Decoking Atmospheres on Alumina-Forming Alloys

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Introduction

- Steam cracking of hydrocarbons is one of the most important processes for manufacturing many base chemicals.
- Carbon buildup (or coking) on stainless steel tubes at high temperatures = high operational costs in ethylene production.
- What is the best atmosphere to decoke (or remove the carbon) these tubes?
- What is the effect of decoking atmosphere on the alloys?
- Two alloys were evaluated: Alumina-forming alloy (AFA) vs Chromia-forming alloy (CFA)

Experimental Procedure

Pre-oxidation (obtain oxide layer)
- 100% Steam
- Temp: 850°C
- Time: 12 h

Coking (carbon deposition)
- 30:1 H₂:C₂H₆
- Temp: 950°C
- Time: 50 h

Decoking (removal of carbon)
- Variable atmosphere
- Temp: 850°C
- Time: 12 h

Decoking reaction:
\[ \text{O}_2 + C = \text{CO}_2 \]

Three decoking atmospheres were tested:
- 100% Steam \( P_{O_2} = 10^{-6} \text{ atm} \)
- Steam – Air \( P_{O_2} = 10^{-3} \text{ atm} \)
- 100% Air \( P_{O_2} = 10^{-0.6} \text{ atm} \)

Results

Decoked

<table>
<thead>
<tr>
<th>Mass change (mg/cm²)</th>
<th>AFA</th>
<th>CFA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low ( P_{O_2} )</td>
<td><img src="AFA_Low_PO2.png" alt="Image" /></td>
<td><img src="CFA_Low_PO2.png" alt="Image" /></td>
</tr>
<tr>
<td>Moderate ( P_{O_2} )</td>
<td><img src="AFA_Moderate_PO2.png" alt="Image" /></td>
<td><img src="CFA_Moderate_PO2.png" alt="Image" /></td>
</tr>
<tr>
<td>High ( P_{O_2} )</td>
<td><img src="AFA_High_PO2.png" alt="Image" /></td>
<td><img src="CFA_High_PO2.png" alt="Image" /></td>
</tr>
</tbody>
</table>

Analysis

- AFA alloy lost mass after being decoked in all three environments.
- CFA alloy gained mass after each decoking treatment, indicating further oxidation and possibly no carbon removal.
- SEM analysis indicates that AFA and CFA alloys did not change drastically in appearance.
- High PO₂ atmosphere removed .023% in AFA alloys and added .0066% in the CFA being the atmosphere with highest removal content

Conclusion

- In terms of carbon removal, the High PO₂ decoking atmosphere seems to have best results
- Future investigations on XRD is needed to characterize oxide layer change

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Figure 1: Representation of carbon buildup.

Figure 2: Alumina-forming alloys (AFA) vs Chromia-forming alloys (CFA)

Figure 3: Images of coked and decoked procedure for AFA and CFA alloys. Scale bar at ~2 cm.

Figure 4: SEM microstructure after each decoking procedure for AFA and CFA alloys.

Figure 5: Average change of mass after each decoking treatment. Negative values indicate that mass decreased.