The Recent Developments in the HiGee Technology

Prof. Jian-Feng Chen

Research Center of the Ministry of Education for High Gravity Engineering & Technology
Beijing University of Chemical Technology,
Beijing, China
Venice, Italy
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Outline

1. Introduction
2. Fundamentals of HiGee (High Gravity) Technology
   - Hydrodynamics
   - Mass transfer
   - Micromixing
3. Applications of HiGee Technology
   - Case Studies
     - Engineering of Nanoparticles
     - Reaction Process Intensification
     - Separation process Intensification
**Introduction**

**what is PI & what could be beneficial**

**Process intensification?**

Innovation on process and equipments, lead to:

- reduction of equipment size dramatically
- reduction of process units operations

**Benefit of PI**

- **product quality improvement**
- energy saving and cost reduction
- resource consumption reduction
- pollution reduced
- safety improvement

**Process Industries**
What could PI do?

- Chemical Industries
- Nanomaterials
- Energy-oil and gas
- Environment
- Life Science

Mass, heat transfer
Mixing and Reaction engineering

Process Intensification

Process Industries
Importance of Micromixing
(mixing at molecular scale)

Liquid phases complex and fast reactions

\[ A + B = R \]  (instantaneous reaction)

\[ R + A = S \]  (fast reaction)

Ratio of reactants: \( A: B = 1:1 \) (mol)

**Chemical reaction** : A molecular-scale process

Selectivity: \( X_R \) — two extremes

- \( X_R = 0\% \)
- \( X_R = 100\% \)

Classical reaction engineering theory can’t explain the above case. Why? How?
Micromixing controlled processes

Micromixing

Dominate and control

Fast chemical process ($t_R < t_M$)

Reactor Design & Scale-up

Nanomaterials (PSD, Morphology)

Polymerization (MWD)

Organic reaction (selectivity)

Fundamental of Engineering, PI?
High Gravity (HiGee) Technology — RPB

In 1979, Dr. C. Ramshaw invented RPB to intensify mass transfer for G-L separation process.

- European Patent, 0002568, 1979
Our research work

- Fast Reaction
- Fundamental Research
- Separation Process
- Reaction Coupled with Separation
- Nanomaterials
- Mass, Heat Transfer Mixing and Reaction Engineering
- Process Intensification
- High Gravity Technology
(1) Fluid Flow in RPB
Visualization of fluid flow in RPB

- **Liquid flow pattern**

  - **Film flow + pore flow**
    - $N < 600$ rpm (15-60g)

  - **Droplet flow**
    - $N > 800$ rpm (>100g)

# Liquid flow-film thickness

<table>
<thead>
<tr>
<th>Radius m</th>
<th>L m³/h</th>
<th>Speed rpm</th>
<th>Liquid film thickness μ m</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.15</td>
<td>1.5</td>
<td>450</td>
<td>17</td>
</tr>
<tr>
<td>0.15</td>
<td>1.5</td>
<td>500</td>
<td>16</td>
</tr>
<tr>
<td>0.15</td>
<td>1.5</td>
<td>600</td>
<td>14</td>
</tr>
<tr>
<td>0.15</td>
<td>1.5</td>
<td>750</td>
<td>11</td>
</tr>
<tr>
<td>0.15</td>
<td>1.5</td>
<td>900</td>
<td>4</td>
</tr>
<tr>
<td>0.15</td>
<td>1.5</td>
<td>1050</td>
<td>2</td>
</tr>
</tbody>
</table>

\[
\delta = 4.20 \times 10^8 \frac{\nu L}{a_f \omega^2 R}
\]

- **L** — flow volume rate
- **ω** — Angular velocity
- **R** — radius diameter
- **ν** — kinetics viscosity

---

## Droplet diameter

### Mean diameter

\[
d_i = B \left( \frac{\sigma}{\omega^2 R \rho} \right)^{\frac{1}{2}}
\]

- \(\sigma\) — liquid surface tension
- \(\omega\) — Angular velocity
- \(R\) — radius diameter
- \(\rho\) — liquid density

\[B = 0.5 - 0.9\]

<table>
<thead>
<tr>
<th>Speed rpm</th>
<th>L m³/h</th>
<th>Mean diameter mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>1.0</td>
<td>0.111</td>
</tr>
<tr>
<td>1000</td>
<td>1.75</td>
<td>0.140</td>
</tr>
<tr>
<td>1000</td>
<td>2.5</td>
<td>0.192</td>
</tr>
<tr>
<td>800</td>
<td>1.0</td>
<td>0.204</td>
</tr>
<tr>
<td>800</td>
<td>1.75</td>
<td>0.203</td>
</tr>
<tr>
<td>800</td>
<td>2.5</td>
<td>0.238</td>
</tr>
<tr>
<td>600</td>
<td>1.0</td>
<td>0.229</td>
</tr>
<tr>
<td>600</td>
<td>1.75</td>
<td>0.253</td>
</tr>
<tr>
<td>600</td>
<td>2.5</td>
<td>0.276</td>
</tr>
</tbody>
</table>
Residence time distribution in RPB

- Electric conductivity probes are mounted on the rotor, which rotate with the rotor
- The signal transformed by electric brushes
- In-situ measurement

Typical residence time curves

Residence time vs. Liquid flow rate

- 600rpm
- 800rpm

Residence time vs. Gas flow rate

- G=0
- L=1.0m³/h
- L=2.5m³/h

Residence time vs. Rotating speed

- G=0
- L=1.0m³/h
- L=2.5m³/h
(2) Mass transfer in RPB
Average mass transfer coefficients in different zones

Out of the rotor
inside the rotor
Inner edge of rotor

Mass transfer coefficient measured by water deaeration (liquid phase control)

Average mass transfer coefficient on two kinds of packing
Based on our visual study, when rotating speed is over 800rpm, liquids exist mainly in the form of droplets.

Modeling of CO₂ absorption in RPB

Mass balance in droplet

\[
\frac{D_L}{R^2} \frac{d}{dR} \left( R \frac{d c}{d R} \right) - k_1 (c - c_e) = 0
\]

\[
\frac{\partial c}{\partial t} = 0
\]

\[
c (d / 2) = c_0
\]

\[
\frac{d c}{d R} \bigg|_{R=0} = 0
\]

\[
k_G \frac{R T}{a_G D_G} = 2 R e_G^{0.7} S c_G^{1/3} \left( a_T d_p \right)^{-2.0}
\]

Absorption rate

\[
N_{CO_2} = K_G a (P - c_H) = K_G \frac{6 \varepsilon_L}{d} (P - c_H)
\]

Gas phase mass balance

\[
\frac{1}{K_G} = \frac{1}{k_G} + \frac{H}{k_L}
\]

\[
G_{\text{mass}} d \left( \frac{y}{1-y} \right) = N_{CO_2} 2 \pi r h d r
\]

Main assumption
1. Steady-state condition prevails.
2. The amount of water in gas-phase is neglected.
3. The plug-flow condition is applicable to both gas and liquid phases.
4. The pressure drop in the RPB is neglected.
5. Isothermal absorption takes place in the RPB.

Result
(concentration of outlet gas)

\[
c = (c_0 - c_e) \frac{d}{2R} \sinh \left( \sqrt{\frac{k_1 R}{D_L}} \right) \sinh \left( \sqrt{\frac{k_1 d}{D_L}} \right) + c_e
\]

\[
k_L (c_0 - c_e) = D_L \frac{d c}{d R} \bigg|_{R=d/2}
\]

Runge-Kutta method
Experimental

Benfield solution (un-promoted) to absorb CO₂

\[ CO_3^{2-} + H_2O \rightleftharpoons OH^- + HCO_3^- \]  
*Instantaneous reaction*

\[ CO_2 + OH^- \xrightleftharpoons[k_{OH}]{k_{-OH}} HCO_3^- \]  
*Rate-controlling step*

\[ CO_2 + CO_3^{2-} + H_2O \rightleftharpoons 2HCO_3^- \]  
*Total reaction*
Most of the predicted $y_0$ (mole fraction of CO$_2$ in outlet gas) agreed well with the experimental data with a deviation within 10%.
Effect of operation parameters on mass transfer coefficient \( K_G \)

Effect of the liquid flow rate on volumetric mass transfer coefficient in RPB

Effect of the gas flow rate on volumetric mass transfer coefficient in RPB

Effect of the rotating speed on volumetric mass transfer coefficient in RPB

Effect of the temperature on volumetric mass transfer coefficient in RPB

Mass Transfer capacity in various devices
Fundamental research

(3) Micromixing in RPB
Experimental setup for micromixing

Parallel-Competition Reactions

\[ A + B \rightleftharpoons R \]
\[ C + B \rightleftharpoons S \]

RPB with radial sampling tubes

Experimental Results - segregation index

iodide-iodate reaction

\[
\begin{align*}
H_2BO_3^- + H^+ &\rightleftharpoons H_3BO_3 \\
5I^- + IO_3^- + 6H^+ &\rightleftharpoons 3I_2 + 3H_2O \\
I^- + I_2 &\rightleftharpoons I_3^-
\end{align*}
\]

Effect of rotating speed on \(X_S\)

Effect of liquid flow rate on \(X_S\)

\(N=600\) rpm, \(a=12\) C\(_{H^+}\) = 0.2 mol/L

\(N=1200\) rpm, \(a=12\) C\(_{H^+}\) = 0.2 mol/L

\(N=900\) rpm, \(a=7.2\) C\(_{H^+}\) = 0.16 mol/L

\(V_A=6\) L/min, \(V_A=9\) L/min
Micromixing efficiency in RPB - Modeling

Relationship of $X_s$ and $t_m$ in our experimental condition

$\tau_{M} = 0.1 \text{ ms}$

c.f, in conventional stirred tank

$\tau_{M} = 5-50 \text{ ms}$

Summary (fundamental)

Two unique advantages: most intensified mass transfer and micromixing in RPB
Application Fields of HiGee Technology

Micromixing controlled processes
- Nanoparticle Syntheses
- Fast reaction
- polymerization

Mass-Transfer limited processes
- CO$_2$
- H$_2$S/CO$_2$
- Deoxygenation of Water
- SO$_2$
- Dedusting
Application I:

Nanoparticles Syntheses
— Engineering of Nanoparticles
Nanoparticles – building block for nano-system

- **Nano-catalysts for Chem. Ind.**
- **Nanoparticles for IT**
- **Nano-electrode for energy**
- **Medical nano-device**
- **Drug nanoparticles for Inhalation**

• Materials in particles form > 70%

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Mechanism

Process of particle formation

How to Engineer the nanoparticles with cost effective way?

Reactive precipitation

Three different distribution

Problem:

\[ \tau_M = 5 \sim 50 \text{ms}, \quad \tau = 1 \text{ms} ; \]

\[ \tau_M > \tau \quad \text{— in micromixing control zone} \]

→ Difficulties in control
PSD, scale-up effect

Fig. 5 Influence of feed point location on PSD
\((t_i = 480 \text{s})\)

**Engineering of nanoparticles — Micromixing**

**Requirements**

Intensified micromixing \(=\) uniform PSD + nano-sized & mass transfer

**Mechanism**

A + B → P ↓

- **Nucleation rate:**
  \[ \frac{dN}{dt} = K_N (c_P - c^*)^a, \]
  \( a = 5 \sim 18 \)

- **Crystal growth rate:**
  \[ \frac{dl}{dt} = k_G (c_P - c^*)^b, \]
  \( b = 1 \sim 3 \)
**Principles for precipitator design**

**Micromixing characteristic time $\tau_M$**

$$\tau_M = k \left( \frac{\nu}{\varepsilon} \right)^{1/2}$$

**Nucleation characteristic time $\tau$**

$$\tau = \frac{6d^2 n^*}{D \ln S}$$

**Principles**

- When $\tau_M < \tau$, ideal reactor for fast reaction process, easy to control (ideal environment)

- When $\tau_M > \tau$, non-uniform environment, difficult to control (non-ideal environment)
High Gravity Technology — RPB

Ideal reactor for nanoparticles synthesis

\[ \tau_M < \tau \]

\[ \tau_M = 0.1\text{ms} \]

\[ \tau = 1\text{ms} \]
Particle size and morphology control of nanoparticles

Particle size control

\[ \text{CO}_2 + \text{Ca(OH)}_2 = \text{CaCO}_3 + \text{H}_2\text{O} \]

Effect of high gravity level on particle size

Morphology control

- Needle
- Spindly
- Cubic
- Flaky

\[ L = 0.3 \text{m}^3/\text{h} \]
\[ G = 0.42 \text{m}^3/\text{h} \]
\[ c_{A_0} = 73 \text{kg/m}^3 \]
Comparison of PSD of cubic CaCO$_3$ prepared by HGRP and commercial product

Prepared by HGRP

30nm narrow distribution

Commercial product by conventional

75nm wide distribution
From idea to commercialization

Nanoparticles production by High Gravity Technology

- 1997, 40 t/a
- 2000, 3000 t/a
- 2001, 10000 t/a
- Price: €400 /ton

<table>
<thead>
<tr>
<th>Scale</th>
<th>Volume / batch (m³)</th>
<th>Carbonation time (min)</th>
<th>Mean size (nm)</th>
<th>Variance</th>
<th>Production capacity (t/a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bench</td>
<td>3</td>
<td>12~20</td>
<td>25~36</td>
<td>0.22~0.38</td>
<td>4.7</td>
</tr>
<tr>
<td>Mini-Pilot</td>
<td>80</td>
<td>20~25</td>
<td>15~30</td>
<td>0.15~0.27</td>
<td>110</td>
</tr>
<tr>
<td>Full scale</td>
<td>2800</td>
<td>22.5</td>
<td>30</td>
<td>0.23</td>
<td>4000</td>
</tr>
</tbody>
</table>

No scale-up effect!
Application of nanoparticles - nanocomposite

Inorganic Nanoparticles → Dispersion → Formulation → Processing → End products

Invention: Core-shell particles technique

Mixing in master batch preparation method

Effect:
- High content of inorganic nano-particles in the master batch (75%)
- Nano-dispersion was reached, mechanical property increased significantly
### PP nanocomposite for bumper

Beijing Yanshan Petrochemical Corp. (Sinopec)

<table>
<thead>
<tr>
<th>item</th>
<th>Unit</th>
<th>Original PP (Audi)</th>
<th>PP nanocomposite</th>
<th>increase (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Charpy noched impact strength</td>
<td>23℃ KJ/m²</td>
<td>67.0</td>
<td>81.4</td>
<td>21.4</td>
</tr>
<tr>
<td>-20℃ KJ/m²</td>
<td></td>
<td>12.0</td>
<td>30.1</td>
<td>150</td>
</tr>
<tr>
<td>Flexural modulus</td>
<td>MPa</td>
<td>763</td>
<td>909</td>
<td>30.0</td>
</tr>
<tr>
<td>Flexural strength</td>
<td>23℃ MPa</td>
<td>17.0</td>
<td>18.8</td>
<td>10.6</td>
</tr>
<tr>
<td>-40℃ MPa</td>
<td></td>
<td>48.2</td>
<td>74.8</td>
<td>55.2</td>
</tr>
<tr>
<td>Tensile yield strength</td>
<td>MPa</td>
<td>15.7</td>
<td>16.2</td>
<td>3.2</td>
</tr>
<tr>
<td>Elongation at break</td>
<td>%</td>
<td>530</td>
<td>613</td>
<td>15.7</td>
</tr>
<tr>
<td>Melting index</td>
<td>g/10min</td>
<td>8.3</td>
<td>12.9</td>
<td>55.4</td>
</tr>
</tbody>
</table>

Both impact strength and flexural modulus are increased remarkably.
Applications of Rubber nanocomposites

Nanocomposites for sole of adidas shoes

- Raising the performance of UV anti-ageing resistance
- Improving the additives dispersion in shoes matrix

Nanocomposites for latex gloves

500% tensile modulus is increased 112%
(5%-7.5% CaCO₃ nanoparticles)

Nanocomposites for silicone sealant

Tensile strength is 50% higher than Japanese products, and 80% higher than home-made products

China-Baiyun Company
Nano-coating for paper

Mechanical Property

Gurley stiffness of paper is increased by 47.9%

Applications

Gurley stiffness of paper is increased by 47.9%

By Weyerhaeuser Company, USA
Monodispersed nanoparticles dispersion

**nano Cu / Oil**

- 2-8nm (5nm)
- Cu in oil: 15%
- Transparent, stable
- Capacity: 100t/a

**Nano CaCO₃ / Oil**

- 10nm
- Solid in oil: 30%
- Transparent, stable
- Production capacity: 1000t/a

**Nano metal oxide**

(cooperation with NanoMaterials Technology Pte. Ltd., Singapore)

**Good transparency**

53% 48% 43% 39% 35% 24%

Solid content
(disperse medium = organic solvent)

Patents: ZL200410037885.9 ; 200610165009.3
Potential Applications

- E-paper
- magnetic fluid
- cosmetics
- rubber
- lubricating oil
- chemical fiber
- plastic
- drug
- glass
- paint

Mono-dispersed nanoparticles

etc

......

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The visible transmittance of the film is less than 1% with 10% ZnO, while the film has the same transparence as the sample without ZnO.
ZnO/polycarbonate nanocomposites

**ZnO in MEK**

SEM

**ZnO/PC film**

\[ \text{ZnO/PC} = 12\% \]

Trasmittance of ZnO/PC nanocomposites with different ZnO content

Trasmittance of ZnO/PC compared with that of UV-blocking PC film from US commercial source

ZnO/PC film

US PC-223R
ZnO/acrylic polyurethane nanocomposites

ZnO in EtAc

SEM (ZnO/AC-PU film)

Trasmittance of ZnO/AC-PU nanocomposites with different ZnO content

ZnO/AC-PU = 5%

Blank
Future of drug nanoparticles

- **Poor-water-soluble drugs**: enhancing solubility and dissolution rates of solid oral formulations

  - **Nernst-Noyes-Whitney equation**:

    \[
    \frac{dC}{dt} = \frac{DS(C_s - C_t)}{V\delta}
    \]

    - \(d\) — dissolution rate; \(C\) — solubility; \(S\) — specific surface area

  - **Pulmonary delivery inhaled drug**: realizing the deep lung deposition to increase the efficiency
    Particle Size: < 500-2000 nm

- **Potential worldwide market**: 480 B USD, 50% share made by nanotechnology (NNI, 2000, USA)
Drugs Nanoparticles prepared by Higee Technology

- **Anticancer drug**
- **Antiasthma drug**
- **Adrenal corticosteroid**
- **Antibiotic drug**
- **Lipid-lowering drug**
- **Immunization drug**
- **Antihyperlipemia drug**
- **Hepatoprotective drug**
Application II:

Fast Reactions

Intensification of micromixing & mass transfer limited reactions
Application II — Fast Reactions

(1) Polymerization
- Isobutylene Isoprene Rubber (IIR)
Cationic polymerization - micromixing limited

- **Synthesis of IIR**

  ![Chemical结构](attachment:image.png)

  - Fast reaction (< 1s)
  - Low temperature
  - High exothermic
Chain-growth in polymerization is first-order reaction, the characteristic reaction time is

\[ t_{1/2} = \frac{\ln 2}{k_p} \]

\[ 0.01 \text{~to~} 0.1 \text{~ms} \]

<table>
<thead>
<tr>
<th>Conventional stirred tank reactor</th>
<th>RPB</th>
</tr>
</thead>
<tbody>
<tr>
<td>( t_m )</td>
<td>5~50 ms</td>
</tr>
</tbody>
</table>

\( t_m > t_{1/2} \) Nonhomogeneous micro-environment

\( t_m \leq t_{1/2} \) Homogeneous micro-environment

Choose RPB
Experimental setup

RPB process for Polymerization of IIR

Flow chart of Polymerization of IIR

1-N₂ cylinder; 2-refrigerant tank; 3-isobutene, isoprene and dichloromethane tank; 4-aluminium chloride and dichloromethane tank; 5-metering pump; 6-RPB; 7-IIR tank

RPB size (rotator): Dₒ=258mm, Dᵢ=150mm, H=50mm
Effect of rotating speed on MWD in RPB

$N \geq 1200 \text{ r} \cdot \text{min}^{-1}$

<table>
<thead>
<tr>
<th>$T_P$</th>
<th>$N_L$</th>
<th>$U_1$</th>
<th>IB</th>
<th>IP</th>
<th>$[\text{AlCl}_3]$</th>
<th>V R</th>
</tr>
</thead>
<tbody>
<tr>
<td>173</td>
<td>45</td>
<td>2.36</td>
<td>2.7</td>
<td>0.05</td>
<td>0.011</td>
<td>10</td>
</tr>
</tbody>
</table>

$M_w/M_n$ vs $N$

- 2.72 at 600 $\text{r} \cdot \text{min}^{-1}$
- 2.13 at 900 $\text{r} \cdot \text{min}^{-1}$
- 1.99 at 1200 $\text{r} \cdot \text{min}^{-1}$
- 1.93 at 1500 $\text{r} \cdot \text{min}^{-1}$
Effect of packing thickness on MWD in RPB

\[ N_L \geq 45 \]

<table>
<thead>
<tr>
<th>N</th>
<th>U_1</th>
<th>IB</th>
<th>IP</th>
<th>[AlCl_3]</th>
<th>V R</th>
</tr>
</thead>
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<td>1200</td>
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<td>10</td>
</tr>
</tbody>
</table>

Higee tech. by Chen
Modeling and experiment results of IIR polymerization

Polymerization of IIR

- **Chain-initiation:**
  
  \[
  I + LA \rightleftharpoons I^+ LA^- \\
  I^+ LA^- + M_1 \xrightarrow{k_i} P_i^+ LA^- 
  \]

- **Chain-growth:**
  
  \[
  P_n^+ LA^- + M_1 \xrightarrow{k_n,M_i} P_{(n+1)}^+ LA^- \\
  P_n^+ LA^- + M_2 \xrightarrow{k_{P,M_2}} P_{2(n+1)}^+ LA^- 
  \]

- **Chain-transfer:**
  
  \[
  P_n^+ LA^- + M_1 \xrightarrow{k_{n,M_i}} P_{n1} + P_i^+ LA^- 
  \]

- **Chain-termination:**
  
  \[
  P_n^+ LA^- \xrightarrow{k_t} P_{n2} + LA 
  \]

**Reaction characteristics:**

1. very low reaction temperature
2. reaction time < 1s
3. activation energy < 0

\[M_n = \frac{W}{n} = \frac{\sum n_i M_i}{\sum n_i} = 2 \times \left( \sum ([C_i] \times M_{w,C_i}) + \sum ([E_i] \times M_{w,E_i}) + [A] \times M_{w,A} \right) / [A] + \sum [E_i] \]

**Calculation of mean molecular weight**

- **Experimental (T):**
  
  - 193K
  - 183K
  - 173K

- **Simulation**

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• Chen J.F., Gao H., Zou H.K., Chu G.W., et al., *AIChe J.* (2009, Accepted)
Comparison of Higee polymerization with conventional technology

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Conventional</th>
<th>RPB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (K)</td>
<td>173~177</td>
<td>173~193</td>
</tr>
<tr>
<td>Residence time (s)</td>
<td>1800~3600</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Operation cycle (h)</td>
<td>24~60</td>
<td>2~3</td>
</tr>
<tr>
<td>Material flow velocity (m·s⁻¹)</td>
<td>4~7</td>
<td>2~3</td>
</tr>
<tr>
<td>Material circulation</td>
<td>YES</td>
<td>NO</td>
</tr>
<tr>
<td>Isobutene density (%, V)</td>
<td>30~35</td>
<td>15~25</td>
</tr>
<tr>
<td>Isoprene density (%, V)</td>
<td>2.5~3</td>
<td>2~3</td>
</tr>
<tr>
<td>Operation pressure (KPa)</td>
<td>240~380</td>
<td>100</td>
</tr>
<tr>
<td>Product number average molecular weight (×10⁵)</td>
<td>≥1.5</td>
<td>1~3</td>
</tr>
<tr>
<td>Product molecular weight distribution index</td>
<td>2.5~3.1</td>
<td>2~2.7</td>
</tr>
</tbody>
</table>
Application II — Fast Reactions

(2) MDI production
Applications of MDI

- MDI - diphenylmethane diisocyanate products
- MDI is the most important raw material in polyurethane (about 50%)
- Polyurethane ranks the fifth in world's plastic production
- Excellent heat insulation, elasticity, abrasion resistance and oil resistance properties of polyurethane

Applications of MDI:

- Sofa seat
- Refrigerator freezer
- Auto materials
- Submarines' and armored vehicles' coating
- The rockets' insulation
- Shoemaking
- Olympic Venues
- Qinghai-Tibet railway embankment
- Spandex
- Energy conservation
Condensation reaction – key process in MDI production

**Condensation reaction**

\[
\text{H}_2\text{N} + \text{HCHO} \xrightarrow{\text{HCl}} \text{H}_2\text{N}\left[\text{CH}_2\text{N} - \text{H} \right]_\text{n}\text{CH}_2\text{N}\text{H}_2
\]

**Interconversion reaction**

\[
\text{H}_2\text{N}\left[\text{CH}_2\text{N} - \text{H} \right]_\text{n}\text{CH}_2\text{N}\text{H}_2 \xrightarrow{\text{HEAT}} \text{H}_2\text{N}\left[\text{CH}_2\text{N} - \text{H} \right]_\text{n}\text{CH}_2\text{N}\text{H}_2
\]

**Reaction characteristics:** micromixing controlled

1. Condensation reaction is rapid, strongly exothermic, complex reactions
2. Formaldehyde is poorly dispersed for the high viscosity. Many by-products are easily generated (such as 2-methylaniline, n-methyl composites, etc.), which affect the quality of target product, and even block the pipeline (trouble)
3. Effective dispersion and temperature control of formaldehyde are very important to improving the quality of polyamines.

**Challenges:** Demand for fast molecular mixing

Commercial application of innovative HiGee reactors for MDI production

Benefit: capacity increased 50%, from 160K to 240K t/a, energy saving about 20%, impurity content reduced by 30%, blocking problem solved
Application II — Fast Reactions

(3) Reaction coupled with separation process

Case — Hypochlorous Acid Production (mass transfer limited)
Industrial application

Hypochlorous acid production by Dow Chemical Co

Reaction:

\[ \text{Cl}_2 (g) + \text{NaOH} (l) = \text{NaCl} (l) + \text{HOCl} (l) \quad \text{(target product, fast reaction)} \]

\[ 2\text{HOCl} (l) + 2\text{NaOH}(l) = \text{NaClO} (l) + \text{NaCl} + \text{H}_2\text{O} \quad \text{(side reaction, fast)} \]

- **DOW** Cooperated with our group, we provided engineering design fundamentals of RPB (such as liquid distributor, pressure drop and equipment dimension, etc.), developed the industrial technology of hypochlorous acid production with high gravity reaction and separation method.

- **Benefit:**
  - HClO yield increased by 10%
  - Equipment investment saved by 70%
  - Cl₂ recycle volume reduced 50%

(In courtesy of DOW Chemical Co.)
Application III:

Separation processes
(1) Deoxygenation of Water
Deoxygenation of oilfield feeding water

- Oxygen content required in oilfield
  Feeding water: <50ppb

- **Conventional method:** vacuum packed tower, single or two stages, large equipment volume and high investment, oxygen content > 100ppb, chemical treatment needed to further remove O₂

- Higee technology has obvious advantages over conventional ones

- Particularly suitable for offshore oil platform

Conventional technology: vacuum packed tower
The first known example of its (RPB’s) commercial use was reported in 1997 by Shengli Oil Field in China, where 1.5-m-dia. rotating strippers replaced 30-m-high vacuum towers for the deaeration of water....

<table>
<thead>
<tr>
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<th>Vacuum deoxygenation</th>
<th>Higee deoxygenation</th>
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<tbody>
<tr>
<td>Oxygen in water supply</td>
<td>6~12</td>
<td>6~12</td>
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<tr>
<td>Oxygen in water after</td>
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<td>50ppb</td>
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<tr>
<td>treatment</td>
<td>tower)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>50~200ppb (two</td>
<td></td>
</tr>
<tr>
<td></td>
<td>towers in series)</td>
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</tr>
<tr>
<td>Ground space</td>
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<td>0.4</td>
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<tr>
<td>Land requirement</td>
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<tr>
<td>Equipment weight</td>
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<td>0.2</td>
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<tr>
<td>Equipment height</td>
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<tr>
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<tr>
<td>Power consumption</td>
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</table>
Application III — Separation processes

(2) Flue Gas Treatment (desulfurization)
Design data basis
(Fujiang Petroleum Refinery Co.)

Gas to be treated
feeding rate: 11 t/h, $t = 40^\circ C$, $p = 1.1$Mpa.
Composition of dry gas: $H_2S \leq 2.27\%$  $CO_2 \leq 3.72\%$

Absorption solution - recycled deficient amine solution:
Composition: $H_2S \leq 1.0$wt$\%$  $CO_2 \leq 0.5$wt$\%$
Amine solution flow rate: 13-16 t/h, $t = 40^\circ C$, $p = 1.1$Mpa.

Requirement: Gas after desulfurization: $H_2S \leq 20$mg/NM$^3$

Reactive absorption:
$2HOC_2H_2-NH_2 + H_2S = (HO-C_2H_4-NH_3)_2S=2HOC_2H_4-NH_3HS$
D=1.2 m
H=1.42 m
Rotor:
D_i=0.35 m
D_o=0.9 m

H=33 m
D=1.2 m
H_{\text{packing}}=12 m
V_{\text{packing}}=14 m^3
Desulfurization effects of RPB vs. conventional PBT

- **X**: days of experiment; **Y**: outlet $H_2S$ index (ppm)

- **Without RPB**:
  - High $H_2S$ index
  - Low and steady $H_2S$ index, meet requirement

- **With RPB**:
  - $H_2S$ index reduced again

- **Stop RPB**:
  - Unstable and high $H_2S$ index

- **Turn on RPB again**:
  - $H_2S$ index increased again

- **Stop RPB again**:
  - $H_2S$ index increased again
Application to fertilizer plant

Benefit: absorption solution recycle volume reduced by 50%
(3) Polymer devolatilization
Polymer devolatilization by HiGee

Content of Volatile, wt%

Rotating speed, rpm

97.5%

<table>
<thead>
<tr>
<th>Equipment</th>
<th>Pressure /Pa</th>
<th>Time</th>
<th>Efficiency/%</th>
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<tr>
<td></td>
<td></td>
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<tr>
<td>HiGee</td>
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<tr>
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<tr>
<td></td>
<td>550</td>
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Conclusions

- **HiGee** can tremendously intensify micromixing and mass transfer
- **HiGee** is a cutting-edge technology platform for process intensification, including nanoparticles syntheses, reaction, separation, mixing, and emulsification
- **HiGee** technology is ready for industrial innovation of chemical processes limited by micromixing and mass transfer
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  - Nanomaterials Technology Pte. Ltd., Singapore
  - DOW Chemicals Co., USA
  - BASF AG., Germany
  - Dow Corning Co. USA
Welcome to visit Beijing (China)

The Bird's Nest  and The Water Cube
End

Thank you for your attention!

Contact: chenjf@mail.buct.edu.cn