Methane Conversion to Olefins, Higher Hydrocarbons and Oxygenates in Low Temperature Non-Equilibrium Plasmas

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Abstract

The goal of this project is the development of novel, economical, processes for the conversion of natural gas to more valuable projects such as methanol, ethylene and other organic oxygenates or higher hydrocarbons. The methodologies of the project are to investigate and develop low temperature electric discharges and electric field-enhanced catalysis for carrying out these conversions. In the case of low temperature discharges, the conversion is carried out at ambient temperature which in effect trades high temperature thermal energy for electric energy as the driving force for conversion. The low operating temperatures relax the thermodynamic constraints on the product distribution found at high temperature and also removes the requirements of large thermal masses required for current technologies. With the electric field-enhanced conversion, the operating temperatures are expected to be below those currently required for such processes as oxidative coupling, thereby allowing for a higher degree of catalytic selectivity while maintaining high activity.

Results indicate both dielectric (barrier) and non-dielectric discharges can be advantages with different product selectivities. Catalytic materials of the mixed metal oxide and zeolitic classes have also been found to be effective. Current work is related to catalyst screening, understanding power utilization and its relationship to reactor configuration, oxygen utilization, hydrocarbon chain building and in-situ condensable product removal.

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Natural Gas Conversion to Higher Value Chemicals at Low Temperatures

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Contract DE-FG21-94MC31170

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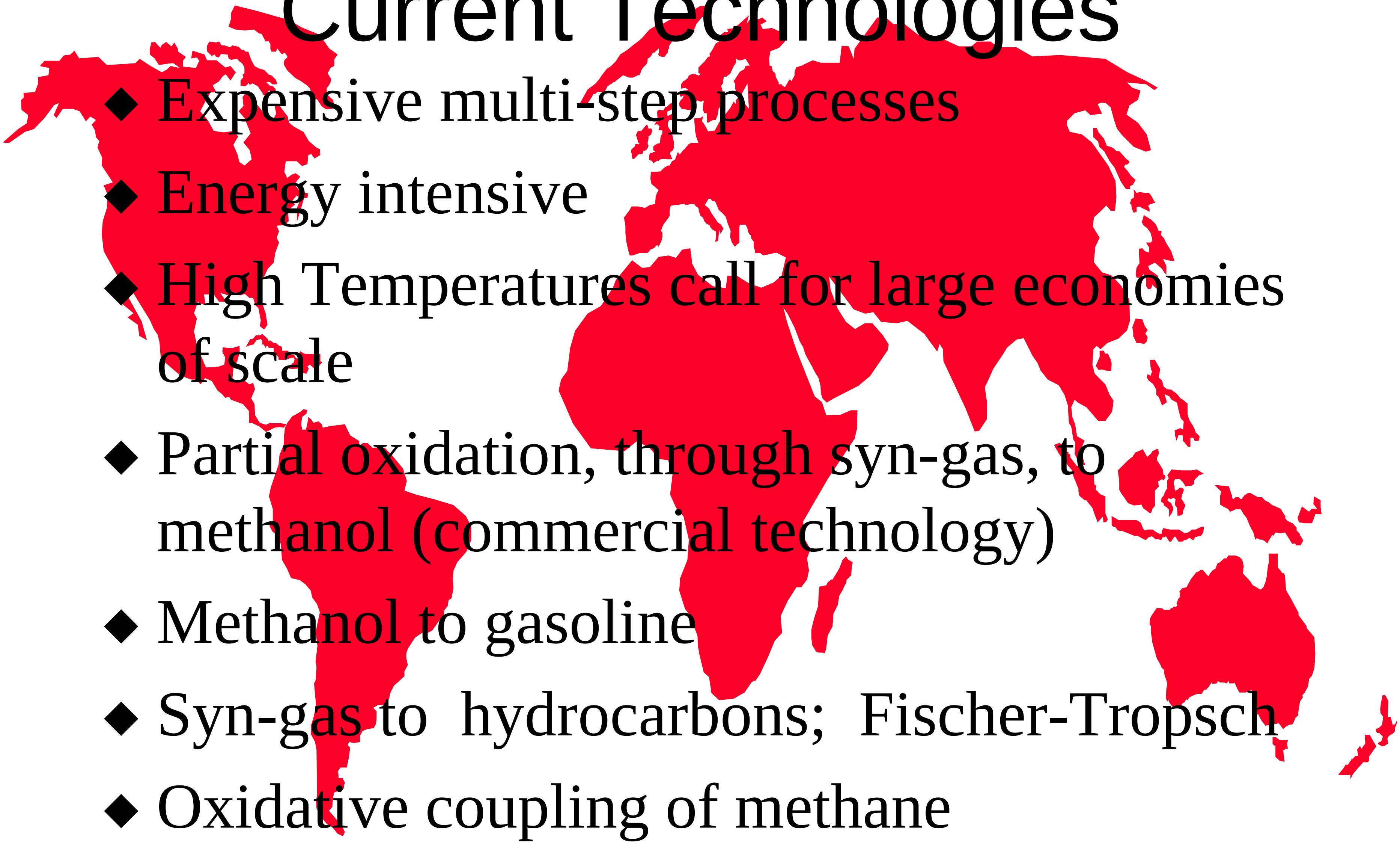
Current Technologies



- Expensive multi-step processes
- Energy intensive
- High Temperatures call for large economies of scale
- Partial oxidation, through syn-gas, to methanol (commercial technology)
- Methanol to gasoline
- Syn-gas to hydrocarbons; Fischer-Tropsch
- Oxidative coupling of methane

Desirable Alternatives

- One-step partial oxidation
- One step to higher hydrocarbons
- Lower energy requirements
- Small economies of scale for remote or small resources: liquids production

Low Temperature Plasma Reactors

- Ambient to a few hundred degrees C
- Atmospheric pressure, so far
- AC or DC currents feasible
- With or without catalysts
- Oxygen activation, when present
- Favorable thermodynamics
- Small scale feasibility

Tubular Reactor Configuration

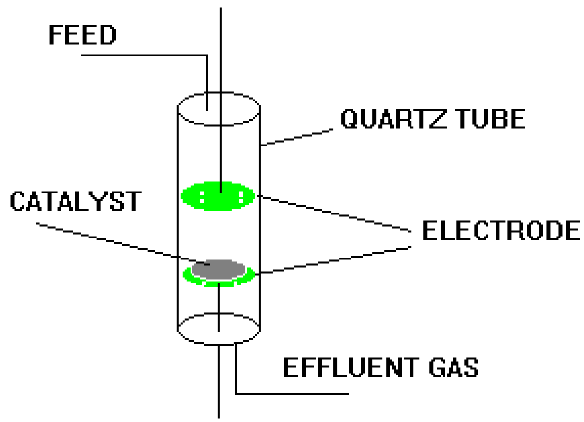


FIGURE 4 CLOSEUP REACTOR

Laboratory Results
No Catalyst, No Dieletric

- Ambient feed temperature, methane + oxygen feed, ~5kV AC
  – Methane conversion, 40 percent
  – C2 selectivity, 47 percent
  – C2 yield 18 percent
  – C_2H_4/C_2H_6 ~.0.5-2, depends on temperature
  – CO/CO_2 10:1or better

Laboratory Results
Na-Y Zeolite, No Dielectric

- 100 ºC, methane + oxygen, ~ +5kV DC
  - 18 percent methane conversion
  - 40 percent C2 selectivity
  - 11 percent yield
  - high CO/CO_2 ~ 40:1
  - ethylene/ethane ~20:1
- Other catalysts examined

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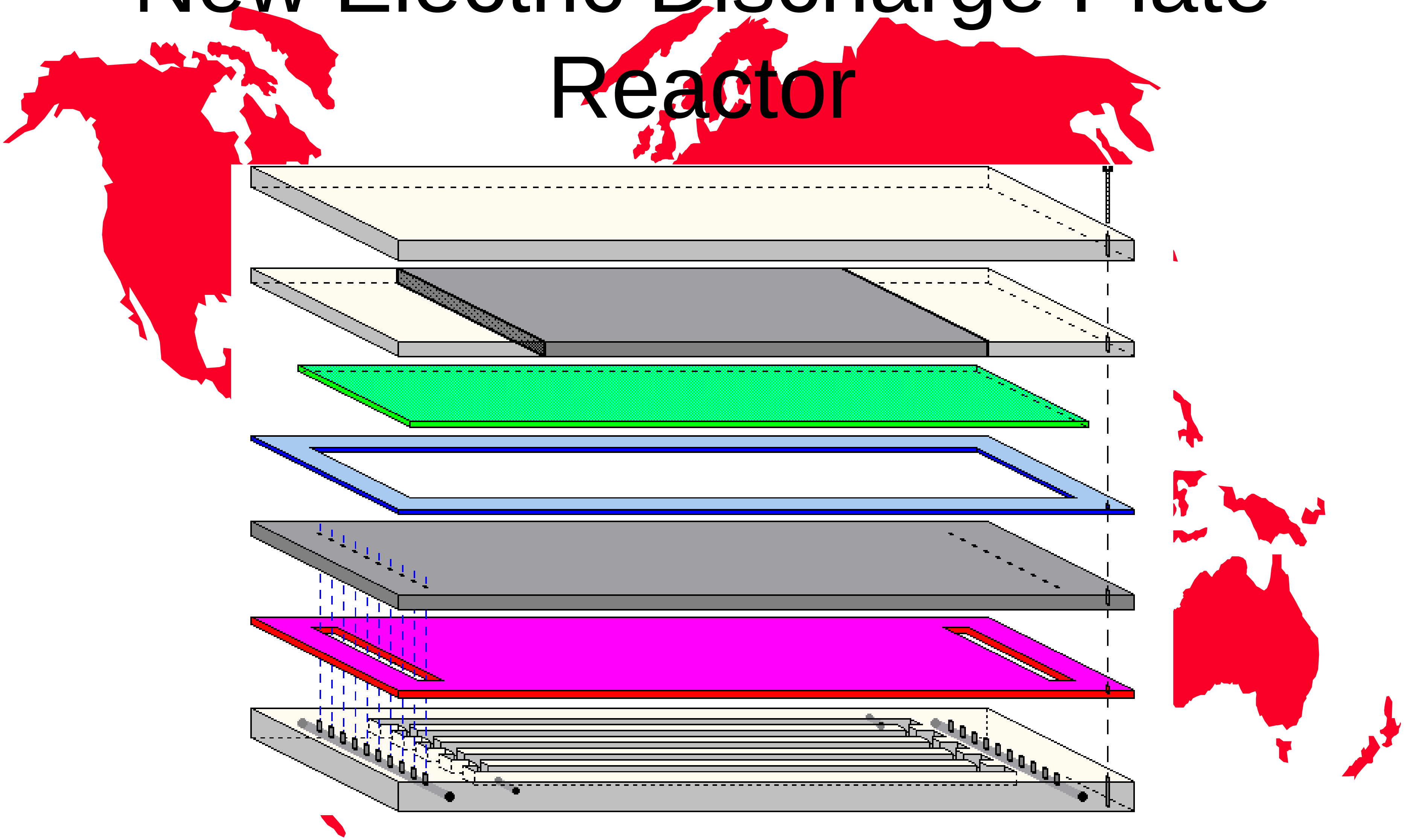
New Electric Discharge Plate Reactor



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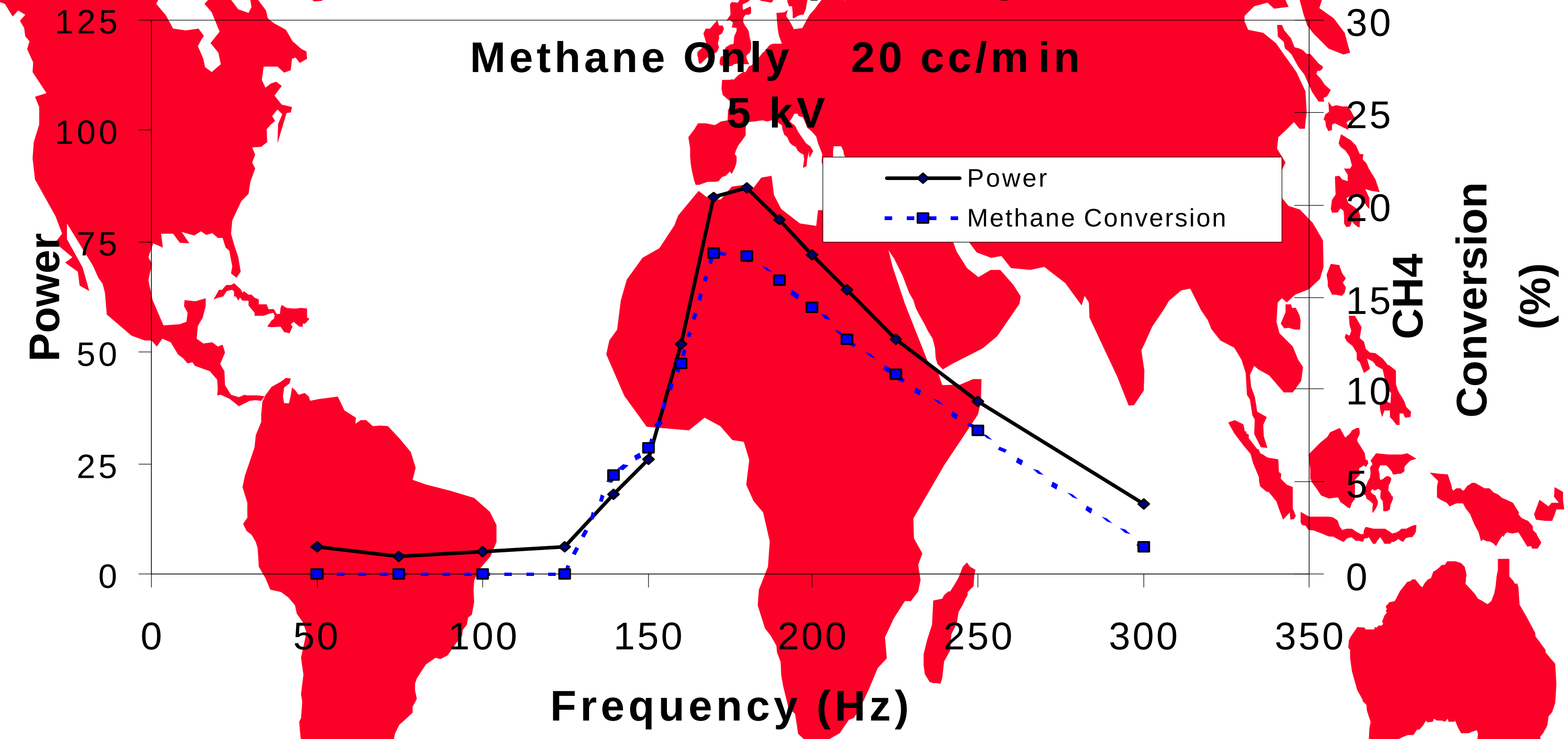
Laboratory Results with Glass Dielectric

- Ambient temperature, 10-18 kV AC, low conversion range so far (less than 25 % to minimize condensation in the reactor)
  - Selectivity to methanol+methyl formate+formic acid 55-60 percent (ca. 50 % aqueous solution)
  - CO/CO_2 2-3:1
  - CO_2 inhibition observed
  - Higher severity may not reduce selectivity

Laboratory Results with Glass Dielectric

- 5-10kV, No Oxygen
- 55 % conversion to Higher Hydrocarbons
- C2, C3, C4
- third body enhancement of rates
- long residence times, presently
- studying reaction/reactor variable effect on power

Power and Methane Conversion vs. Frequency



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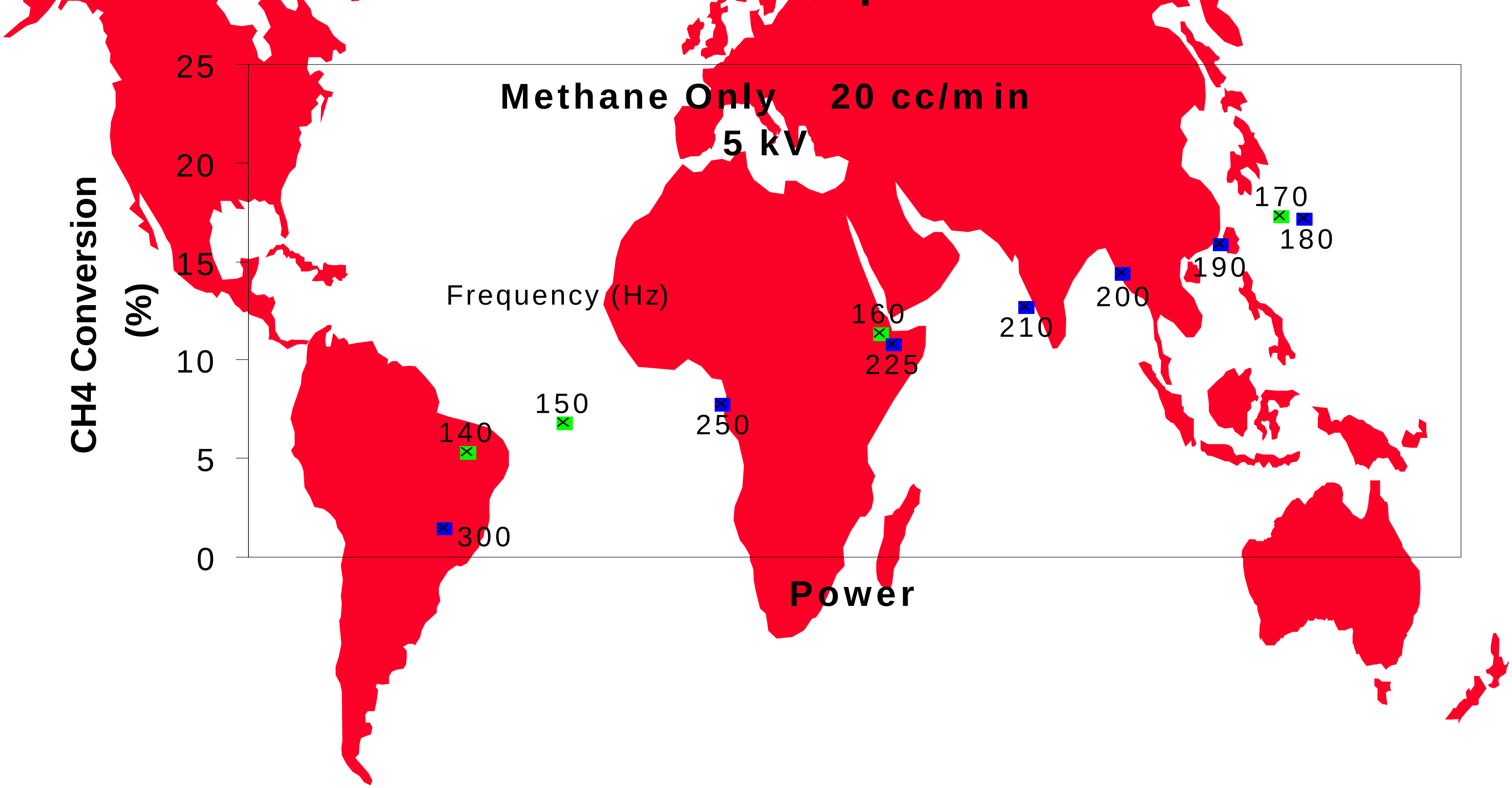
Methane Conversion vs. Power
at Various Frequencies



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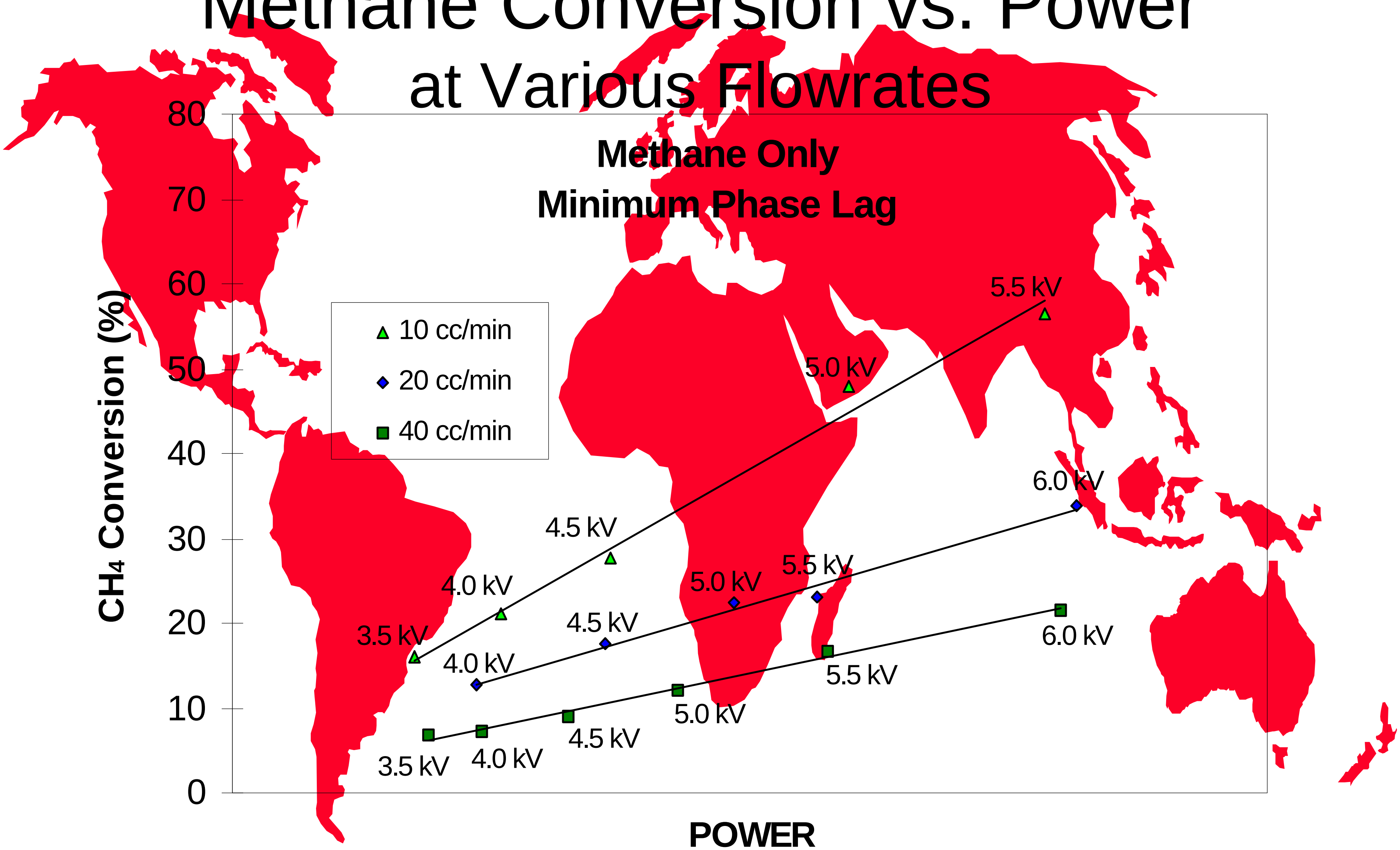
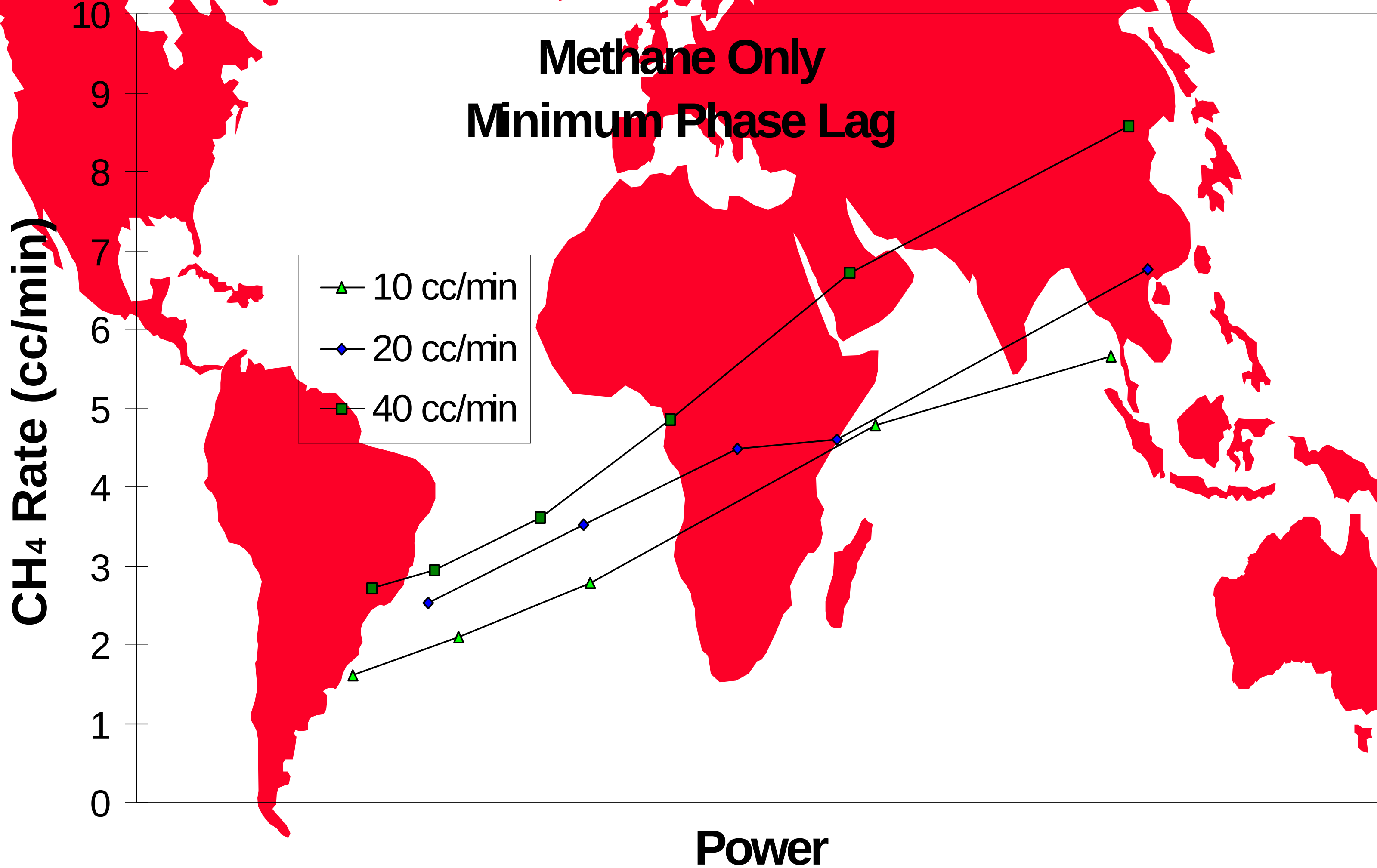
Methane Conversion vs. Power at Various Flowrates



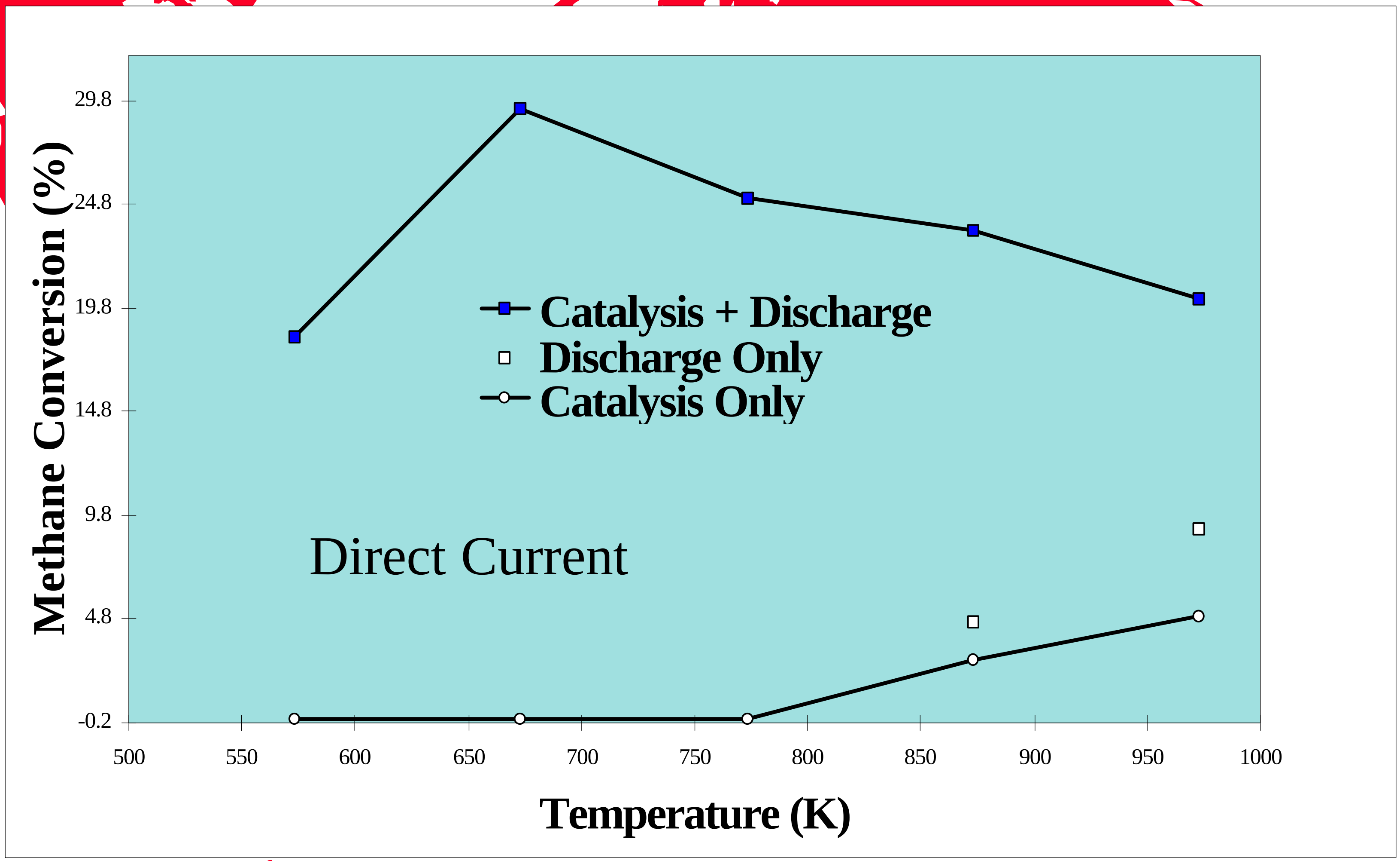
Methane Rate vs. Power
at Various Flowrates



Continuing Research

- Continuing to improve laboratory results
- Power utilization
- Expanding to examine reforming with CO_2
- Use of Air
- Higher pressures

PPC/CEP over CaO/NaOH



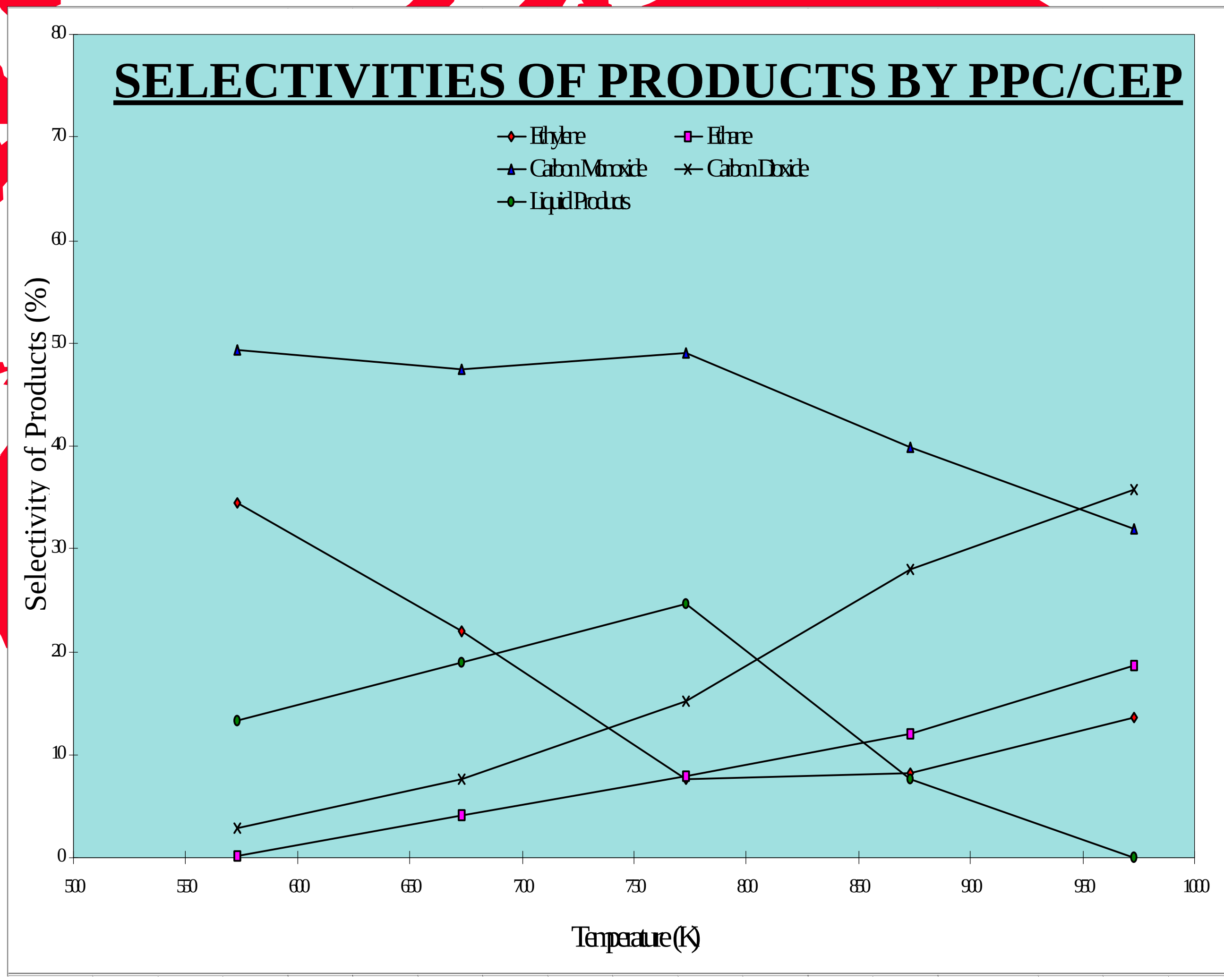
THE EXPERIMENTAL RESULTS ON CaO/NaOH

100 cm^3/min

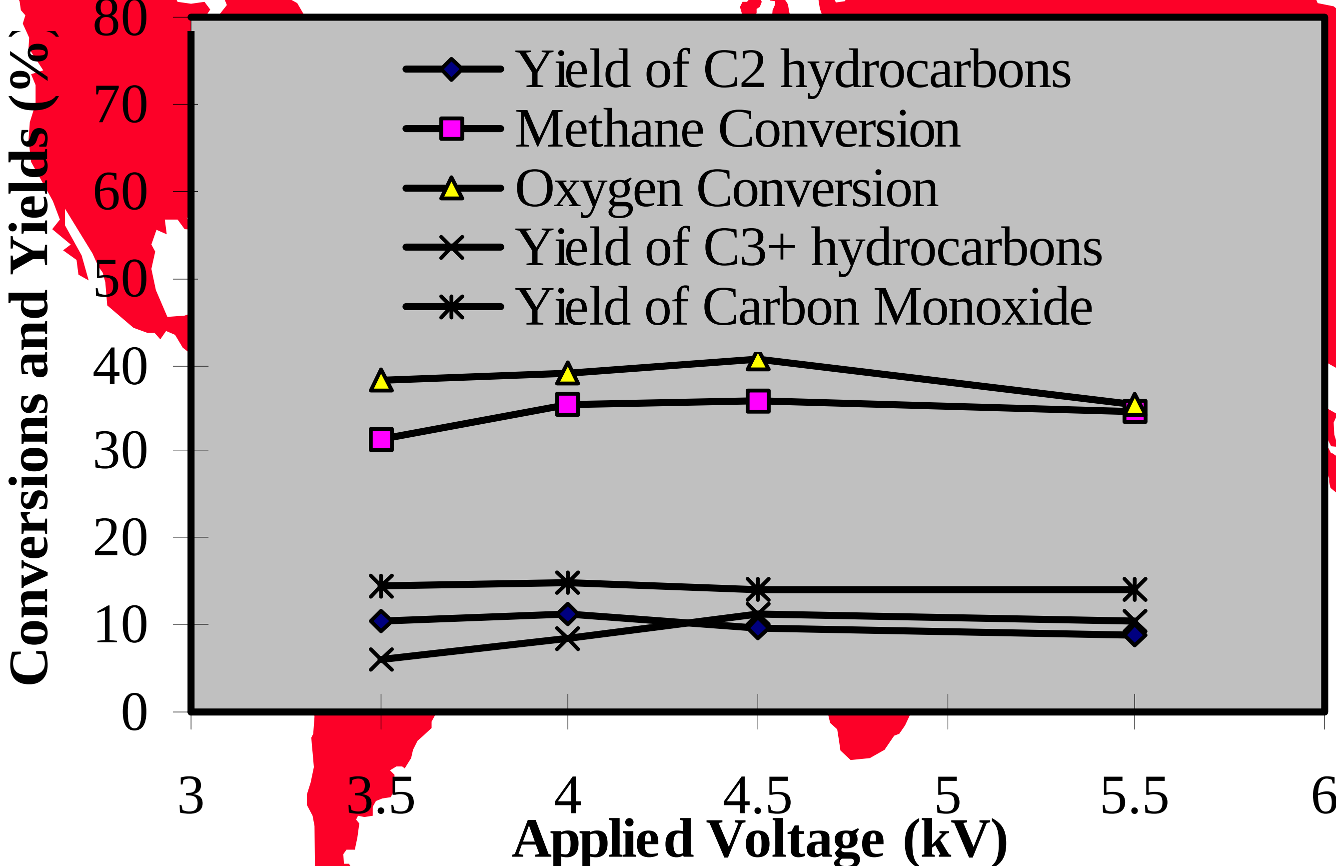
CH_4 /O_2 : 4/1

remote corona

catalyst weight: 0.1 g



Experimental Results on PPC/CEP over NaOH Treated Y Zeolite



50 cm^3/min

4/1 of CH_4/O_2

473 K

0.1 g catalyst

remote corona

Direct Current

Sample CO Run

- Voltage = 8.5 kV
- Frequency = 100 hz
- Total Feed Flowrate = 200 cc/min
- Methane/Oxygen =3:1
- CH_4 flowrate = 120 cc/min
- O_2 Flowrate = 40 cc/min
- CO Flowrate = 40 cc/min

CO Experimental Results

CO Flowrate (cc/min)	Mole % CH_4 Conversion	Mole % CO Conversion	Mole % O_2 Conversion	% CO Selectivity	% CO_2 Selectivity
0	20.2	0.0	67.0	15.3	12.2
10	17.0	0.0	63.09	6.6	20.5
20	18.6	4.7	65.7	0	23.8
40	19.8	8.1	78.1	0	31.2
60	17.9	7.4	74.0	0	36.9

CO Experimental Results

CO Flowrate (cc/min)	% Methanol Select.	% Methyl Formate Select.	% Formic Acid Select.	% Formalde-hyde Selectivity	Org. Liq. Sum	% Ethane Selcct.
0	15.0	10.3	15.8	11.5	52.6	3.7
10	17.3	14.7	12.9	12.0	56.9	4.9
20	17.0	12.2	13.5	11.6	54.3	5.2
40	15.5	11.5	12.5	9.6	49.1	6.9
60	12.1	12.4	3.7	5.8	34.0	8.0

CO_2 EXPERIMENTS

CH_4/O_2 = 3:1, Total Feed Flowrate = 200 cc/min

CO_2 Flowrate (cc/min)	Freq. (hz)	Voltage (kV)	% CH_4 Conver-sion	% CO_2 Conver-sion	% Oxygen Conver-sion	% Select. CO	% Select. CO_2
0	100	8.5	20.2	0.0	67.0	15.2	12.1
0	200	16.0	13.6	0.0	48.1	18.2	15.3
10	100	8.5	14.9	0.0	53.4	22.8	13.6
20	200	16.0	14.6	0.0	49.7	26.7	6.8
40	200	16.0	19.4	1.54	65.9	36.9	0
40	100	9.75	24.2	.03	82.3	37.3	0
60	100	8.5	22.2	3.3	70.6	42.2	0

CO_2 Experimental Results

CH_4/O_2 = 3:1, Total Feed Flowrate = 200 cc/min

Flowrate (cc/min)	Freq. (hz)	Voltage (kV)	% Select. Methan-ol	% Select. Methyl Formate	% Select. Formic Acid	% Select. Formal-dehyde	Or. Liq. Sum	% Et. Selec
0	100	8.5	15.0	10.0	15.8	11.5	52.3	3.7
0	200	16.0	13.3	8.8	16.0	11.9	50.9	4.7
10	100	8.5	14.3	9.4	10.0	11.8	45.5	4.5
20	200	16.0	14.4	11.0	18.6	11.7	55.7	4.3
40	200	16.0	11.0	19.1	19.6	11.5	61.2	4.8
40	100	9.75	11.1	15.5	18.7	11.8	57.1	4.6
60	100	8.5	11.1	7.6	7.3	8.4	34.4	3.5

O_2 Absent Experimental Results

Total feed Flowrate = 200 cc/min, Voltage = 16 kV, Freq. = 200 hz

Flowrate (cc/min)	He, CO, and/or CO_2 Flowrate (cc/min)	% Methane Conver-sion	% CO Selectivity	% CO_2 Selectivity	% Ethane Selectivity
200	0	3.3	0.0	0.0	48.7
150	50 He	3.5	0.0	0.0	56.6
150	50 CO_2	3.4	44.6	0.0	37.4
150	50 CO	3.4	0.0	1.3	82.2
120	40 CO 40 CO_2	16.7	56.7	0.0	23.2

Essentially No Organic Liquids

O_2 Absent Experimental Results

Total feed Flowrate = 200 cc/min, Voltage = 16 kV, Freq. = 200 hz

Flowrate (cc/min)	He, CO, and/or CO_2 Flowrate (cc/min)	% Methane Conver-sion	% CO Conver-sion	% CO_2 Conver-sion	% Ethane Conver-sion
200	0	3.3	0	0	0
150	50 He	3.5	0	0	0
150	50 CO_2	3.4	0	1.2	0
150	50 CO	3.4	.1	0	0
120	40 CO 40 CO_2	16.7	0	3.0	0

Essentially No Organic Liquids

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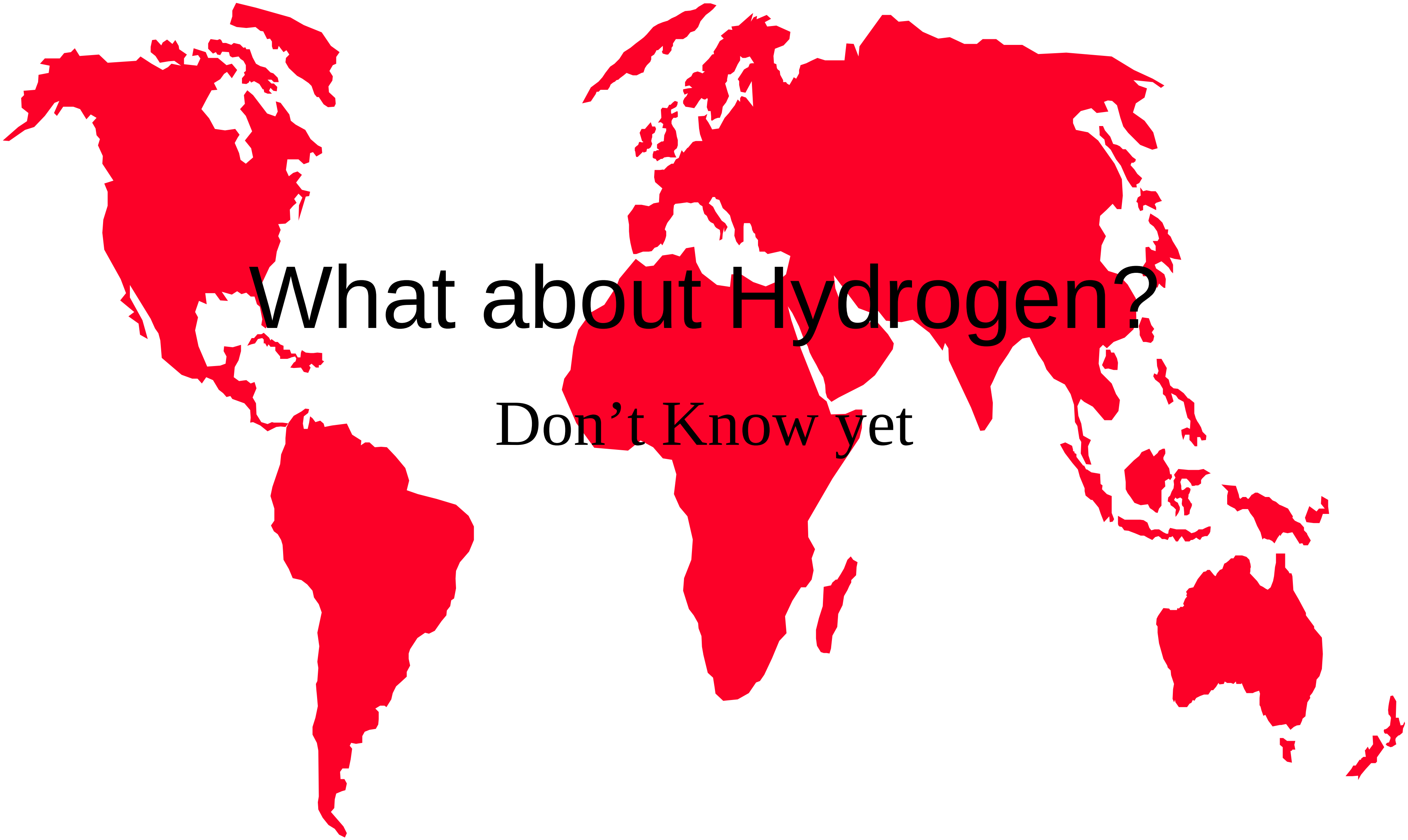

What about Hydrogen?

Don’t Know yet

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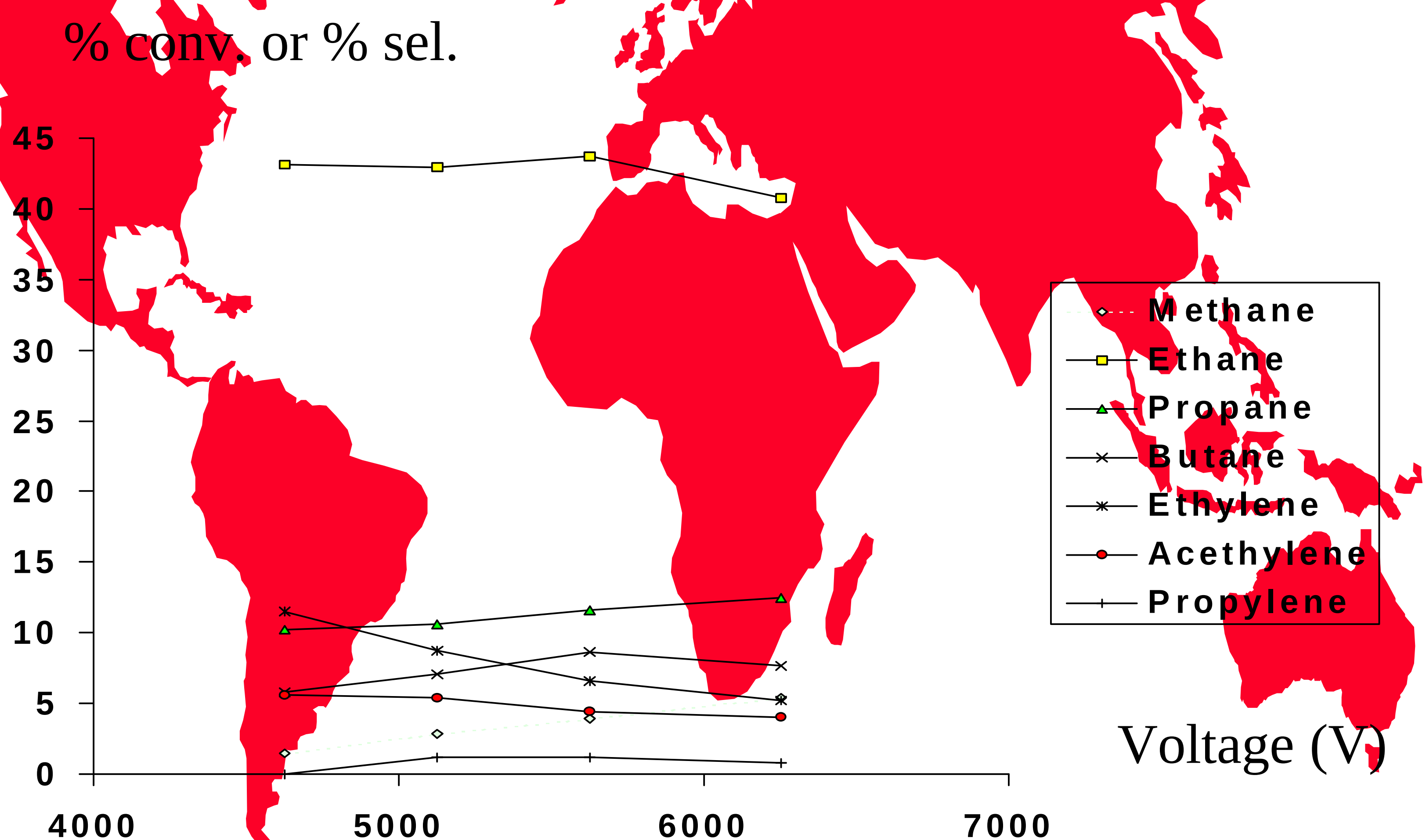
Pure Methane System



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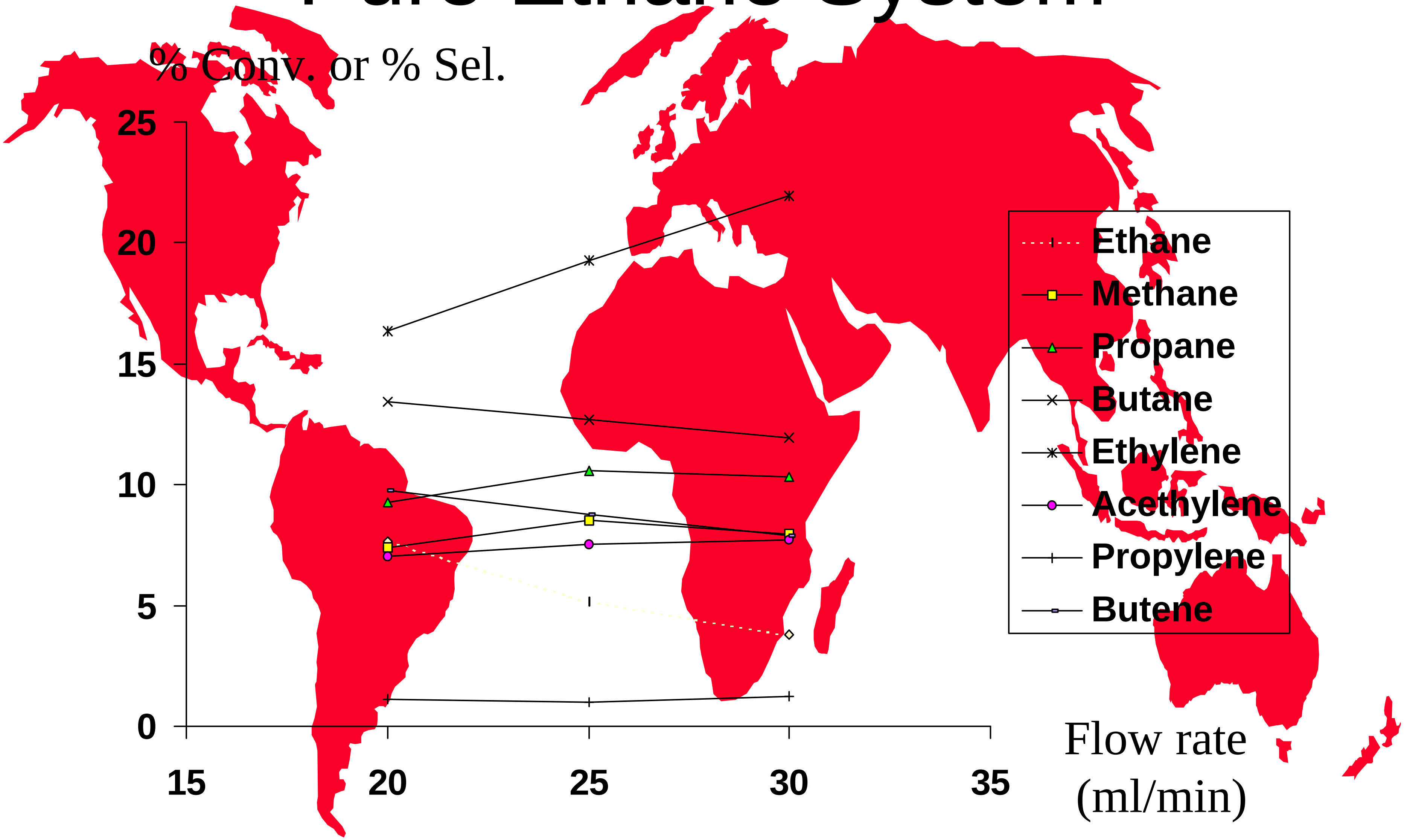
Pure Ethane System



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Pure Propane System