

PENNSTATE



Chemical Conversion and Utilization of CO₂ from Fossil Fuel Combustion

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**DOE NETL Workshop on Carbon Sequestration Science
May 22-24, 2001, Pittsburgh, PA, USA**

World CO₂ Emissions from the Consumption of Fossil Fuels during 1980-1997 (in Million Metric Tons of Carbon)

World Regions	1980	1985	1990	1995	1997.0
North America	1484.2	1439.0	1561.4	1643.9	1725.8
Central and South America	173.0	167.8	187.4	226.1	242.5
Western Europe	1022.1	979.3	1011.2	957.8	990.2
Eastern Europe & Former U.S.S.R.	1111.4	1233.4	1297.9	878.1	851.8
Middle East	137.2	162.8	200.8	248.1	264.0
Africa	145.7	173.1	198.4	226.0	236.4
Far East and Oceania	977.2	1157.4	1429.9	1813.4	1921.1
World Total	5050.8	5312.8	5886.9	5993.4	6231.7

Sources: DOE, EIA, 1998, 1999

U.S. CO₂ Emissions from Different Sectors (Million Metric Tons of Carbon)

CO2 Emissions Sources	1980	1985	1990	1995	1997
CO2 from Residential Sector	248.4	245.8	253.1	270.3	286.5
CO2 from Commercial Sector	178.3	189.7	206.8	217.9	237.2
CO2 from Industrial Sector	484.6	424.7	454.1	465	482.9
CO2 from Transportation Sector	378.1	384.4	432.1	458.5	473.1
CO2 from End-Use Total	1289.4	1244.6	1346.1	1411.7	1479.6
CO2 from Electric Utilities*	418.4	439	476.9	495.3	523.4

*Electric Utility emissions are distributed across end-use sectors.

Sources: DOE, EIA, 1998, 1999

U.S. CO₂ Emission from Electricity-Generating Units (Million Metric Tons of Carbon)

CO2 Emissions Sources	1990	1995	1997
Coal-Fired Units at Electric Utilities	409.9	434.3	471.3
Petroleum-Fired Units at Electric Utilities	25.3	13.0	15.0
Gas-Fired Units at Electric Utilities	39.2	44.5	36.0
Other Units at Electric Utilities	1.2	0.8	1.0
Emissions at Electric Utilities, Total	475.5	492.7	523.4
Coal-Fired Units at Nonutilities	17.8	24.6	25.3
Petroleum-Fired Units at Nonutilities	4.3	7.3	7.4
Gas-Fired Units at Nonutilities	39.2	57.6	53.2
Other Units at Nonutilities	37.4	45.9	48.4
Emissions at Nonutilities, Total	98.7	135.5	134.4
CO2 from Coal-Fired Units, Total	427.7	458.9	496.6
CO2 from Petroleum-Fired Units, Total	29.6	20.3	22.4
CO2 from Gas-Fired Units, Total	78.4	102.1	89.3
CO2 from Other Units, Total	38.5	46.8	49.4
Total CO2 Emissions from Generators	574.2	628.1	657.7

Sources: DOE, EIA, 1998, 1999

1990-1999 U.S. GHG Emissions

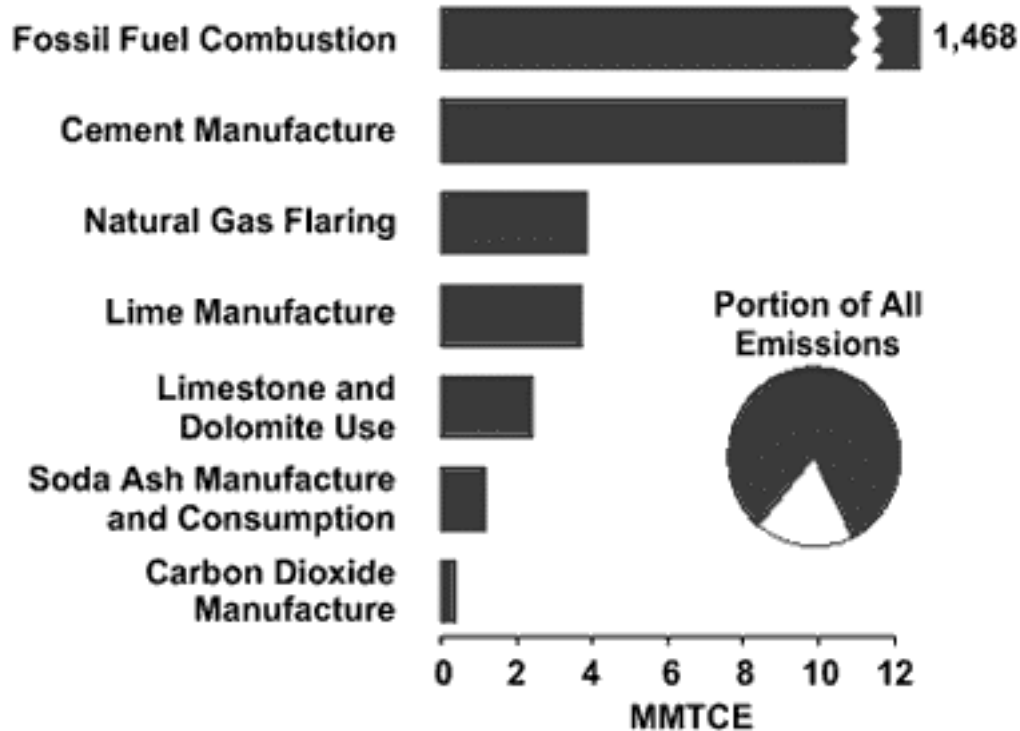
(Million Metric Tons Carbon Equivalent)

Gas	1990	1995	1997	1999-P
Carbon Dioxide	1,351	1,435	1,505	1,527
Methane	182	179	172	165
Nitrous Oxide	99	106	104	103
HFCs, PFCs, and SF6	24	29	35	38
Total	1,655	1,748	1,816	1,833

Source: AER, EIA, U.S. DOE, October 31, 2000. Note: Carbon Equivalent based on global warming potential.

1998 U.S. Sources of CO2 Emissions

(Million Metric Tons Carbon Equivalent)

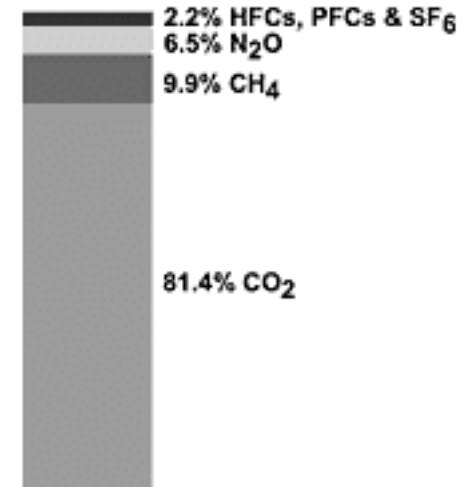


Portion of All Emissions

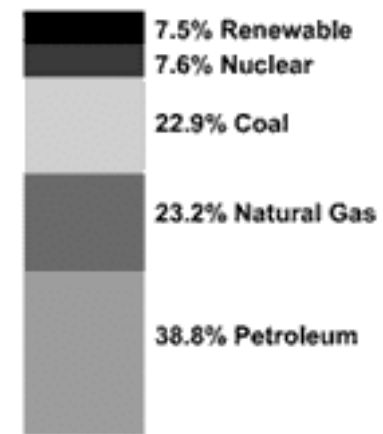


(Million Metric Tons Carbon Equivalent)

Source: U.S. EPA website, Viewed May 7, 2001. URL: <http://www.epa.gov/globalwarming/emissions/national/co2.html>.

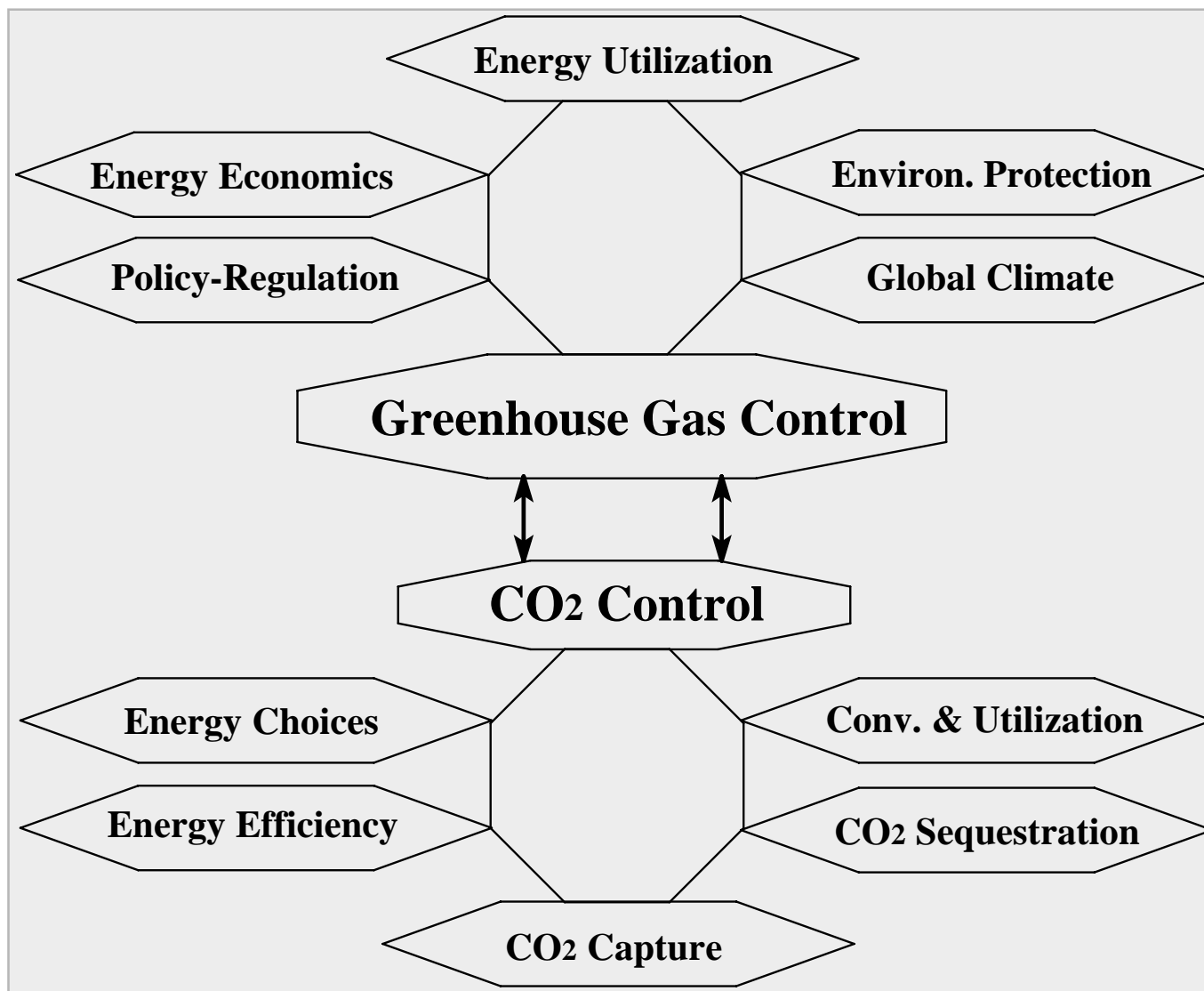


1998 US GHG Emissions
Source: US EPA, 2001

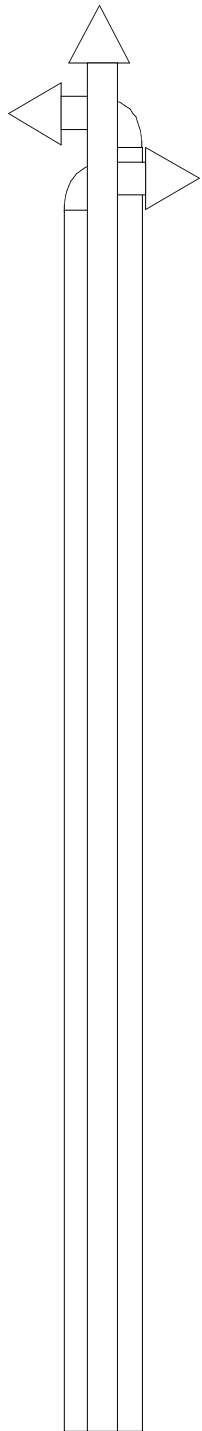


1998 US E Consum
Source: AER, USDOE, 2001

GHG Control & Related Areas



Source: C. Song. Am. Chem. Soc. Symp. Ser., 2001



Objectives of CO₂ Conversion & Utilization

Use CO₂ for environmentally-benign physical and chemical processing

Use CO₂ to produce industrially useful chemicals and materials

Use CO₂ to recover energy and reduce its emission to the atmosphere

Use CO₂ recycling to conserve carbon resources for sustainable development



Critical R&D Issues of CO₂ Conversion & Utilization

To make use of CO₂ based on the unique physical or chemical properties of CO₂

To produce useful chemicals and materials using CO₂ as a reactant or feedstock

To replace a hazardous or less-effective substance in existing processes with CO₂ as an alternate medium or solvent or co-reactant or a combination of them

To use CO₂ for energy recovery while reducing its emissions to the atmosphere by sequestration

To recycle CO₂ as C-source for chemicals and fuels

To convert CO₂ under geologic-formation conditions into “new fossil” energies

Source: C. Song. Am. Chem. Soc. Symp. Ser., 2001

CS/PSU/NETL 5/01



Barriers & Challenges for Promoting CO₂ Conv & Utilization

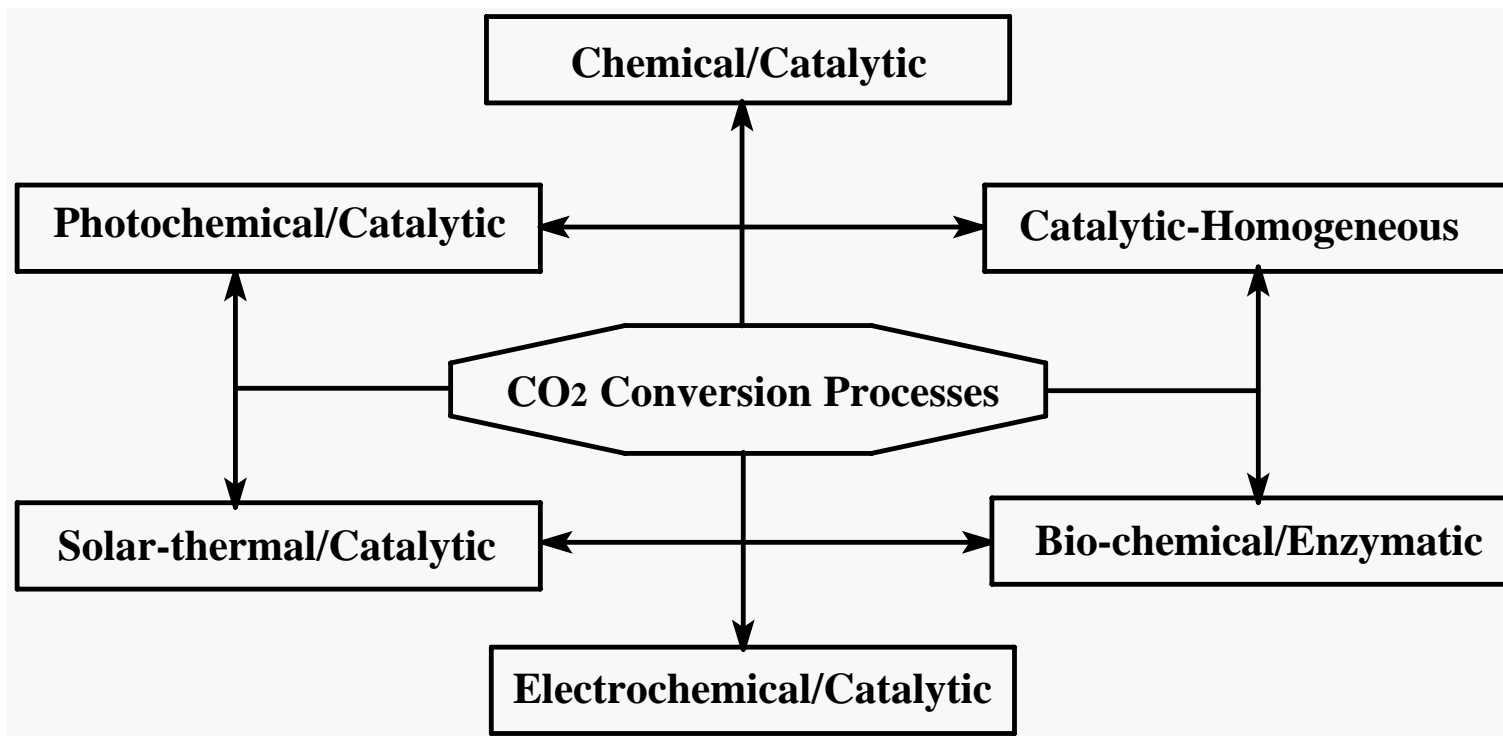
Costs of CO₂ capture, separation, purification, and transportation to user site.

Energy requirements of CO₂ chemical conversion (plus source & cost of H₂ if involved).

Market size limitations, and lack of investment-incentives for CO₂-based chemicals.

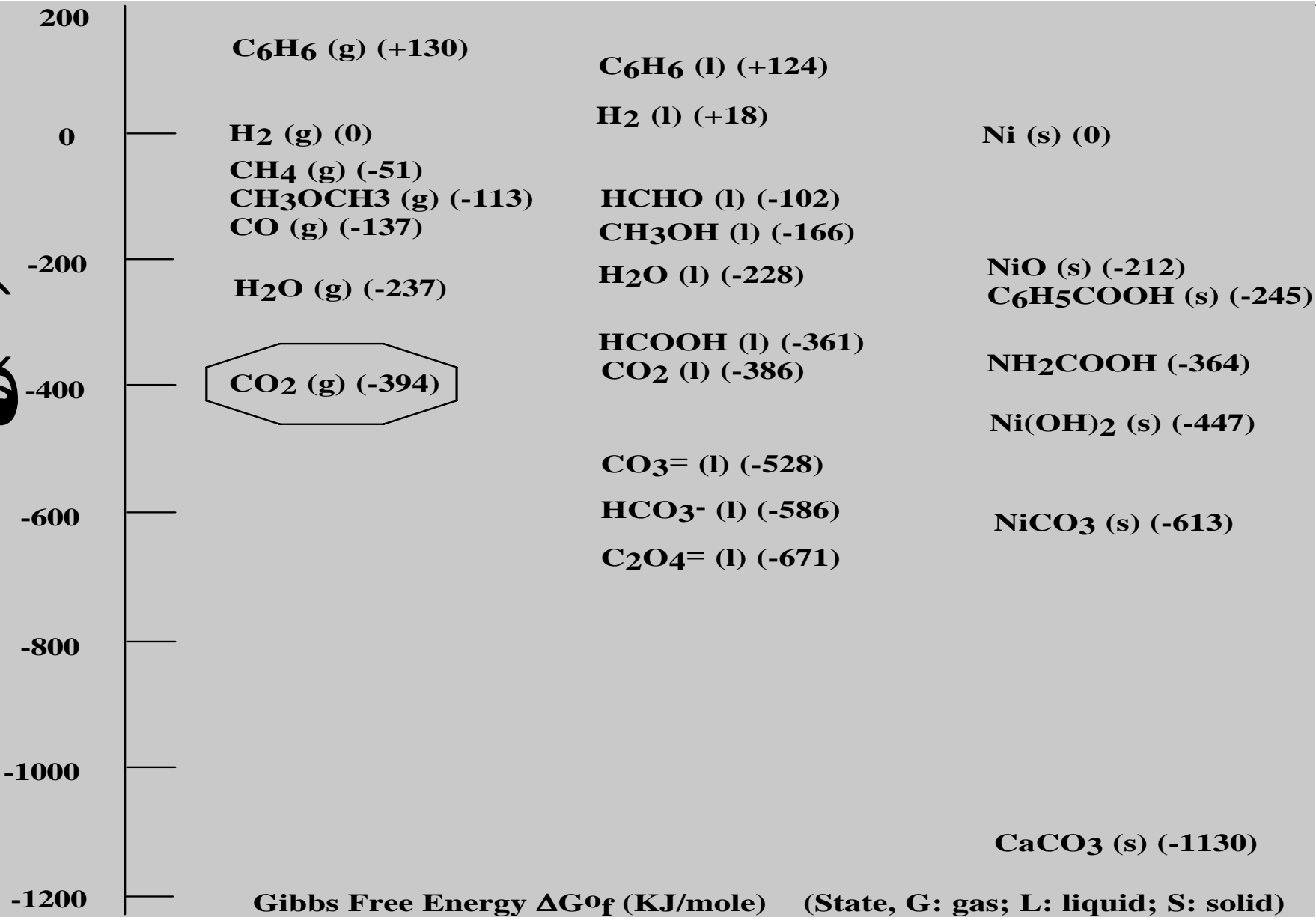
Socio-economical driving forces do not facilitate enhanced CO₂ utilization.

Chemical Processes for CO₂ Conv

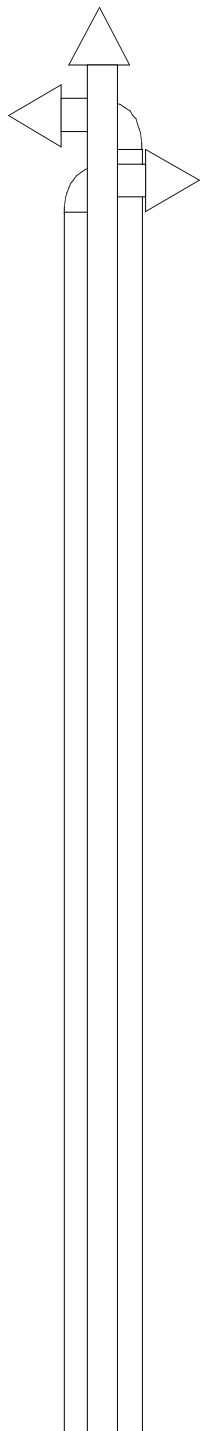


Source: C. Song. Am. Chem. Soc. Symp. Ser., 2001

Thermodynamics of CO₂ Conversion



Source: C. Song. Am. Chem. Soc. Symp. Ser., 2001



Strategies for CO₂ Conversion & Utilization

Select concentrated CO₂ sources for CO₂ capture; aim for on-site/nearby uses if possible.

Convert CO₂ along with other co-reactants into industrially useful chemical products.

Take value-added approaches for CO₂ sequestration coupled with utilization.

Fix CO₂ into environmentally-benign organic polymer materials or inorganic materials.

Use CO₂ to replace a hazardous or less-effective substance in existing chemical processes for making products with significant volumes.

Source: C. Song. Am. Chem. Soc. Symp. Ser., 2001

CS/PSU/NETL 5/01

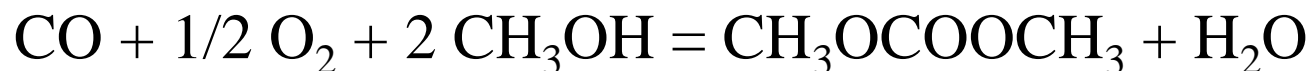
Chemical Synthesis Using CO₂

Synthesis of Dimethyl Carbonate (Phosgene Substitution)

Conventional Route (SNPE, 1970s):



New DMC Process by EniChem – 12000 tons/Yr



New Ube Chemical Process – 3000 tons/Yr

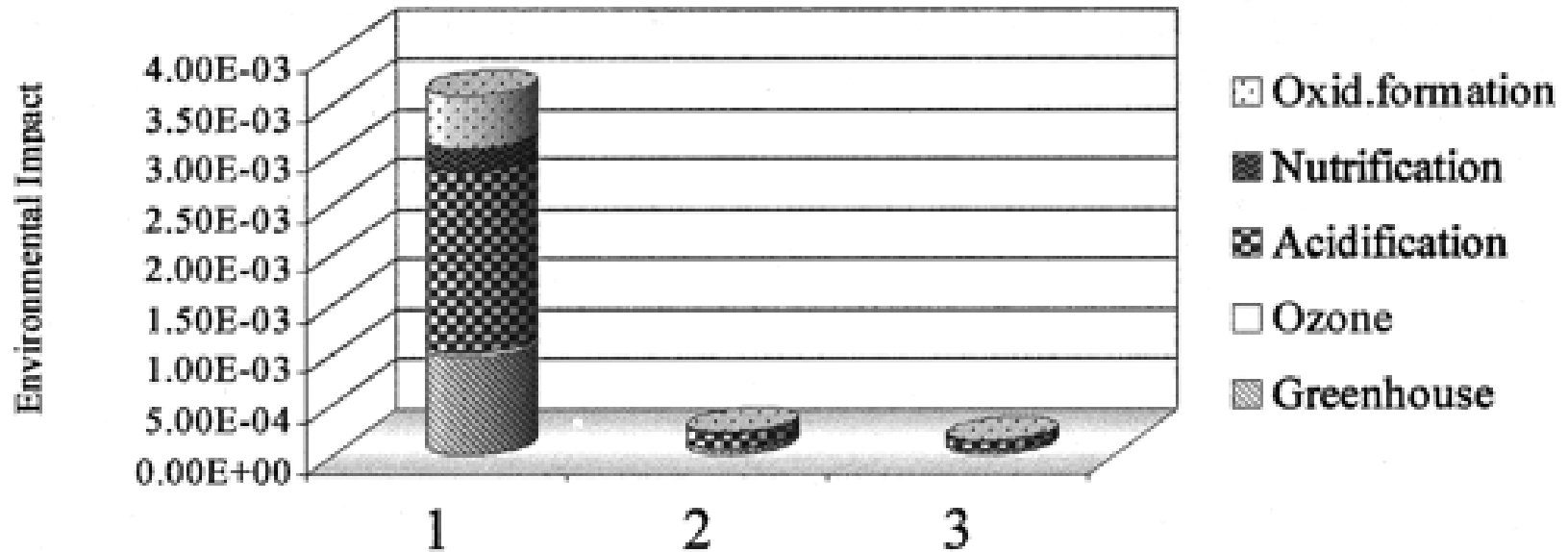


New CO₂-Based Route



Env. Benefits of Synthesis Using CO₂

[Case of Dimethyl Carbonate Synthesis]

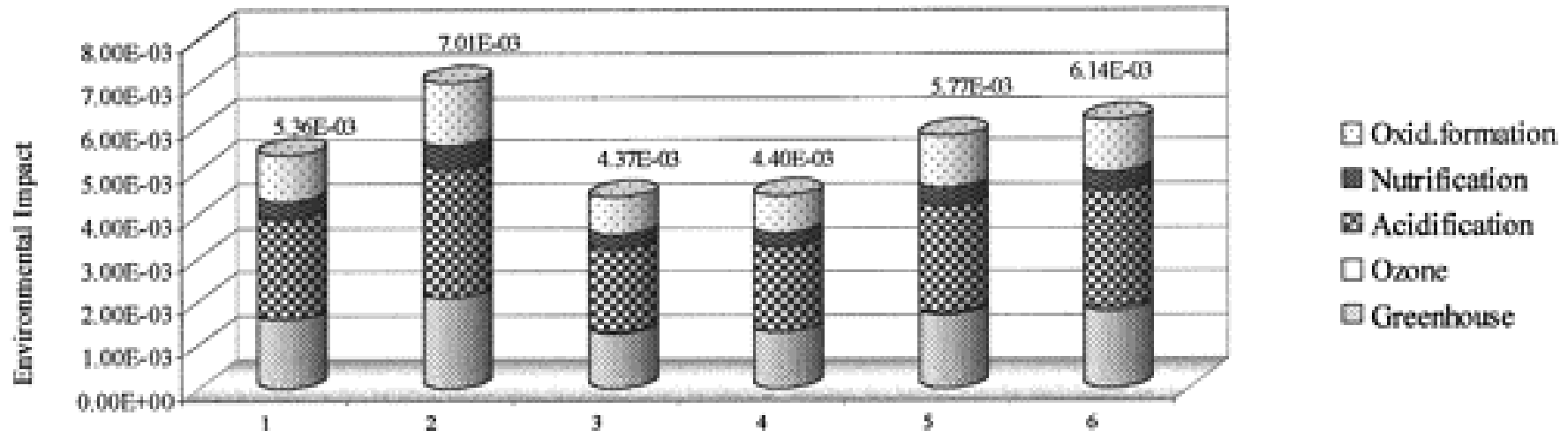


1: DMC from phosgene and methanol; 2: DMC from urea and methanol;
3: DMC from methanol and CO₂.

Source: Aresta, M.; Dibenedetto, A.; Tommasi, I. Energy & Fuels, 2001, 15, 269.

Env. Benefits of Synthesis Using CO₂

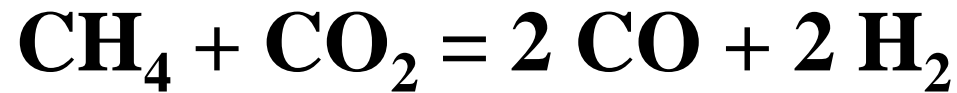
[Case of Methanol Synthesis]



- 1= methanol from CO₂ + H₂ (with CO₂ and H₂ from LNG steam reforming)
- 2= methanol from CO + H₂ (with CO and H₂ from LNG steam reforming)
- 3= methanol from CO₂ + H₂ (with 20% CO₂ recovered by MEA)
- 4= methanol like in reaction 3 (with 20% CO₂ recovered by refrigeration)
- 5= methanol from mix 75% CO + H₂ and 25% CO₂ + H₂ (with 75% CO₂ recovered by refrigeration)
- 6= methanol like in reaction 5 (with 75% CO₂ recovered by MEA)

Source: Aresta, M.; Dibenedetto, A.; Tommasi, I. Energy & Fuels, 2001, 15, 269.

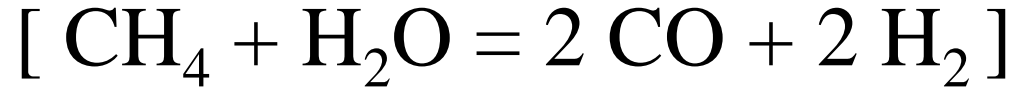
CO₂ Reforming of CH₄



Endothermic, $\Delta H = 247 \text{ KJ/mole}$

Being Widely Studied Worldwide

Requires 20% more energy than SMR



Problems with CO₂ Reforming of CH₄

Severe carbon formation, especially at HP by TEOM, prevents its commercial development.

Low H₂/CO ratios limit its large-scale application for F-T & MeOH synthesis.

Some Reviews on Chemical Conversion

Aresta, M.; Dibenedetto, A.; Tommasi, I. Developing Innovative Synthetic Technologies of Industrial Relevance Based on Carbon Dioxide as Raw Material. Energy & Fuels, 15: 269-273, 2001.

Halmann, M. M.; Steinberg, M. Greenhouse Gas Carbon Dioxide Mitigation: Science and Technology. Lewis Publishers, Boca Raton, Fl, 1999, 568 pp.

Aresta M. Perspectives of Carbon Dioxide Utilisation in the Synthesis of Chemicals. Coupling Chemistry with Biotechnology. STUD SURF SCI CATAL 114: 65-76, 1998

Arakawa H. Research and Development on New Synthetic Routes for Basic Chemicals by Catalytic Hydrogenation of CO₂. STUD SURF SCI CATAL 114: 19-30, 1998

Audus H; Oonk H. An Assessment Procedure for Chemical Utilisation Schemes Intended to Reduce CO₂ Emissions to Atmosphere. ENERG CONV MANAGE 38: S409-S414 Suppl. S 1997



Chemical Conversion and Utilization of CO₂ **[Some Recent ACS Symps on Chemical Aspects]**

Am. Chem. Soc. Symp. on “Greenhouse Gas Control and Utilization” (Co-chairs: C. Song, M. Aresta, and K. Y. Lee), ACS Spring 2001 National Meeting in San Diego, Published in Am. Chem. Soc. Div. Fuel. Chem. Prepr., 2001, Vol. 46, No. 1.

Am. Chem. Soc. Symp. on “CO₂ Conversion and Utilization” (Co-chairs: C. Song, A. M. Gaffney, and K. Fujimoto), ACS Spring 2000 National Meeting in San Francisco, Published in Am. Chem. Soc. Div. Petrol. Chem. Prepr., 2000, Vol. 45, No. 1.

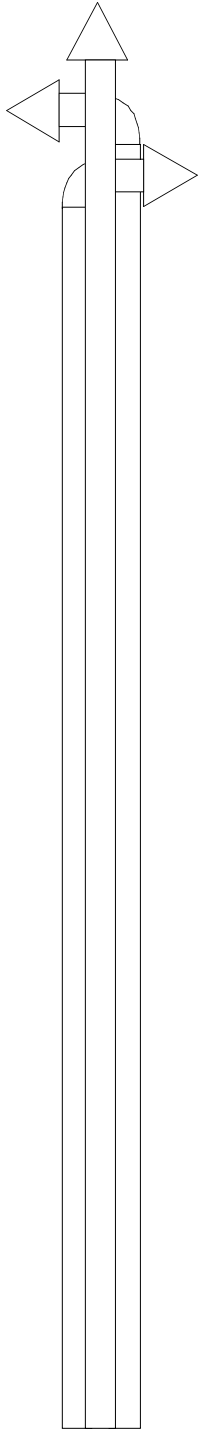
Energy & Fuels April 2001 “CO₂ Capture, Utilization and Sequestration” (Co-chairs: R. M. Enick and R. P. warzinski) 2001, Vol. 15, No. 2.

Proceedings of International Conference on Carbon Dioxide Utilization (1991- Nagoya, Japan; 1993-Bari, Italy; 1995-Oklahoma, US; 1997-Kyoto, Japan;

US Market for CO₂-Based Chemicals & Materials & Hypothetical Upper Limit of Future Demand

Chemicals & Materials	1999 U.S. Production ^a	Metric Tons (Tonnes)
Synthetic Plastics:	80,727 millions of lb	36,650,058
Synthetic Fibers	10,219 millions lb	4,639,426
Synthetic Rubbers	2,414 thousands of metric tons	2,414,000
	1. Polymers Subtotal (1999) =	37,584,996 as C 43,703,484 as Comp
Ammonia (reference for urea)	14,972 thousands of tons	13,579,604
Urea for fertilizer	5,453 thousands of tons	4,945,871
Urea for chemicals (1999) ^{a,b}	18,660 millions of lb ^b	8,471,640
Urea for chemicals (1994) ^c	15.90 billions of lb (7,952 thousands of tons)	7,218,600
	2. Urea-equivalent CO₂(1999)=	2,686,185 as C 9,839,508 as CO ₂
Methanol for chemicals (1994) ^c	12.18 billions of lb	5,529,720
	3. MeOH-Equivalent CO₂(1999)^f	2,428,590 as C 8,895,937 as CO ₂
CO ₂ – Liquid+Solid (1994) ^{c,d}	11.80 billions of lb (5,899 thousands of tons)	5,357,200
	4. Liq+Sol CO₂ (1999)^e	1,711,143 as C 6,267,924 as CO ₂
Ultimate U.S. CO ₂ demand for chemicals & materials	Total US Potential (1+2+3+4) =	44.4 MMT as C 162.8 MMT as CO ₂
Ultimate world CO ₂ demand for chemicals & materials	Estimated for World Potential	177.6 MMT as C 651.3 MMT as CO ₂

Source: C. Song. Am. Chem. Soc. Symp. Ser., 2001



Role of CO₂ in Chemical Conversion

Source of Carbon for Industrial Chemicals

Fixation CO₂ as Monomer in Polymer Materials

Source of Active “Oxygen”

Co-reactant for Reforming of Hydrocarbons

Gasifying Agent for Coal and Coke

Mild Oxidant for Chemical Reactions

Reaction Medium & Reactant in SC-CO₂

Replace Acids for Neutralizing Alkaline Wastes

Replace Acids for Neutralizing Alkaline Wastes

For Mineral Carbonation & Carbonates

CO₂ for New “Fossil” in Geologic Formations

[Besides beverage and foods use, and biomass]

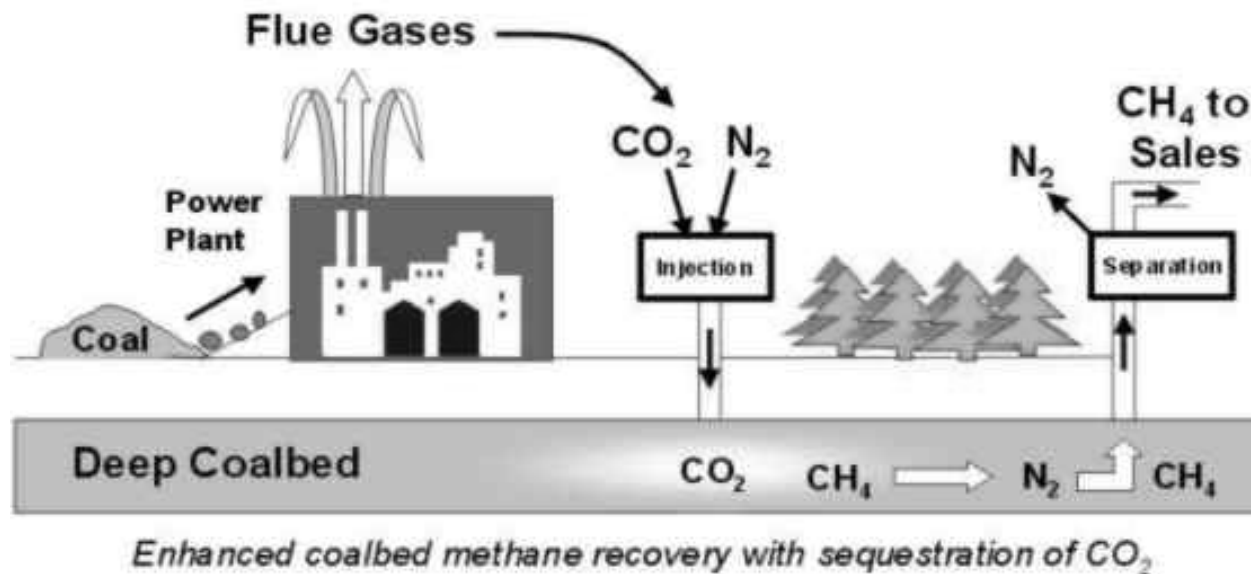
U.S. Transportation Fuels Market & Hypothetical Upper Limit of US Demand for CO₂-Based Fuels

U.S. Fuels	1999 Daily Production ^a	1999 Annual Production	Total Annual Production ^b	C-Equivalent of Annual Prod ^c
	Million barrels per day	Million barrels per Year	Million Metric Tons (Tonnes)	Million Metric Tons (Tonnes)
Gasoline	8.38	3058.7	354.8	301.6
Distillate Fuels (Diesel, etc)	3.55	1295.8	171.0	145.4
Jet Fuel	1.67	609.6	77.4	65.8
	Total = 13.60 [12.75 in transportation]		Subtotal =	512.8
			1997 US Electric Utilities Annual CO₂ Emissions	523.4 as C

Source: C. Song. Am. Chem. Soc. Symp. Ser., 2001

Value-Added CO₂ Sequestration-Utilization (CO₂-Enhanced Recovery of Oil & Gas)

CO₂-Enhanced Coal Bed methane Recovery



Source: IEA, <http://www.ieagreen.org.uk/>, May 5, 2001

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**Tri-reforming: A New Process Concept for
Conversion and Utilization of CO₂ in Flue
Gas without Pre-separation***

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Pennsylvania State University
University Park, PA, USA**

***Source: C. Song, Chemical Innovation, 2001, 31, 212-26.**



Challenges of Using CO₂ in Flue Gases from Power Plants

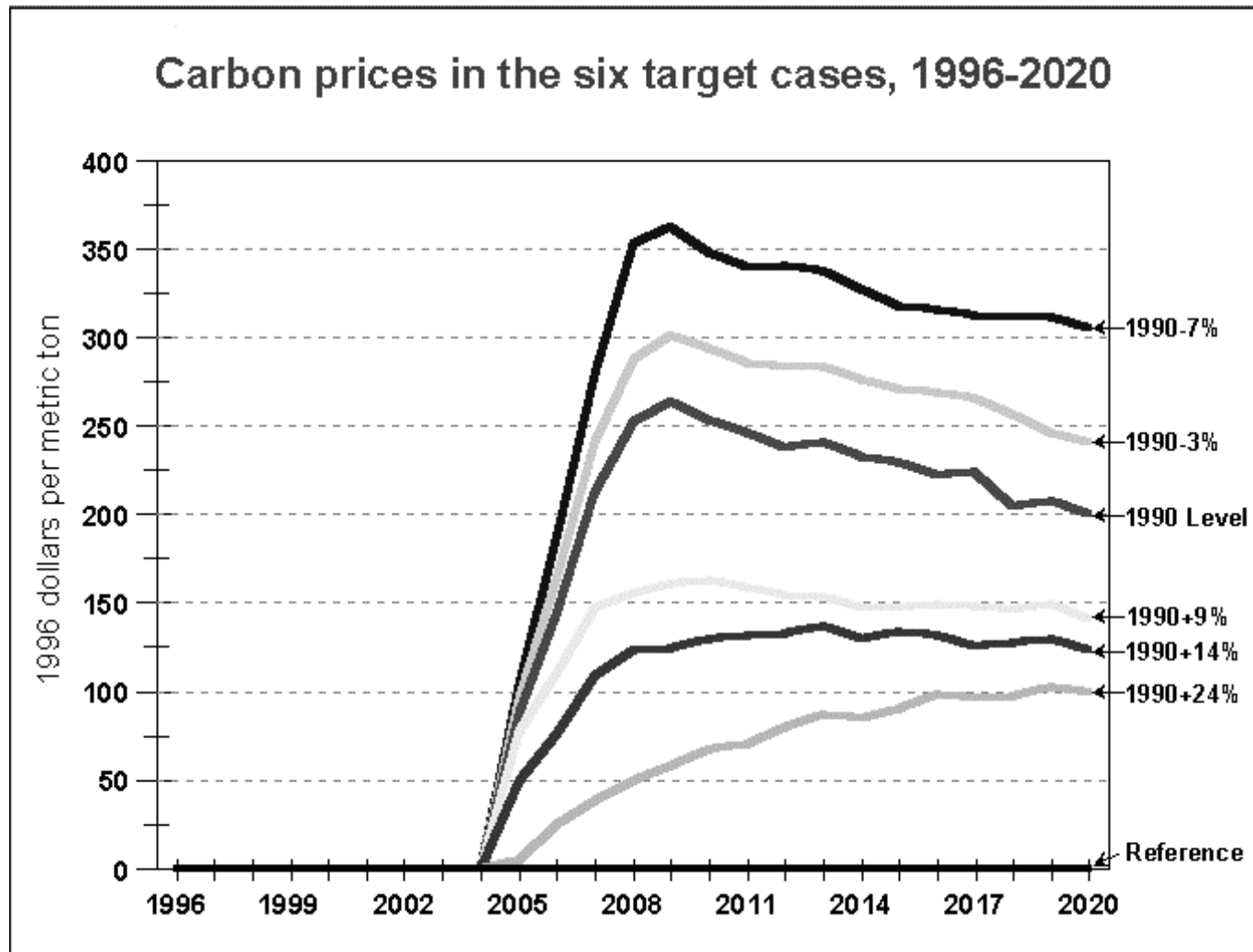
Flue gases from power plants contain O₂, H₂O, in addition to CO₂ and inert N₂ and other components.

Separation of CO₂ from flue gases is an expensive operation.

CO₂ separation accounts for 2/3 of the cost for carbon sequestration according to DOE.

Other issues concerning CO₂ separation

Prices for Reduction of CO₂ Emission in US



The carbon price required to reduce U.S. energy-related carbon emissions ranges from \$67 to \$348 per metric ton in 2010 (1996 dollars)

Source: Impacts of the Kyoto Protocol on U.S. Energy Markets and Economic Activity, EIA, US DOE, Oct 1998.

Idea for CO₂-Based Tri-generation of Chemicals, Fuels, and Electricity

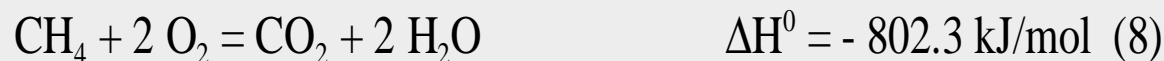
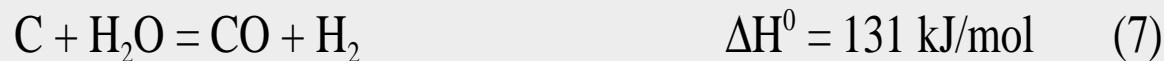
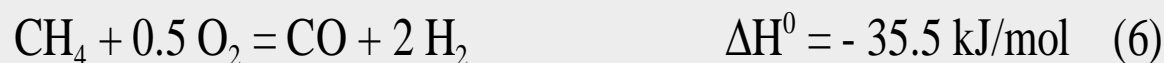
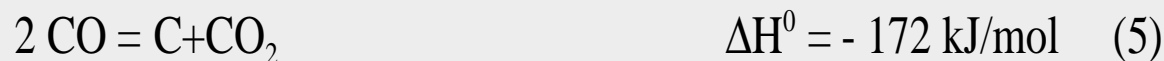
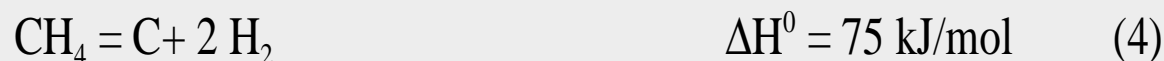
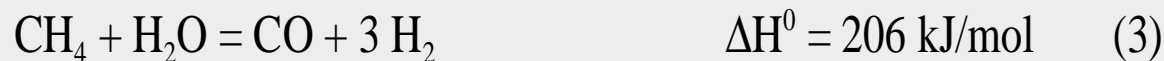
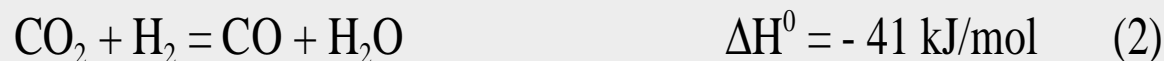
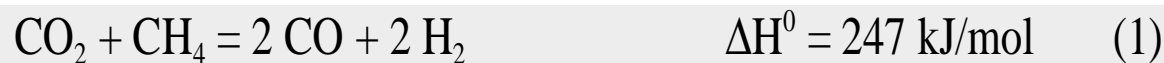
Can we design a chemical system where the expensive CO₂ pre-separation from flue gases is not necessary?

Can we use the CO₂ in flue gas along with H₂O and O₂ directly for producing industrial useful products?

Is it possible to use waste heat in power plants for CO₂ conversion?



Energetics of CO₂ Conv into Syngas



**W. Pan, C. Song. Calculations on energetics under various conditions,
to be published in 2001**

Conceptual Flow of Proposed Tri-Reforming Process Using CO₂ in Flue Gas

Flue Gases

Coal-Fired

12-14% CO₂

8-10% H₂O

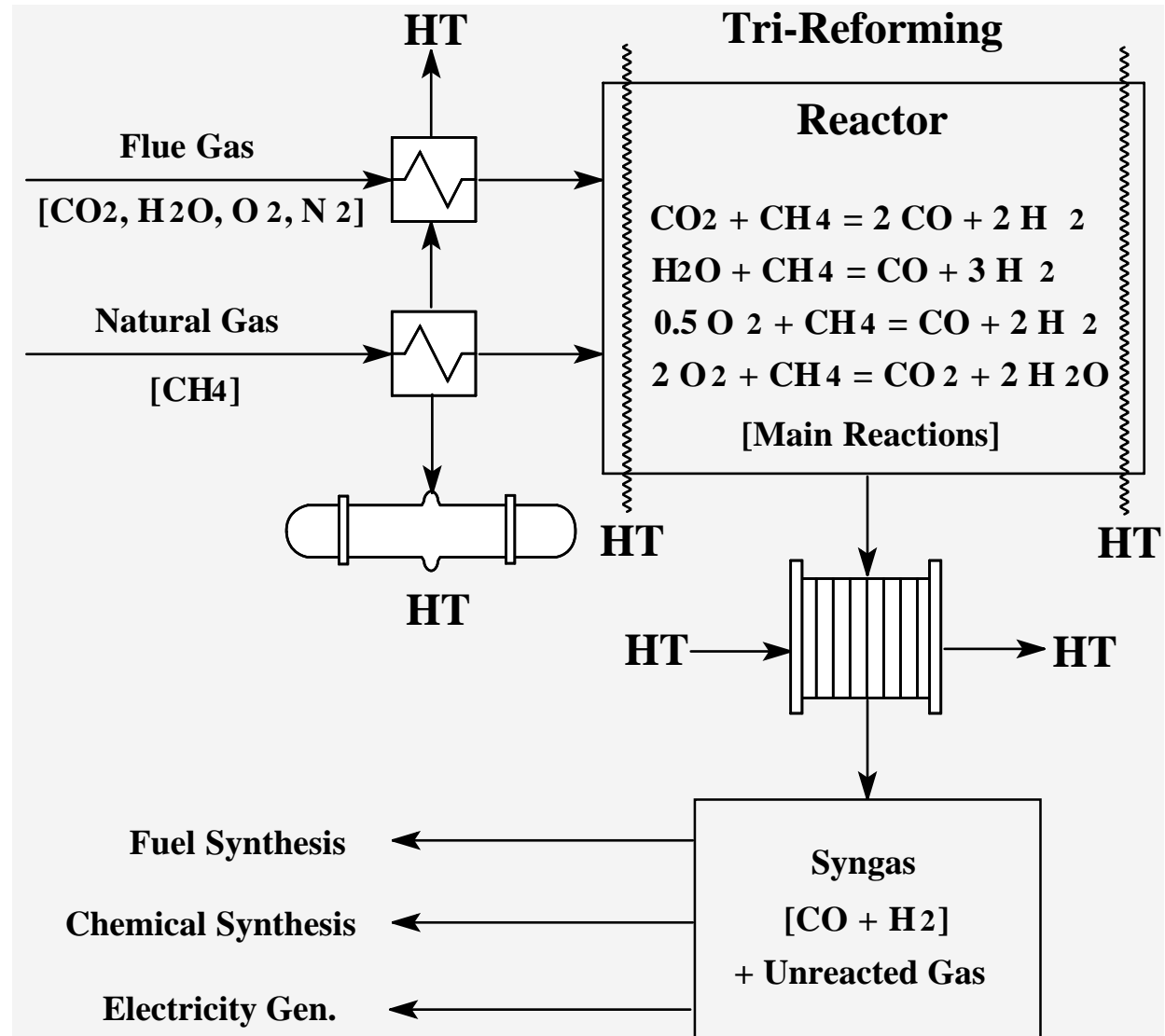
3-5% O₂

N.Gas-Fired

8-10% CO₂

18-20% H₂O

2-3% O₂

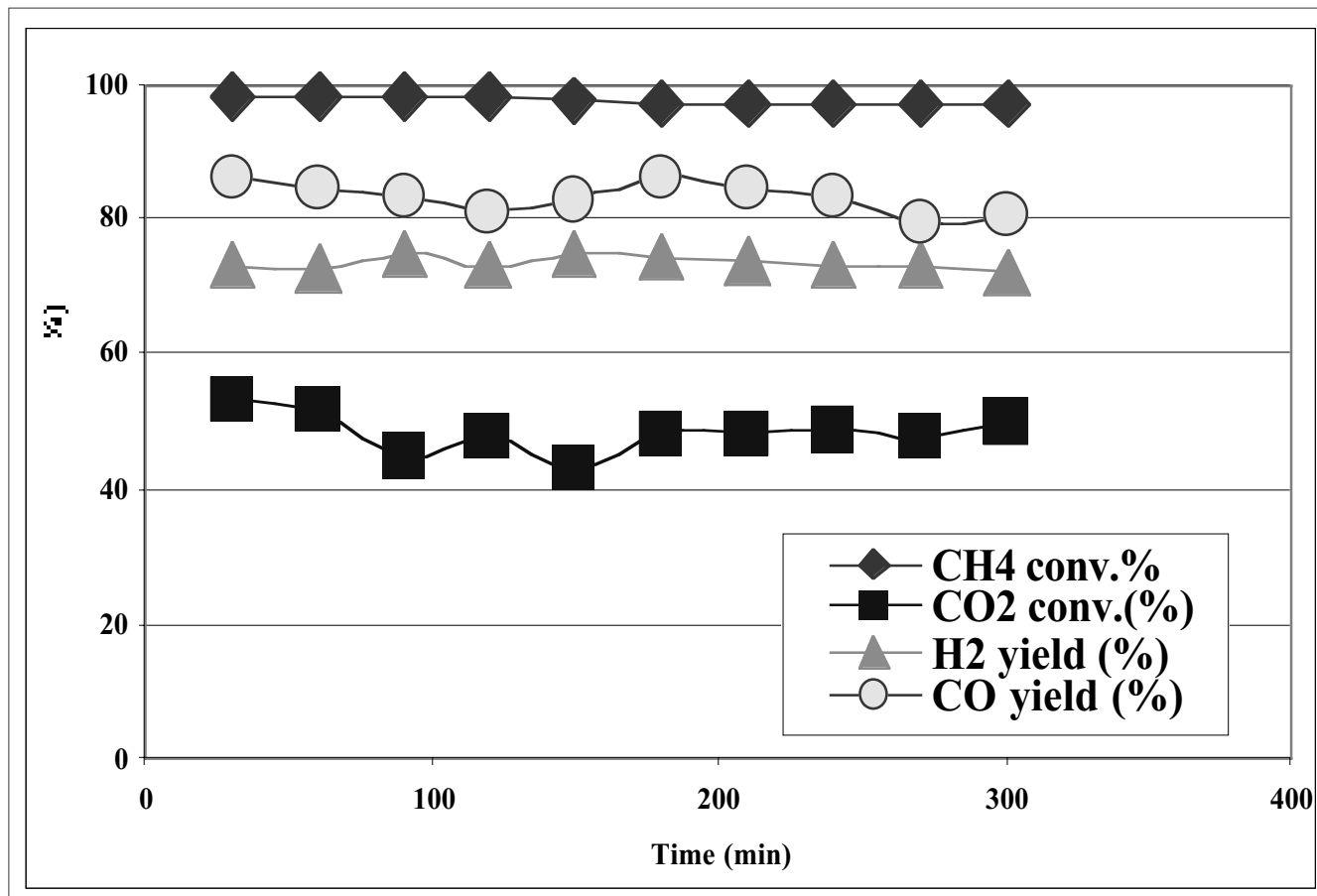


Tri-reforming Reactor System at PSU



Tri-reforming: Experimental Work

(Tri-reforming of CH_4 at 850 °C and 1 atm over Haldor-Topsoe R67 catalyst)



*Source: C. Song, Chemical Innovation, 2001, 31, 212-26.

Comparison of Catalysts Used after Tri-reforming and CO₂ Reforming

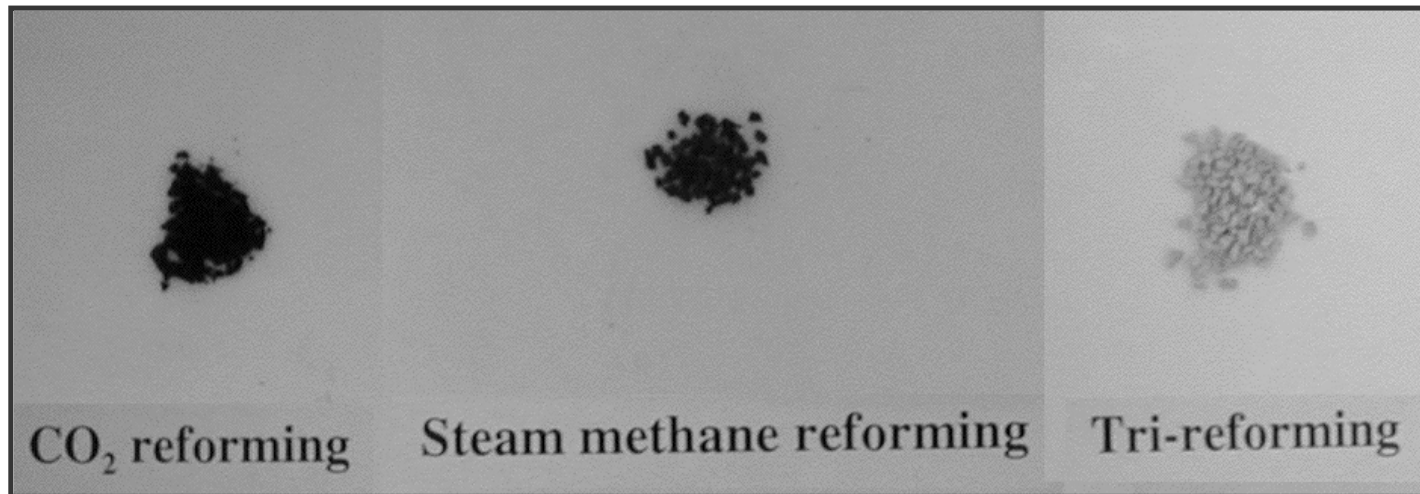


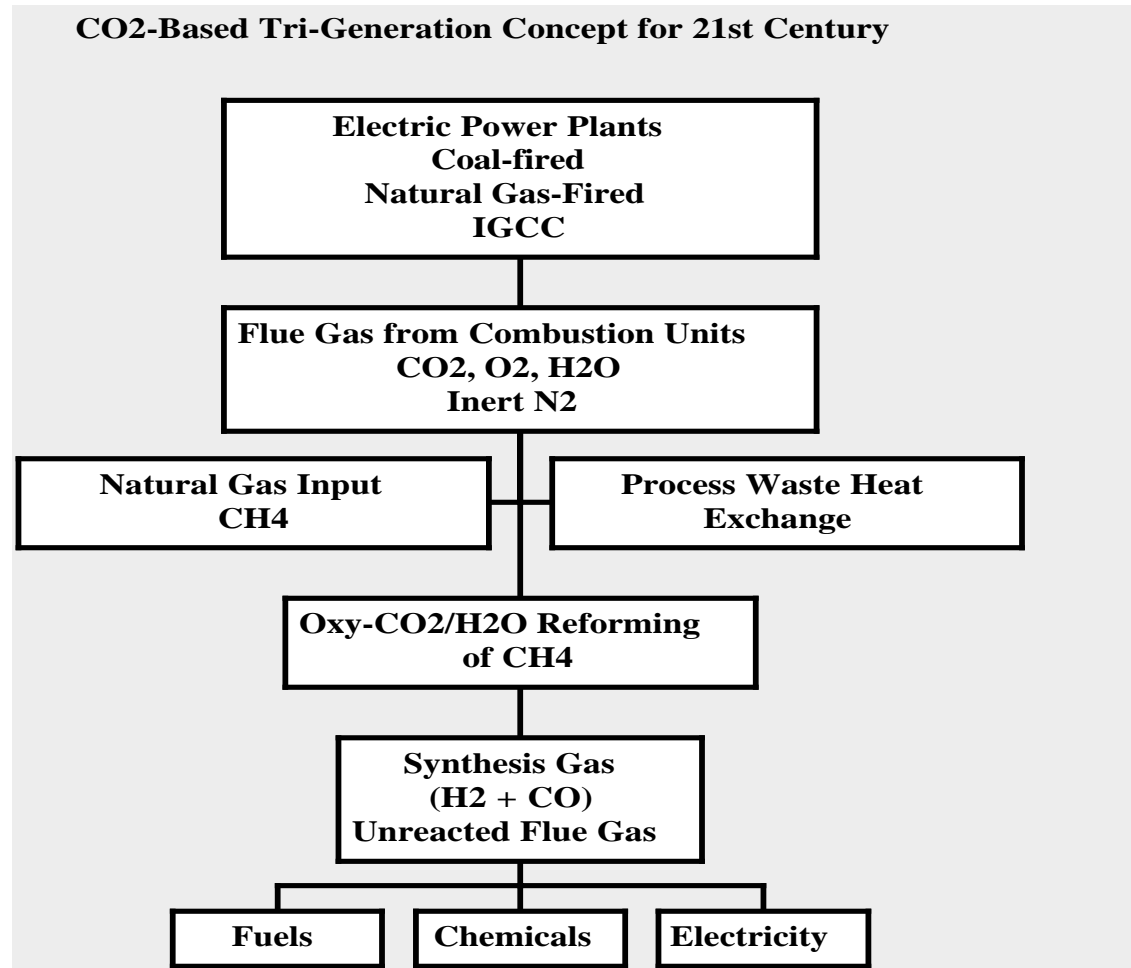
Photo of used Haldor-Topsoe R67 catalyst after CO₂ reforming, steam methane reforming and tri-reforming at 1 atm and 850 °C



Advantages of Proposed Tri-reforming

- ⌘ **Direct use of CO₂ in waste flue gases of power plants without CO₂ separation and purification.**
- ⌘ **Taking advantage of H₂O and O₂ impurities in flue gases, for more energy efficient reforming.**
- ⌘ **Produces synthesis gas with desired H₂/CO ratios (1 ~ 2) that are difficult to achieve by conventional SMR. [“Imported CO₂” is needed in industry].**
- ⌘ **Eliminate or largely reduce coke formation, common in dry reforming, by using O₂ and H₂O.**
- ⌘ **Proactive/advantageous use of greenhouse gas.**
- ⌘ **New process concept for large-scale syngas prod.**
- ⌘ **Challenges: catalyst, process, E, feed+prod, etc.**

Tri-reforming for CO₂-Based Tri-generation



C. Song. Proc. 16th Ann. Internat. Pittsburgh Coal Conf., Pittsburgh, PA

Oct 11-15, 1999, Paper No. 16-5.



Advantages of Proposed Tri-Generation

- u Start with synthesis gas from tri-reforming of natural gas using flue gas of power plants.**
- u Synthesis of chemicals such as alcohol, acetic acid, ether, olefins, and hydrogen, etc.**
- u Production of ultra-clean hydrocarbon fuels by Fischer-Tropsch method; production of oxygenated fuels such as alcohols and ethers.**
- u Additional generation of electricity, by using syngas, hydrogen, and waste heat, by gas turbine generator, fuel cells, and others.**
- u Challenges: paradigm shift; ind. boundaries; E aspects; processing aspects**



Critical Research Issues on Tri-reforming

Feasibility as a new process concept for syngas production

Catalyst formulation for enhanced CO₂ conversion in the presence of oxygen

Energy and low-temp heat management, and inert gas (N₂) management

System integration incorporating gas processing and utilization



Acknowledgments

AER, IEO, MER, EIA-WWW, Energy Information Administration, U.S. Department of Energy (DOE)

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Howard Herzog, Massachusetts Institute of Technology

Michelle Aresta, University of Bari, Italy

Robert Warzinski, National Energy Technology Lab, DOE