

Two-Step Methane Conversion to Alkynes and Dienes

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CeraMem Corporation

- **S-Corporation**

- + Founded in 1986
- + Original Focus: Develop and commercialize ceramic membrane products
- + Seed Financing: Primary through U.S. Government SBIR grants

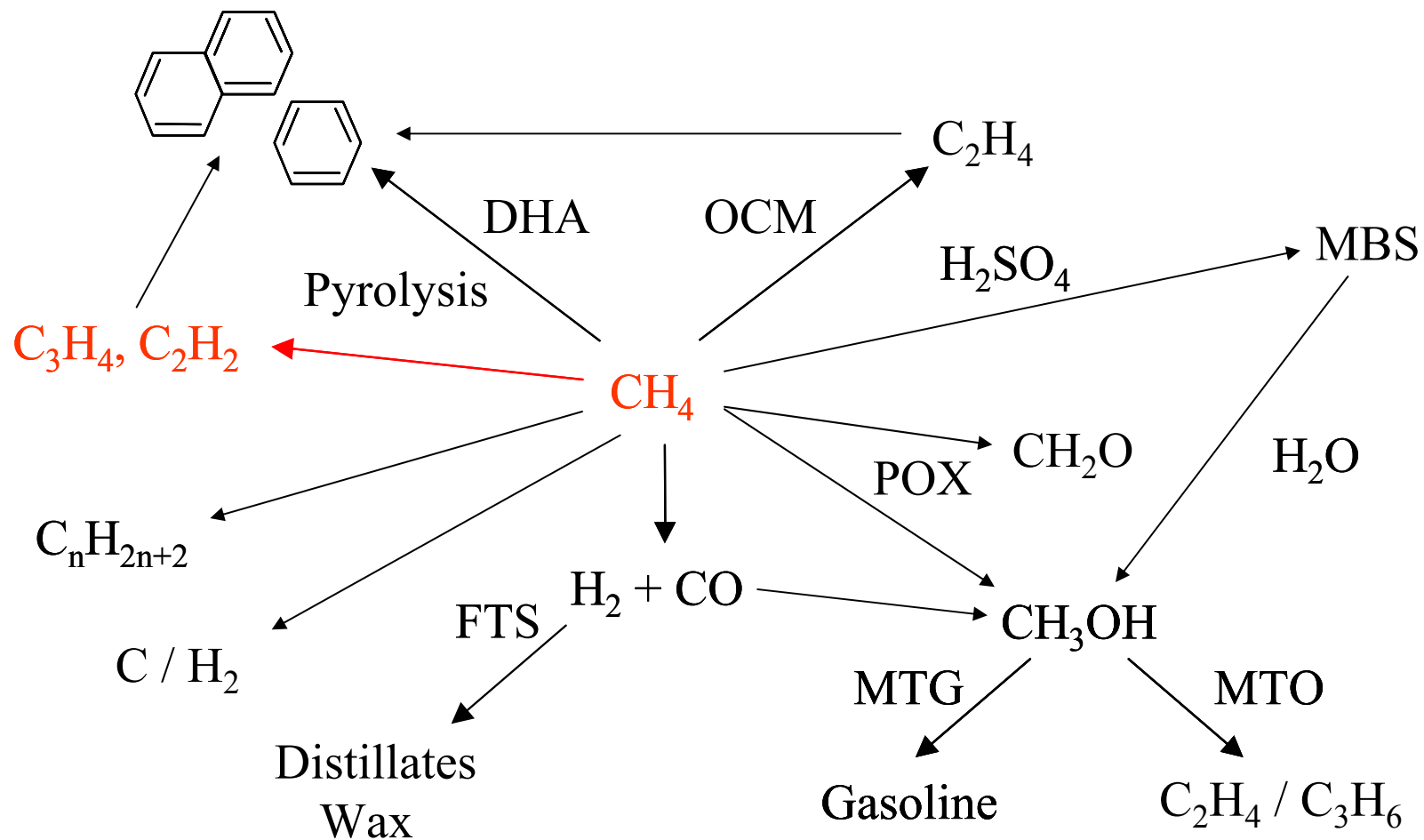
- **Current Technology Areas**

- + Ceramic and Metallic Membranes
 - > Microfiltration / Ultrafiltration / Nanofiltration / Pervaporation; and
 - > High-Temperature Gas Separation;
- + Heterogeneous Catalysis & Reaction Engineering;

- **Previous Joint Ventures:**

- + CeraMem Separations (with Exxon Chemical & Corning); and
- + CeraFilter Systems (with Ahlstrom Pyropower)

Motivation: Natural Gas Monetization via Selective Conversion



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Acetylene is Primarily Produced from Natural Gas and Calcium Carbide

Acetylene Consumption in 2000 = 404 Metric Tons *

Manufacturing Process	% of Capacity *
Natural Gas Partial Oxidation	57
Calcium Carbide Hydrolysis	25
Ethylene Co-Product (Cracking)	18

* Data refer only to the United States, Western Europe and Japan.
J.Lacson, U.Löchner and G.Toki, "CEH Product Review: Acetylene," 2001.

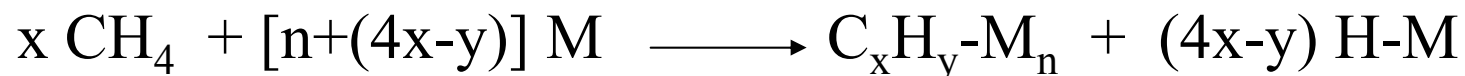
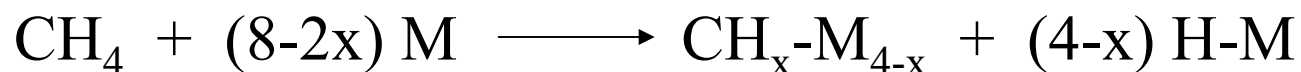
An Opportunity Exists to Develop More Efficient Technology

	CH ₄ Pyrolysis Technologies				
	CaC ₂	Arc	Partial Oxidation	HFPP	CeraMem
Temperature (K):	2,500-2,800	18,000	2,000	3,000	< 2,000
Electricity(Btu/lb_m C₂H₂):	31,000	18,750	540	19,600	60
Methane Req.(lb_m CH₄/lb_m C₂H₂):					
For Conversion to C ₂ H ₂	0.0	2.9	4.0	1.5	1.2
For Power Generation	<u>0.0</u>	<u>1.8</u>	<u>0.1</u>	<u>1.9</u>	<u>0.6</u>
Total:	0.0	4.7	4.1	3.4	1.8
Per Pass CH ₄ Conv. (%):	---	82	91	39	≥ 80
Selectivity to C ₂ H ₂ (%):	≥ 99.6%	52	79	83	≥ 99.6%
Effluent C₂H₂ Conc. (%):	---	15	8	15	72
CO Emissions (lb_m/lb_m C₂H₂)	1.1	0.0	1.6	0.0	0.0
Waste (lb_m/lb_m C₂H₂)	1.9	0.0	0.0	0.0	0.002

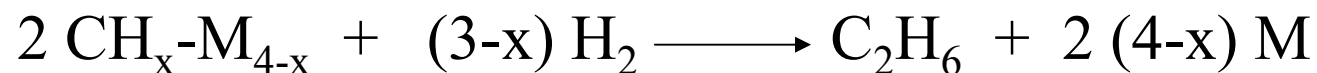
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Two-Step Methane Homologation is Not Economically Viable

Step 1. Dissociative CH₄ Adsorption

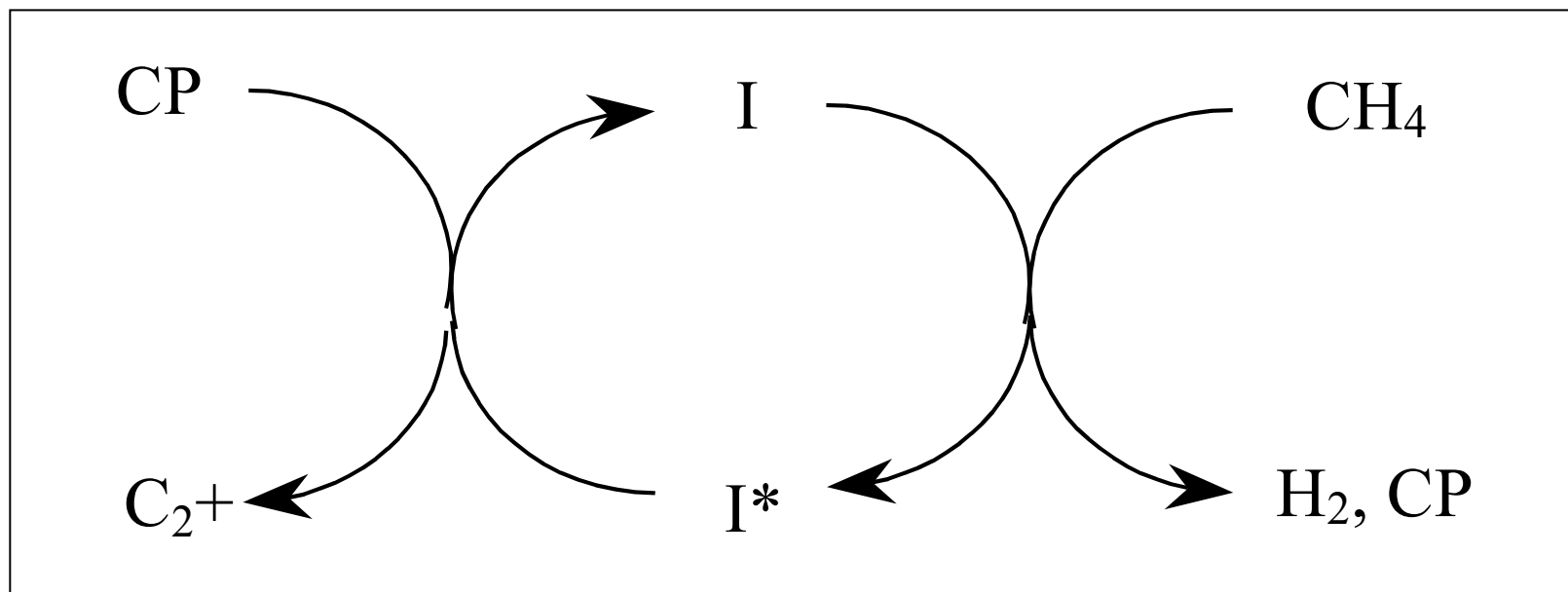


Step 2. Hydrogenation & Recombinative Desorption



NSF SBIR Grant # DMI-9861211; *Catal.Lett.*, **66** (2000) 113; *J.Catal.*, **189** (2000) 238.

CeraMem's New Technical Approach Selectively Yields Alkynes or Dienes



I/I* = Intermediates
CP = Co-Product
C₂+ = Alkyne or Alkene Product

Natural Gas Conversion: Pyrolysis

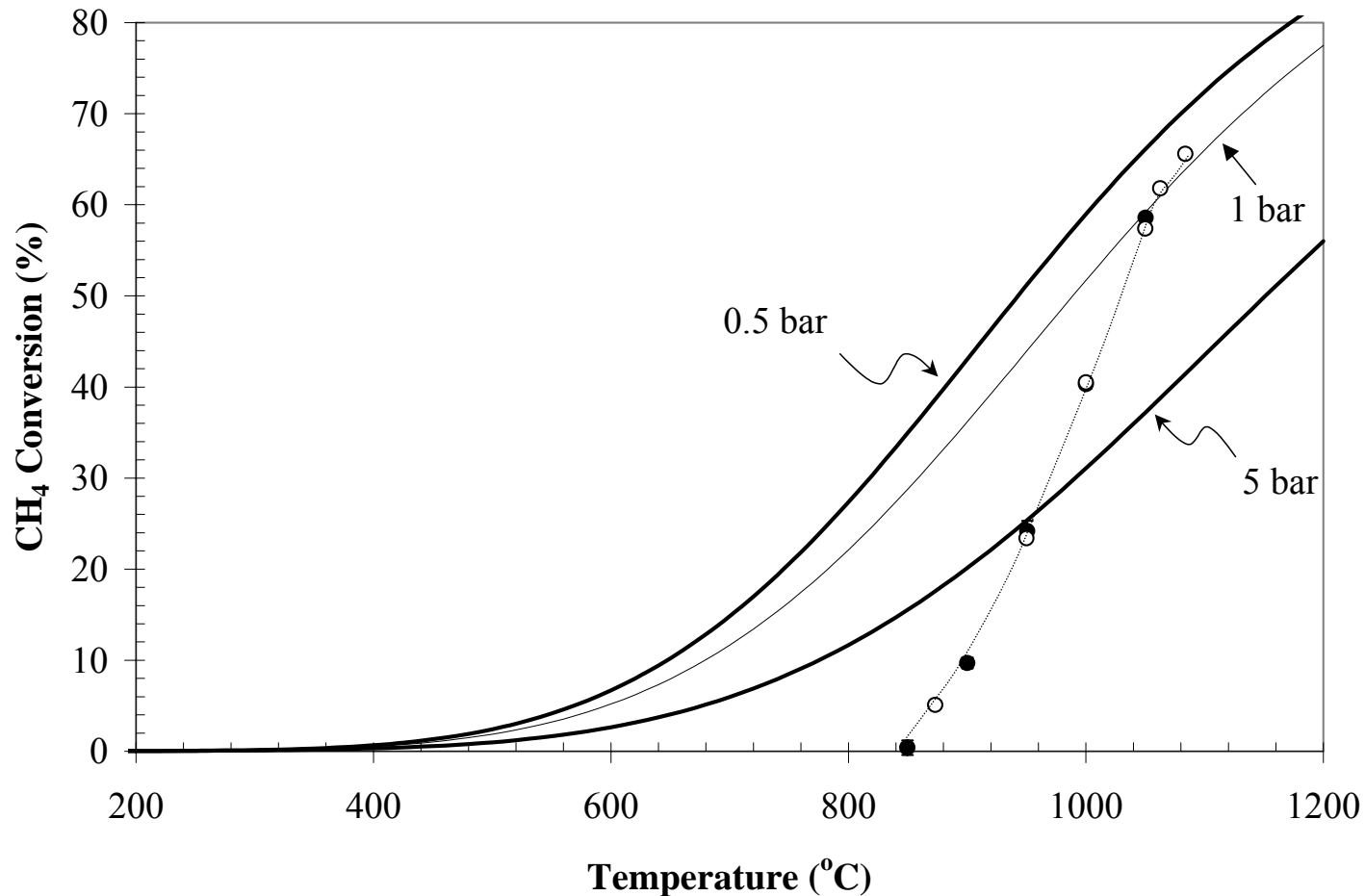


Figure 8. CH₄ conversion to C₂H₂, C₂H₄, C₂H₆, C₆H₆, and H₂ at thermodynamic equilibrium as a function of temperature and pressure (solid curves without symbols are calculated values). Experimental data (○,●) were obtained by CeraMem from two independent experiments using a CH₄ pressure of 0.5 bar and a contact time of 60 seconds. Source: Report DOE/ER-83161-3.

I/I* Materials

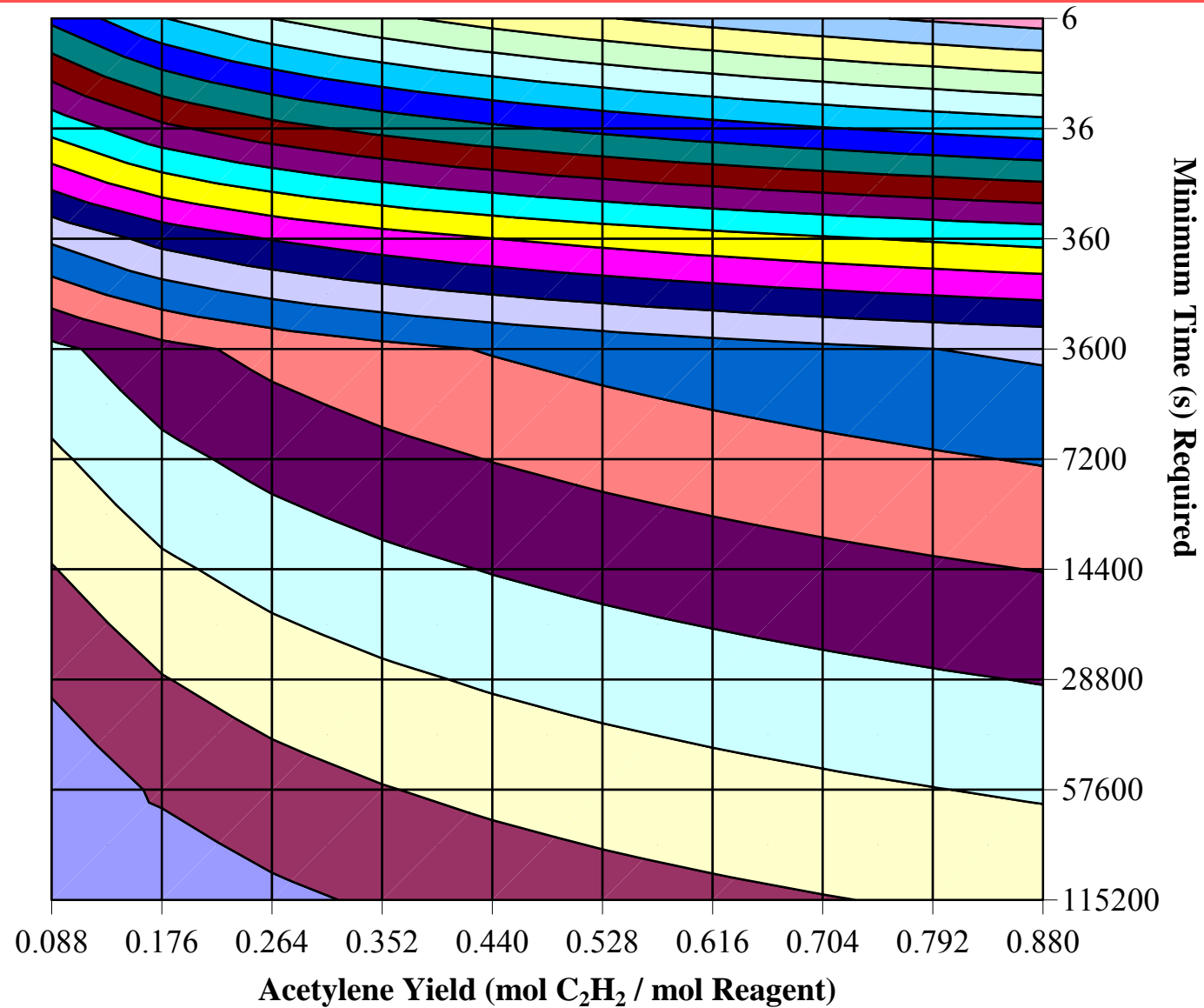
Catalyze Natural Gas Conversion

Cycle #	Conversion (%)				
	CH ₄	C ₂ H ₆	C ₃ H ₈	C ₄ H ₁₀	CO ₂
1	76	98	100	100	100
2	69	100	100	100	100
3	69	100	100	100	100

Reaction Conditions: T = 830°C; P = 1.1 atm; τ = 8 sec
(94.9% CH₄; 2.4% C₂H₆; 0.2% C₃H₈; 0.1% C₄H₁₀; 1.6% N₂; 0.7% CO₂)

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Model Developed to Predict Acetylene Yield



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C₂H_x Yield High Relative to Two-Step CH₄ Homologation

Table 1. Observed acetylene production for CeraMem's most advanced intermediate (I/I*) developed in the Phase II program compared with (a) that developed in the Phase I program, and (b) ethylene production observed during two-step methane conversion over Ru/Al₂O₃.^c

Intermediate (I/I*)	Experimental Results ^a		C ₂ H ₂ Yield / Cycle (mol C ₂ H ₂ /mol I/I*)
	μmol C as C ₂ H _x /g/I/I*	S (%) ^b	
Ru/Al ₂ O ₃ ^c	2.2 ^c	48 ^c	0.0001 ^c
CeraMem "Phase I"	493 ± 88	99.8 ± 0.1	0.01
CeraMem "Phase II"	10,090 ± 338	99.4 ± 0.3	0.43

^a Reported uncertainties are non-biased standard deviations ($\pm 1\sigma_{n-1}$) and are based on two or more experimental measurements.

^b Selectivity within the hydrocarbon fraction is reported on a carbon atom basis.

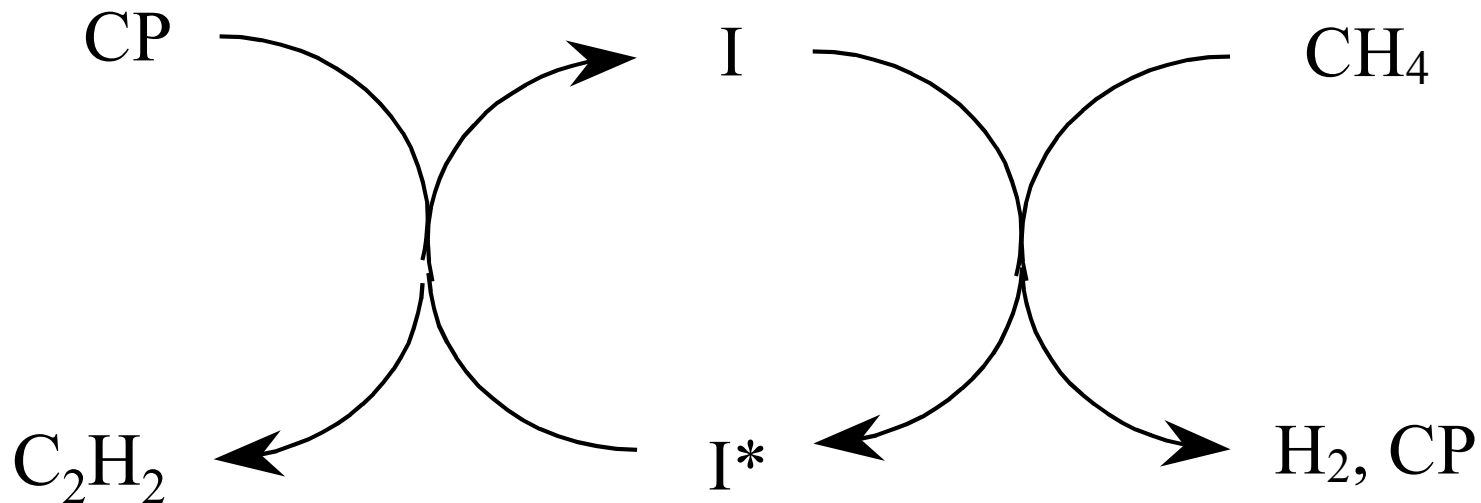
^c Data refer to the production of ethylene using Ru/Al₂O₃ via two-step CH₄ conversion (L.Guczi, G.Stefler, Zs.Koppány, L.Borkó, S.Niwa and F.Mizukami, *Appl.Catal.A:General*, **161** (1997) L29).

High Acetylene Yield Decreases with Each Process Cycle

Cycle #	Yield (mole C ₂ H ₂ / mole I/I*)		
	T1	T2	T3
1	0.22	0.35	0.43
2	0.21	0.31	0.26
3	0.13	0.09	0.005

Summary

CeraMem has developed an indirect, cyclic process for the selective conversion of natural gas to acetylene, mediated by a series of novel materials (I/I*), that is potentially more efficient than existing technology options.



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