04	5.43	94.53	2.13	2.98	94.89
NaHCO ₃ test run (0.1-40 ppm in feed)									
361	0.09	6.15	93.75						
KHCO ₃ test run (0.1-40 ppm in feed)									
391				0.20	3.93	95.86			

7.4.2. Fresh and Contaminated FTS Catalysts

To determine if contaminant ions (e.g., Na⁺, K⁺, and Cl⁻) were retained on the surface of the Fe-FT catalyst during FTS, some of the slurry from the reactor containing Fe-FT catalyst was washed several times with hot o-xylene to remove slurry residue from the catalyst's surface and then analyzed using ICP. The results of these elemental analyses are summarized in Table 26. A portion of the water, oil and wax products that accumulated during FTS was also periodically

collected and analyzed by ICP during high-concentration contaminant testing (e.g., in the 20-100 ppmw range) to determine if the contaminant was being adsorbed by the catalyst. The calculated theoretical maximum concentrations of Na^+ , K^+ or Cl^- on the surface of the Fe-FT catalyst (assuming that all of the contaminant(s) fed during the test was adsorbed and retained by the Fe-FT catalyst) are also provided in the table for comparison. The results of the elemental analyses indicated that only small quantities of these contaminant ions adsorbed onto the surface of the catalyst during testing. However, the concentrations of contaminants on the Fe-FT catalyst could have theoretically reached 0.4-1.5 wt.% if the entire quantity fed was adsorbed and retained by the catalyst during testing. This explains why essentially no changes in catalyst activity or selectivity were observed during the Fe-FT catalyst experiments that were conducted in the presence of these contaminants.

After the long-term FTS runs that examined the impact of 0-40 ppmw NaHCO_3 or KHCO_3 on the Fe-FT catalyst, the theoretical maximum concentrations of Na^+ and K^+ ions adsorbed on catalyst were calculated to be 0.4% and 1.51% by the end of testing (after 361 or 392 h). However, the elemental analyses results determined that only 300-400 ppmw Na^+ or K^+ ions were present on the Fe-FT catalyst surface, which is only 2.6-7.6% of the calculated maximum theoretical values. These results clearly indicate that the uptake of contaminants by the Fe-FT catalyst under FTS conditions was very low, which is consistent with the FTS reaction results discussed above.

Similar results were obtained for the Fe-FT catalyst after the KCl test. The concentrations of K^+ and Cl^- in the Fe-FT catalyst after testing were 800 and 111 ppm, which are just 1.5-10% of the calculated maximum theoretical values. Note that the K^+ concentrations measured by ICP listed in Table 26 are referred to as 'extra' because they were obtained by subtracting the concentration of K^+ measured in the fresh catalyst (without exposure to KCl) from the concentration in the catalyst tested with the contaminant. For the Fe-FT catalyst sample after the NaCl test run, the ICP results shown neglect Na^+ or Cl^- ions on the catalyst surface, even if the calculated concentrations are as high as 5.9 or 9.1%, respectively. This could be due to the small amounts of samples obtained following o-xylene washing and extraction for this run, which could have resulted in a larger analysis error.

7.4.3. Contaminants in the FTS Products

ICP analysis was performed to measure the concentrations of contaminant ions (e.g., Na^+ , K^+ or Cl^-) in the FTS products (i.e., water, oil and wax) and the results are listed in Table 27. It is interesting that Na^+ , K^+ or Cl^- ions were detected in all phases of the FTS products from the four contaminant test runs on the Fe-FT catalyst. However, from the data shown in Table 28, most of the contaminant ions were retained in the slurry in the reactor (>90% in most cases), with the remaining (<10%) distributed between the oil- and aqueous-phases. This further suggests that the contaminant ions injected online into the CSTR reactor in the aqueous solution did not strongly adsorb on the Fe-FT catalyst surface under slurry FTS conditions, and that their impact on catalyst behavior could differ compared to the addition of trace amounts of these contaminants directly onto the catalyst or fed in the syngas.

Furthermore, Table 28 indicates that the concentrations of Cl^- ions present in the aqueous and oil phases were similar at about 2-10%. The concentrations of Na^+ and K^+ ions detected in the oil phase were similar to that of the Cl^- ion; however, the concentrations of Na^+ and K^+ ions in the aqueous phase were quite small (<1%), although the reasons for this are not well understood. One possibility is that the alkali ions could potentially adhere more easily to hydrocarbons (or more likely the oxygenates) than Cl^- ions.

Closure of the mass balances for the contaminant ions was quite challenging because of inherent errors in the analytical instruments and methods used to measure the concentrations of these trace impurities and the relatively few number of samples which were collected. Nevertheless, the material balance closure for Na^+ or K^+ were calculated and found to fall within 90-150%, which may be attributed primarily to the errors caused by the large dilution factors used in the ICP analysis of the different samples. The mass balance closure ranges for the contaminant ions were relatively large as compared to those for the elemental C, H and O species in the FTS reaction products, which usually fell within 98-101%. However, considering that we were dealing with trace quantities of contaminant ions, the errors encountered in this study should not impact the conclusions discussed above.

8. Techno-economic Trade-off Study

In Task 5 of this project, we carried out an assessment of the economic trade-off between catalyst deactivation by the contaminants in coal-biomass derived syngas and the cost of a warm-gas cleanup system to protect the catalysts based on the long-term catalyst-contaminant test results of Task 3. In commercial operation, catalysts are replaced (or regenerated) after a certain operational period. The requirement for syngas cleaning is therefore based on economic considerations: investment in syngas cleaning versus accepting decreased production due to poisoning of the catalyst. In this task, a system analysis was carried out to identify the critical deactivation rates for each catalyst-contaminant pair that would trigger the installation of a syngas clean-up and purification system.

This system analysis took several critical factors into consideration that could impact the process economics and the decision making process; the catalyst poisoning rates derived from the experimental studies, the cost of the FT and WGS catalysts, the cost of catalyst replacement, the cost of spent catalyst disposal or recycling, labor rates, and the loss of revenue due to reduced production rates and reactor downtime. This was simplified by calculating the replacement rate for the WGS and FT catalysts when no guard bed is used against the replacement rate when there are no contaminants present in the syngas feed (the normal deactivation rate). The cost of the guard beds (cleanup beds) are expected to be less than 50% of the annual catalyst replacement costs. The ratio of the cost of warm-gas sulfur removal sorbent to sour shift catalyst is less than 50% (DOE/NETL-2010-1397 and DOE/NETL-PED-IGCC-98-002).

The results of the long-term bench-scale tests were used to determine the rate of deactivation for each catalyst-contaminant pair. The deactivation rate for each contaminant was calculated based on the increase in CO concentration in the product gas: the difference between the absolute percentage change (on a dry basis) per hour during exposure to the contaminant and the absolute percentage change during the baseline test in clean syngas (on a dry basis) per hour.

8.1. HT-WGS Catalyst

From the results of the long-term bench-scale evaluation studies on the iron-based HT-WGS catalyst (Task 3, Subtask 1), the contaminants that significantly inhibit or deactivate the HT-WGS catalyst are H_2S , AsH_3 and PH_3 .

8.1.1. H_2S

The deactivation rate of the catalyst during exposure to syngas containing 85 ppmv H_2S was 0.04%/h, and the HT-WGS catalyst would therefore completely deactivate and need to be replaced every 2 months instead of at the standard annual replacement rate of 25% (i.e., 4 yr life). Hence, the cost of catalyst replacement during exposure to 85 ppmv H_2S would be 24 times higher than normal whereas a typical warm-gas desulfurizing system containing a material such as zinc titanate or Z-sorb (Phillips 66) would only cost about 50% of the normal annual catalyst makeup cost, providing a savings of more than 20 times the annual catalyst replacement cost.

8.1.2. AsH_3

The deactivation rate of the catalyst during exposure to 1 ppmv AsH_3 in the syngas was 0.003%/h, and the HT-WGS catalyst would therefore completely deactivate and need to be replaced every 22 months instead of at the standard annual replacement rate of 25% (i.e., 4 yr

life). Hence, the cost of catalyst replacement during exposure to 1 ppmv AsH₃ would be 2.2 times higher than normal whereas a typical AsH₃ cleanup system would cost significantly less. TDA Research has developed a warm-gas AsH₃ sorbent for syngas cleanup in another DOE project (DE-FG02-08ER85211), which may be suitable for use to protect the HT-WGS catalyst.

8.1.3. PH₃

The deactivation rate of the catalyst during exposure to 1 ppmv PH₃ in the syngas was 0.003%/h, and the HT-WGS catalyst would therefore completely deactivate and need to be replaced every 23 months instead of at the standard annual replacement rate of 25% (i.e., 4 yr life). Hence, the cost of catalyst replacement during exposure to 1 ppmv PH₃ would be 2.1 times higher than normal whereas a typical PH₃ cleanup system would cost significantly less. TDA Research has developed a warm-gas PH₃ sorbent for syngas cleanup in another DOE project (DE-FG02-08ER85211), which may be suitable for use to protect the HT-WGS catalyst.

8.2. LT-WGS Catalyst

From the results of the long-term bench-scale evaluation studies on the copper/zinc-oxide-based LT-WGS catalyst (Task 3, Subtask 2), the contaminants in syngas that significantly inhibit or deactivate the LT-WGS catalyst are H₂S, AsH₃, PH₃, NaCl and KCl.

8.2.1. H₂S

The deactivation rate of the catalyst during exposure to 88 ppmv H₂S in the syngas was 0.017%/h, and the LT-WGS catalyst would therefore completely deactivate and need to be replaced every 4 months instead of at the standard annual replacement rate of 25% (i.e., 4 yr life). Hence, the cost of catalyst replacement during exposure to 88 ppmv H₂S would be 12 times higher than normal whereas a typical warm-gas desulfurizing system containing a material such as zinc titanate or Z-sorb (Phillips 66) would only cost about 50% of the normal annual catalyst makeup cost, providing a savings of more than 10 times the annual catalyst replacement cost.

8.2.2. AsH₃

AsH₃ has a greater impact on the LT-WGS catalyst than on the HT-WGS catalyst. The deactivation rate of the catalyst during exposure to 1 ppmv AsH₃ in the syngas was 0.005%/h, and the LT-WGS catalyst would therefore completely deactivate and need to be replaced every 14 months instead of at the standard annual replacement rate of 25% (i.e., 4 yr life). Hence, the cost of catalyst replacement during exposure to 1 ppmv AsH₃ would be 3.4 times higher than normal whereas a typical AsH₃ cleanup system would cost significantly less. TDA Research has developed a warm-gas AsH₃ sorbent for syngas cleanup in another DOE project (DE-FG02-08ER85211), which may be suitable for use to protect the LT-WGS catalyst.

8.2.3. PH₃

PH₃ has an even greater impact on the LT-WGS catalyst than on the HT-WGS catalyst. The deactivation rate of the catalyst during exposure to 1 ppmv PH₃ in the syngas was 0.007%/h, and the LT-WGS catalyst would therefore completely deactivate and need to be replaced every 9 months instead of at the standard annual replacement rate of 25% (i.e., 4 yr life). Hence, the cost of catalyst replacement during exposure to 1 ppmv PH₃ would be 5.3 times higher than normal whereas a typical PH₃ cleanup system would cost significantly less. TDA Research has developed a warm-gas PH₃ sorbent for syngas cleanup in another DOE project (DE-FG02-08ER85211), which may be suitable for use to protect the LT-WGS catalyst.

8.2.4. NaCl

The deactivation rate of the catalyst during exposure to NaCl was comparable to the baseline deactivation rate in clean syngas during the bench-scale studies. Also, the tests were run with 10 wt.% NaCl mixed directly in with the catalyst, which is considered to be an extreme exposure to NaCl. Hence, we expect the low concentration of NaCl vapor present in coal-biomass derived syngas to have no impact on the performance of the LT-WGS catalyst.

8.2.5. KCl

The deactivation rate of the catalyst during exposure to 10 wt.% KCl (mixed in directly with the catalyst) was 0.007%/h, and the LT-WGS catalyst would therefore completely deactivate and need to be replaced every 10 months instead of at the standard annual replacement rate of 25% (i.e., 4 yr life). Hence, the cost of catalyst replacement during exposure to 10 wt.% KCl would be 5 times higher than normal. However, the vapor pressure of KCl at the industrial LT-WGS conditions will be in the lower ppb levels and therefore may not actually have an impact on the performance of the LT-WGS catalyst in that setting.

8.3. Co-FT Catalyst

From the results of the long-term bench-scale evaluation studies (Task 3, Subtask 3), the contaminants that significantly inhibit or deactivate the Co-FT catalyst are AsH₃, NH₄OH, NaCl, KNO₃, HNO₃, HCl, and HBr. The non-gaseous contaminants were introduced into the CSTR in an aqueous solution that was co-fed with the syngas at the rate of 1.0 ml/h via a syringe pump.

8.3.1. AsH₃

The deactivation rate of the catalyst during exposure to 300 ppbv AsH₃ in the syngas was 0.049%/h, and the Co-FT catalyst would therefore completely deactivate and need to be replaced every 1.5 months instead of at the standard annual frequency (i.e., 1 yr life). Hence, the cost of catalyst replacement during exposure to 300 ppbv AsH₃ would be 8.5 times higher than normal whereas a typical AsH₃ cleanup system would cost significantly less. TDA Research has developed a warm-gas AsH₃ sorbent for syngas cleanup in another DOE project (DE-FG02-08ER85211), which may be suitable for use to protect the Co-FT catalyst. At a concentration of 1 ppmv in the syngas, AsH₃ would have an even greater impact on catalyst activity, and in that case the required rate of catalyst replacement would be 28 times the normal frequency.

8.3.2. HCl

The deactivation rate of the catalyst during exposure to 500 ppbv HCl in the syngas was 0.008%/h, and the Co-FT catalyst would therefore completely deactivate and need to be replaced every 9 months instead of at the standard annual frequency (i.e., 1 y life). Hence, the cost of catalyst replacement during exposure to 500 ppbv HCl would be 1.4 times higher than normal, and therefore a clean-up system would not be justified. However, when exposed to a concentration of 1 ppmv HCl in the syngas, the deactivation rate would double and the required catalyst replacement rate would be 2.6 times higher than normal, making the use of a cleanup system favorable.

8.3.3. HBr

The deactivation rate of the catalyst during exposure to 10 ppmv HBr in the syngas was 0.034%/h, and the Co-FT catalyst would therefore completely deactivate and need to be replaced every 2 months instead of at the standard annual frequency (i.e., 1 yr life). Hence, the

cost of catalyst replacement during exposure to 10 ppmv HBr would be 6 times higher than normal and a clean-up system would be needed. At higher levels of HBr i.e., 20 and 100 ppmv, the life of the catalyst would be reduced to less than 2 months and 1 month, respectively, further increasing the required catalyst replacement rate or the need for a clean-up system.

8.3.4. Aqueous NH_4OH

The CO conversion dropped but remained stable after a few hours of exposure to $\text{NH}_4\text{OH}_{(\text{aq})}$ (50 ppmv NH_4NO_3 in 1.0 ml/h H_2O) and there was no change in selectivity. However, the decrease in CO conversion increased with NH_4OH concentration.

8.3.5. Aqueous HNO_3

The deactivation rate of the catalyst during exposure to 500 ppb $\text{HNO}_{3(\text{aq})}$ was 0.015%/h, and the Co-FT catalyst would therefore completely deactivate and need to be replaced every 3 months instead of at the standard annual frequency (i.e., 1 yr life). Hence, the cost of catalyst replacement during exposure to 500 ppb aq. HNO_3 would be 3.9 times higher than normal and a clean-up system would be needed. At higher levels of HNO_3 , i.e. 1 ppm, the life of the catalyst would be reduced to less than 1.5 months, further increasing the catalyst replacement rate to 8.6 times the normal rate.

8.3.6. Aqueous KNO_3

The deactivation rate of the catalyst during exposure to 10 ppm $\text{KNO}_{3(\text{aq})}$ was 0.037%/h, and the Co-FT catalyst would therefore completely deactivate and need to be replaced every 2 months instead of at the standard annual frequency (i.e., 1 yr life). Hence, the cost of catalyst replacement during exposure to 10 ppm aq. KNO_3 would be 6.5 times higher than normal and a clean-up system would be needed. Upon exposure to 500 ppm $\text{KNO}_{3(\text{aq})}$ for only 100 h, the Co-FT catalyst would be completely deactivated.

8.3.7. Aqueous NaCl

There was no deactivation during exposure to 100 ppm $\text{NaCl}_{(\text{aq})}$ in the bench-scale test. However, during exposure of Co-FT catalyst to 400 ppm $\text{NaCl}_{(\text{aq})}$ the catalyst deactivated at a measureable rate (0.091%/h), and the Co-FT catalyst would therefore completely deactivate and need to be replaced in less than a month instead of at the standard annual frequency (i.e., 1 yr life). Hence, the cost of catalyst replacement during exposure to 400 ppm $\text{NaCl}_{(\text{aq})}$ would be 16 times higher than normal. However, such high concentrations of $\text{NaCl}_{(\text{aq})}$ may not be seen at the Co-FT synthesis reactor unless there is an accumulation of NaCl in the liquid products through absorption from the syngas feed. However, this is not realistic since the vapor pressure of NaCl under industrial Co-FT conditions is very low.

9. Summary & Conclusions

Altogether we evaluated four different catalysts; commercial ferrochrome high-temperature WGS catalyst (HT-WGS, Shiftmax 120™, Süd-Chemie), low-temperature copper/zinc-oxide WGS catalyst (LT-WGS, Shiftmax 230™, Süd-Chemie), and in-house prepared iron- and cobalt-based Fischer-Tropsch synthesis catalysts (Fe-FT & Co-FT, UK-CAER). We first evaluated the interaction of these catalysts with fifteen different contaminants commonly found in coal-biomass derived syngas (H_2S , NH_3 , HCN , AsH_3 , PH_3 , HCl , NaCl , KCl , As_3 , NH_4NO_3 , NH_4OH , KNO_3 , HBr , HF , and HNO_3) in a thermodynamic analysis, and then determined the effect of each of these contaminants on the long-term performance of the catalysts at their typical industrial operating conditions in bench-scale experiments that typically lasted for >100 h. The physical and chemical interactions of the contaminants with each tested catalyst were subsequently examined using various analytical tools (e.g., BET, XRD, ICP-AA, and chromatography). We used the catalyst deactivation rates determined from the long-term tests as a basis for a techno-economic analysis to identify the critical deactivation rates for each catalyst-contaminant pair that would trigger the installation of a syngas clean-up and purification system.

In this project, TDA Research, Inc. collaborated with a team at the University of Kentucky Center for Applied Energy Research (UK-CAER) led by Prof. Burt Davis. The experiments on the impact of contaminants on low- and high-temperature WGS catalysts were carried out at TDA Research and the cobalt- and iron-based FTS catalyst studies were conducted primarily at UK-CAER. UK-CAER also performed the bulk of the post-testing catalyst characterization, which provided insight into the inhibition/poisoning mechanisms.

Because of the difficulties in simulating gas streams that contain all the primary coal and biomass contaminants and evaluating the impact of these species on catalytic activity, we adopted a tiered approach to provide a cost-effective, repeatable, reliable methodology and understanding of the fouling/poisoning processes that included the following tasks: (1) thermodynamic modeling identified the contaminants that could react with the active phase and the promoters used in the FT and WGS catalyst formulations and could degrade their performance, (2) bench-scale experiments using commercial and generic (prepared in-house) WGS and FT catalyst formulations were performed to measure their catalytic activity and deactivation rates in the presence of selected major contaminant species under representative reaction conditions (in these experiments we also measured the adsorption/chemisorption characteristics of the contaminant species), (3) thorough physical and chemical characterization of the catalyst samples that were exposed to the contaminants was conducted to develop a fundamental understanding of the poisoning mechanisms, (4) an engineering analysis was carried out to assess the cost trade-off between investing in a proactive contaminant control system versus not taking any action (i.e., to write-off the incurred catalyst replacement cost and the revenue loss for the reduced production rates due to chemical poisoning).

We completed a detailed thermodynamic analysis in Task 2 (the project management plan was developed in Task 1) to evaluate the impact of potential contaminants in the syngas generated by coal and biomass co-gasification on the WGS and FT catalysts. We evaluated the impact of single contaminants at reaction conditions on each of the metal or metal oxide species present in the catalysts and observed that all of the contaminants included in the study showed some impact on each of the catalysts. However, the condensation and deposition products will be formed upstream in the heat exchangers and process pipelines rather on the catalyst, since the catalyst does not take part in these deactivation mechanisms. If we eliminated these condensation and deposition mechanisms, then we could categorize the contaminants into

groups depending on their potential to cause major or minor impact, derived from the results of the thermodynamic study.

In Task 3 we evaluated the interaction of the fifteen different contaminants (H_2S , NH_3 , HCN , AsH_3 , PH_3 , HCl , NaCl , KCl , AS_3 , NH_4NO_3 , NH_4OH , KNO_3 , HBr , HF , and HNO_3) with the four different catalysts in bench-scale experiments that typically lasted for >100 h. An extensive experimental campaign was undertaken to evaluate the impact of anticipated contaminants in the synthesis gas generated by coal and biomass co-gasification on the components (e.g., the active phases, promoters, and supports) and activity, selectivity, and lifetime of each catalyst. Most of the contaminants included in the HT- and LT-WGS catalyst experimental studies appeared to adsorb onto these catalysts because they were not detected downstream of the catalyst beds during testing. However, it is possible that some of the contaminants (such as NH_3) were removed in the steam condenser prior to the analysis point.

The results of the LT- and HT-WGS catalyst-contaminant tests can be summarized as follows:

- Syngas that contained 4.5 ppmv AsH_3 impacted the selectivity and conversion of the HT-WGS catalyst because it adsorbed onto it.
 - AsH_3 had an even greater impact on the LT-WGS catalyst.
- H_2S slowly degraded both the LT- and HT-WGS catalysts over time.
 - The CO conversion remained stable over the LT-WGS catalyst after the introduction of 10 ppm H_2S .
- A mixture of H_2S (60 ppmv) and NH_3 (38 ppmv) did not impact the performance of the HT-WGS but did impact the activity of the LT-WGS catalyst
- PH_3 appreciably impacted the performance of the WGS catalysts.
- Moderate levels of NH_3 did not impact the performance of either of the WGS catalyst and the CO conversion remained stable after the introduction of up to 100 ppmv NH_3 .
- No change in performance for either of the catalysts was observed following a long induction period after the introduction of 10 ppmv HCN .
- In tests run with alkali salts (NaCl or KCl) directly intermixed with the catalysts, virtually no effect was observed on the HT-WGS catalyst, but the activity of the LT-WGS catalyst decreased very slowly.

In many cases for the HT-WGS catalyst, the contaminant had no discernable effect on the catalyst's activity or selectivity during the timeframe of our tests. Those specific contaminants (NH_3 , NaCl , KCl , and HCN) may not be problematic in an industrial setting, but their lack of impact could have been attributed to a combination of the low concentration of the impurity and the duration of the test, which may not have been long enough to saturate the catalyst and affect its performance.

Most of the contaminants included in this study had little or no impact on the LT-WGS catalyst, but the impact of H_2S , AsH_3 , and PH_3 was significant. Also, H_2S , AsH_3 , PH_3 , NH_3 , H_2S , HCN all appeared to adsorb onto the catalyst. The alkali salts were physically mixed in with the catalyst and inhibited the WGS reaction slightly. However, because the vapor pressures of both NaCl and KCl are negligible at the reaction temperatures of this study, it is unlikely that these contaminants will impact any of the catalysts. NH_3 and H_2S together also poisoned the LT-WGS catalyst, although it took awhile to saturate the catalyst with adsorbed H_2S .

In binary contaminant tests, the effect of introducing mixtures of H_2S and NH_3 into the syngas on the catalytic activity of the commercial LT- and HT-WGS catalysts was evaluated. We observed a decrease in the performance of the LT-WGS catalyst following a short induction period after

introducing a combination of NH_3 (38 ppmv) and H_2S (60 ppmv) into the syngas feed. H_2S conclusively adsorbed onto the HT-WGS catalyst during the single-contaminant test, and it also noticeably adsorbed when it was co-fed with ammonia. This combination of NH_3 and H_2S in the syngas feed resulted in H_2S uptake by the HT-WGS catalyst until it appeared to saturate the bed, as evidenced by H_2S breakthrough after only a few hours on-stream. Interestingly, very little decrease in CO conversion activity was observed during the test, even after more than half of the feed concentration of H_2S was detected in the WGS product stream.

The results of the bench-scale contaminant impact study carried out on the UK-CAER Co-FT catalyst showed that all of the contaminants impacted FTS over this catalyst to some extent with the exception of NaCl and HF. An aqueous solution of each compound, including chloride salts and bicarbonates, was injected into the reactor as the source of contaminant ions in syngas. The results of the contaminant experiments clearly established that poisoning of Co-FT synthesis catalysts is very complex and depends upon a number of factors. This makes it a demanding task to define experiments that focus on a specific feature of catalyst poisoning. It also appeared that, irrespective of its source (e.g., NH_3 , KNO_3 , or HNO_3), ammonia tended to suppress Co-FT catalyst activity to a moderate degree at all of the concentration levels examined. Neither the mode of deactivation nor the strength of the poisoning effect (e.g., reversibility) is known at this time. For example, the impact of the nitrate ion appeared to be influenced by its ability to undergo hydrogenation to water and ammonia, and that its impact was in fact due to the effect of ammonia. Furthermore, the loss of activity of the Co-FT catalyst in clean syngas (no contaminants) due to the accumulation of FTS reaction products made it difficult to know when to begin the poisoning study and how to differentiate between the impact of the contaminants on CO conversion and the normal rate of decline in activity.

The effect of NaCl, KCl, NaHCO_3 and KHCO_3 (0.1- 100 ppmw) contaminants co-fed with syngas on the performance of the UK-CAER high-alpha Fe-FT catalyst was studied at 260 and 270 °C. These contaminants had no significant impact on the Fe-FT catalyst and its activity. The hydrocarbon selectivities of the catalyst also did not significantly change while Na^+ , K^+ , Cl^- ions were continuously fed during tests that lasted between 72-144 h. The activity and selectivity results for the FTS reaction indicated that there was essentially no impact on the Fe-FT catalyst activity and selectivity when up to 100 ppmw halide compounds (NaCl and KCl), or up to 40 ppmw alkali bicarbonates (NaHCO_3 and KHCO_3) were co-fed with the syngas feed at both 260 °C and 270 °C. This suggests that neither the alkali ions (i.e., Na^+ or K^+) nor chloride ion (i.e., Cl^-) adsorbed strongly enough onto the catalyst surface to deactivate it during the FTS reaction in the CSTR, (if they are assumed to physically block the Fe active sites or change the electronic character of the Fe-FT catalyst).

Extensive characterization of the physical attributes and chemical compositions of the catalysts both before and after testing was conducted in Task 4 to identify any changes that occurred due to the catalyst-contaminant interactions during the long-term tests. Some of the contaminants adsorbed on the catalysts or reacted with them, which caused a reduction in performance during testing. These catalyst samples were subsequently examined using analytical techniques such as BET, XRD, ICP-AA, and chromatography.

BET analysis showed that the surface areas, pore volumes, and pore diameters of both the LT- and HT-WGS catalysts all decreased during both single and combined H_2S and NH_3 contaminant tests. These reductions were probably due to sintering and pore filling by the impurity, especially in the case of sulfur.

The Fe-based HT-WGS catalyst was evaluated with XRD after testing in syngas that contained 1 ppmv PH_3 , or 2 ppmv H_2S , or both H_2S (60 ppmv) and NH_3 (38 ppmv). The peaks became sharper during testing, which was indicative of crystal growth and sintering. However, the concentration of any new phases that may have formed were too low to detect. After testing the copper/zinc-oxide-based LT-WGS catalyst (Shiftmax 230) in syngas that contained either 3-33 ppmv NH_3 or 0-88 ppmv H_2S there were a few unidentified new phases that appeared, with significant differences apparent between the catalyst tested in NH_3 versus H_2S . The broad semi-amorphous peaks between $35\text{--}40^\circ$ 2θ for the fresh catalyst almost disappeared for the catalyst tested in H_2S . In contrast, for the catalyst tested in NH_3 , these peaks became more resolved and crystalline.

The XRD patterns for two different LT-WGS tests in syngas containing binary H_2S (60 ppmv or 500 ppmv) and NH_3 (38 ppmv) contaminant mixtures showed several new sulfide peaks compared to the XRD pattern for the fresh catalyst. The patterns for the tested catalysts showed several distinct new peaks compared to the XRD pattern for the fresh catalyst. The additional small peaks at $\sim 30^\circ$ and between $45\text{--}50^\circ$ 2θ on the catalysts exposed to H_2S were most likely sulfides, and as previously noted the large semi-amorphous peaks between $35\text{--}40^\circ$ 2θ for the fresh catalyst were almost gone in the tested samples. There were also some subtle differences in the peak shapes and the phases that formed between the catalysts tested at low or high H_2S concentrations and those tested in single (H_2S or NH_3) versus binary contaminant mixtures (H_2S and NH_3). Broad, low-intensity peaks indicated that the Fe-FT catalyst was primarily nanocrystalline and amorphous prior to testing.

ICP-AA spectroscopy and other methods (e.g., chromatography) were used to analyze for all of the elements of interest (i.e., Fe, Cu, S, K, Na, P, As, Cl, C, H, and N) on both the fresh WGS and FT catalysts and the catalyst samples that were exposed to contaminants during the long-term tests. For the HT-WGS catalyst, the catalysts that were subjected to testing in syngas with co-fed contaminants displayed higher concentrations of the elements that composed that contaminant relative to the composition of the fresh catalyst in the cases of H_2S (484 ppm sulfur compared to 132 ppm sulfur in the fresh catalyst), NaCl (9.51% sodium compared to 488 ppm and 9.65% chlorine compared to 0.13%), PH_3 (0.44% phosphorus compared to 196 ppm), KCl (8.67% potassium compared to 52 ppm and 6.05% chlorine compared to 0.13%), and AsH_3 (1819 ppm arsenic compared to 11 ppm). For the other elements (i.e., N, H, and C), the results indicated either no measurable increase in the concentration of the contaminant in question, or a decrease in its concentration (e.g., C with HCN) within the limits of experimental error for the analysis technique.

For the Cu-based LT-WGS catalyst, the samples of catalyst that were subjected to contaminant exposure tests also contained higher concentrations of the elements that compose the contaminant of interest relative to the fresh catalyst in the cases of H_2S (2.37% sulfur relative to 84 ppm in the fresh catalyst), NaCl (8.83% sodium relative to 397 ppm and 15.6% chlorine relative to 0.08%), $\text{NH}_3 + \text{H}_2\text{S}$ (3.02% sulfur relative to 84 ppm), and AsH_3 (259 ppm arsenic relative to 9 ppm). For the other elements (i.e., N, H, P, and C), the results indicated no measurable increase in the concentration of the contaminant in question within the limits of experimental error for the analysis technique.

ICP and chromatographic analyses of the HT- and LT-WGS catalysts exposed to the alkali contaminants (i.e., Na^+ , K^+ and Cl^-) showed much higher levels of these residual metals after testing compared to the other contaminants since each of the alkalis was introduced by mixing its crystalline powder directly with the catalyst rather than feeding it into the catalyst bed in the gas phase. For the Fe-FT catalyst, the results of the elemental analyses indicated that only

small quantities of these contaminant ions adsorbed onto the surface of the catalyst during testing. However, the concentrations of contaminants on the Fe-FT catalyst could have theoretically reached 0.4-1.5 wt.% if the entire quantity fed was adsorbed and retained by the catalyst during testing. This explains why essentially no changes in catalyst activity or selectivity were observed during the Fe-FT catalyst experiments that were conducted in the presence of these contaminants.

After the long-term FTS runs that examined the impact of 0-40 ppmw NaHCO_3 or KHCO_3 on the Fe-FT catalyst, 300-400 ppmw Na^+ or K^+ ions were present on the Fe-FT catalyst surface, which is only 2.6% (Na^+) and 7.6% (K^+) of the maximum theoretical values. The concentrations of K^+ and Cl^- in the Fe-FT catalyst after FTS testing in the presence of KCl were also low (800 and 111 ppm), respectively, which are just 1.5% (Na^+) and 10% (K^+) of the calculated maximum theoretical values. These results clearly indicate that the uptake of these contaminants by the Fe-FT catalyst under FTS conditions was very low, which explains why they did not affect FTS during the long-term tests.

ICP analysis of the alkali contaminant ion (e.g., Na^+ , K^+ or Cl^-) concentrations in the FTS products (i.e., water, oil and wax) from the four different contaminant test runs on the Fe-FT catalyst detected Na^+ , K^+ or Cl^- ions in all phases of the FTS products. However, most of the contaminant ions were retained in the wax slurry in the reactor (>90% in most cases), with the remaining (<10%) distributed between the oil- and aqueous-phases. This further suggests that the contaminant ions injected on-line into the CSTR reactor in the aqueous solution did not strongly adsorb onto the Fe-FT catalyst surface under slurry FTS conditions, and that their impact on catalyst behavior could differ compared to the addition of trace amounts of these contaminants directly onto the catalyst or fed in the syngas.

A techno-economic study was carried out for Task 5 that evaluated the cost trade-off between cleaning up the coal-biomass derived syngas versus the added costs of catalyst replacement due to poisoning. Using the experimentally determined rates of catalyst deactivation from the long-term syngas-contaminant tests performed in Task 3, we carried out a system analysis to identify the critical deactivation rates that would trigger the requirement to install a warm-gas cleanup system downstream of the gasifier and upstream of the CBTL process. Anticipated catalyst lifetimes during exposure to the various contaminants were determined from the results of the long-term syngas-contaminant tests. This trade-off analysis showed that the use of a contaminant removal system would be economically justified in many cases to reduce the cost of premature catalyst replacement due to poisoning.

The results of this project enabled us to determine the sensitivity of the WGS and FT catalysts used in CBTL processes to the contaminants in coal-biomass derived syngas, provided information on the long-term cumulative degradation and service life for these catalysts, and will enable DOE and FT technology developers to assess the risk of catastrophic damage if higher than planned levels of these contaminants slip through syngas clean-up systems. The results of this work can help guide follow-on research to investigate potential catalyst improvements and/or process modifications needed to ultimately reduce the capital and operating expenses associated with producing drop-in liquid transportation fuels from coal-biomass derived syngas mixtures. The findings of this investigation will also be critical in establishing failure mode and effect criteria for coal-biomass co-gasification clean-up systems that operate in FTS plants.

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