Investigation of Effects of Contaminants on the Performance of Coal and Biomass to Liquids (CBTL) Process Catalysts

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International Pittsburgh Coal Conference

September 20-23, 2009 – Pittsburgh, PA

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Outline

- Coal and Biomass contaminants
- Thermodynamic Analysis
- Preliminary Catalyst Testing
- Sorbent Development for Contaminant Control

Project Objective

- **The objective is to evaluate the impact of various contaminants present in the coal and biomass-derived synthesis gas on the performance of commercial WGS and FT catalysts**
- **Four catalysts**
  - Fe-based high temperature WGS catalyst
  - Cu/ZnO-based low temperature WGS catalyst
  - Fe-based FT catalyst
  - Co-based FT catalyst
- **Approach**
  - Identify the potent poisons using thermodynamic simulation
  - Bench-scale tests to document degradation using the worst poisons
  - Characterization
  - Trade-off analysis

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Coal Syngas Contaminants

- **Coal derived synthesis gas contains a myriad of trace metal contaminants**

Typical Metal Contaminants in Coal

Coal Type	Hg (ppm)	As (ppm)	Se (ppm)	Cd (ppm)
Pittsburg	0.11	4.1	0.6	0.06
Elkhorn/Hazard	0.13	4.0	3.1	0.31
Illinois No.6	0.22	2.7	2.2	0.15
Wyodak	0.19	1.3	1.6	0.30

Bool et al., 1997

- **Arsenic has been shown to be a potent catalyst poison**
  - Formation of iron and cobalt arsenides is favorable at FT conditions
- **Mercury can potentially form metal amalgams with active catalyst materials**
- **Sulfur is also present at high levels in coal**

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Biomass Contaminants

- **Biomass co-gasification is expected to introduce a host of additional contaminants**
- **Additional source of sulfur, halides and nitrogen**

Typical Contaminants in Biomass

Fuel	Wheat	Oat	Barley	Carinata
Moisture (%)	8.4	7.8	8.5	7.3
Ash (%, dry)	4.8	3.8	6.9	4.9
Ca (%, dry)	0.35	0.72	0.34	0.61
Cl %, dry)	0.27	0.05	0.79	0.05
K (%, dry)	1.2	0.6	2.3	1.4
S (%, dry)	0.17	0.14	0.21	0.26
Si (%, dry)	0.79	0.27	0.81	0.05

- **Biomass co-gasification may introduce volatile salts of K and Na**
  - **These may include KCl, K_2SO_4, and NaCl**
- **PH_3 and $Si(OH)_4$ may be also contaminate the synthesis gas**
  - **Silica condensation can block active sites and porosity**
  - **Phosphorus has been identified as a poison for nickel-based electrocatalyst**

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Other Syngas Contaminants

Contaminant	Concentration (ppmv)
Arsenic, as AsH_3	<0.2
Halogens {Cl & F}	~0
Chlorine	120
CH_3F	2.55
CH_3Cl	2.01
HCl	<1
CH_3SCN	2.14
Acetonitrile	<0.5
PH_3	1.91
Antimony	<0.07
Cadmium	0.011
Beryllium	<0.025
Chromium	<6
Mercury	<0.17
Sodium	320
Thiophene	1.61
Vanadium	<0.025
Lead	0.26
Zinc	9

adapted from DOE FOA (DE-PS26-05NT42470)

- **Syngas Contaminants that are present in various gasifier streams**
- **List adapted from FOA from the High Temperature Electrochemistry Research Center to investigate the impact of coal impurities on the operation of solid oxide fuel cells**
- **Some of these contaminants may also affect the WGS and FT Catalysts**

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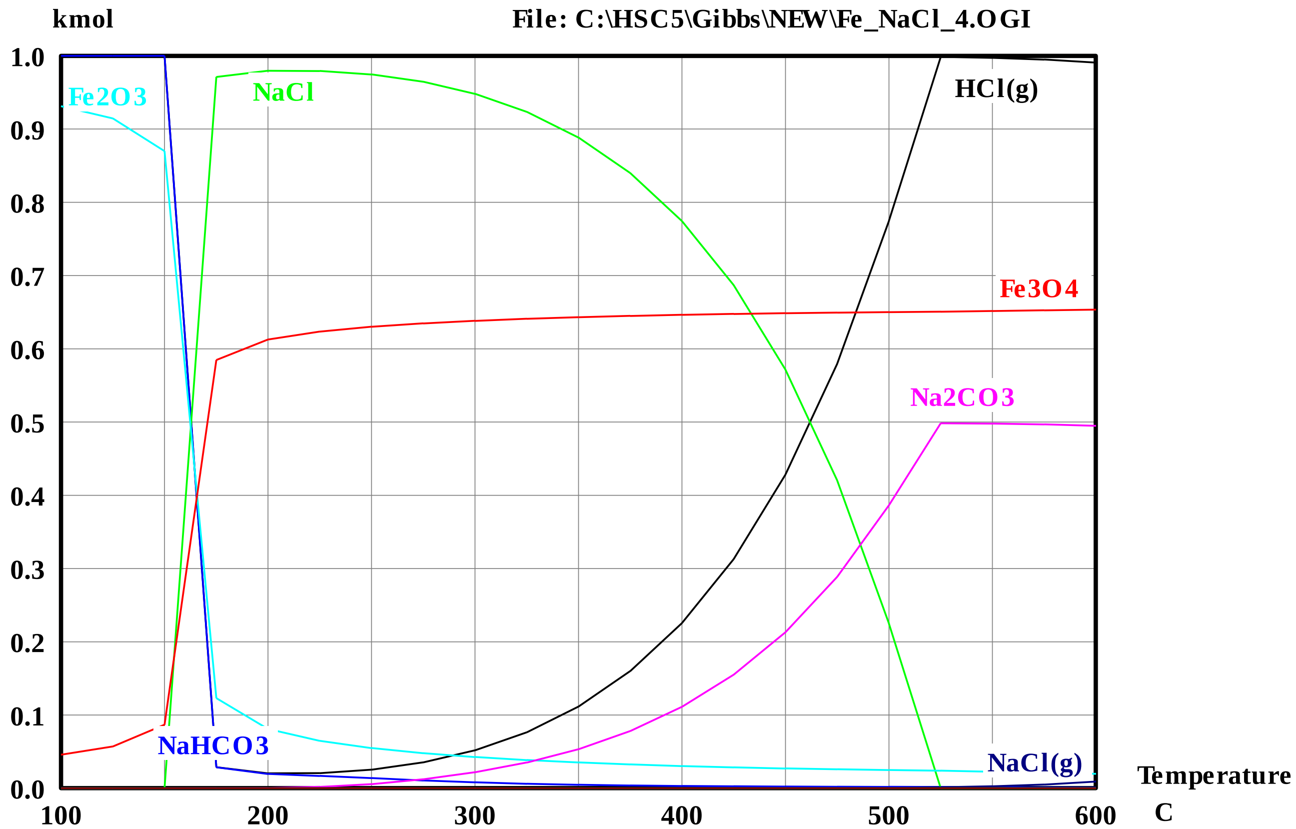
Thermodynamic Analysis

Effect of Na on Fe-catalyst

Baseline Cond.: P= 40 atm, H_2= 27.8%, CO = 36.1%, CO_2= 16.7%, H_2O= 15%, CH_4= 4.4%, vol.

Fe_2O_3 + NaCl



- **Thermodynamic analysis results indicate no interaction between Fe-Na**
- **Potential condensation of NaCl on catalyst surface between 150-520°C**

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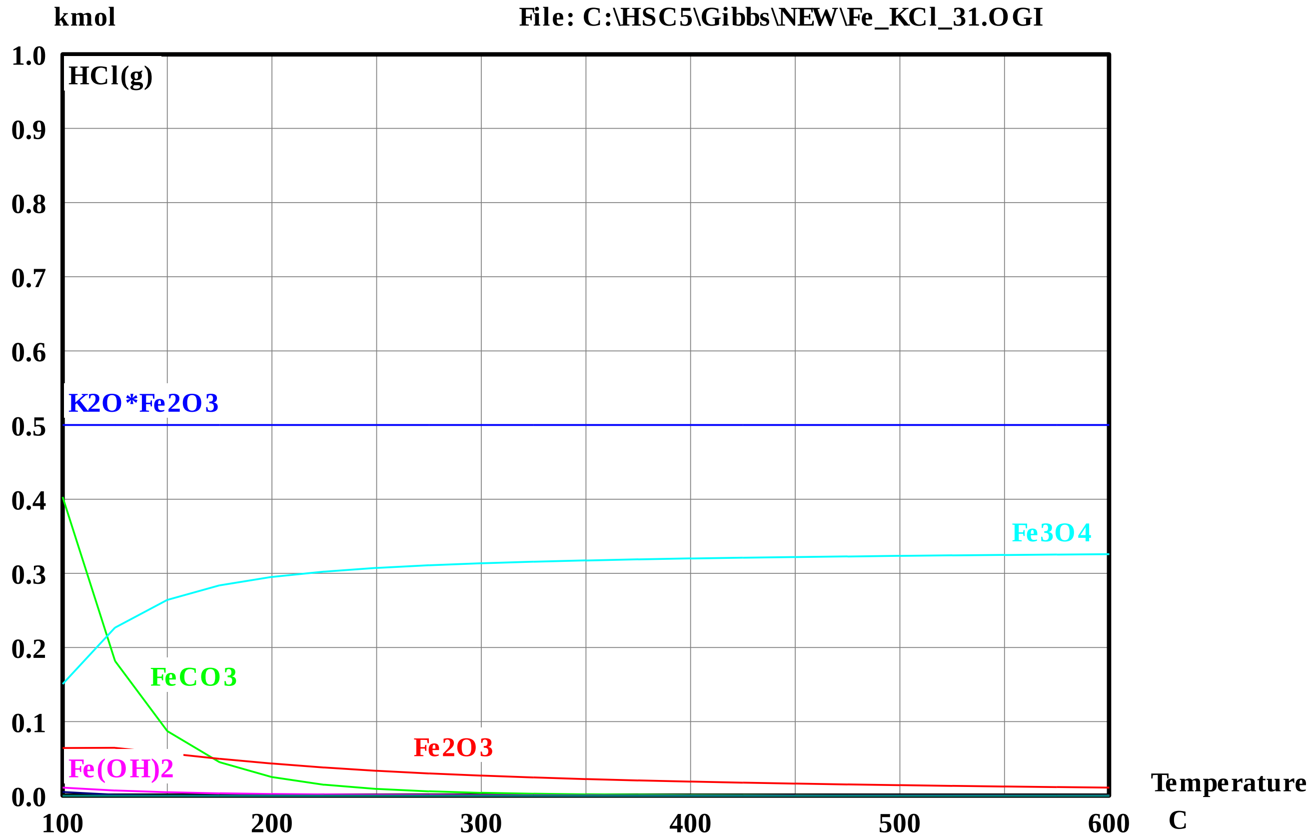
Effect of K on Fe-catalyst

Baseline Cond.: P= 40 atm, H_2= 27.8%, CO = 36.1%, CO_2= 16.7%, H_2O= 15%, CH_4= 4.4%, vol.

Fe_2O_3 + KCl



- **Thermodynamic analysis results indicate an interaction between Fe-K to form a mixed oxide**
- **KCl gets converted to HCl(g) no condensation**

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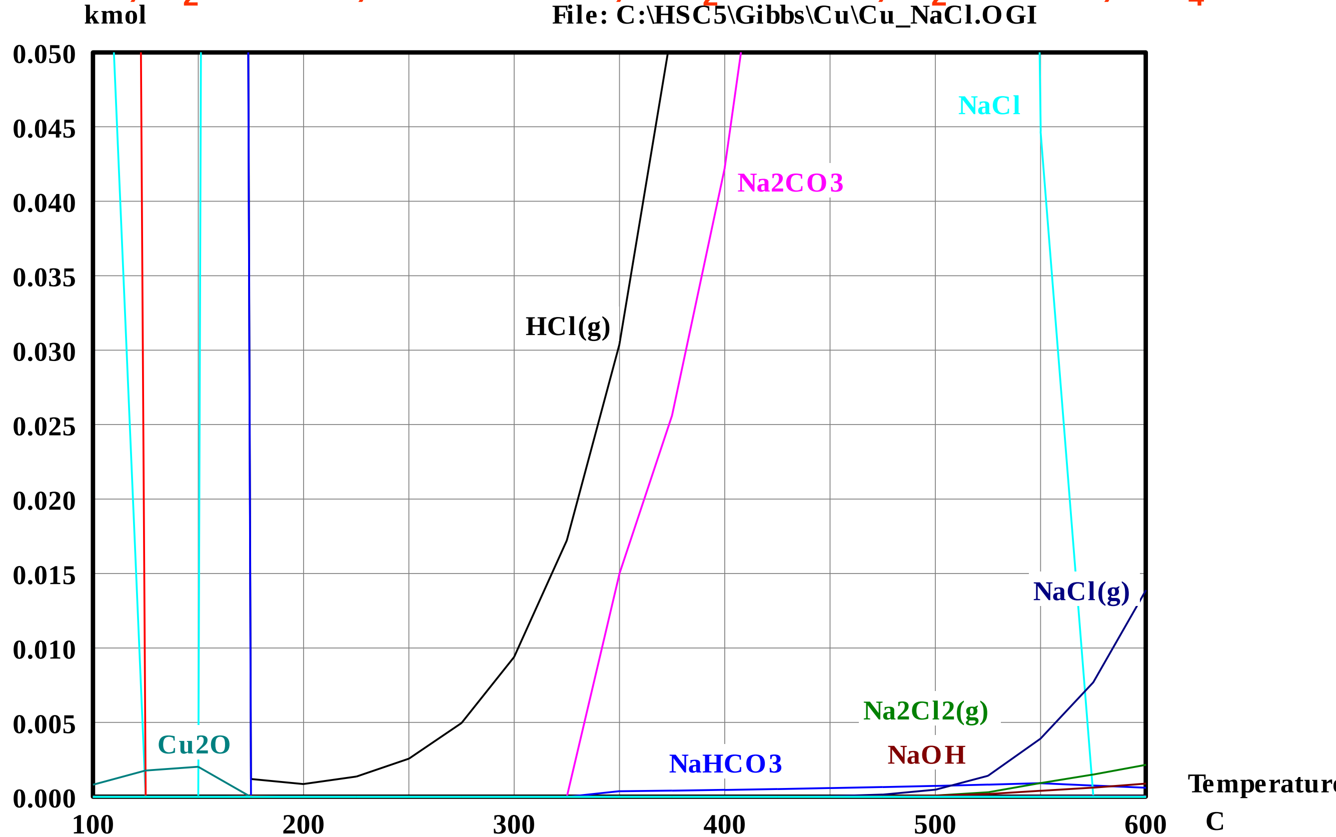
Effect of Na on Cu-catalyst

Baseline Cond.: P= 40 atm, H_2= 27.8%, CO = 36.1%, CO_2= 16.7%, H_2O= 15%, CH_4= 4.4%, vol.

CuO + NaCl



- **Thermodynamic analysis results indicate no chemical interaction between Cu-Na**
- **Potential condensation of NaCl on Cu surface between 150-570°C**

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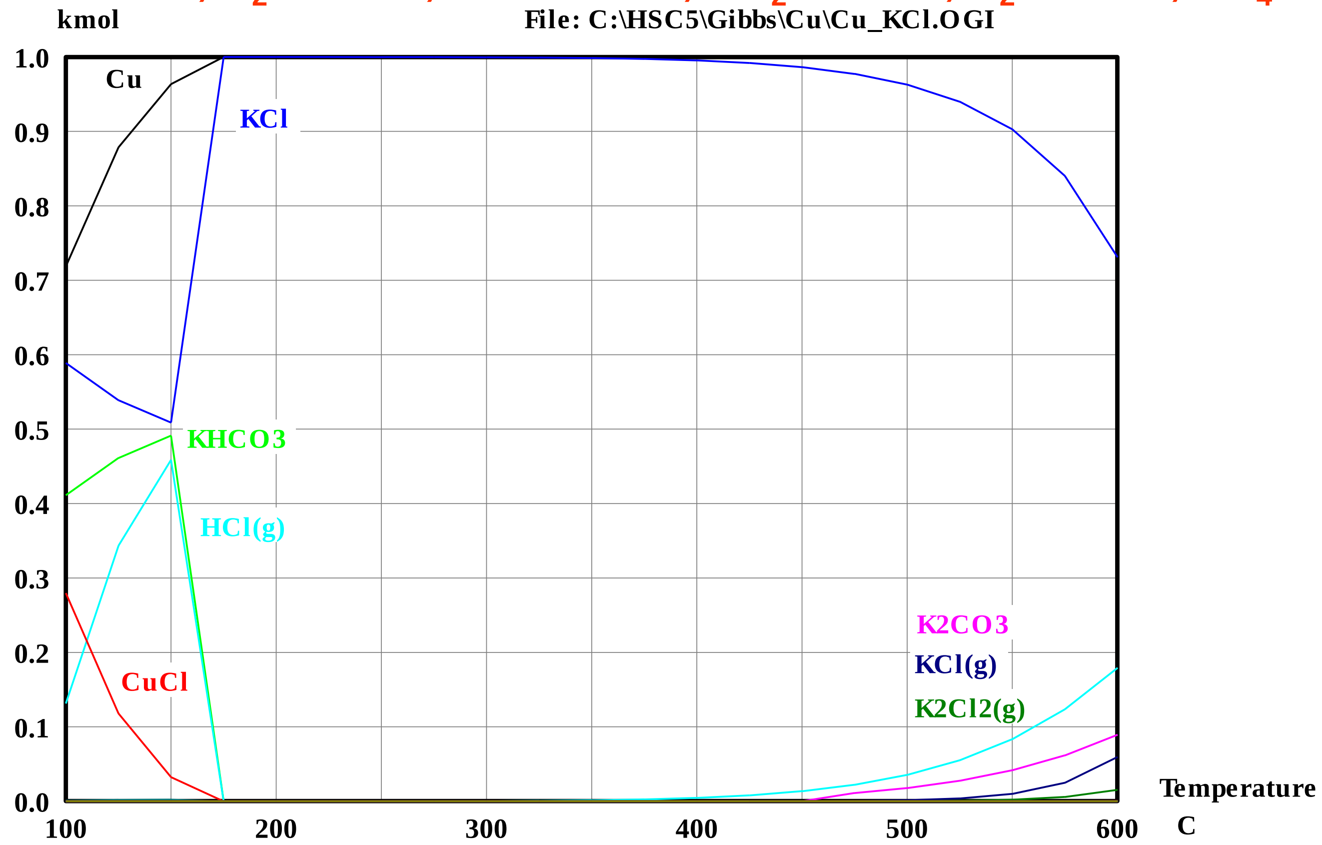
Effect of K on Cu-catalyst

Baseline Cond.: P= 40 atm, H_2= 27.8%, CO = 36.1%, CO_2= 16.7%, H_2O= 15%, CH_4= 4.4%, vol.

CuO + KCl



- **Thermodynamic analysis results indicate no chemical interaction between Cu-K**
- **Potential condensation of KCl on Cu surface at all temperatures**

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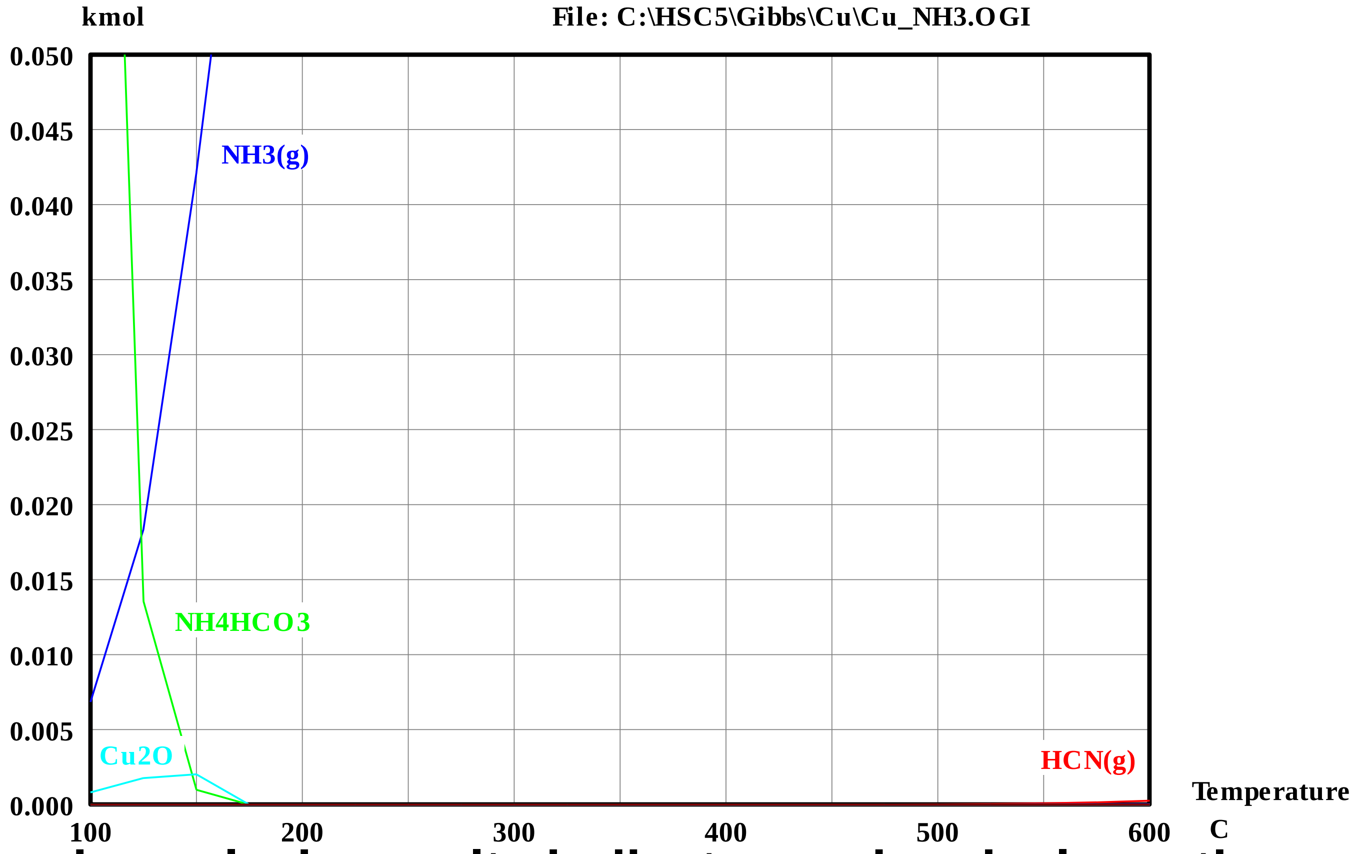
Effect of N on Cu-catalyst

Baseline Cond.: P= 40 atm, H_2= 27.8%, CO = 36.1%, CO_2= 16.7%, H_2O= 15%, CH_4= 4.4%, vol.

$CuO + NH_3$



- **Thermodynamic analysis results indicate no chemical reaction between Cu-NH_3**
- **Weak Chemical interactions like p-complexation are known to occur bewteen Cu^{1+} and NH_3**

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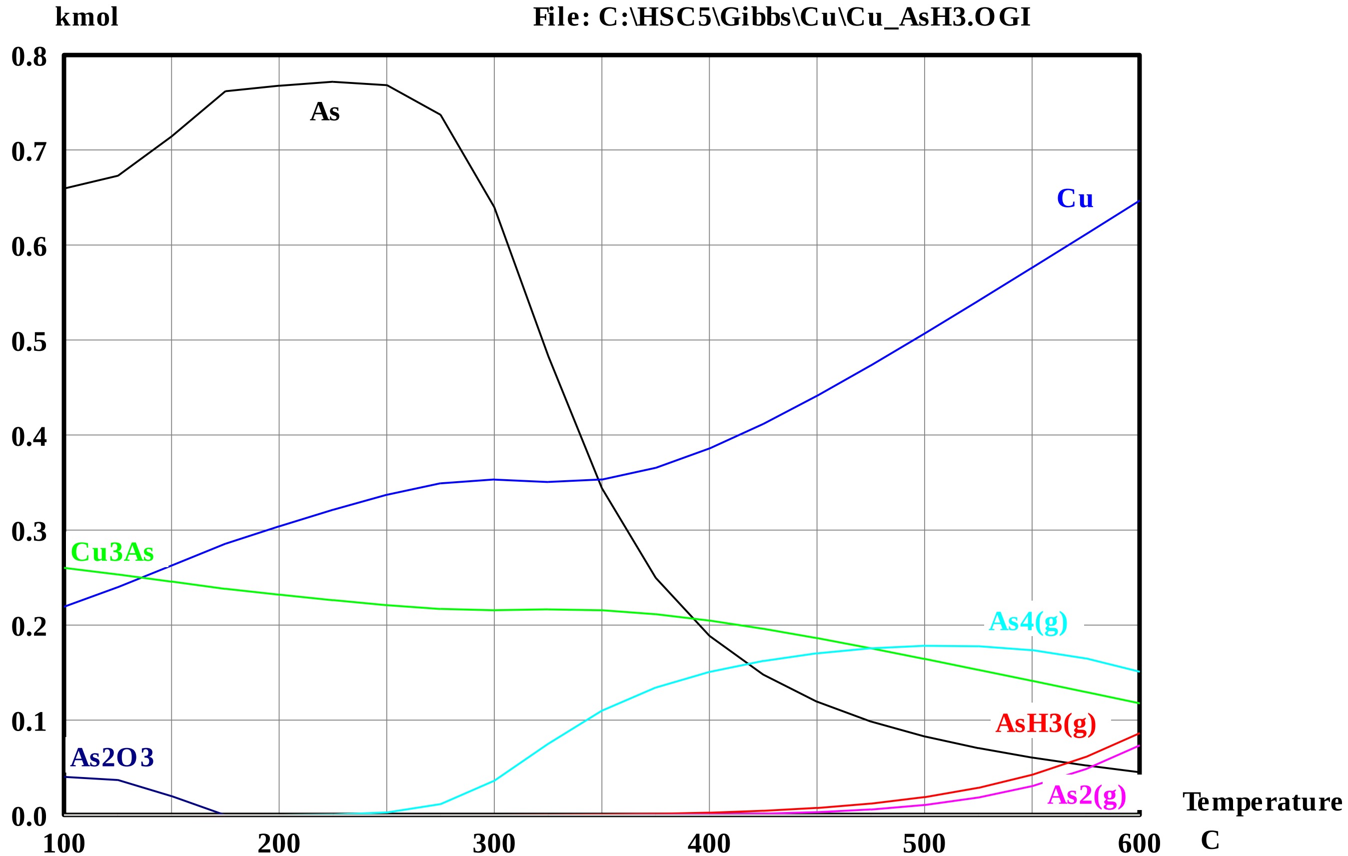
Effect of As on Cu-catalyst

Baseline Cond.: P= 40 atm, H_2= 27.8%, CO = 36.1%, CO_2= 16.7%, H_2O= 15%, CH_4= 4.4%, vol.

CuO + AsH_3



- Thermodynamic analysis results indicate formation of a copper arsenide phase
- Potential condensation of As metal on Cu surface

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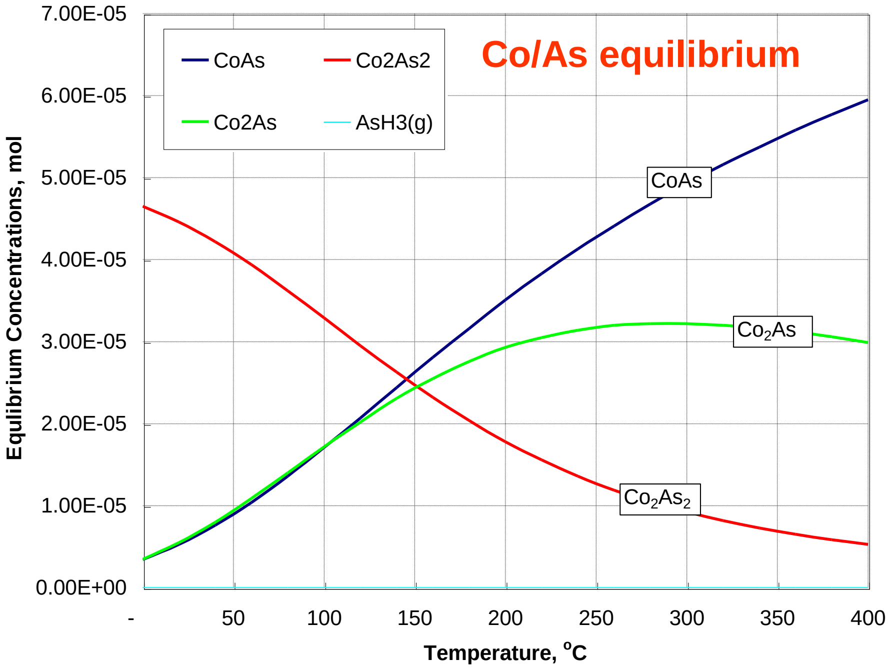
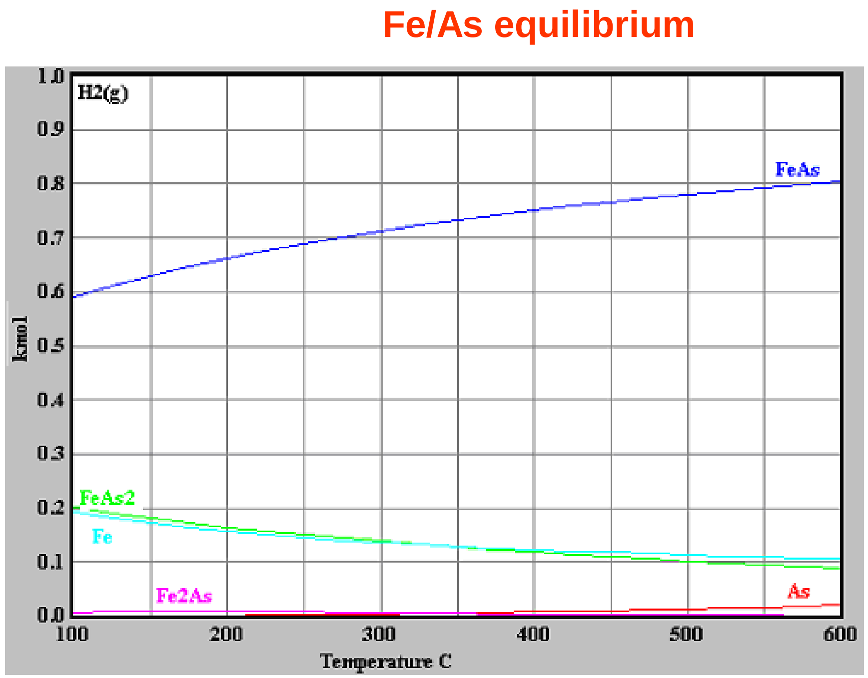
Effect of As on FT-catalyst

Baseline Cond.: P= 40 atm, H_2= 27.8%, CO = 36.1%, CO_2= 16.7%, H_2O= 15%, CH_4= 4.4%, vol.





- **Arsenic forms various complexes with metals like Fe, Co; key ingredients of WGS, and Fischer-Tropsch catalysts**
  - Blocking of active site by irreversible chemisorption (or chemical reaction)

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Catalyst Testing

- Initial Testing on Each Catalyst
  - Evaluation of space velocity on conversion
  - Ideal operating condition is under full utilization of catalyst
    - Fast response of effects of contaminants
- Feed composition
  - HT-WGS at given composition
    - Water
  - LT-WGS at equilibrium output of HT-WGS at test conditions

Gas Composition		
	HT-WGS	LT-WGS
H_2	20.6%	43.2%
CO	26.8%	4.5%
CO_2	12.3%	34.4%
CH_4	3.3%	2.9%
H_2O	37.0%	15.0%

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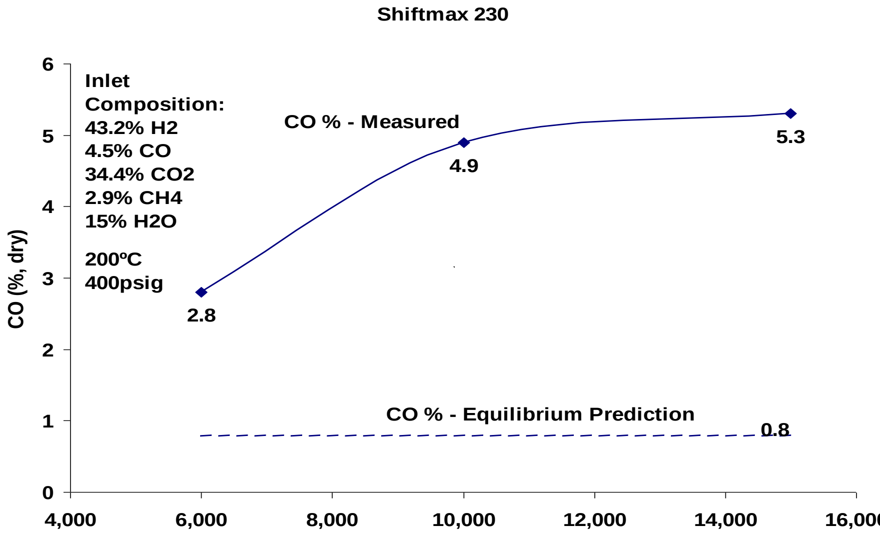
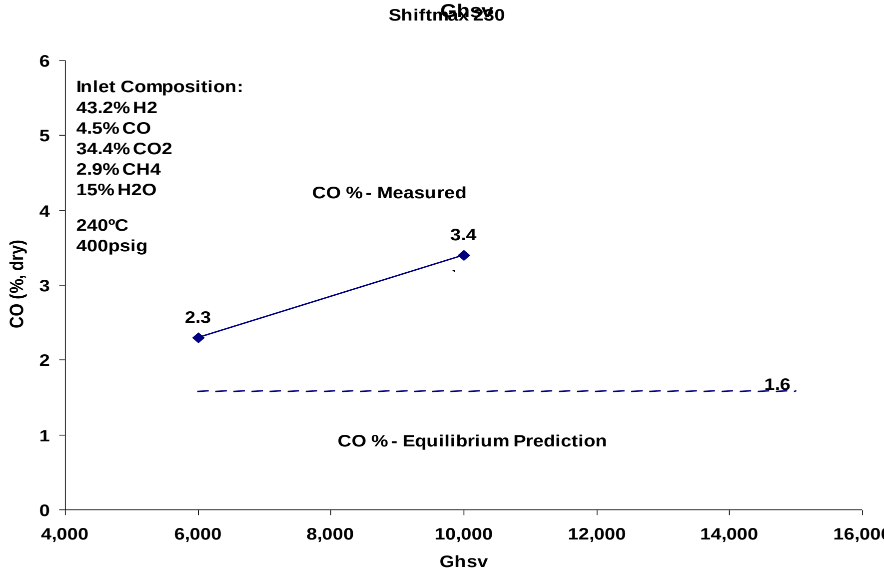
Space Velocity Test

- **Low-Temperature WGS Catalyst**
  - **Sud-Chemie ShiftMax 230® Cu/Zn-based**

- **Space Velocity Testing at 6,000h^{-1}, 10,000h^{-1}, 15,000h^{-1}**

- **Data Shown for CO conversion versus equilibrium**
  - **Substantial methanation in both tests**





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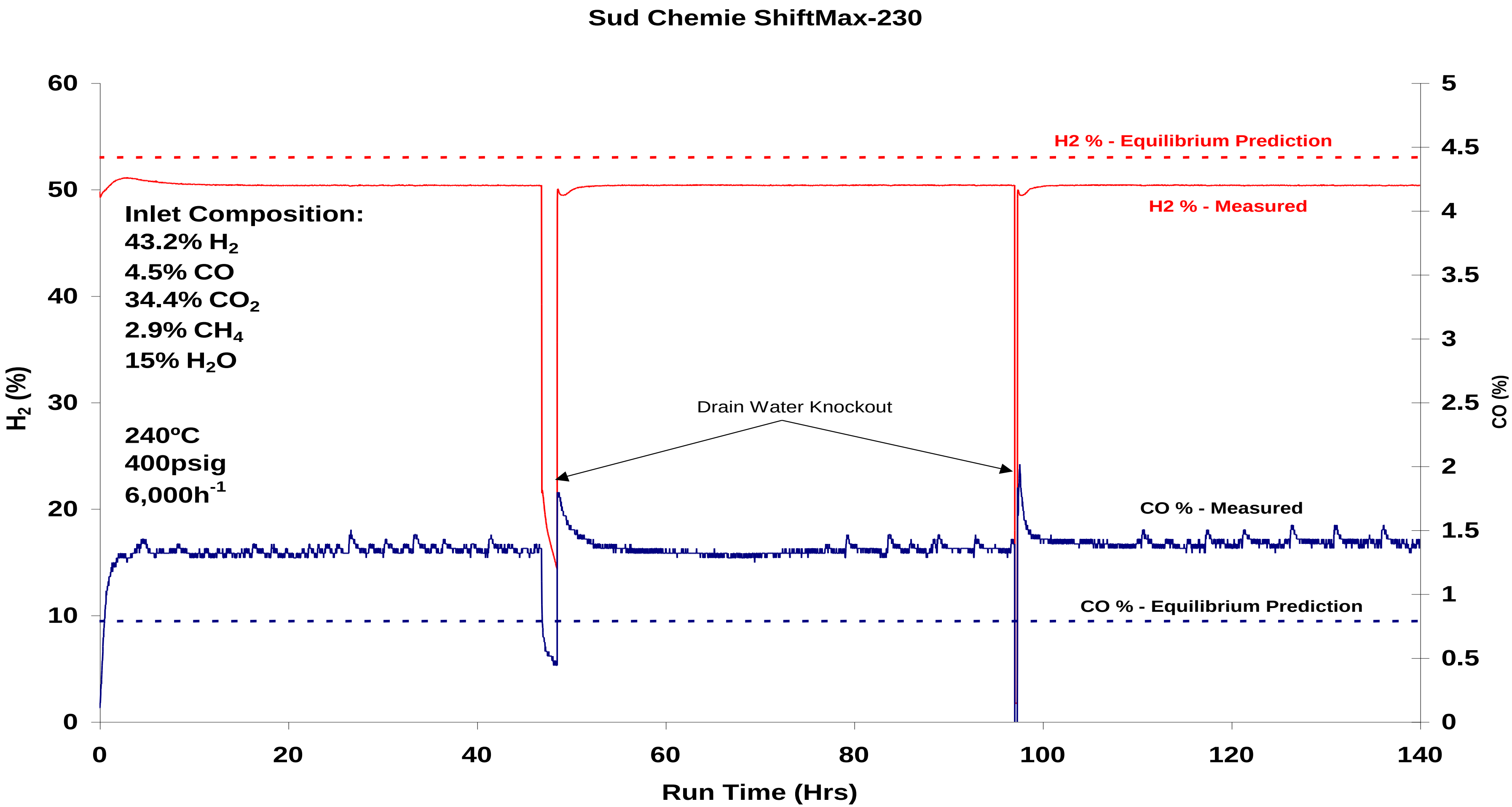
LT-WGS Baseline



- **Steady conversion over 140 hour run**
- **Future work involves testing the catalyst activity and selectivity in presence of various contaminants**

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Sorbent Development for Removal of Trace Contaminants

TDA's Warm Temperature Sorbent

Potential Poisons for FT Catalysts

Impurity	Tolerance Level	Source
Sulfur	0.2 ppm 1 ppmv 60 ppb	Dry, 1981 Boerrigter, *et al*, 2002 Turk, *et al*, 2001
Halides	10 ppb	Boerrigter, *et al*, 2002
Nitrogen	10 ppmv NH3 0.2 ppmv NOx 10 ppb HCN	Turk, *et al*, 2001

- **TDA's developing a warm temperature CO_2 sorbent**
- **The sorbent can be surface modified to increase its nitrogen, sulfur and trace contaminant removal capacity**
- **Nitrogen, sulfur, and CO_2 are removed in a regenerable manner**
- **As and halides are removed in an expendable manner**

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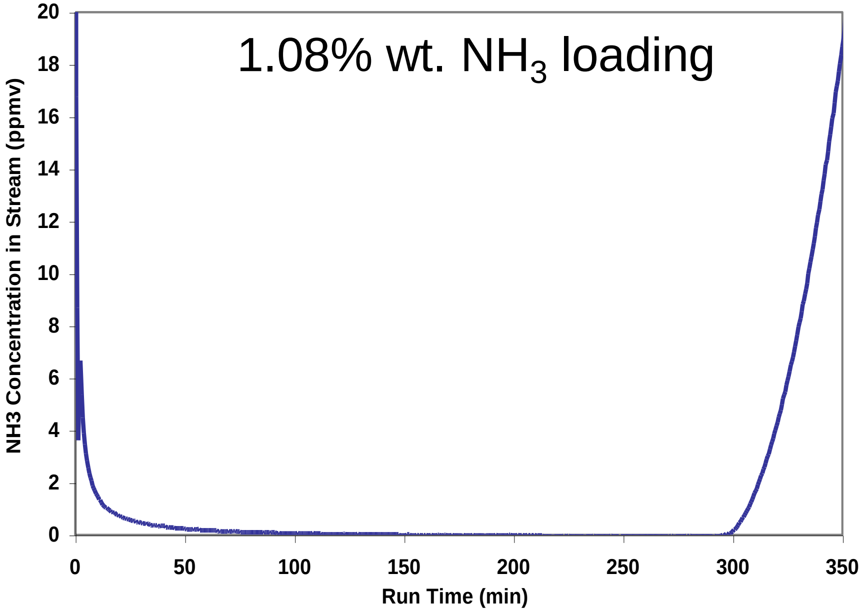
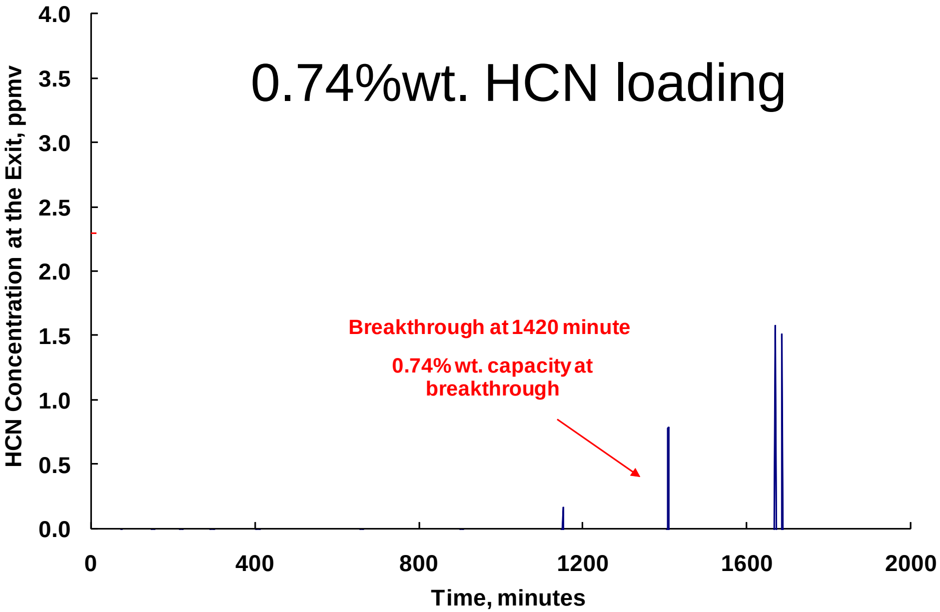
Ammonia Removal

70 ppmv NH_3, in simulated syngas, T= 180°C, P= 500 psig, GHSV= 180,000 h^{-1}



5 ppmv HCN, in simulated syngas T= 220°C, P= 500 psig, GHSV= 10,000 h^{-1}



- **NH_3 and HCN breakthrough curves with surface modified TDA's warm temperature CO_2 sorbent**

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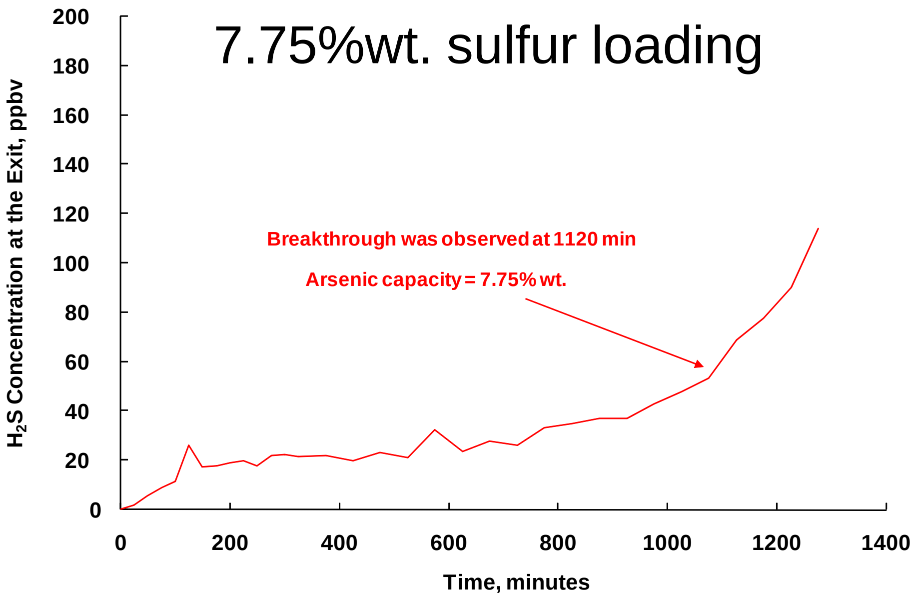
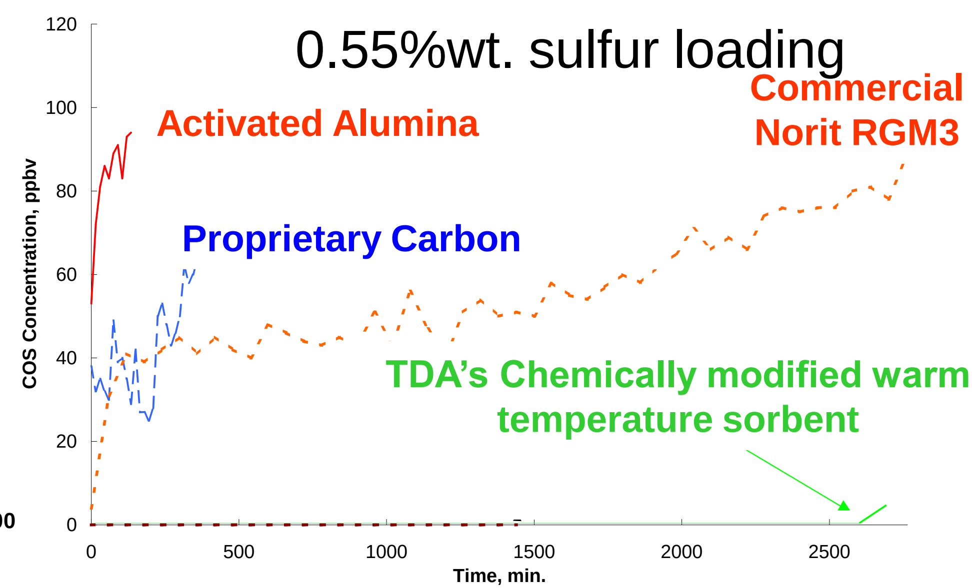
H_2S and COS Adsorption

20 ppmv H_2S, 1.5 ppmv AsH_3 in simulated syngas, T= 220°C, P= 500 psig, GHSV= 60,000 h^{-1}



2 ppmv COS, in simulated syngas T= 220°C, P= 500 psig, GHSV= 10,000 h^{-1}

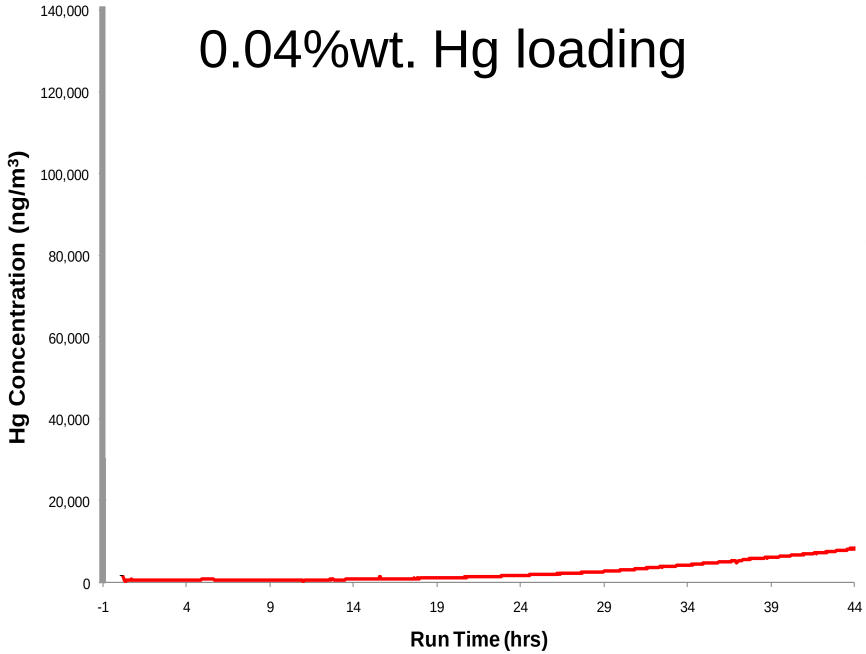


- **H_2S and COS breakthrough curves with surface modified TDA's warm temperature CO_2 sorbent**

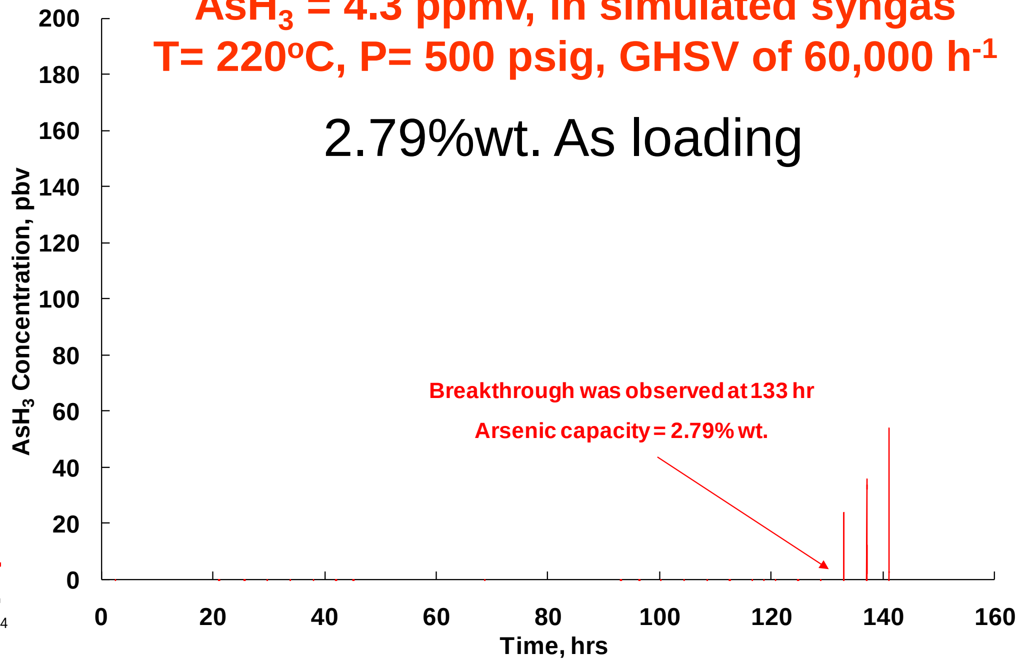
Hg and As Adsorption

- **Hg and As breakthrough curves with surface modified TDA's warm temperature CO_2 sorbent**

Hg Inlet Conc.= 140,000 ng/m^3, in simulated syngas
T= 220°C, P= 500 psig, GHSV of 60,000 h^{-1}



AsH$_3$ = 4.3 ppmv, in simulated syngas
T= 220°C, P= 500 psig, GHSV of 60,000 h^{-1}



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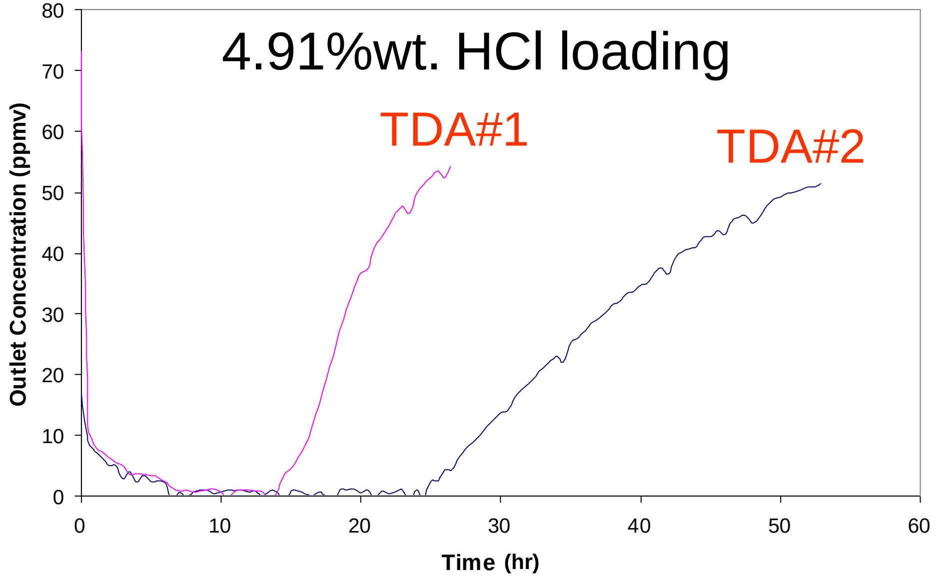
HCl Adsorption

5 ppmv HCl, in simulated syngas
T= 220°C, P= 500 psig, GHSV= 60,000 h^{-1}



- **HCl breakthrough curve with surface modified TDA's warm temperature CO_2 sorbent**

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Removal of Trace Contaminants

- **TDA's warm temperature CO_2 sorbent modified with different functional groups to capture trace contaminants simultaneously at warm gas temperatures ~ 430F**

Contaminant	Sorbent Capacity
Hg	0.04%
NH_3	1.08%
H_2S	7.75%
HCl	4.91%
HCN	0.78%
AsH_3	2.79%