RAPIC PROJECT:

TOWARD COMPETITIVE HEAT EXCHANGER/REACTOR

ANR Sustainable Chemistry Conference | Zoé ANXIONNAZ-MINVIELLE

19TH SEPTEMBER 2012
Chemical syntheses = f(T)
Heat transfer limitations in batch reactors

Transposition from batch to plug flow continuous reactors and heat and mass transfer intensification:
• Continuous production
• Quality enhancement
• Safer process
• Environmental-friendly
Plate heat exchanger/reactors

- Industrial well-known plate heat exchanger technology
- Compact technology
- Demonstrated in the 1-10kg/h range…
- …But expensive apparatuses

**RAPIC Project to develop an innovative and low-cost component**

**Scientific and technical challenges:**
- Compacity vs. Residence time?
- Scale-up x10 up to x100
- Low-cost manufacturing technique
• Funded by the French National Research Agency
• Consortium: CEA LITEN, Rhodia, Fives Cryo, LGC et LTN
• Budget: 1,9 M€ / 4 ans

**Objectives:**

• To develop an innovative and **low-cost** component
• To comply with the implementation constraints of **exo/endo**thermal reactions
• To be as close as possible to **mature technologies** of the heat exchanger sector
• To respect the **cost constraints** imposed by the market
1. End-user specifications
2. Design of a basic HEX/reactor
3. Optimization of the design
4. Lab-scale pilots
Rhodia chemical reaction target:

- Homogeneous liquid-phase exothermal reaction
- Adiabatic temperature rise = 200°C
- Residence time = 2-3 min
- Isothermal reactor: max temperature rise = 10°C

\[
\frac{U \cdot A}{V_{\text{fluid}}} = 580 \text{ kW} \cdot \text{m}^{-3} \cdot \text{K}^{-1}
\]

- Lab-scale: 1-10 kg.h\(^{-1}\)
- Production scale: 100-4000 kg.h\(^{-1}\)

- Assessment of a maximal cost to be equivalent to the industrial batch process
  → cost assessment from reactants to building
Process side
- Straight stainless steel tubes (8/10mm)
- Twisted inserts
- Copper matrix
- 2x25 process plates (1.25 x 0.8 x 0.02 m$^3$) and 60 tubes/plate

 Cooling side
- Straight perforated fins (h=0.4mm – e=0.5mm)
- 51 plates

 Reactor
- 580 kW.m$^{-3}$.K$^{-1}$
- $V_{\text{reactor}} = 1.44$ m$^3$
- $\Delta P = 7$ bars
Manufacture of the 1st concept mock-up:
- To validate the pre-sizing correlations
- To assess the manufacture costs

Overall cost equivalent to a batch reactor (6 kT/year)

2nd step objective: more efficient, compact and cheaper heat exchanger/reactor:
- Modification of channel cross-section shape
- Structuration of the channel geometry (2D)
Objectives:

- Manufacturing qualification processes:
  - Machining, fins bending
  - Brazing, hot isostatic pressing
- Thermo-hydraulic characterizations
  - Flow structure: pressure drops, RTD
  - Heat and mass transfers

Overall dimensions:

- ~320 x 130 x 20 mm$^3$
- Material: 316L, copper, PMMA
- Milli-reaction channel
2D-structure of the reaction channel

Process side

Utility side
PMMA mock-ups: flow characterization in the 2D reaction channel

Thermo-hydraulic performances
- Global mixing
- Thermal performances

2D-structure of the reaction channel

Flow hydrodynamics
- Residence Time Distribution
- Pressure drops

PhD Thesis
LGC/CEA
2D-structure of the reaction channel
LAB-SCALE MOCK-UPS

Tubes inserted in a copper matrix

Manufacturing techniques

d=8 mm
Twisted inserts
$V_{\text{fluid}}=301 \text{ mL}$
$L_{\text{dev}}=2.88 \text{ m}$

Bended tubes in a solid matrix

$2\times4 \text{ mm}^2$
$V_{\text{fluid}}=34 \text{ mL}$
$L_{\text{dev}}=4.67 \text{ m}$
Manufacturing techniques

2x4 mm²

\[ V_{\text{fluid}} = 23 \text{ mL} \]
\[ L_{\text{dev}} = 2.21 \text{ m} \]

\[ h_{\text{fin}} = 5.1 \text{ mm} \]
\[ L_{\text{fin}} = 1.54 \text{ mm} \]
\[ V_{\text{fluid}} = 102 \text{ mL} \]
\[ L_{\text{dev}} = 0.9 \text{ m} \]
Experimental characterizations

Flowrate (kg.h⁻¹)

Pump power (W)

UA/V (kW.K⁻¹.m⁻³)
Experimental characterizations

\[ \text{Pe} = 40 \text{ to } 150 \]

Iodide-iodate method with adaptive procedure*
FROM THE MOCK-UPS TO THE PILOTS

- Integration of cooling plates
- 2 manufacturing techniques
- 10 kg/h range
- Tests with exothermic reactions

Process plate (x3):
- Straight circular tube with twisted inserts
- Copper matrix
- HIP technique

Cooling plate (x4):
- Stainless steel herringbones
- Brazing techniques
- Dimensions: 800 x 400 x 70 mm³
- Fluid volume = 1.17 L
Oxidation reaction:

\[ 2 \text{Na}_2\text{S}_2\text{O}_3 + 4\text{H}_2\text{O}_2 \rightarrow \text{Na}_2\text{S}_3\text{O}_6 + \text{Na}_2\text{SO}_4 + 4\text{H}_2\text{O} \]

\[ \Delta H_r = -586.2 \text{kJ.mol}^{-1} \text{ of Na}_2\text{S}_2\text{O}_3 \]

<table>
<thead>
<tr>
<th></th>
<th>Process fluid</th>
<th>Cooling fluid</th>
<th>Conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>( Q_p ) (L.h(^{-1}))</td>
<td>Re</td>
<td>( t_r ) (s)</td>
<td>( T_{u,\text{in}} ) (°C)</td>
</tr>
<tr>
<td>14.0</td>
<td>2500</td>
<td>6.9</td>
<td>39.7</td>
</tr>
<tr>
<td>7.0</td>
<td>1300</td>
<td>13.8</td>
<td>39.7</td>
</tr>
<tr>
<td>7.0</td>
<td>1500</td>
<td>13.8</td>
<td>59.4</td>
</tr>
</tbody>
</table>
Comparison with batch reactors

Data of the oxidation reaction experiments ($T_u=49^\circ C$), heat generated:
$Q/V=14 \cdot 10^3$ kW.m$^{-3}$

Heat that could be removed in a batch reactor

(1$L<V<1m^3$ - $\Delta T=45^\circ C$ – $U_{max}=500$ W.m$^2$.K$^{-1}$)

<table>
<thead>
<tr>
<th>Volume (m$^3$)</th>
<th>1.10$^{-3}$</th>
<th>1.10$^{-2}$</th>
<th>0.001</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diameter (m)</td>
<td>0.08</td>
<td>0.2</td>
<td>0.4</td>
</tr>
<tr>
<td>Height (m)</td>
<td>0.2</td>
<td>0.3</td>
<td>0.8</td>
</tr>
<tr>
<td>$A$ (m$^2$)</td>
<td>0.055</td>
<td>0.22</td>
<td>1.13</td>
</tr>
<tr>
<td>$Q_{max}/V$(kW.m$^3$)</td>
<td>1200</td>
<td>500</td>
<td>250</td>
</tr>
</tbody>
</table>

Impossible operating conditions in a batch reactor!
• Design assistance
• Operating conditions optimization
• Reaction implementation in safe conditions
Ac. + KOH \( \rightarrow \) intermediate \( \rightarrow \) Final product

- Batch process
- Operating times >3h to keep \( T < 40°C \)
- Secondary products = 0.2%

<table>
<thead>
<tr>
<th>Flowrate (kg/h)</th>
<th>5</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Res. time (s)</td>
<td>73</td>
<td>480</td>
</tr>
<tr>
<td>% 2\text{ndary} Prod.</td>
<td>1.3 (( T_{\text{inlet}} = 60°C ))</td>
<td>0</td>
</tr>
<tr>
<td>T_{\text{outlet}} = 32°C)</td>
<td></td>
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</table>
Costs assessments

Estimated costs = 0.4 to 0.6 of an eq. Batch reactor
Design, manufacture and tests of 3 plate heat exchanger/reactors

- Low manufacturing costs
- Additional gains thanks to the transposition from batch to continuous process
- Severe operating conditions vs. Residence time
- Tests in industrial conditions (Rhodia reaction)

Outlooks

- Manufacturing techniques transfer
- Scale-up x100
- Multiphase applications (G/L, L/L)
Thank you!

zoe.minvielle@cea.fr