Stability and Regenerability of Catalysts for the Destruction of Tars Formed During Black Liquor and Biomass Gasification

Pradeep K. Agrawal (P.I.)
School of Chemical Engineering
Georgia Institute of Technology
Atlanta, Georgia 30332

Scott Sinquefield, Kristiina Iisa
Institute of Paper Science and Technology
Atlanta, Georgia 30318

Project ID: DE-FC07-00ID 13875

Black Liquor Colloquium
Park City, Utah
May, 2003
Staff and Budget

**Staff**

- Dr. Pradeep Agrawal, Ga Tech, PI
- Dr. Kristiina Iisa
- Dr. David Dayton, NREL
- Dr. Scott Sinquefield, IPST
- Dr. Viboon Sricharoenchaikul, IPST and Ga Tech
- Dr. Xiaoyan Wu, IPST
- Anil Amlani, Ga Tech MS Student
- Mary Minton, Ga Tech
- Irais Passariello, Ga Tech

Duration: 3 years ending Feb 2003
1. Objective
2. Background
3. Experimental
4. Results and Discussions
5. Conclusions
6. Future Work
7. Path Forward
1. Overall Objectives

- To screen catalyst candidates for the destruction of tar species.
- To examine the effect of sulfur on catalytic activity.
- To study the role of alkali species in catalyst performance.
- To understand the effect of operating conditions on carbon deactivation.
- To develop and test pathways for catalyst regeneration.
- To study selected catalysts in a pilot scale operation.
2. Background

**Formation of Tars** 0.5 – 5% of carbon in BL forms tars. Tars will foul processing equipment and gas turbines. Tars are lost energy. Many tar compounds are carcinogenic.

**BL Tar Species** are mostly monoaromatic and polyaromatic ring compounds from incomplete breakdown of lignin (Sricharoenchaikul, PhD thesis 2001).

**Tar Removal Methods**
- **physical:** cooling towers, scrubbers, filters
- **thermal:** thermal cracking and partial oxidation
- **catalytic:** tar destruction on catalysts at relatively low temperature, surpassing former two methods due to high destruction efficiency, low cost, compatible operating conditions with gasification, lower effluent to environment
Catalytic tar removal

Steam reforming reactions

\[ \text{C}_6\text{H}_6 + 6\text{H}_2\text{O} = 6\text{CO} + 9\text{H}_2 \] \hspace{1cm} (1)
\[ \text{C}_6\text{H}_6 + 12\text{H}_2\text{O} = 6\text{CO}_2 + 15\text{H}_2 \] \hspace{1cm} (2)

Water – gas shift reaction

\[ \text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2 \] \hspace{1cm} (3)

Catalysts: (dozens were tested)

- Ni-SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3}, Pd, Pt, Ru-Al\textsubscript{2}O\textsubscript{3} (sulfur poisoning)
- WS\textsubscript{2} (active with sulfur but poisoned by alkali)
- Sulfided CoMoO\textsubscript{x}-Al\textsubscript{2}O\textsubscript{3} (active with both S and Na)

Goal of the final year (January 2002 – February 2003)

Investigate the performance of catalyst, Sulfided CoMo-Al\textsubscript{2}O\textsubscript{3}, vs. long-run time and regeneration times, particle size, temperature and steam level; pilot operation.
3. Experimental

Diagram of the catalytic reactor system and the ceramic Reactor
4. Results and Discussions

Deactivation Test

1.3 mol% steam level (Figure 1)
- a linear conversion-time decreasing trend;
  catalyst activity reduces from 0.28 to 0.05 after running 300 hours, 82% activity loss
- CO/(CO+CO₂) also reduces with time

2.1 mol% steam level (Figure 2)
- catalyst activity gradually reduces from 0.61 to 0.27 after 300 hours, 56% activity loss
- Higher steam level can prolong the catalyst life

Note: Industrial steam levels will be higher
Figure 1  Conversions (based on COx) and CO/COx change vs. operation time. Conditions: catalyst particle size: 180 ~ 250 µm; feed: benzene/2300 ppm, steam/1.3 mol%, helium/balance; temperature: 800ºC; catalyst amount: 0.4 g catalyst diluted in 2.0 g inert sand, W/F_{Benz}: 0.747 lb-cat.hr/mol
Figure 2  Conversions (based on COx) and CO/COx change vs. operation time. Conditions: catalyst particle size: 180 ~ 250 µm; feed: benzene/2300 ppm, steam/2.1 mol%, helium/balance; temperature: 800°C; catalyst amount: 1.0 g catalyst diluted in 5.0 g inert sand, W/F_{Benz} : 3.74 lb-cat.hr/mol
Catalyst Regeneration

Regeneration of deactivated catalyst: two-step treatment
  a. oxidization of coke
    feed: air/water/helium ~ 25.0/2.0/73.0 mol%,
    200ml/min, 450°C, 8 hours
  b. sulfidation of catalyst
    feed: 10.0 mol% H₂S with balance hydrogen,
    80ml/min, 550°C, 2 hours.

- Regeneration treatment → complete recovery of catalyst activity;
- No permanent loss of catalyst activity after regeneration twice
  (Figure 3)
- Coke formation – key factor leading to deterioration in catalyst
  activity
Figure 3  Conversions (based on COx and benzene consumption) change vs. operation time. Conditions: catalyst particle size: 180 ~ 250 µm; feed: benzene/2300 ppm, steam/2.1 mol%, helium/balance; temperature: 800°C; catalyst amount: 1.0 g catalyst diluted in 5.0 g inert sand, W/F_{Benz}: 3.74 lb-cat.hr/mol
Influence of catalyst size

Two catalyst sizes: 90 ~ 125 and 180 ~ 250 μm

Smaller catalyst particle size → higher conversion  
  intra-particle mass transport significantly influences catalytic  
  results for the larger catalyst particles (Figure 4)

Influence of Temperature

Reactions (1) and (2): strongly endothermic

Increasing temperature  
  → conversion of benzene increases (Figure 5)  
  → CO/(CO+CO₂) increases (Figure 6)
Figure 4  Profiles of conversion vs. time for different particle sizes. Conditions: catalyst particle sizes/90 ~ 125 µm and 180 ~ 250 µm; feed: benzene/2300 ppm, steam/1.3 mol%, helium/balance; temperature: 800°C; catalyst amount: 0.4 g catalyst diluted in 2.0 g inert sand, $W/F_{\text{Benz}}$ : 0.747 lb-cat.hr/mol
Figure 5 Conversions change vs. temperature. Conditions: catalyst particle size: 180 ~ 250 µm; feed: benzene/2300 ppm, steam/2.1 mol%, helium/balance; temperature: 700 ~ 900°C; catalyst amount: 1.0 g catalyst diluted in 5.0 g inert sand, $W/F_{\text{Benz}}$: 3.74 lb-cat.hr/mol

$E_a \sim 78.8$ kJ/mol
Figure 6  Ratio of CO to total COx changes vs. temperature
Influence of Steam Level

Increasing steam level (Figure 7)
→ conversion based on benzene consumption nearly unchanged
→ conversion based on produced COx increases
→ reducing coke deposition

Steam level in syngas from gasifier >> 5mol%, keeping catalyst lasting longer

More steam favors CO₂ generation (Figure 8)
(from reaction (2) and (3))
Figure 7 Conversions change vs. steam level. Conditions: catalyst particle size: 180 ~ 250 µm; feed: benzene/2300 ppm, steam/0.5 ~ 5.0 mol%, helium/balance; temperature: 800ºC; catalyst amount: 1.0 g catalyst diluted in 5.0 g inert sand, \( W/F_{\text{Benz}} \): 3.74 lb-cat.hr/mol.
Figure 8 Concentration of COx and ratio of CO/(CO+CO2) change vs. steam level.
5. Conclusions from Prior Years

- Group VIII transition metals (Ni, Pt, Pd, Ru) are active for steam reforming of Tar, but are irreversibly poisoned by sulfur.

- WS\textsubscript{2} and CoMoS showed promise as sulfur-tolerant catalysts. WS\textsubscript{2} was irreversibly poisoned by Na.

- Various active (MoS\textsubscript{2}, MoO\textsubscript{2}) and inactive (Na\textsubscript{2}MoO\textsubscript{4}) phases can be formed depending on the feed conditions; it is important to understand the transformations between different phases as the deactivated catalysts undergo regeneration attempts.
Conclusions from the final year

- Slow carbon deactivation for MoCoS catalyst
- Steam level affects coke deposition and catalyst deactivation significantly
- Temperature strongly influences benzene conversion
- Intra-particle mass transport exerts an evident effect on catalytic reaction
- Complete catalytic activity recovery by air oxidation/sulfidation treatment
6. Future Work

- Industrial sulfur and water levels.
- Optimize the CoMoS alloy, and the support structure for surface area.
- Kinetics model for tar destruction (99+% conversion)
- Improve understanding of the regeneration of carbon-deactivation and the cycling of various phases between reaction, regeneration and resulfiding.
- Carbon deactivation kinetics model
- Testing with real BLG syn gas using bench scale tar generator under construction
- Pilot testing using a slip stream of syn gas from a real gasifier (Big Island, New Bern, Ferco)