CHEMRAWN XVI Conference
Consultation Forum

Innovation Stage: the way pure to the applied chemistry

Transformation of the old process: Ethylbenzene to Styrene with CO_2 dilution

MIN CHE CHON

Chon International Co., Ltd.

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_2O_3-K_2O-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)

Company	Capacity	Location	Starting year	Process Licensor
YNCC	140	Yeochon	1986, 1995	Badger Eng.
LG Chemical	330	Yeochon	1990, 1991	Lummus/Monsanto
SK Oxychemical	300 260	Ulsan Ulsan	1991 1997	Badger/Mobil/ARCO* ARCO
Dongbu Chemical	210	Ulsan	1978, 1989	Monsanto/Lummus
Samsung GC	590	Daesan	1991, 1996	Badger
Hyundai PC	325	Daesan	1991, 1996	Badger Raytheon
Total	2,155 →	2.5 Mt/year capacity (Year 2001)		

*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 H_2 from dehydrogenation with O_2

; Overcome the contamination of mixing the steam and O_2

Need for very selective and stable catalysts for oxidation of 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

SODECO$_2$® Technology Development

SODECO$_2$® (Styrene from Oxidative Dehydrogenation via CO_2):

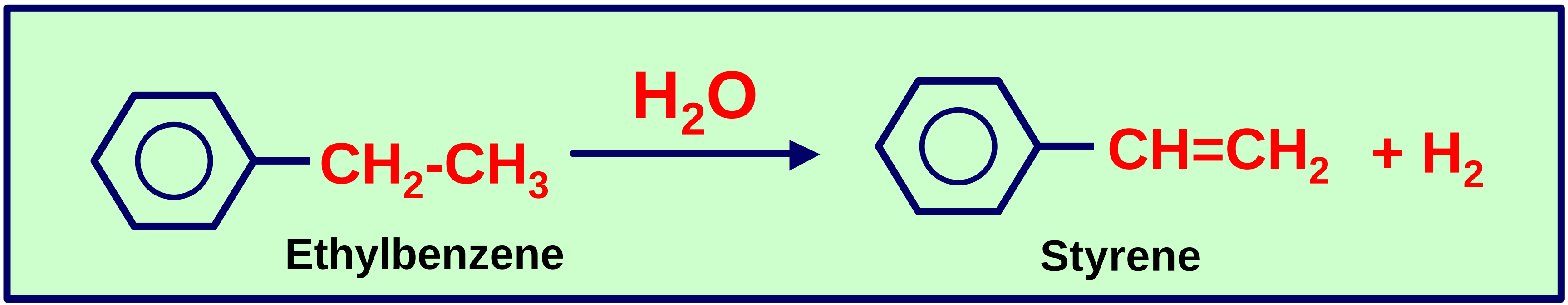
Styrene Monomer Process via Oxidative Dehydrogenation of Ethylbenzene using Carbon Dioxide as Soft Oxidant

Source of CO_2 ----- By Product CO_2 discharged from Petrochemical Industry

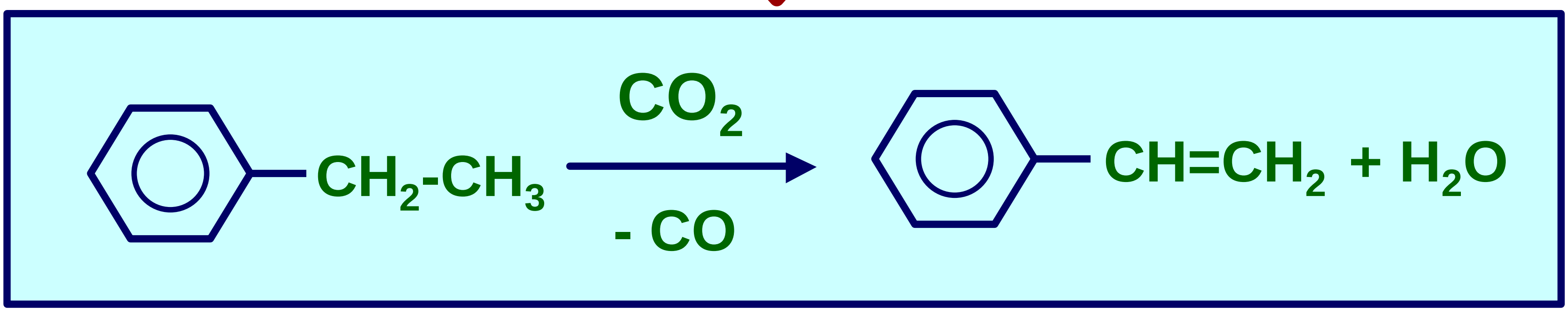
Developed by: Dr. S. E. Park and his group KRICT

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 CO_2: 49.1 J/ mol·K at 673K (37.0 J/mol·K at 673K for H_2O and 33.2 J/mol·K at 673K for 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

Characteristics	Steam	Oxygen	Carbon Dioxide
Function	Not oxidant Diluent	Strong oxidant Not Diluent	Soft oxidant Diluent
Heat capacity	Medium (37.0 J/mol·K at 673K)	Low (33.2 J/mol·K at 673K)	High (49.1 J/mol·K at 673K)
Heat capacity	High selectivity Catalyst stability Coke resistance Keeping oxidationstate	High activity Exothermic Less deactivation	High selectivity Activity enhancement Equilibrium shift Cheap carrier gas
Disadvantage	Expensive diluent Highly endothermic High latent heat High operation cost	Low selectivity Dangerous Hot spot	Not commercialized Endothermic Catalyst deactivation

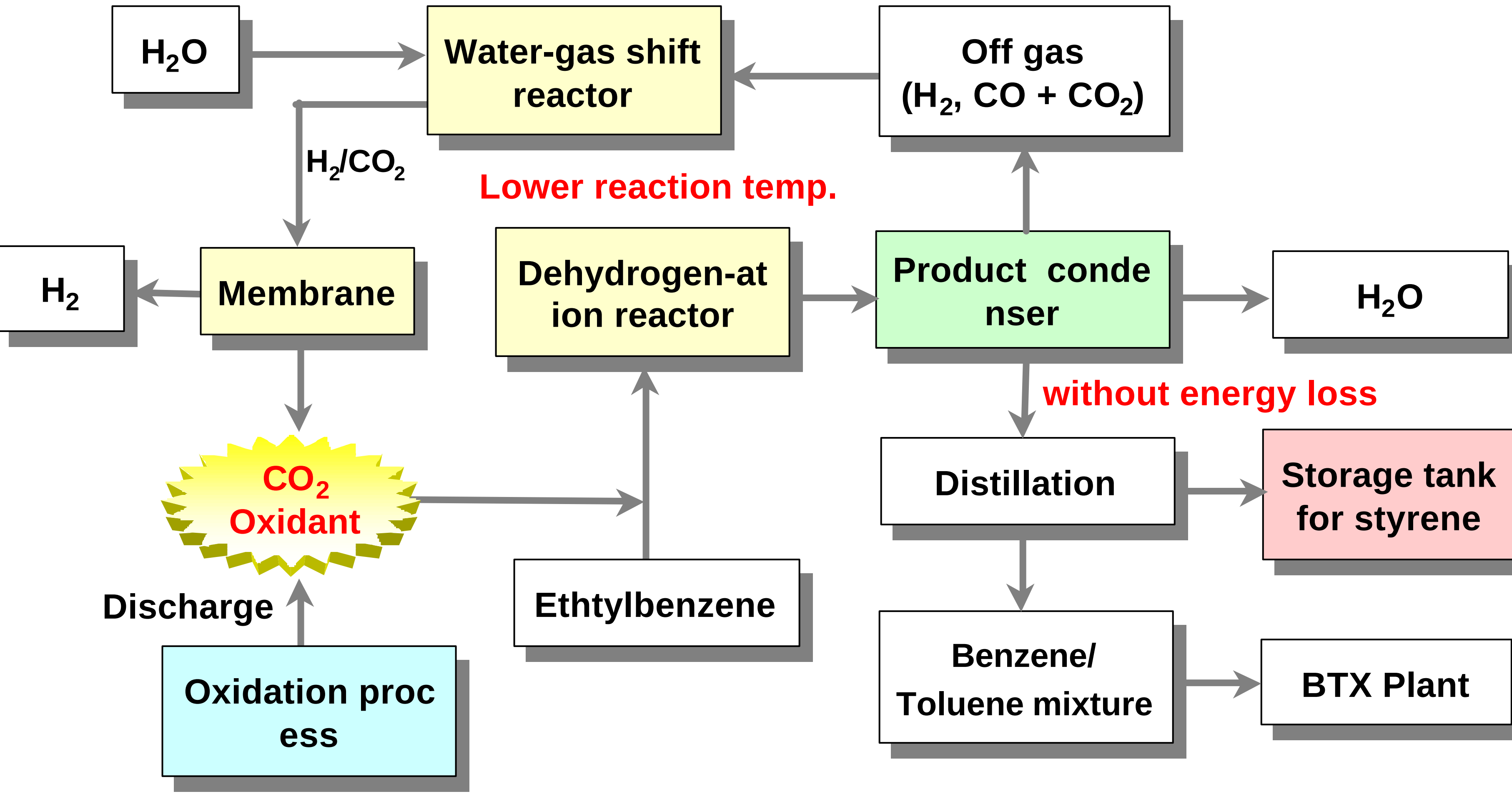
Characteristics of SODECO$_2$® Process

1. Direct utilization of CO_2 as a by-product discharged fr om petrochemical industry (Self-sufficiency of CO_2)
2. Utilization of CO_2 as soft oxidant to alleviate chemical equilibrium of ethylbenzene dehydrogenation
3. Selective dehydrogenation process using CO_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)

andidate 1

Schematic Diagram of $SODECO_2$® Process

$SODECO_2$® (Styrene via Oxidative Dehydrogenation of Ethylbenzene with CO_2)

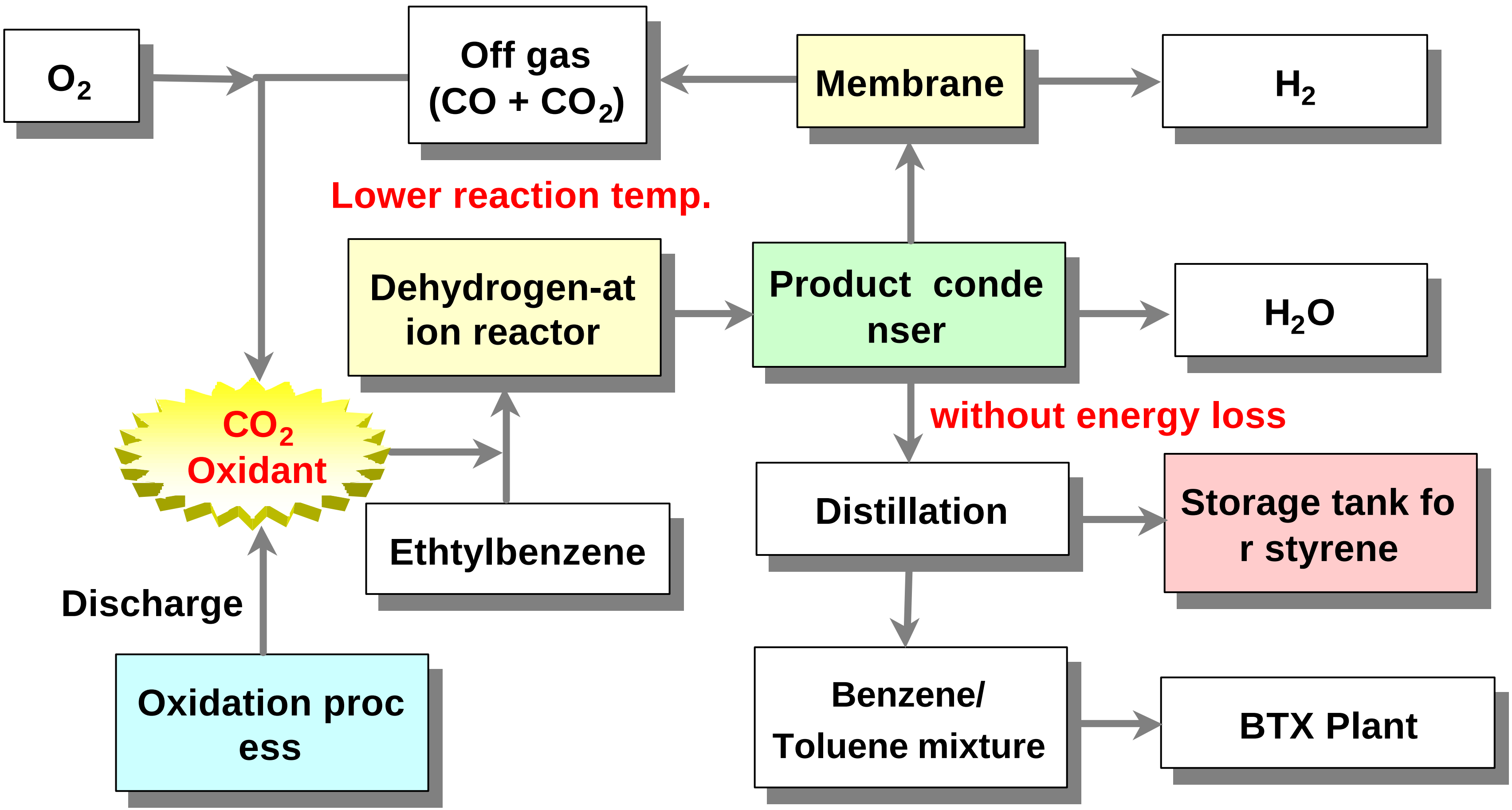


*Korea Patent Appl. 02-11418 (2002.3.4), EU Patent Appl. 03004382.2 (2002.3.3)

andidate 2

Schematic Diagram of SODECO$_2$® Process

SODECO$_2$® (Styrene via Oxidative Dehydrogenation of Ethylbenzene with CO_2)

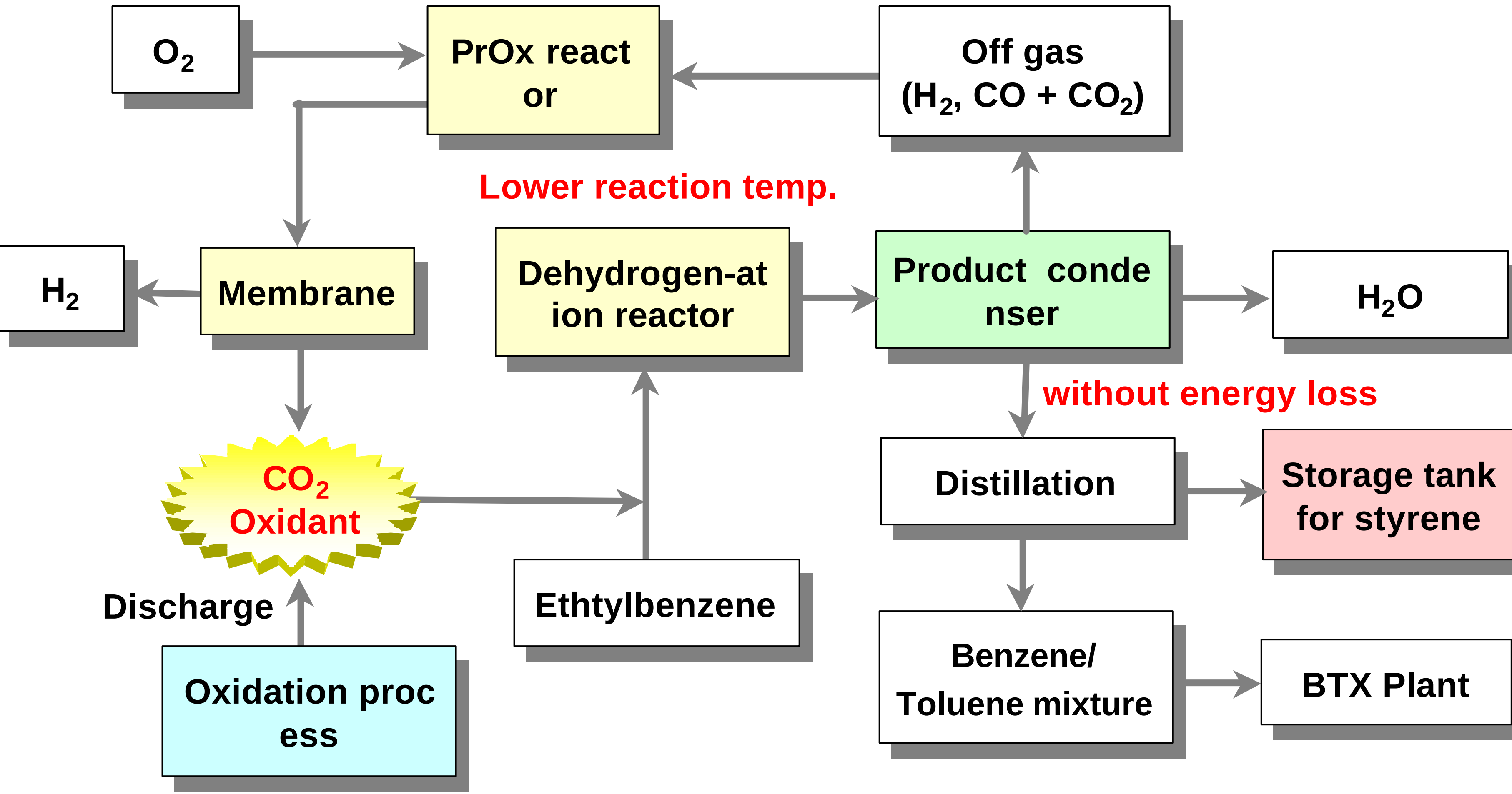


*Korea Patent Appl. 02-11418 (2002.3.4), EU Patent Appl. 03004382.2 (2002.3.3)

andidate 3

Schematic Diagram of SODECO$_2$® Process

SODECO$_2$® (Styrene via Oxidative Dehydrogenation of Ethylbenzene with CO_2)



*Korea Patent Appl. 02-11418 (2002.3.4), EU Patent Appl. 03004382.2 (2002.3.3)

Development of Commercial EBD catalysts

Function	Generation			
	1st (~1960)	2nd (~1980)	3rd (~2000)	SODECO$_2$®
Main Component	Fe/K	Fe/K	Fe/K	New Catalyst for EB dehydro-genation with CO_2 as an oxidant
Chemical Promoter	Cr	Ce	Ce, Ce-Zr	
Textual Promoter		W,Cu	Mg	
Selectivity Promoter	-	-	Mo	
Others (Binder, etc.)	Ca	Ca	Ca	
Commercial catalysts	-	BASF/Shell	NGC, etc.	KRICT
Catalytic Activity[a]	< 55	55 ~ 60	60 ~ 65	> 65 ~ 80

[a]Styrene yield, %

Catalyst for SODECO$_2$® Process

Function	Component	
Active Phase	Fe_3O_4	V_2O_5
Activity Promoter	Mn	-
Stability Promoter	Mo	Sb
Structural stabilizer	Ca ,Mg	Mg
Catalyst Support	Promoted-Al_2O_3, ZrO_2	

Comparison of catalytic performance between commercial and CO_2-SM catalyst

Catalyst	Commercial (steam)	CO_2-EBD
Temperature (°C)	SOR: 625-575(600) EOR: 655-605(630)	SOR: 525 – 575 EOR: not fixed
Pressure (atm)	0.75	0.75
Space velocity (LHSV, h^{-1})	0.75-1.0	1.0
Carrier/EB (molar)	8-12	2-10
Styrene yield (%)	60-66	55 – 65
Styrene selectivity (%)	94.0-96.5	97.0 – 98.0
Catalyst lifetime	2 years	?
Others	Only H_2 product	$X(CO_2)$ = 40-45% CO/H_2 = 1.0-1.5

SOR : Start-of-run; EOR : End-of-run

Scale-up Study vof $SODECO_2$® Process from Lab to Mini Pilot

Microactivity Test Unit

Bench-scale

Mini Pilot

		Micro(Lab.)	Bench	Pilot
Reactor	*F* (in.)	3/8	1/2	2
	length(ft.)	1	3	4
Catalyst volume		15ml	500ml	4 liter
Shape of catalyst		granule	spheroid	Tablet

Characteristics of Reactor Systems

Equipment	Micro uint	Bench scale	Mini Pilot
CO_2 Feed	Mass flow controller Cylinder gas (R-grade)	Mass flow controller Cylinder gas (R-grade)	Mass flow controller CO_2 from EG/EO Plant
EB Feed	Syringe pump	LC pump	LC pump
Pre-heater	Preheating Zone	Pre-heater (electric) wi th mixer	Pre-heater (electric) with mixer
Temperature control	Single heating zone	5-zoned heater with PID controller	5-zoned heater with PID controller
Product analysis	Gas component; on-lined GC(TCD) Liq. component; Condensed to GC(FID)	Gas component; on-lined GC(TCD) Liq. component; Condensed to GC(FID)	Gas component; on-lined GC(TCD) Liq. component; Condensed to GC(FID)

Bench Scale Unit for Ethylbenzene Dehydrogenation with CO_2

Design SM Production Capacity : 2.5 Ton / yr

Catalyst volume = 500 ml Shape :spheroid (*F*=3mm)

LHSV = 1.0 h^{-1}, CO_2/EB = 5/1, 50% yield @ 560°C

SM Production via SODECO$_2$® Process @ Pilot-scale system

Annual SM Production : 20 Ton / yr

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

P = 0.75 atm, LHSV = 1.0 h^{-1}, CO_2/EB = 5/1,

CO_2 Conv.= 42% @ 560°C (Dual 4 Tubes of Bench scale)

Comparison of economical properties for EBD processes

Basis for calculation : 0.6Mt-SM/yr

	$SODECO_2$®	Conventional
Temperature(°C)	560	600
SM Selectivity(%)	96.5	95.0
Economic effect	$ 2.7 M	
Loss of latent heat	66 %	100%
Cost for super-heated steam		$ 17 M
Energy saving	$ 6.6M	
Total	$ 9.3 M	

Project Financing

✓ **Critical Technology-21 Program**

Greenhouuse 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

Related Publications

? Patents

- "Catalyst for Dehydrogenating Aromatic Hydrocarbons with Carbon Dioxide," U.S. Patent 6, 034,032, U.S.Patent 6,037,511(2000).

- "Dehydrogenation of Alkylaromatic Hydrocarbons using Carbon Dioxide as Soft Oxidant" 2 003-13139(Korea), 2003-057644(Japan), 03004382.2 (Europe), U.S. Patent *under application*

- 4 Patents of Korea

? Research Papers

Environ. Challenge and Greenhouse Control in 21C, Green Chem (2003), Catal. Today,(2003), Res. Chem, Intermed, 28, 461,(2002), Catal. Commun., **3, 227 (2002);** ***Appl. Organomet. Chem.,*** **14, 815 (2001);** ***J. Catal.,*** **195, 1 (2000);** ***Catal. Lett.,*** **65, 75 (2000);** ***Catal. Lett.,*** **69, 93 (2000);** ***Res. Chem. Intermed.,*** **25(5), 411 (1999);** ***Chem. Lett.,*** **(10), 1063 (1998) etc.**

? Presentations

ACS Keynote Lecture(2001), ACS Fuel Chem. Div. (1996), ACS Fuel Chem. Div. (2002), 5th,6th, 7th Int.Conf.Carbon Dioxide Util. (1999, 2001, 2003)

Dr. Sang-Eun Park

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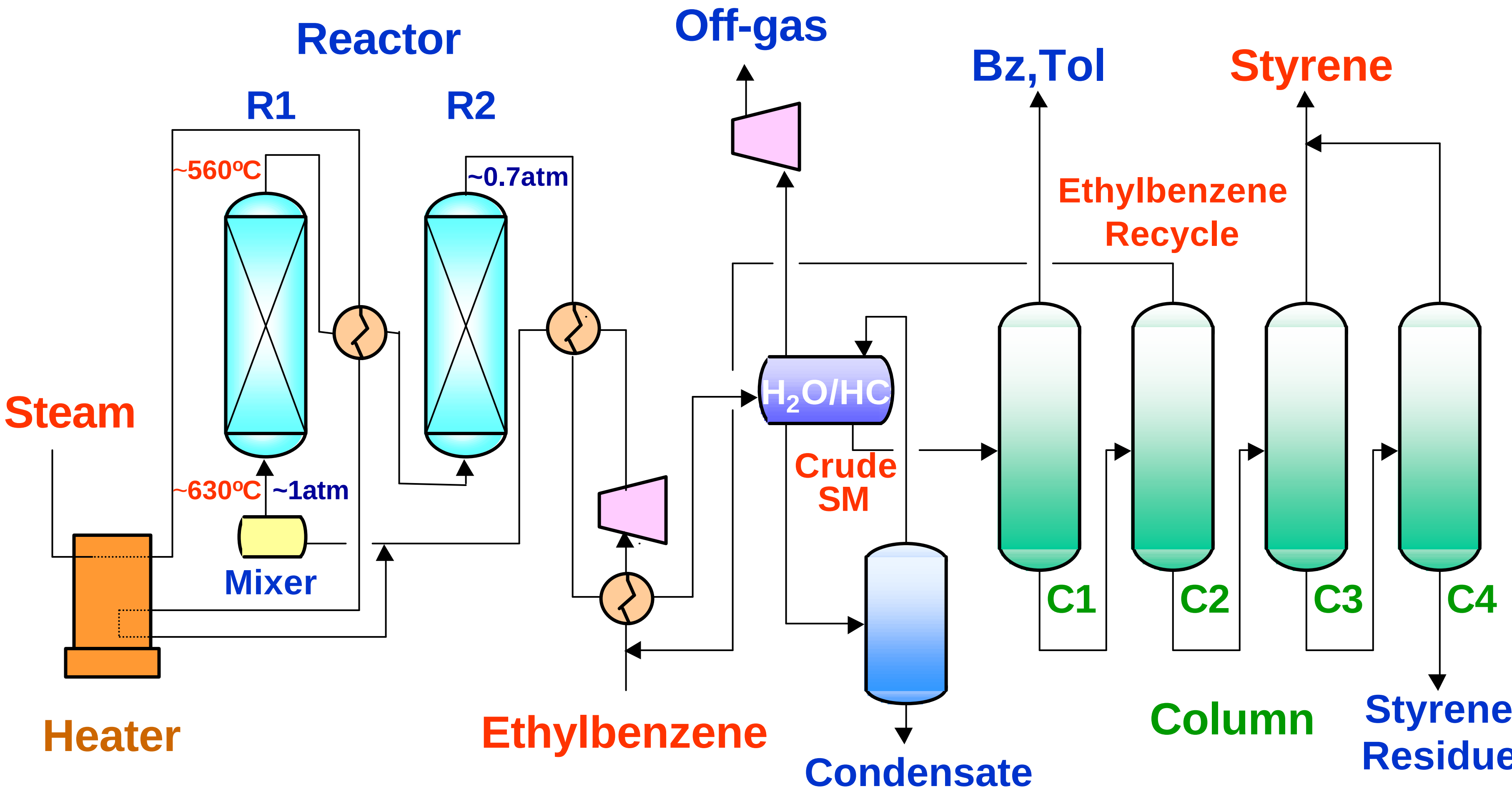
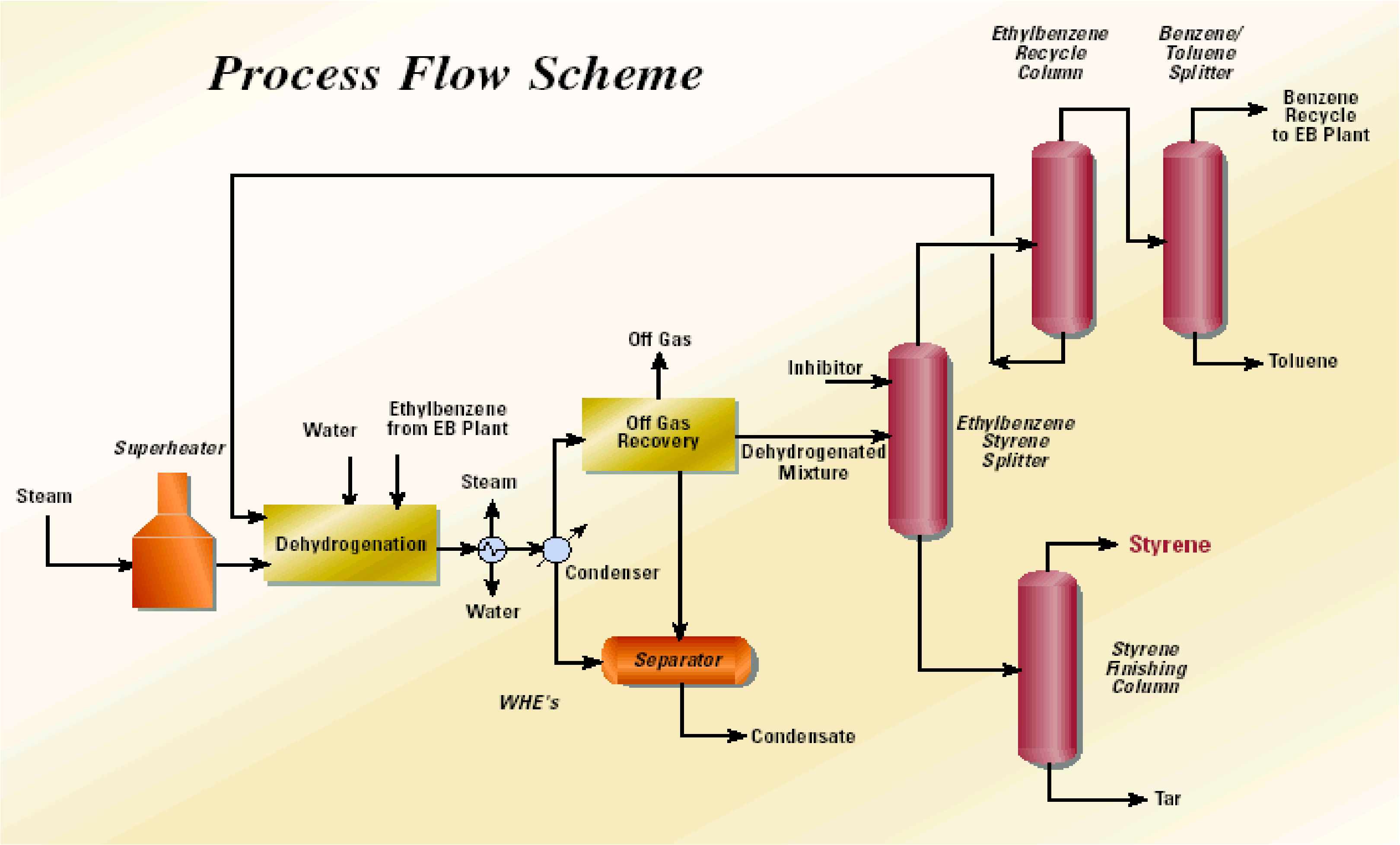
Year	Organization	Title	Others
1977-1984	Central Research Inst. Of Chon Engineering Co.	Chief Researcher	Chemical Engineering Design Process Development
1984-1986	Dept. of Chemistry, Texas A&M Univ.	Researcher Associate	Post Doc.
1987-1987	Dept. of Chemistry, KAIST	Visiting Researcher	
1987-present	KRICT	Senior Researcher to Director	

PFD for Conventional Styrene Monomer Process

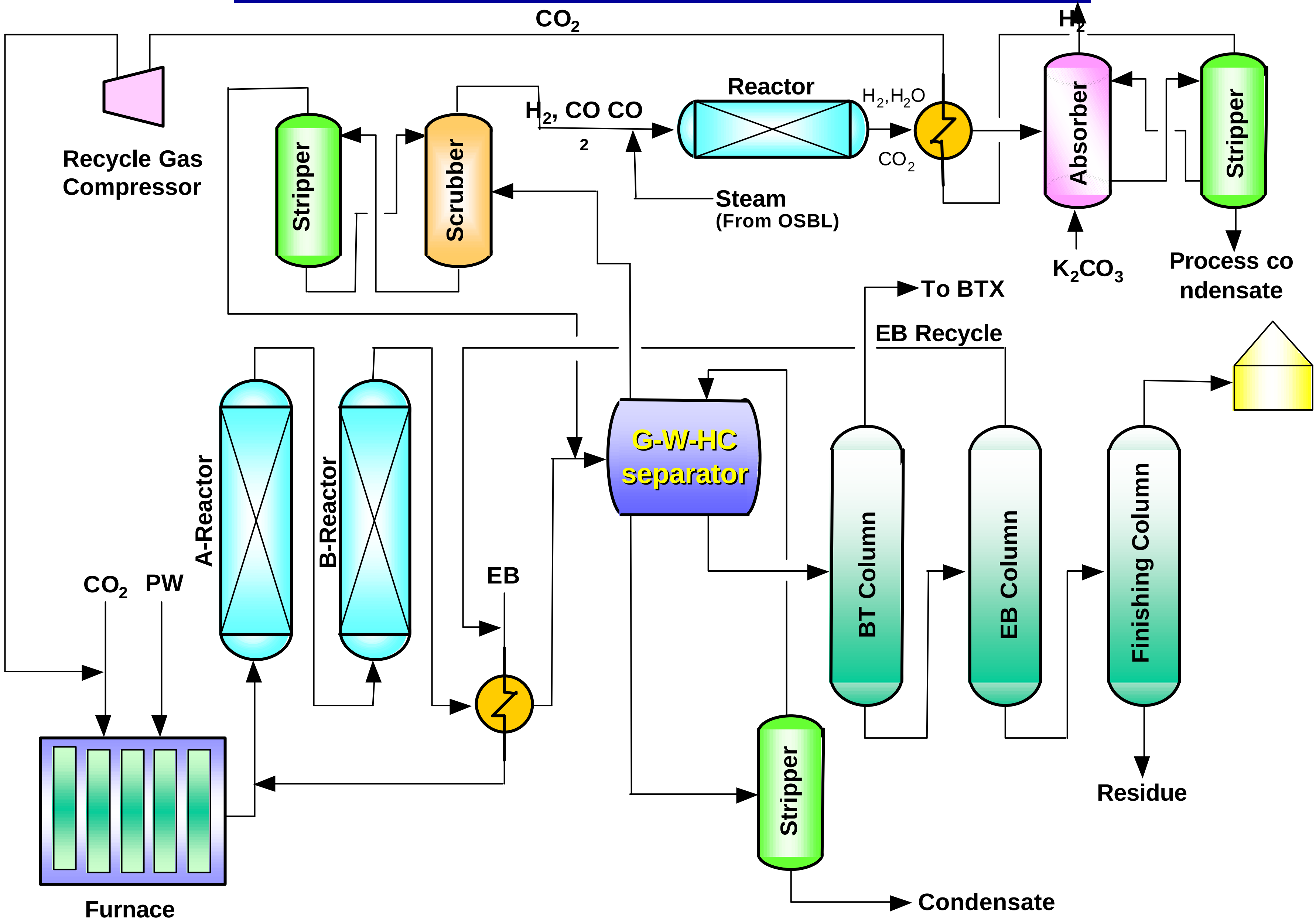


*Energy cost for superheated steam: 15 M dollar for 0.6 Mt-SM/year capacity

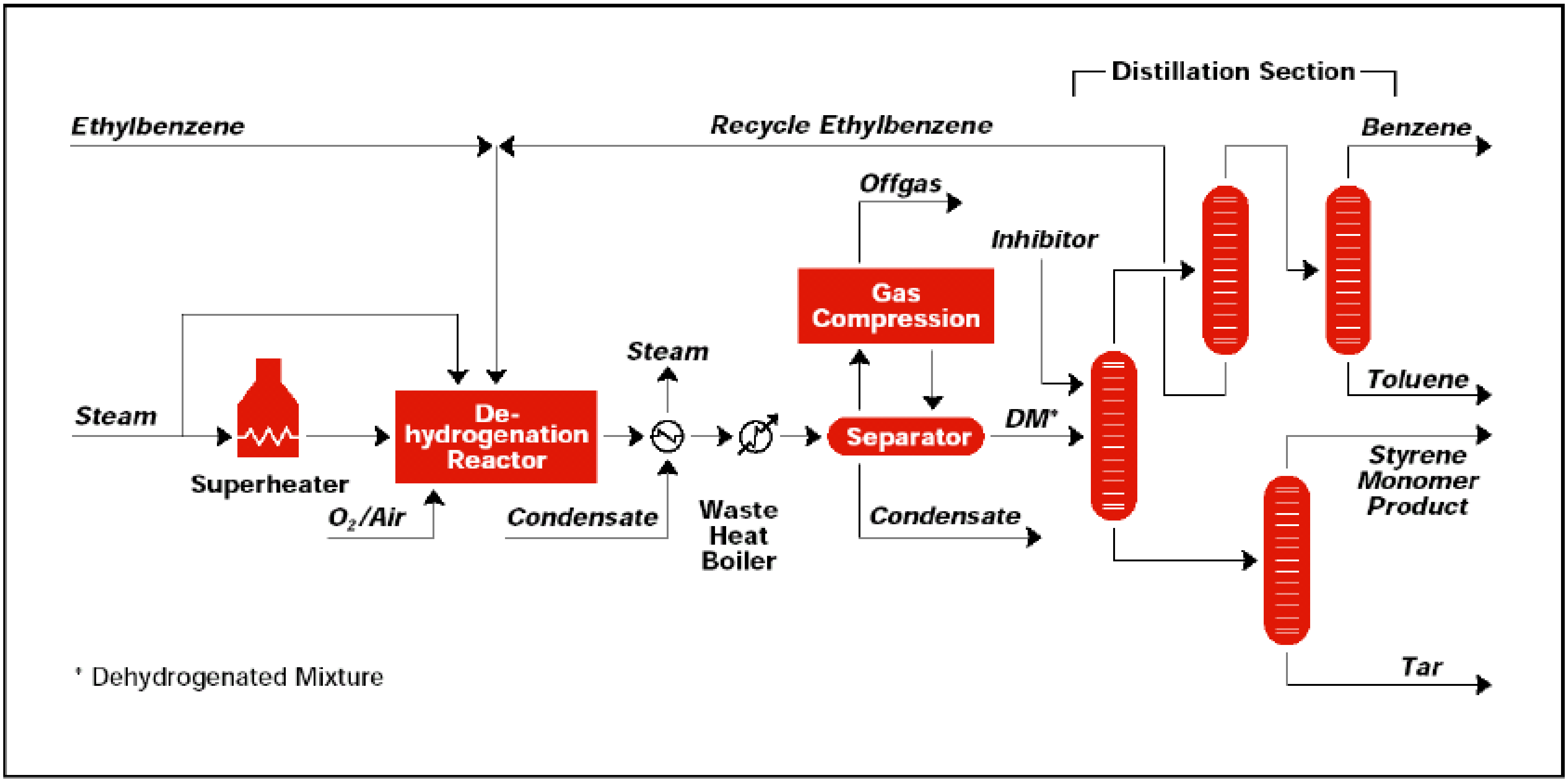
Lummus/UOP Classic SMTM Process



PFD of SODECO$_2$® Process

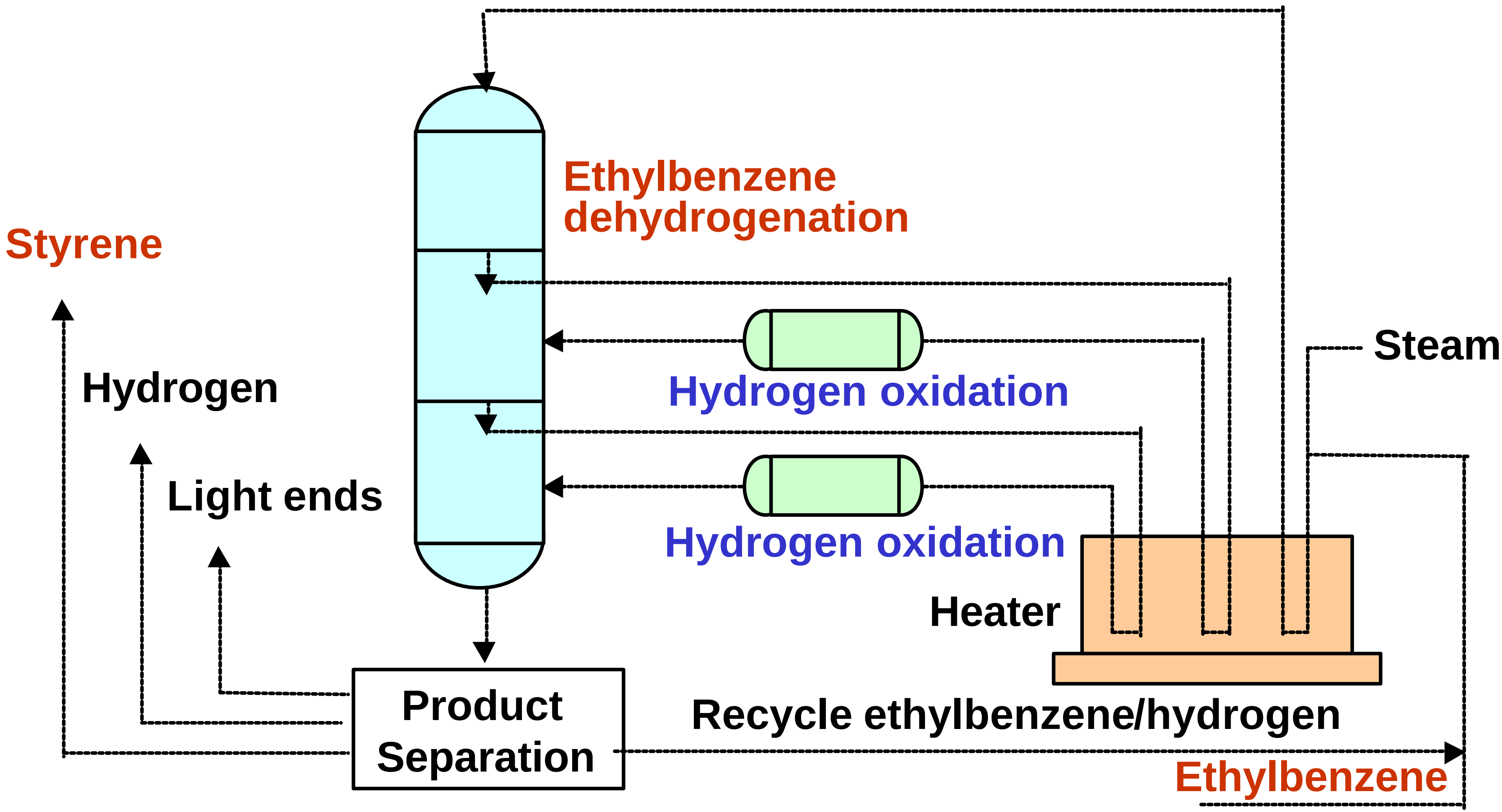


Lummus/UOP-SMART Process;
(Styrene Monomer Advanced Reheat Technology)



The SMART SM™ process combines oxidative reheat technology with adiabatic dehydrogen ation technology to produce high purity (99.85 wt% minimum) styrene monomer (SM) from e thylbenzene.
This results in EB conversion of more than 80%, as well as eliminating the costly interstage r eheater and reducing superheated steam requirements.

UOP-SMART Process

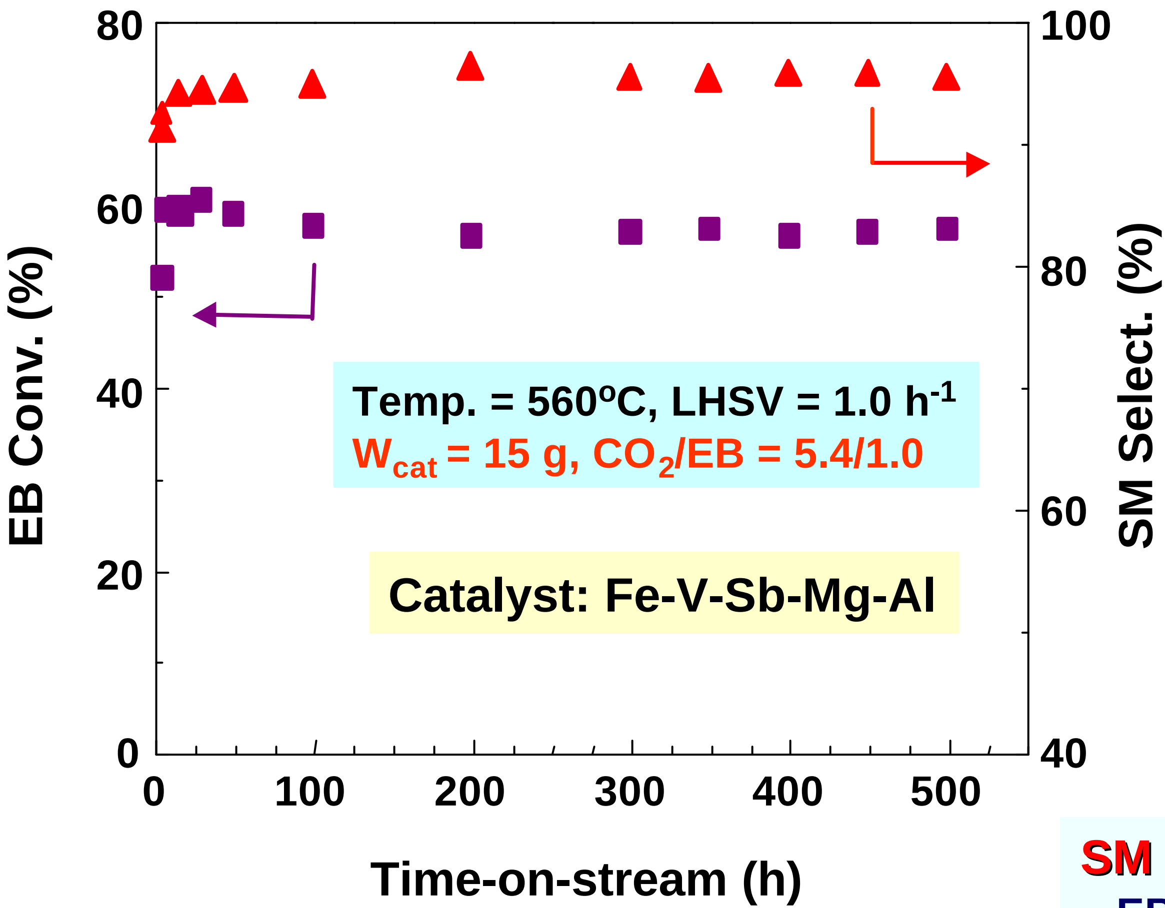


Purity of CO_2 by-product from Ethylene Oxide (EO) Process

Component	Case1	Case2
CO_2	99.46%	99.9%
H_2O	0.51%	-
O_2	50ppm	100ppm
N_2	50ppm	100ppm
Methane	-	300ppm
Ethylene	140ppm	200ppm
Ethane	80ppm	100ppm

*Separation of EO and CO_2 through absorption process to purify EO product

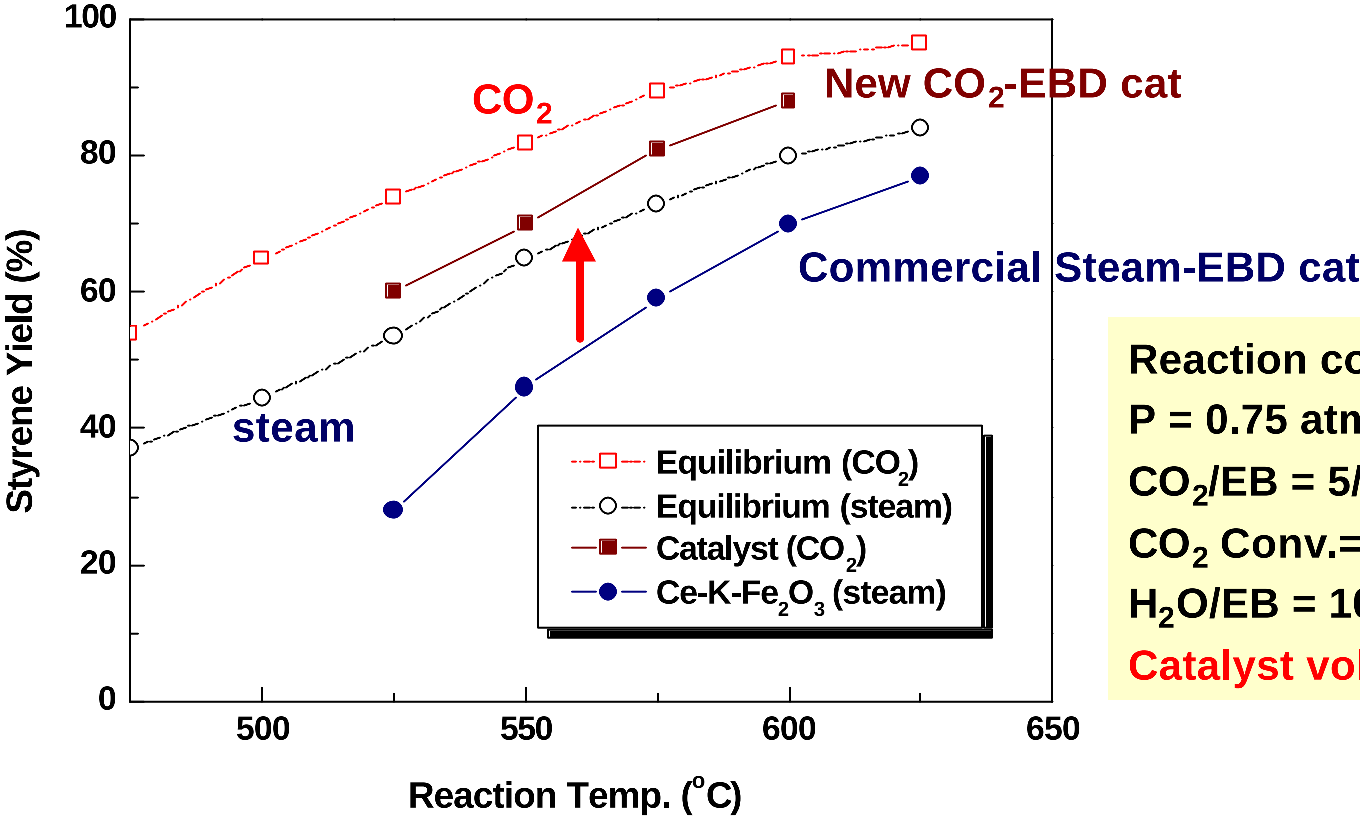
Catalytic Activity in EBD with CO_2 in Bench-scale



SM Production

- EB Feeding : 30cc/hr
- SM Yield : ~ 60%
- SM Production = 370g/day

New CO_2-EBD catalyst vs. Commercial steam-EBD catalyst



Reaction condition:

P = 0.75 atm, LHSV = 1.0 h^{-1},

CO_2/EB = 5/1 (CO_2 Cat.)

CO_2 Conv.= 42% @ 560°C

H_2O/EB = 10/1 (Steam Cat.)

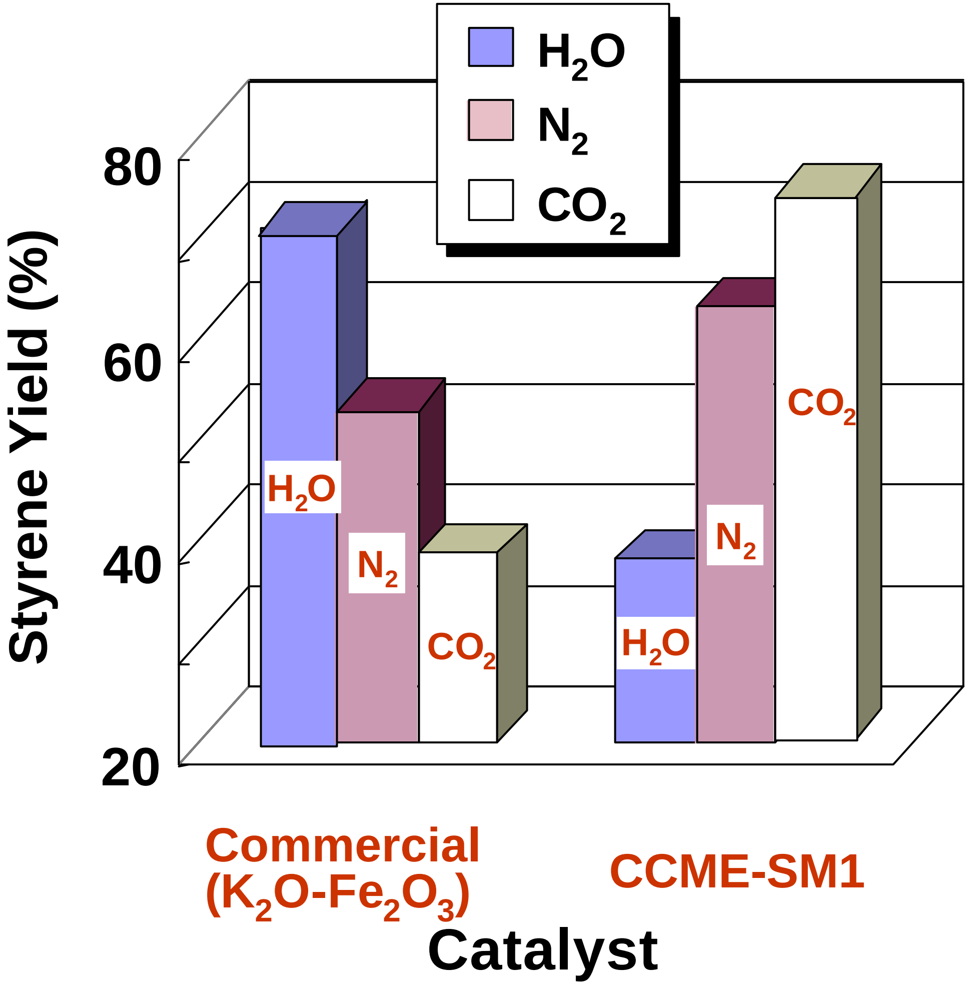
Catalyst volume = 4 L

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)

*** Korea Patent Appl. 02-11418 (2002.3.4), EU Patent Appl. 03004382.2 (2002.3.3)**

Comparison of styrene yields in steam-EBD and CO_2-EBD catalysts



Catalyst : Fe-V-Sb-Mg-Al

Reaction conditions:
- Temp. = 600^{o}C,
- LHSV = 1.0 h^{-1}
- $H_2O(N_2)/EB$ = 8/1;
- CO_2/EB = 5.4/1

*US Patent 6,037,511(2000) for catalyst; US Patent 6,034,032 (2000) for process

Simplified Reaction Equations of EB Dehydrogenation via *SODECO₂*® and conventional

- ***Oxidative* Dehydrogenation of EB via *SODECO$_2$*® Process**

$$CO_2 \xrightarrow[[\ \ ]^*]{} CO + [O]_s$$

$$C_6H_5CH_2CH_3 + [O]_s \longrightarrow C_6H_5CH{=}CH_2 + H_2O$$

$$C_6H_5CH_2CH_3 + CO_2 \longrightarrow C_6H_5CH{=}CH_2 + CO + H_2O$$

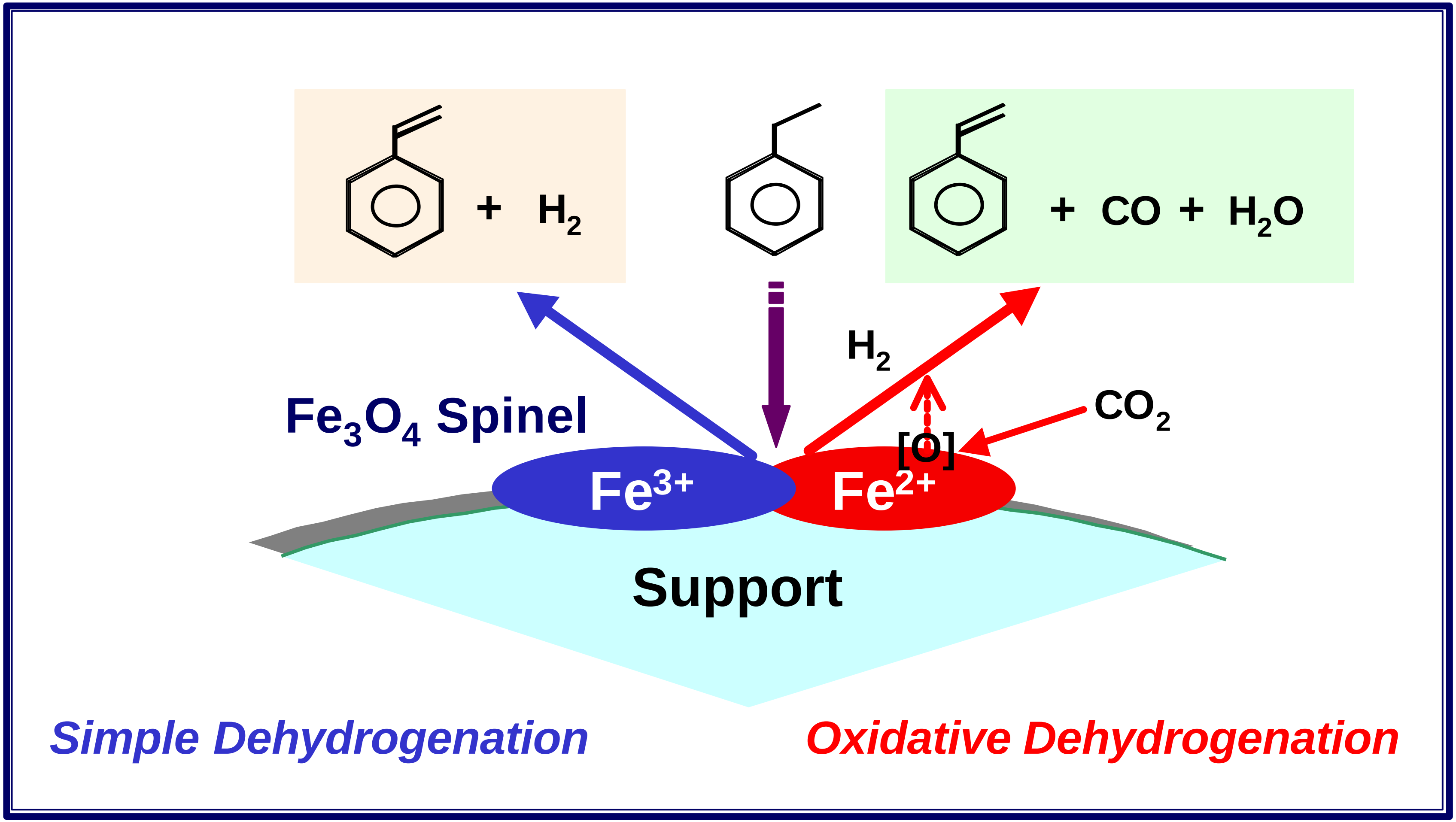
[ ]* : a surface vacancy

$[O]_s$: a lattice oxygen atom

- ***Simple* Dehydrogenation of EB with *Steam***

$$C_6H_5CH_2CH_3 \xrightarrow[Steam]{} C_6H_5CH{=}CH_2 + H_2$$

Mechanism for Oxidative Dehydrogenation of EB with CO_2 over Iron-oxide catalyst



S.-E. Park et.al. , AIChE 2000 Spring Meeting, Atlanta, GA, Mar. 9 - 12, 2000.

SODECO$_2$® Technology Development

SODECO$_2$® (Styrene from Oxidative Dehydrogenation via CO_2):
New process for styrene production with CO_2 discharged from oxidation process

Discharge of 0.556 tone of carbon dioxide per 1 tone of ethylene oxide (EO)
Purity of CO_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_2 330,000 t/year in EO process)

Creation of New Chemical Industry by Utilization of Carbon Dioxide Discharged from Chemical Process