Caprolactam Recovery from Nylon-6 via Reactive Extrusion

nylon 6  \rightarrow  \varepsilon\text{-caprolactam}
Previous Works

- Ammonolysis
- Hydrolysis
  - Steam only
  - Acid + steam
  - Base + steam
- Pyrolysis
  - No catalyst
  - Base-catalyzed
# Base-catalyzed Pyrolysis

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>% Catalyst</th>
<th>Reactor</th>
<th>Time</th>
<th>Temp. °C</th>
<th>Pressure</th>
<th>Yield</th>
<th>% Purity</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaOH</td>
<td>1</td>
<td>semi-batch</td>
<td>4.5 hr</td>
<td>250</td>
<td>3 mmHg</td>
<td>90.5</td>
<td>unknown</td>
</tr>
<tr>
<td>K₂CO₃</td>
<td>0.5-2.5</td>
<td>semi-batch</td>
<td>various</td>
<td>270-300</td>
<td>25 mbar</td>
<td>95</td>
<td>98</td>
</tr>
<tr>
<td>KOH on alumina</td>
<td>5 w/w</td>
<td>fluidized bed</td>
<td>&lt; 1 hr</td>
<td>330-360</td>
<td>-</td>
<td>85</td>
<td>90</td>
</tr>
<tr>
<td>eutectic NaOH/KOH</td>
<td>10</td>
<td>cycled spheres</td>
<td>75-300 mins</td>
<td>290-350</td>
<td>-</td>
<td>99</td>
<td>99</td>
</tr>
</tbody>
</table>

Depolymerization Methods - Pyrolysis

National Renewable Energy Lab (NREL)

- CRNI TSE
- 2 minutes residence time
- Nylon 6 carpet strips with $\text{K}_2\text{CO}_3$
- 67% crude yield
Objectives

- Assess catalysts
  - Different bases: same conditions
  - Screen using dynamic Thermogravimetric Analysis (TGA)
  - As little catalyst as possible

- Effective depolymerization reactor
Catalyst Screening

- Mixed catalysts and pure nylon in Haake Rheomix® 600
  - 240°C
  - 5 mins
  - Under N₂
  - 10% wt of polymer
- Grind into powder
- Dynamic TGA
  - 25-500°C
  - Heating @ 10°/min
TGA Results: Hydroxides

Weight loss fraction

KOH
CsOH
NaOH
Pure Nylon 6

Temperature (°C)

200 250 300 350 400 450 500
TGA Results: Carbonates

![Graph showing the weight loss fraction of different carbonates with temperature.](image)

- $K_2CO_3$
- $Na_2CO_3$
- CR $Ca_2CO_3$
- $Cs_2CO_3$
- Pure Nylon 6
TGA Results: Selected Catalysts

- 10% KOH
- 1% KOH
- 10% $\text{K}_2\text{CO}_3$
- 1% $\text{K}_2\text{CO}_3$
- Pure Nylon 6
Kinetics from TGA

ASTM E 1641 – 99

- Assumes 1\textsuperscript{st} order
- Iterative process
  - Activation Energy
  - Pre-exponential

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<tr>
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<tr>
<td>Pure</td>
<td>3.65E+04</td>
<td>6.15E+03</td>
<td>1197</td>
<td>264</td>
<td>65</td>
</tr>
<tr>
<td>1% KOH</td>
<td>21</td>
<td>7</td>
<td>2</td>
<td>0.9</td>
<td>0.3</td>
</tr>
<tr>
<td>1% K\textsubscript{2}CO\textsubscript{3}</td>
<td>130</td>
<td>42</td>
<td>15</td>
<td>6</td>
<td>2</td>
</tr>
<tr>
<td>cr Ca\textsubscript{2}CO\textsubscript{3}</td>
<td>1079</td>
<td>270</td>
<td>75</td>
<td>23</td>
<td>8</td>
</tr>
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Extruders inherent capabilities:

- Good melting of polymers & temperature control
- Control over residence time distribution
- Excellent dispersive and distributive mixing
- Continuous processing

Counter-rotating Non-intermeshing Twin Screw Extruder (CRNI TSE)

- High degree of backflow
- High interfacial area for devolatilization/Superior vent performance
## Residence Time

### Time to 90% Conversion (min)

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### Exit Age Distribution (time-1)

Graph showing time to 90% conversion at different temperatures and flow rates.
Product Collection
GC Results

ION TRACE. Flagging=Scan Number & Area. Max.Scan=1675#30:01.94. Integ=[Det:1%, Hgt:0.5V, Wid:3-50, Res:3%]. Total Ion Current. Max.Int.=24.43895.
SCAN GRAPH.

Scan 571#10:13.76 - 576#10:19.15. Sub=579#10:22.37 - 591#10:35.28. 100% Int.=0.20936. Ei. POS. 0.209360.20936

Low Resolution M/z

Intensity (%age)

42.1 51.1 55.1 67.1 68.1 84.1 85.1 113.1

MS Results
Key Parameters and Variables

- Screw configuration
- Barrel temperatures
- Vacuum level
- Product rate/Screw speed ratio
Summary

- Pure nylon: degradation onset ~ 400°C
- With catalyst: onset between 250-300°C
- Hyroxides
  - CsOH & KOH most effective
- Carbonates
  - Cs₂CO₃ and K₂CO₃ most effective
  - Carpet Ratio CaCO₃ decreases onset
- Cs⁺ bases more expensive than K⁺ bases
  - KOH and K₂CO₃ seem to be the best candidates
    - 10% KOH and K₂CO₃ have similar onset Temperature
    - 1% catalyst as effective as 10%
- Twin screw extruder as reactor
  - Sufficient residence time
  - Pure caprolactam
  - Still trying to optimize the yield
Fin
### Miscellaneous

- **caprolactam** $0.90-\$0.98/lb
- **K_2CO_3** $0.40/lb
- vapor pressure of caprolactam 1.9 E-3 mm Hg at 25 °C

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<th>Specifications</th>
<th>ε-caprolactam</th>
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<tr>
<td>Freezing point (dry basis) (°C)</td>
<td>69.0 (minimum)</td>
</tr>
<tr>
<td>Percen transmission at 410 nm (65wt % aq. sol'n)</td>
<td>92.0 (minimum)</td>
</tr>
<tr>
<td>Permanganate number</td>
<td>7 (maximum)</td>
</tr>
<tr>
<td>Moisture (%)</td>
<td>0.10 (maximum)</td>
</tr>
<tr>
<td>Iron (as Fe) (ppm)</td>
<td>0.5 (maximum)</td>
</tr>
<tr>
<td>Volatile bases (as NH3) (ppm)</td>
<td>5 (maximum)</td>
</tr>
<tr>
<td>Ignition residue (ppm)</td>
<td>10 (maximum)</td>
</tr>
<tr>
<td>Water insoluble</td>
<td>passes test</td>
</tr>
<tr>
<td>Cyclohexanone omine (ppm)</td>
<td>10 (maximum)</td>
</tr>
<tr>
<td>Free alkalinty (meq kg-1)</td>
<td>0.04 (maximum)</td>
</tr>
</tbody>
</table>

http://www.epa.gov/ttn/atw/hlthef/caprolac.html
Chemical market reporter Oct. 28, 2004
Nylon 53%
CaCO₃ 30%
PP 7%
SBR 10%
Depolymerization Methods - Ammonolysis

- Nylon in ammonia at high temperatures and pressures
- 81% monomer recovery
- Numerous by-products

**Depolymerization Methods - Hydrolysis**

- **Non-catalyzed**: steam only
  - Less than 10% contaminant
  - 3 hours
  - 94.4% pure caprolactam, but only 89.7% overall yield
  - Further purification required

- **Acid Catalyzed**: 5-35wt% mineral acids with steam
  - 96.4% yield
  - Cannot be used with mixed material

- **Base catalyzed**: alkali and alkaline earth oxides, hydroxides, carbonates, etc. with steam
  - 98% yield
  - By-products present

Miller, B. U.S. Patent 2,840,606 (1958)