Transformation of the old process:
Ethylbenzene to Styrene with CO\(_2\) dilution
Conventional Process for Styrene Production

- Worldwide Capacity for Production of Styrene Monomer: more than **20 Mt/year** (2.3 Mt/year in Korea)
  More than 90%: Ethylbenzene Dehydrogenation with Steam

- Commercial Catalyst: Fe$_2$O$_3$-K$_2$O-CeO$_2$ with additives

- **Role of Steam in Ethylbenzene Dehydrogenation (EBD)**
  - Shift of the equilibrium towards higher conversions
  - Supply for heat of reaction with superheated steam
  - Decrease of the amount of coke by steam gasification

- **Drawbacks of EBD Process with Steam**
  - High energy consumption during the condensation of steam due to high latent heat of water
  - Catalyst deactivation in the presence of CO$_2$ as a by-product
  - The need for high steam-to-ethylbenzene ratio
## Production of Styrene Monomer in Korea

### Year 1999 (Unit: 1000 T/Y)

<table>
<thead>
<tr>
<th>Company</th>
<th>Capacity</th>
<th>Location</th>
<th>Starting year</th>
<th>Process Licensor</th>
</tr>
</thead>
<tbody>
<tr>
<td>LG Chemical</td>
<td>330</td>
<td>Yeochon</td>
<td>1990, 1991</td>
<td>Lummus/Monsanto</td>
</tr>
<tr>
<td>SK Oxychemical</td>
<td>300, 260</td>
<td>Ulsan</td>
<td>1991</td>
<td>Badger/Mobil/ARCO*  ARCO</td>
</tr>
<tr>
<td>Dongbu Chemical</td>
<td>210</td>
<td>Ulsan</td>
<td>1978, 1989</td>
<td>Monsanto/Lummus</td>
</tr>
<tr>
<td>Samsung GC</td>
<td>590</td>
<td>Daesan</td>
<td>1991, 1996</td>
<td>Badger</td>
</tr>
<tr>
<td>Hyundai PC</td>
<td>325</td>
<td>Daesan</td>
<td>1991, 1996</td>
<td>Badger Raytheon</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>2,155</strong></td>
<td></td>
<td></td>
<td><strong>2.5 Mt/year capacity (Year 2001)</strong></td>
</tr>
</tbody>
</table>

*Dehydrogenation process of MBA (Methyl benzyl alcohol)*
Problems of Conventional EBD Process

Problems

1. High Energy Consumption by Use of Excess Steam
   – estimated to 10% of production cost
2. Low equilibrium conversion of ethylbenzene to styrene
   due to limitation of thermodynamic equilibrium
3. Increase in risk to crack of the reactor and preheater
   due to high temperature operation
4. Catalyst deactivation with evaporation of potassium

Suggestion for conventional process

*New process using carbon dioxide as soft oxidant*
Alternative Processes for Styrene Production

• Oxidative dehydrogenation with oxygen
  ; Higher yield by shift of the dehydrogenation equilibrium
  Flammable, Need for two catalysts with an oxidation Pd or Pt

2. Selective oxidation of $\text{H}_2$ from dehydrogenation with $\text{O}_2$
  ; Overcome the contamination of mixing the steam and $\text{O}_2$
  Need for very selective and stable catalysts for oxidation of $\text{H}_2$ and
  at high temperature

3. Membrane process
  ; Oxidative dehydrogenation avoiding the flammability
  Need for effective permeability of membrane

4. Oxidative dehydrogenation with carbon dioxide
SODECO₂® Technology Development

SODECO₂® (Styrene from Oxidative Dehydrogenation via CO₂):

Styrene Monomer Process via Oxidative Dehydrogenation of Ethylbenzene using Carbon Dioxide as Soft Oxidant

Source of CO₂ ------ By Product CO₂ discharged from Petrochemical Industry

Developed by: Dr. S. E. Park and his group KRICT
CCME (Catalysis Center for Molecular Engineering)
New Development in Dehydrogenation Process using Carbon Dioxide as Soft Oxidant

Conventional process

New development
Advantages of Carbon Dioxide in Dehydrogenation

1. Role of soft oxidant to remove hydrogen as a product (less dangerous than oxygen)
2. High heat capacity of $\text{CO}_2$: 49.1 J/mol·K at 673K
   (37.0 J/mol·K at 673K for $\text{H}_2\text{O}$ and $33.2$ J/mol·K at 673K for $\text{O}_2$)
3. High selectivity to styrene (97%)
4. Activity Enhancement (high conversion)
5. Equilibrium shift to give lower reaction temperature
6. Cheaper gas than steam or oxygen
## Comparison of Carrier Gases for Dehydrogenation of Hydrocarbons

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Steam</th>
<th>Oxygen</th>
<th>Carbon Dioxide</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Function</strong></td>
<td>Not oxidant Diluent</td>
<td>Strong oxidant Not Diluent</td>
<td>Soft oxidant Diluent</td>
</tr>
<tr>
<td><strong>Heat capacity</strong></td>
<td>Medium (37.0 J/mol·K at 673K)</td>
<td>Low (33.2 J/mol·K at 673K)</td>
<td>High (49.1 J/mol·K at 673K)</td>
</tr>
<tr>
<td><strong>Disadvantage</strong></td>
<td>Expensive diluent Highly endothermic High latent heat High operation cost</td>
<td>Low selectivity Dangerous Hot spot</td>
<td>Not commercialized Endothermic Catalyst deactivation</td>
</tr>
</tbody>
</table>
Characteristics of SODECO\textsubscript{$2$}® Process

1. Direct utilization of CO\textsubscript{2} as a by-product discharged from petrochemical industry (Self-sufficiency of CO\textsubscript{2})
2. Utilization of CO\textsubscript{2} as soft oxidant to alleviate chemical equilibrium of ethylbenzene dehydrogenation
3. Selective dehydrogenation process using CO\textsubscript{2} (1.5\% high in styrene selectivity)
4. Energy saving effect against conventional process (33\% saving effect: 6.5 M dollar for 0.6 Mt-SM/year)
5. High activity at lower temperature (Release of risk in crack of reactor materials)
**Schematic Diagram of SODECO₂® Process**

SODECO₂® (Styrene via Oxidative Dehydrogenation of Ethylbenzene with CO₂)

- **H₂O** → Water-gas shift reactor → Off gas (H₂, CO + CO₂)
- **H₂/CO₂** → H₂ (Membrane) → Dehydrogenation reactor → Product condenser → H₂O
- **CO₂** (Oxidant) → Discharge
- **H₂O** → Water-gas shift reactor
- **H₂** → Membrane
- **H₂O** → Water-gas shift reactor

Lower reaction temp.

- Without energy loss
- Distillation → Benzene/Toluene mixture → Storage tank for styrene → BTX Plant

*Candidates 1

**Schematic Diagram of SODECO₂® Process**

SODECO₂® (Styrene via Oxidative Dehydrogenation of Ethylbenzene with CO₂)

- **O₂** → **Dehydrogenation reactor** → **Off gas (CO + CO₂)** → **Membrane** → **H₂**
- **CO₂ Oxidant** → **Oxidation process** → **Ethylbenzene** → **Discharge**
- **Product condenser** → **Distillation** → **Benzene/Toluene mixture** → **BTX Plant**
- **Storage tank for styrene**

*Lower reaction temp. without energy loss*

---

Schematic Diagram of SODECO₂® Process

SODECO₂® (Styrene via Oxidative Dehydrogenation of Ethylbenzene with CO₂)

O₂ → PrOx reactor → Off gas (H₂, CO + CO₂)

H₂ → Membrane → Dehydrogenation reactor

CO₂ Oxidant

Discharge → Ethylbenzene

Oxidation process

Product condenser → Distillation → Storage tank for styrene

Benzene/Toluene mixture → BTX Plant

Lower reaction temp.

without energy loss

# Development of Commercial EBD catalysts

<table>
<thead>
<tr>
<th>Function</th>
<th>Generation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Main Component</td>
<td>Fe/K</td>
</tr>
<tr>
<td>Chemical Promoter</td>
<td>Cr</td>
</tr>
<tr>
<td>Textual Promoter</td>
<td>W,Cu</td>
</tr>
<tr>
<td>Selectivity Promoter</td>
<td>-</td>
</tr>
<tr>
<td>Others (Binder, etc.)</td>
<td>Ca</td>
</tr>
<tr>
<td>Commercial catalysts</td>
<td>-</td>
</tr>
<tr>
<td>Catalytic Activity$^a$</td>
<td>&lt; 55</td>
</tr>
</tbody>
</table>

$^a$Styrene yield, %
## Catalyst for SODECO₂® Process

<table>
<thead>
<tr>
<th>Function</th>
<th>Component</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Active Phase</strong></td>
<td>Fe₃O₄, V₂O₅</td>
</tr>
<tr>
<td>Activity Promoter</td>
<td>Mn</td>
</tr>
<tr>
<td>Stability Promoter</td>
<td>Mo, Sb</td>
</tr>
<tr>
<td>Structural stabilizer</td>
<td>Ca, Mg, Mg</td>
</tr>
<tr>
<td>Catalyst Support</td>
<td>Promoted-Al₂O₃, ZrO₂</td>
</tr>
</tbody>
</table>
## Comparison of catalytic performance between commercial and CO₂-SM catalyst

<table>
<thead>
<tr>
<th></th>
<th>Commercial (steam)</th>
<th>CO₂-EBD</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Catalyst</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Temperature (°C)</strong></td>
<td>SOR: 625-575(600)</td>
<td>SOR: 525 – 575</td>
</tr>
<tr>
<td></td>
<td>EOR: 655-605(630)</td>
<td>EOR: not fixed</td>
</tr>
<tr>
<td><strong>Pressure (atm)</strong></td>
<td>0.75</td>
<td>0.75</td>
</tr>
<tr>
<td><strong>Space velocity</strong></td>
<td>0.75-1.0</td>
<td>1.0</td>
</tr>
<tr>
<td><strong>(LHSV, h⁻¹)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Carrier/EB (molar)</strong></td>
<td>8-12</td>
<td>2-10</td>
</tr>
<tr>
<td><strong>Styrene yield (%)</strong></td>
<td>60-66</td>
<td>55 – 65</td>
</tr>
<tr>
<td><strong>Styrene selectivity (%)</strong></td>
<td>94.0-96.5</td>
<td>97.0 – 98.0</td>
</tr>
<tr>
<td><strong>Catalyst lifetime</strong></td>
<td>2 years</td>
<td>?</td>
</tr>
<tr>
<td><strong>Others</strong></td>
<td>Only H₂ product</td>
<td>X(CO₂) = 40-45%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CO/H₂ = 1.0-1.5</td>
</tr>
</tbody>
</table>

**SOR**: Start-of-run; **EOR**: End-of-run
Microactivity Test Unit  Bench-scale  Mini Pilot

**Scale-up Study vof SODECO® Process from Lab to Mini Pilot**

<table>
<thead>
<tr>
<th>Micro(Lab.)</th>
<th>Bench</th>
<th>Pilot</th>
</tr>
</thead>
<tbody>
<tr>
<td>F (in.)</td>
<td>1/2</td>
<td>3/8</td>
</tr>
<tr>
<td>Reactor</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>Length (ft.)</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Catalyst volume</td>
<td>500ml</td>
<td>4 liter</td>
</tr>
<tr>
<td>Shape of catalyst</td>
<td>Spheroid</td>
<td>Tablet</td>
</tr>
<tr>
<td></td>
<td>granule (F=1mm)</td>
<td>(F=3mm)</td>
</tr>
</tbody>
</table>
## Characteristics of Reactor Systems

<table>
<thead>
<tr>
<th>Equipment</th>
<th>Micro unit</th>
<th>Bench scale</th>
<th>Mini Pilot</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂ Feed</td>
<td>Mass flow controller Cylinder gas (R-grade)</td>
<td>Mass flow controller Cylinder gas (R-grade)</td>
<td>Mass flow controller CO₂ from EG/EO Plant</td>
</tr>
<tr>
<td>EB Feed</td>
<td>Syringe pump</td>
<td>LC pump</td>
<td>LC pump</td>
</tr>
<tr>
<td>Pre-heater</td>
<td>Single heating zone</td>
<td>Pre-heater (electric) with mixer</td>
<td>Pre-heater (electric) with mixer</td>
</tr>
<tr>
<td>Temperature control</td>
<td></td>
<td>5-zoned heater with PID controller</td>
<td>5-zoned heater with PID controller</td>
</tr>
<tr>
<td>Product analysis</td>
<td>Gas component; on-lined GC(TCD)</td>
<td>Gas component; on-lined GC(TCD)</td>
<td>Gas component; on-lined GC(TCD)</td>
</tr>
<tr>
<td></td>
<td>Liq. component; Condensed to GC(FID)</td>
<td>Liq. component; Condensed to GC(FID)</td>
<td>Liq. component; Condensed to GC(FID)</td>
</tr>
</tbody>
</table>
Bench Scale Unit for Ethyl benzene Dehydrogenation with CO₂

Design SM Production Capacity : 2.5 Ton / yr
Catalyst volume = 500 ml  Shape : spheroid (Φ=3mm)
LHSV = 1.0 h⁻¹, CO₂/EB = 5/1, 50% yield @ 560°C
SM Production via SODECO\textsubscript{2}® Process @ Pilot-scale system

Annual SM Production: 20 Ton / yr

Catalyst volume = 4 L; Shape: Tablet (5 x 3 mm)

\[ P = 0.75 \text{ atm}, \quad \text{LHSV} = 1.0 \text{ h}^{-1}, \quad \text{CO}_2/\text{EB} = 5/1, \]
\[ \text{CO}_2 \text{ Conv.} = 42\% \text{ @ 560°C (Dual 4 Tubes of Bench scale)} \]
Comparison of economical properties for EBD processes

Basis for calculation: 0.6 Mt-SM/yr

<table>
<thead>
<tr>
<th></th>
<th>SODECO$\text{CO}_2^\text{®}$</th>
<th>Conventional</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Temperature(°C)</strong></td>
<td>560</td>
<td>600</td>
</tr>
<tr>
<td><strong>SM Selectivity (%)</strong></td>
<td>96.5</td>
<td>95.0</td>
</tr>
<tr>
<td><strong>Economic effect</strong></td>
<td>$2.7\text{ M}$</td>
<td></td>
</tr>
<tr>
<td><strong>Loss of latent heat</strong></td>
<td>66 %</td>
<td>100%</td>
</tr>
<tr>
<td><strong>Cost for super-heated steam</strong></td>
<td>$6.6\text{ M}$</td>
<td>$17\text{ M}$</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>$9.3\text{ M}$</td>
<td></td>
</tr>
</tbody>
</table>
Project Financing

✓ **Critical Technology-21 Program**
  Greenhouse Gas Research Center
  Financed by the Ministry of Science and Technology

✓ **SGC Daesan Petrochemical Complex**
  Pilot Scale Demonstration Unit for Catalyst Performance Test

✓ **Key to Success**
  Scale-up Technology of Catalyst
  Stable Enough for industrial Application
Patents
- “Dehydrogenation of Alkylaromatic Hydrocarbons using Carbon Dioxide as Soft Oxidant” 2003-13139 (Korea), 2003-057644 (Japan), 03004382.2 (Europe), U.S. Patent under application
- 4 Patents of Korea

Research Papers

Presentations
# Dr. Sang-Eun Park

Affiliation: Korea Research Institute of Chemical Technology  
E-mail: separk@pado.kRICT.re.kr

<table>
<thead>
<tr>
<th>Year</th>
<th>Organization</th>
<th>Title</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>1987-1987</td>
<td>Dept. of Chemistry, KAIST</td>
<td>Visiting Researcher</td>
<td></td>
</tr>
<tr>
<td>1987-present</td>
<td>KRICT</td>
<td>Senior Researcher to Director</td>
<td></td>
</tr>
</tbody>
</table>
PFD for Conventional Styrene Monomer Process

*Energy cost for superheated steam: 15 M dollar for 0.6 Mt-SM/year capacity
Lummus/UOP Classic SMTM Process

Process Flow Scheme

- Superheater
- Water from EB Plant
- Dehydrogenation
- Off Gas Recovery
- Dehydrogenated Mixture
- Ethylbenzene
- Benzene/Toluene Splitter
- Ethylbenzene Recycle Column
- Toluene
- Benzene Recycle to EB Plant
- Styrene
- Styrene Finishing Column
- Condensate
- WHE’s
- Steam
- Condenser

The SMART SM™ process combines oxidative reheat technology with adiabatic dehydrogenation technology to produce high purity (99.85 wt% minimum) styrene monomer (SM) from ethylbenzene. This results in EB conversion of more than 80%, as well as eliminating the costly interstage reheater and reducing superheated steam requirements.
The UOP-SMART Process involves the separation of ethylbenzene and the recycling of ethylbenzene and hydrogen. The process includes:

- **Ethylbenzene dehydrogenation**
- **Hydrogen oxidation**
- **Recycle ethylbenzene/hydrogen**

The process also involves the separation of light ends and the production of styrene.
## Purity of CO₂ by-product from Ethylene Oxide (EO) Process

<table>
<thead>
<tr>
<th>Component</th>
<th>Case1</th>
<th>Case2</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>99.46%</td>
<td>99.9%</td>
</tr>
<tr>
<td>H₂O</td>
<td>0.51%</td>
<td>-</td>
</tr>
<tr>
<td>O₂</td>
<td>50ppm</td>
<td>100ppm</td>
</tr>
<tr>
<td>N₂</td>
<td>50ppm</td>
<td>100ppm</td>
</tr>
<tr>
<td>Methane</td>
<td>-</td>
<td>300ppm</td>
</tr>
<tr>
<td>Ethylene</td>
<td>140ppm</td>
<td>200ppm</td>
</tr>
<tr>
<td>Ethane</td>
<td>80ppm</td>
<td>100ppm</td>
</tr>
</tbody>
</table>

*Separation of EO and CO₂ through absorption process to purify EO product*
Catalytic Activity in EBD with CO$_2$ in Bench-scale

**Graph:**
- **X-axis:** Time-on-stream (h)
- **Y-axis 1:** EB Conv. (%)
- **Y-axis 2:** SM Select. (%)

**Legend:**
- Red triangles: EB Conv.
- Purple squares: SM Select.

**Conditions:**
- Temp. = 560°C, LHSV = 1.0 h$^{-1}$
- $W_{cat} = 15$ g, CO$_2$/EB = 5.4/1.0
- Catalyst: Fe-V-Sb-Mg-Al

**SM Production**
- EB Feeding: 30cc/hr
- SM Yield: ~ 60%
- SM Production = 370g/day
Lowering reaction temperature (up to 50°C) due to alleviation of chemical equilibrium with carbon dioxide

SM Production: 20 M-t/Yr (SM Yield = 65% @ 560°C)

Reaction condition:
P = 0.75 atm, LHSV = 1.0 h⁻¹,
CO₂/EB = 5/1 (CO₂ Cat.)
CO₂ Conv. = 42% @ 560°C
H₂O/EB = 10/1 (Steam Cat.)

Catalyst volume = 4 L

Comparison of styrene yields in steam-EBD and CO$_2$-EBD catalysts

**Reaction conditions:**
- Temp. = 600°C
- LHSV = 1.0 h$^{-1}$
- H$_2$O(N$_2$)/EB = 8/1;
- CO$_2$/EB = 5.4/1

**Styrene Yield (%)**

- **Commercial (K$_2$O-Fe$_2$O$_3$)**
- **CCME-SM1**

*Catalyst: Fe-V-Sb-Mg-Al

Simplified Reaction Equations of EB Dehydrogenation via \textit{SODECO}_2^\textregistered\ and conventional

\textbullet \textbf{Oxidative Dehydrogenation of EB via SODECO}_2^\textregistered\ Process

\[ \text{CO}_2 \xrightarrow{[\text{\ }]^*} \text{CO} + [\text{O}]_s \]

\[ \text{C}_6\text{H}_5\text{CH}_2\text{CH}_3 + [\text{O}]_s \rightarrow \text{C}_6\text{H}_5\text{CH=CH}_2 + \text{H}_2\text{O} \]

\[ \text{C}_6\text{H}_5\text{CH}_2\text{CH}_3 + \text{CO}_2 \rightarrow \text{C}_6\text{H}_5\text{CH=CH}_2 + \text{CO} + \text{H}_2\text{O} \]

\[ [\text{\ }]^* : \text{a surface vacancy} \]

\[ [\text{O}]_s : \text{a lattice oxygen atom} \]

\textbullet \textbf{Simple Dehydrogenation of EB with Steam}

\[ \text{C}_6\text{H}_5\text{CH}_2\text{CH}_3 \xrightarrow{\text{Steam}} \text{C}_6\text{H}_5\text{CH=CH}_2 + \text{H}_2 \]
Mechanism for Oxidative Dehydrogenation of EB with CO$_2$ over Iron-oxide catalyst

Simple Dehydrogenation

Oxidative Dehydrogenation

**SODECO\textsubscript{2}®** (Styrene from Oxidative Dehydrogenation via CO\textsubscript{2}):

New process for styrene production with CO\textsubscript{2} discharged from oxidation process

Discharge of 0.556 tone of carbon dioxide per 1 tone of ethylene oxide (EO)

Purity of CO\textsubscript{2} as a by-product of EO process: > 99% (Others: 0.5% H2O and less than 300 ppm of C1 and C2 hydrocarbons)

Production of EO: 600,000 t/year in Korea (CO\textsubscript{2} 330,000 t/year in EO process)
Creation of New Chemical Industry by Utilization of Carbon Dioxide Discharged from Chemical Process

CO₂ as a by-product in industry

CO₂ utilization

Petrochemical industry (styrene monomer)

Polymerization

CO₂ mitigation
Replacing steam
Energy saving

w/o purification

Processing

Iron oxide waste

Catalyst

Iron mill

Polystyrene