Attrition of methanol to olefins catalyst in a jet cup

Mao Ye
National Engineering Laboratory for MTO, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, China, maoye@dicp.ac.cn

Zhongmin Liu
National Engineering Laboratory for MTO, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, China

Yinfeng Zhao
National Engineering Laboratory for MTO, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, China

Jingai Haoa
National Engineering Laboratory for MTO, Dalian Institute of Chemical Physics, Chinese Academy of Sciences; University of Chinese Academy of Sciences, China

Follow this and additional works at: http://dc.engconfintl.org/fluidization_xv

Part of the Chemical Engineering Commons

Recommended Citation

This Abstract and Presentation is brought to you for free and open access by the Proceedings at ECI Digital Archives. It has been accepted for inclusion in Fluidization XV by an authorized administrator of ECI Digital Archives. For more information, please contact franco@bepress.com.
Attrition of methanol to olefins catalyst in high temperature jet cup

Jingai Hao, Yinfeng Zhao, Mao Ye* and Zhongmin Liu

National Engineering Laboratory for MTO, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, China
Email: maoye@dicp.ac.cn

Fluidization XV, May 22-27, 2016, Fairmont Le Chateau Montebello, Quebec, Canada
Contents

- Background
- Experimental
- Results and discussion
- Conclusions
1. Background: MTO process

- MTO = methanol to olefins (ethylene and propylene)
  - world’s first MTO commercial unit started up in 2010 by DICP
  - currently more than 10 units on stream
  - Turbulent fluidized bed reactor and bubbling fluidized bed regenerator
  - SAPO-34 zeolite catalyst
1. **Background: MTO catalyst**

- **MTO catalyst manufacture**
  - physical properties close to FCC (fluid catalytic cracking) catalyst:
    - density
    - particle size distribution
    - attrition index measured in the laboratory
1. Background: MTO unit

- Catalyst loss rate much lower than that in FCC unit
- Slurry of fines at the bottom of quench tower
1. Background: purpose of this study

- Understand the attrition of MTO catalyst at high temperature
  - Comparison of attrition test methods: high velocity gas jets (ASTM-D5757-11) vs Jet cup
  - Influence of temperature, gas velocity, test time on MTO attrition index

2. Experimental: setup

Conical jet cup

Tab. 1 Properties of sieved catalyst samples

<table>
<thead>
<tr>
<th>Property</th>
<th>value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk density, g/cm³</td>
<td>0.75</td>
</tr>
<tr>
<td>$d_{p50}$, μm</td>
<td>111.7</td>
</tr>
<tr>
<td>$d_{p32}$, μm</td>
<td>106.9</td>
</tr>
</tbody>
</table>
## 2. Experimental: conditions

<table>
<thead>
<tr>
<th>No.</th>
<th>Inlet gas velocity, m/s</th>
<th>Temperature, °C</th>
<th>Time, min</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>88</td>
<td>20</td>
<td>180</td>
</tr>
<tr>
<td>2</td>
<td>114</td>
<td>20</td>
<td>180</td>
</tr>
<tr>
<td>3</td>
<td>139</td>
<td>20</td>
<td>180</td>
</tr>
<tr>
<td>4</td>
<td>158</td>
<td>20</td>
<td>180</td>
</tr>
<tr>
<td>5</td>
<td>88</td>
<td>100</td>
<td>180</td>
</tr>
<tr>
<td>6</td>
<td>114</td>
<td>100</td>
<td>180</td>
</tr>
<tr>
<td>7</td>
<td>139</td>
<td>100</td>
<td>180</td>
</tr>
<tr>
<td>8</td>
<td>158</td>
<td>100</td>
<td>180</td>
</tr>
<tr>
<td>9</td>
<td>139</td>
<td>20</td>
<td>180</td>
</tr>
<tr>
<td>10</td>
<td>139</td>
<td>100</td>
<td>180</td>
</tr>
<tr>
<td>11</td>
<td>139</td>
<td>200</td>
<td>180</td>
</tr>
<tr>
<td>12</td>
<td>139</td>
<td>300</td>
<td>180</td>
</tr>
<tr>
<td>13</td>
<td>139</td>
<td>400</td>
<td>180</td>
</tr>
<tr>
<td>14</td>
<td>139</td>
<td>500</td>
<td>180</td>
</tr>
</tbody>
</table>
2、Experimental: methods

- Attrition index \((AI)\): the weight percent of particles less than 20 μm or 44 μm \((AI_{20}\) and \(AI_{44}\)) after experiments

- A material balance analysis showed that the fine loss was less than 1.5% of the initial sample for all individual test

- Particle size distribution (PSD): Malvern laser particle size analyzer (Mastersizer 3000)

- Particles’ morphology: Scanning electron microscope (SEM, Hitachi TM 3000)
3. Results: effect of operating temperature

Attrition index (after three hours) with temperature (inlet gas velocity 139 m/s for jet up and 424 m/s for high velocity gas jets)

- Attrition index is maximum at 100 °C;
- Attrition at 25 °C may be different from that at high temperature
- Results agree with our previous findings at high gas velocity gas jets

SEM pictures of the remaining particles in jet cup after tests: (a) room temperature, (b) 100 °C, (c) 200 °C, (d) 300 °C, (e) 400 °C, (f) 500 °C.

At room temperature, both fragmentation and abrasion exist; only abrasion at high temperature.
PSD of the samples after tests at different temperatures.

- Attrition mechanism at room temperature and high temperature (above 100°C) is different for MTO catalyst
  - At room temperature, both fragments of 25 μm and fines of 2 μm appear;
  - At high temperature there are mainly fines of 2 μm
3. Results: effect of attrition time

Gwyn formulation

\[ AI = k_1 t^n \]  \hspace{1cm} (1)

- \( k_1 \): attrition rate constant
  - depends on operating conditions.
- \( n \): fitting parameter
  - depends on the attrition mode and material property.
- \( t \): test time

In our previous experiments in air jets (ASTM-), \( n \) was found to be 1.233 for \( Al_{20} \) at room temperature (25\(^\circ\)C), and 1.236 for \( Al_{20} \) at 500 \(^\circ\)C.
3. Results: effect of attrition time

- Attrition index varies with test time at different inlet gas velocities.

![Graphs showing the relationship between attrition index and time for different inlet gas velocities.](image)

Table 3. $k_1$ and $n$ for different inlet gas velocities.

<table>
<thead>
<tr>
<th>Inlet gas velocity, m/s</th>
<th>$AI_{20}$</th>
<th>$AI_{44}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$k_1$, h$^{-1}$</td>
<td>$n$</td>
</tr>
<tr>
<td>88</td>
<td>0.345</td>
<td>1.213</td>
</tr>
<tr>
<td>114</td>
<td>1.284</td>
<td>1.213</td>
</tr>
<tr>
<td>139</td>
<td>3.876</td>
<td>1.213</td>
</tr>
<tr>
<td>158</td>
<td>5.823</td>
<td>1.213</td>
</tr>
</tbody>
</table>

*: Temperature is 373.15 K.
3. Results: effect of attrition time

- Attrition index varies with test time at different temperatures.

![Graphs showing AI20 and AI44 vs. time for different temperatures](image)

Table 4. $k_1$ and $n$ for different temperatures.

<table>
<thead>
<tr>
<th>Temperature, K</th>
<th>$k_1$, h$^{-1}$</th>
<th>$AI_{20}$</th>
<th>$n$</th>
<th>$k_1$, h$^{-1}$</th>
<th>$AI_{44}$</th>
<th>$n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>373.15</td>
<td>4.014</td>
<td>1.213</td>
<td></td>
<td>4.795</td>
<td>1.173</td>
<td></td>
</tr>
<tr>
<td>473.15</td>
<td>2.792</td>
<td>1.213</td>
<td>3.198</td>
<td>1.173</td>
<td></td>
<td></td>
</tr>
<tr>
<td>573.15</td>
<td>2.076</td>
<td>1.213</td>
<td>2.536</td>
<td>1.173</td>
<td></td>
<td></td>
</tr>
<tr>
<td>673.15</td>
<td>1.401</td>
<td>1.213</td>
<td>1.764</td>
<td>1.173</td>
<td></td>
<td></td>
</tr>
<tr>
<td>773.15</td>
<td>0.417</td>
<td>1.213</td>
<td>0.661</td>
<td>1.173</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*: Inlet gas velocity is 139 m/s.
3. Results: effect of attrition time

- Comparison with previous results in high velocity gas jets
  - Parameter $n$:
    - High velocity gas jets: $n=1.233$
    - Jet cup: $n=1.213$
  - Test time $t$: the time to achieve steady attrition
    - High velocity gas jets: 2 hours
    - Jet cup: 15 minutes

- For MTO catalyst the attrition measured by two methods is quantitatively comparable.
- Test time required in jet cup significantly shorter than that in high velocity gas jets
3. Results: Influence of operation conditions in jet cup

A correlation with following formulation is derived:

\[ AI = k_0 e^{-k_3(T-373.15)} U^m t^n \]

<table>
<thead>
<tr>
<th>Parameters</th>
<th>( AI_{20} )</th>
<th>( AI_{44} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_0 )</td>
<td>( 4.65 \times 10^{-8} )</td>
<td>( 5.43 \times 10^{-8} )</td>
</tr>
<tr>
<td>( k_3 )</td>
<td>0.00452</td>
<td>0.00452</td>
</tr>
<tr>
<td>( m )</td>
<td>3.7</td>
<td>3.7</td>
</tr>
<tr>
<td>( n )</td>
<td>1.213</td>
<td>1.173</td>
</tr>
<tr>
<td>( R^2 )</td>
<td>0.986</td>
<td>0.958</td>
</tr>
</tbody>
</table>

Comparison between the experimental results and the predicted \( AI \): (a) \( AI_{20} \), (b) \( AI_{44} \).
Attrition mechanism of MTO catalyst is different for room temperature and high temperature (above 100°C)

- both fragmentation and abrasion exist at room temperature
- abrasion is dominant at high temperature
- attrition test results at room temperature cannot be directly used for high temperature
- fines from abrasion at high temperature are around 2 μm, which is hard to be captured by cyclones.

For MTO catalyst quantitatively comparable results can be obtained in both high velocity gas jets and jet cup method; but jet cup method needs significantly shorter test time

A correlation of MTO catalyst attrition in high temperature jet cup with operation conditions fits the experimental data very well
Thank you for your attention!

National Engineering Laboratory for Methanol to Olefins
Dalian Institute of Chemical Physics, CAS, Dalian 116023, China