Innovation Drives Green Growth:
Advanced Flow Reactor Technology -
Industrial Production Made Real

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Manager Sales – AFR India

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Corning Incorporated

- **Founded:** 1851
- **Headquarters:** Corning, New York
- **Employees:** ~34,000 worldwide
- **2014 Sales:** $10.2B
- **US Fortune 500 Rank (2014):** 343
- Corning is the world leader in specialty glass and ceramics.

Corning Reactor Technologies:

- **Program started:** 2002
- **Business Headquarters:** Avon, France
- Provide innovative Corning® Advanced-Flow™ Reactor products and full engineering services for
  - **Flow Chemical Process Development**
  - **Flow Chemical Industrial Production**
    - Pharma Chemicals
    - Fine Chemicals
    - Specialty Chemicals
    - Base Chemicals
AFR™ Patented Heart-Cell Designs

*Offer fast mixing & superior heat exchange (1000X enhancement)*

**Mixing of Two Liquid Phases**
- Liquid 1: Blue
- Liquid 2: Yellow
- Mixture: Green

![Diagram of Mixing of Two Liquid Phases](image)

**HE Layer**

**Reaction Layer**

**HE area:** 2500 m²/m³

**U × (S/V) ≥ 1 MW/m³.K**

**Corning® Specialty Glass**
AFR™ Reactor Offers Superior G-L, L-L Mass Transfer Performance with Much Lower Energy Consumption (or Pressure-Drops)

MIT-Klavs F. Jensen Group fundamental study of Corning G1 fluidic module, published a series of results (2012-2013)

Consistent mixing and mass transfer from lab to production at same residence time

![Graph showing volumetric mass transfer coefficient vs. residence time](image)

- **LFR 5 t/y**
- **G1, 80 t/y**
- **G2, 250 t/y**
- **G3, 1000 t/y**
- **G4, 2000 t/y**
Replacing batch reactor processes with “continuous-flow” reactor processes: Significant Improvement in Safety
AFR: Revolutionary Improvement vs. Batch

1000 X HE Improvement
100 X Mixing Improvement
1/1000 X Batch Reactor Volume

Seamless Scaleup from Lab to Production

- 25% Readily Convertible
- 25% Not Convertible!
- 25% Convertible with efforts
- 25% with Hybrid Approach

- Not 100% reactions fit to AFR
- Continue requiring innovative process development
- Chemists, ChE, MechE work together
# AFR Provides Comprehensive Solutions from Lab to Production

<table>
<thead>
<tr>
<th>G4 SiC</th>
<th>Lab flow-chemistry R&amp;D (high PH/high T, HF)</th>
<th>Small-production Flow: 15-35 kg/hr (high PH/high T, HF)</th>
<th>Medium production Flow: ~35 kg/hr Annual: 250 t/y</th>
</tr>
</thead>
<tbody>
<tr>
<td>G3</td>
<td>Lab flow-chemistry R&amp;D</td>
<td>Kilo-lab production Flow: 1.5-15 kg/hr</td>
<td>Small production Flow: ~15 kg/hr Annual: 80 t/y</td>
</tr>
<tr>
<td>G2 SiC</td>
<td>Lab flow-chemistry R&amp;D</td>
<td>Kilo-lab production Flow: 0.1-0.6 kg/hr</td>
<td>Small production Flow: ~15 kg/hr Annual: 5 t/y</td>
</tr>
<tr>
<td>G1</td>
<td>Lab flow-chemistry R&amp;D</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LF</td>
<td>Lab flow-chemistry R&amp;D</td>
<td></td>
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</tr>
</tbody>
</table>

| Large production Flow: ~300 kg/hr Annual: **2000 t/y** |
| Large production Flow: ~150 kg/hr Annual: **1000 t/y** |
Corning AFR™ G1 Process Development System Platform

**Chiller** for temperature control:
-20 to 200°C, 2.5 bar

**Corning AFR™ Reactors**
Operating Inlet pressure up to 18 bar

**Dosing Lines** (20 bar)
(S.S. or metal-free pump-heads)

AFR™ G1 Process Development Platform
AFR™ G2 SiC Offers Special Solutions for Highly Caustic at High Temperature, HF Involved Applications

Operating conditions: Temperature = -10 ~ 200C; Inlet Pressure = 0 ~ 18 bars; Flow rate = 50 ~ 500 ml/min

You can open the reactive plates!

Internal volume: 28mL per plate
Corning Launched AFR™ G1 Photo Reactor

- An engineered reactor with all of the benefits from the existing G1 reactor (good mixing, good temperature management, etc).
- Plus:
  - Good control of the light source
    - Position of the LED guarantees homogenous illumination
    - LED temperature control guarantees long lifetime
  - Double illumination guarantees a more efficient use of the light
  - Choice of wavelength
    - 365 nm, 405 nm, etc.
  - Light intensity is tunable
AFR™ technology & manufacturing have received many certificates, and awards in Europe and Asia

- TÜV PED Quality Certificate (G4 SiC)
- China SELO A4 (SiC)
- EU ATEX II 2 G c IIC T4 Certificate (G1, G3) Certificates
- FDA Certificates for compliances
- ISO 14001
- ...

AFR helped Changzhou University win National Grand Award “Challenge Award”

Received 2013 National Innovation Award by China Petroleum & Chemical Industry Federation CPCIF
Corning® AFR™ Reactor Technology is committed to providing global application engineering and commercial support.
Hydrogenation with Pd/C catalyst:
We can dose the slurry (Pd/C G1+solvent or raw materials) into G1 using diaphragm pump, and clean it out with solvent as shown.

Catalyst size < 200 µm, typically 20-100 µm
Selective Hydrogenation of Slurry in Corning® AFR

98% + conversion & selectivity (impurity profiles within spec.)

- highly exothermic (>400 kJ/mol)
- ~30 μm catalyst in slurry
- significant catalyst reduction

Ref: Chemistry Today 27(6), Nov-Dec (2009)
Green Process: Glycerine to Fuel Additives in Corning® AFR
Successful feasibility demonstration for ~1000 mt/y industrial production

- 10% biofuels for transports by 2020 in EU
- 20 millions tons biodiesel capacity in 2009 (EU)
- 10 tons biodiesel => 1 ton Glycerine (by-product)

Convert Glycerine to STBE (Solketal TertButyl Ether) via Solketal

Ref: Chemistry Today – submitted (2010)
Carbonyl hydrogenation to hydroxyl (1)

\[ \text{Conversion vs. reaction time} \]

\[ \text{Catalyst Activity vs. \# of Catalyst Recycles} \]
Carbonyl hydrogenation to hydroxyl (2)

\[
\text{R–C} \xrightleftharpoons{\beta^{-1/4} \Delta} \text{R–C–OH}
\]

✓ Corning AFR delivered better and much stable yield

![Graph showing yield vs. number of experiments]

- AFR Hydrogenation Yield
- Batch Hydrogenation Yield

Number of expt.

Yield
Low Temperature Applications
Energy saving and/or better yield (DCM-B-Pin)

Hans-Rudolf Marti et al, “1st Symposium on Continuous Flow Reactor Technology for Industrial Applications” (October 12, 2009)
Chlorination using AFR

- Targeted product: B
- Batch: -10 °C with fast reaction rate, high heat release, temperature rises rapidly
- By-product C is formed if more Cl2 is fed
- By-product C is explosive potential, unstable
- Product B is unstable, hard to control the reaction ending point
Chlorination Results (1): Batch vs. AFR

Conversion vs. chlorine/SM mole ratio

Yield vs. reaction temperature

Yield vs. SM concentration%

Yield vs. reaction time
AFR for Continuous Production of Y2010A: Simplified process with improved yield and purity

- Organic lubricant additives: **Y2010A** (methylene-bis-dibutylthiocarbamate)
- Market: 3500 t/y,
- 2 step complicated synthesis => 1 step stable synthesis
- Increased yield from 85% to 92%
- Improved purity from 97% to 99%
- Reduced reaction time from 10 hours to 1 minute
- Filed 3 process Chinese patents

### AFR vs. Batch

<table>
<thead>
<tr>
<th>Process</th>
<th>Yield</th>
<th>Purity</th>
<th>Reaction Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>AFR</td>
<td>92%</td>
<td>99%</td>
<td>1 min</td>
</tr>
<tr>
<td>Batch</td>
<td>85%</td>
<td>97%</td>
<td>10 hours</td>
</tr>
</tbody>
</table>

**AFR**

**Batch**

1 Step

2 Steps
Flow Chemistry Helped Deliver Green Continuous Process: Eliminated solvent use & extraction, distillation etc steps

<table>
<thead>
<tr>
<th></th>
<th>HATP</th>
<th>Batch</th>
<th>AFR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yield</td>
<td>67%-75%</td>
<td>Quantitative Yield</td>
<td></td>
</tr>
<tr>
<td>Purity</td>
<td>&gt;97.0%</td>
<td>&gt;97.0%</td>
<td></td>
</tr>
<tr>
<td>B/A Molar Ratio</td>
<td>1.10</td>
<td>1.02</td>
<td></td>
</tr>
<tr>
<td>Production</td>
<td>The quality</td>
<td>Stable</td>
<td></td>
</tr>
<tr>
<td>Stability</td>
<td>varies by</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>batch</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Solvent</td>
<td>Yes</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>Waste Water</td>
<td>Yes</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>Energy Use</td>
<td>Distillation</td>
<td>Min to control Temp</td>
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<tr>
<td></td>
<td>Extraction</td>
<td></td>
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<tr>
<td>Process</td>
<td>Concentration</td>
<td>No. Pump off volatile</td>
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</tr>
<tr>
<td></td>
<td>Drying</td>
<td></td>
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</tr>
<tr>
<td></td>
<td>Fractional</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>Distillation</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

30t/y CMO production in Laviana China (2012)

Courtesy of Laviana
Changzhou University: China National Award for development of flow process of nitro-guanidine
Seamless Scaleup: From G1 to G4:

Process Development in G1

- Process development was done on AFR™ G1 platform
- Optimized mole ratio, reaction temperature, flow rate, residence time, dosing method, and other parameters.
- Project duration: 4 weeks!

Production Realized in G4

- Based on G1 data, Corning designed G4 reactor.
- All parameters are the same except the flow throughput increased by 25 times and led to annual throughput of 2000 tons.
- Absolutely seamless scale-up!
More G4 Production Commissions Happening Globally
Globally - Growing Interest in Corning AFR™ Technology and Applications in Pharma, Fine & Specialty Chemicals
Concluding Remarks

• AFR™ technology is an Inherently Safer Technology (IST) that drastically reduces the consequences of an accident on the plant environment, however it does not prevent using the good & safe practices developed by the chemical industry.
• Successfully demonstrated seamless scale-ups providing customers increased confidence in adopting this technology
• We are proud of seeing our long-list of G4 production projects going on in Asia and Europe
• AFR™ technology and Green Chemistry goes with hand in hand

Contacts: sethiack@corning.com
http://www.corning.com/reactors

...Thank you....
Corning Application Lab in India help customers adopt AFR technologies

Experience the Production Benefits of Continuous-Flow Technology
A Unique Opportunity Brought to You by Corning and Acoris Research (A Division of Hikal Ltd.)