The Role of Fundamentals in Future Directions for the Chemical Industries

Kurt VandenBussche

UOP LLC

CREL 04 meeting

Outline

- Future Directions
- Fundamentals
- Conclusions

Outline

- Future Directions
  - The processing industries today
  - Trends
    - Cost
    - Environment
    - Feedstock
- Fundamentals
- Conclusions

Past Predictions

1876 "This 'telephone' has too many shortcomings to be seriously considered as a means of communication" Western Union Memo

1895 "Heavier-than-air flying machines are impossible" Lord Kelvin, President Royal Society

1920 "The wireless music box (radio) has no imaginable commercial value" David Sarnoffs Associates in response to his urgings for investments in the radio

1943 "I think there's a world market for maybe five computers" Thomas Watson, Chairman IBM

1949 "Computers in the future may weigh no more than 1.5 tons" Popular Mechanics forecasting the relentless march of science.

1977 "There is no reason anyone would want a computer in their home" Ken Olson, President, Chairman and Founder of Digital Equipment

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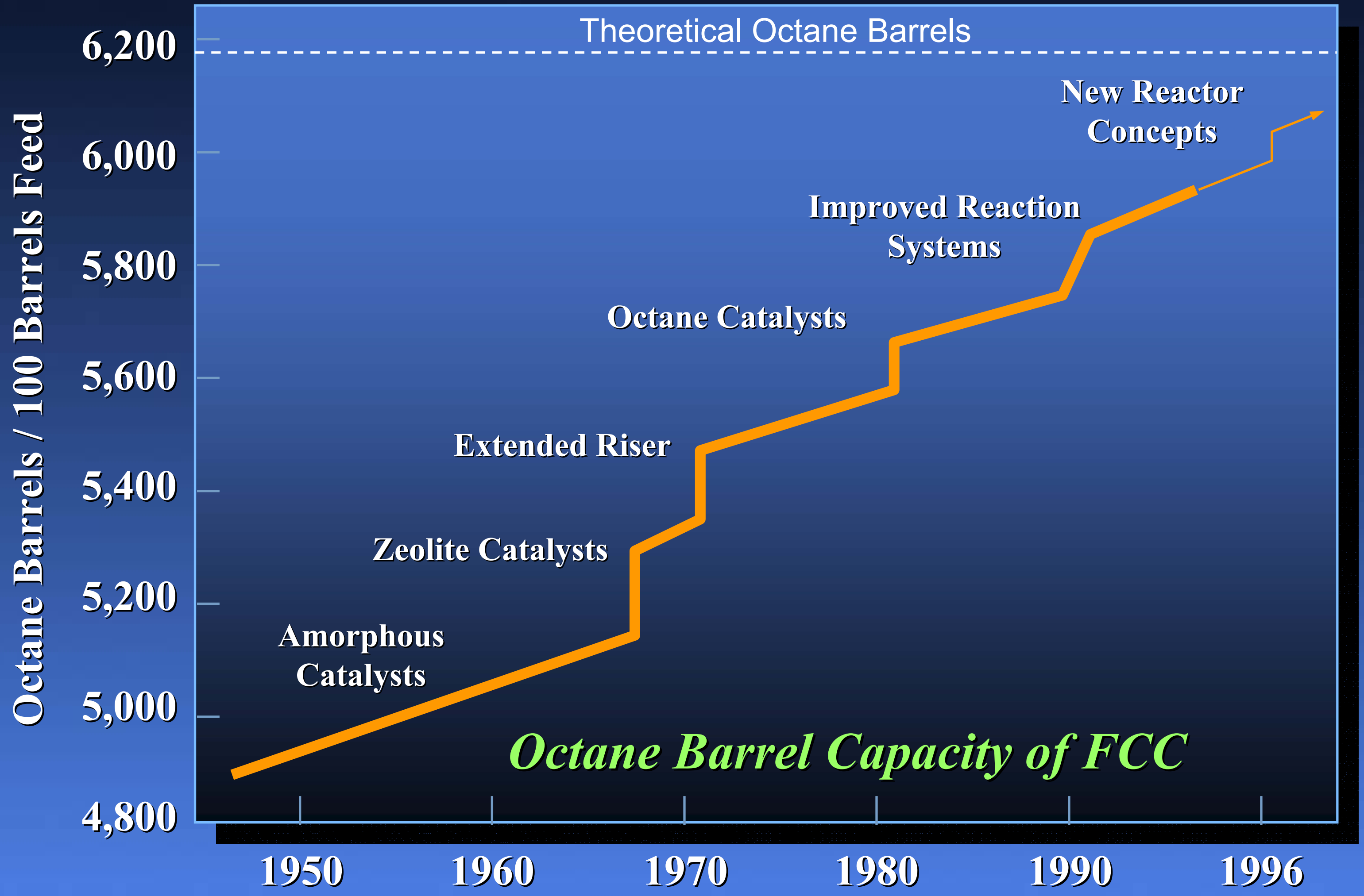
The refining and petrochemical industries today

- Evolution characterized by step-changes
  - 1920 Thermal cracking
  - 1930 Alkylation
  - 1950 Catalytic Reforming
  - 1970 PX/MX/OX separations
  - 1990 Solid Acids for alkylation
  - 2000 Bio based bulk chemicals
- As a rule, technology in the refining and petrochemical industries is mature, growing with GDP

The Importance of Continuous Improvement



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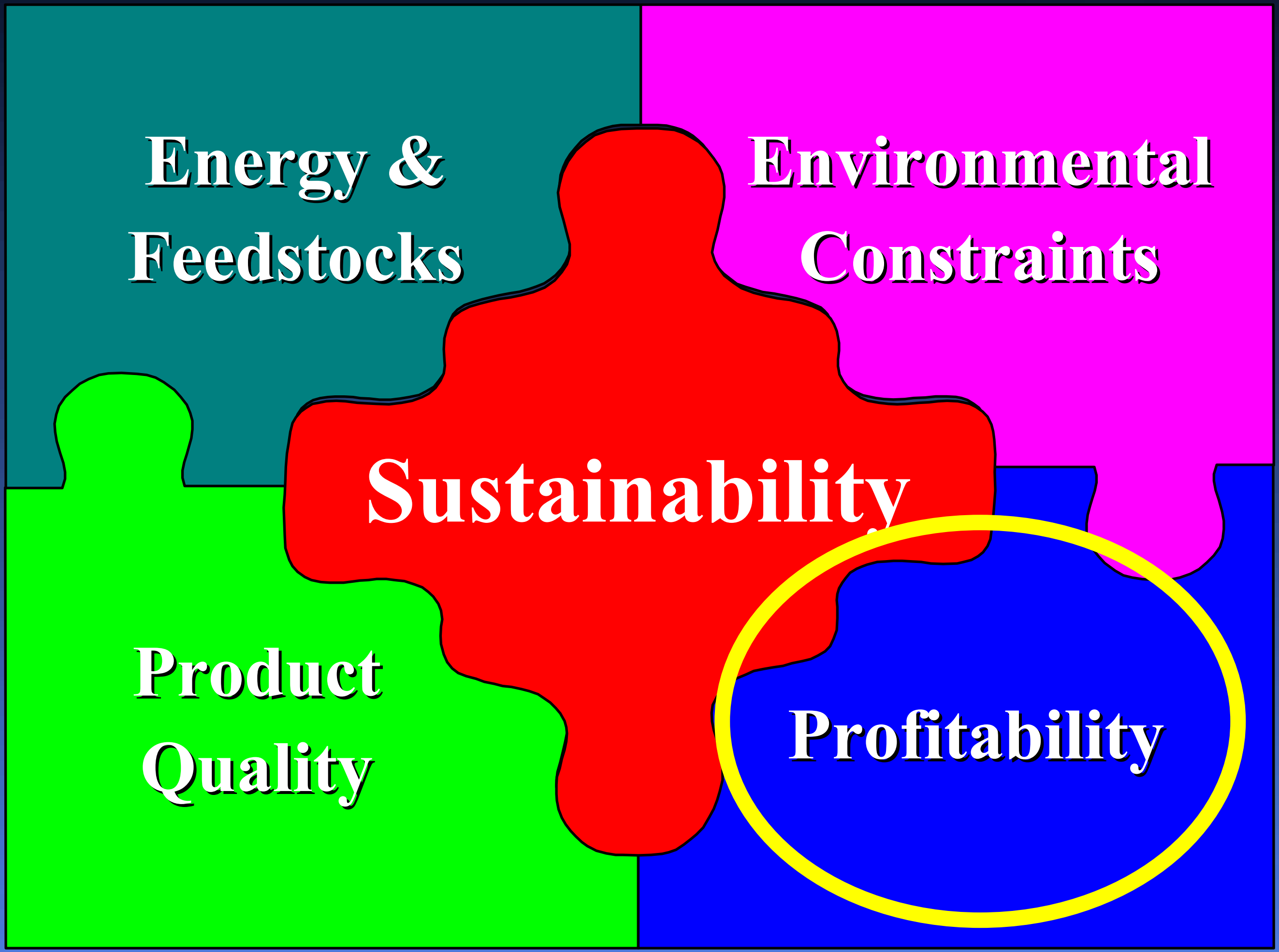
Trends in the Processing Industries



Process Intensification

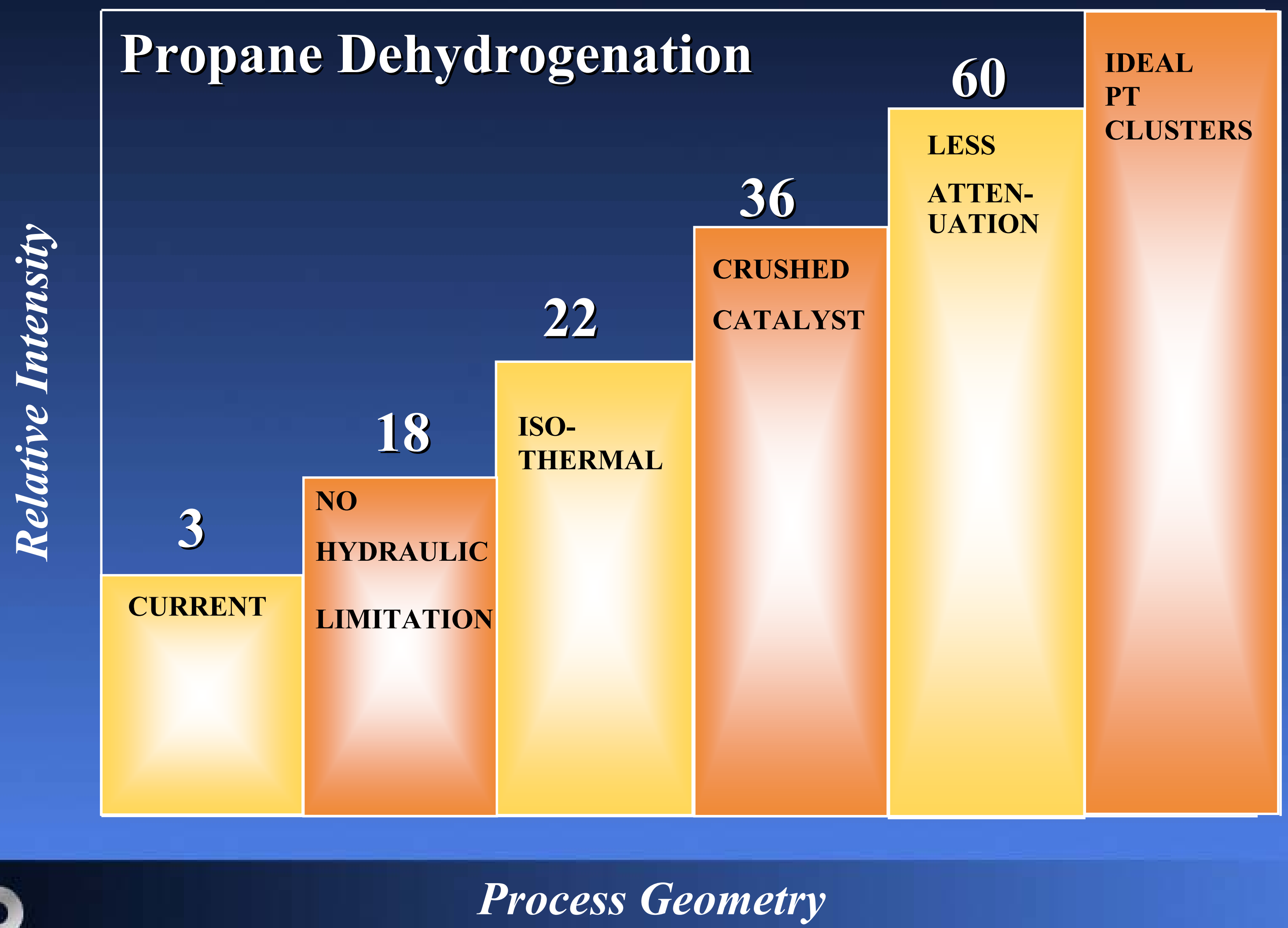
- Coined in the 70's by ICI by Colin Ramshaw
- A series of tools, aimed at
  - reducing the capital cost of production for bulk chemicals
  - at constant or lower variable cost of production.
- Capex scales roughly with footprint or number of unit operations
- Achieved by
  - Combining syntheses, multiple products
  - combining unit operations
  - removing 'limitations' (intensifying)
    - Heat transfer
    - Mass transfer
    - Kinetics
    - Momentum/Pressure drop
    - Gravity…

PI Techniques

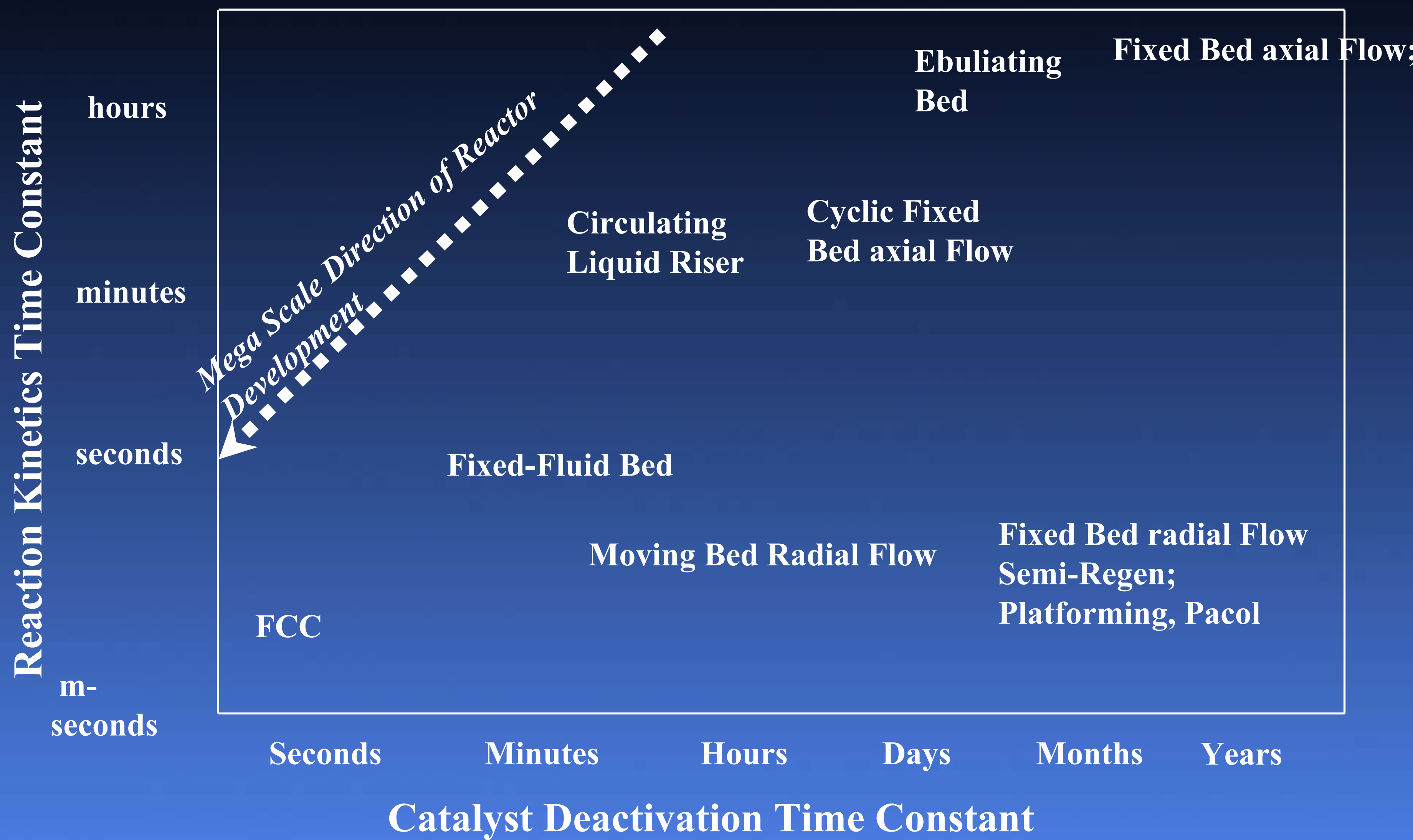
- **Just-in-time manufacture – lower inventories**
- **In-line mixers – lower inventories**
- **Structured column packings – less hold-up**
- **Plate heat exchangers – lower ΔT, less volume**
- **Monolith catalysts – lower ΔT, better mass tfr**
- **Micro-channel reactors – better mass tfr**
- **HiGee fractionation – better mass tfr**

Increasing Commercial Acceptance

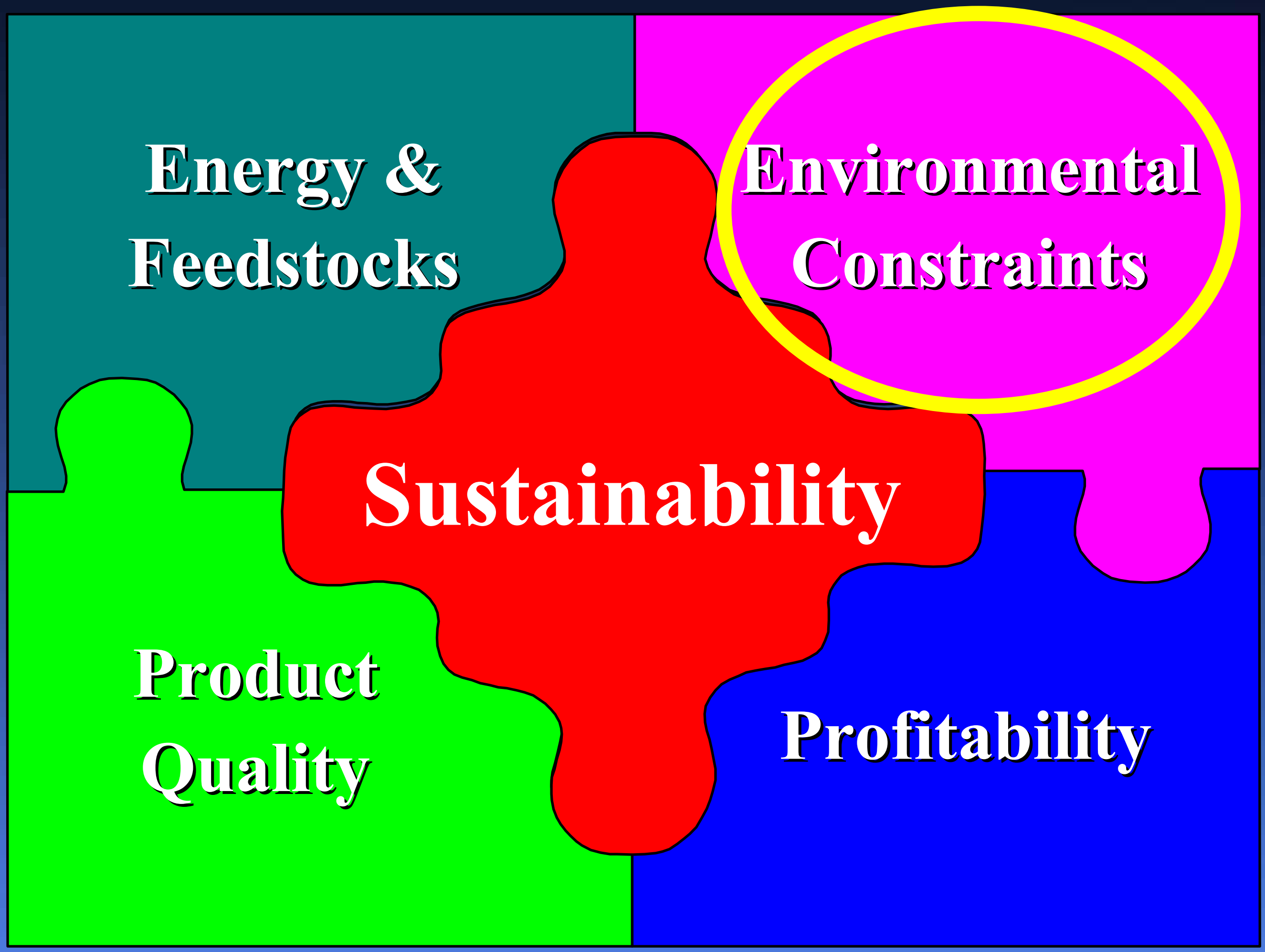
Process Intensification Potential



PI trends in reactor technology



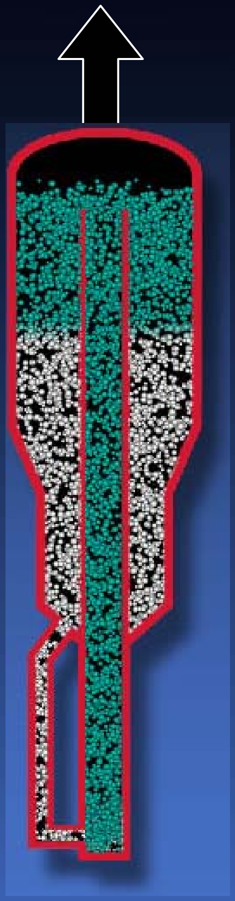
Trends in the Processing Industries



Replacing HF Alkylation

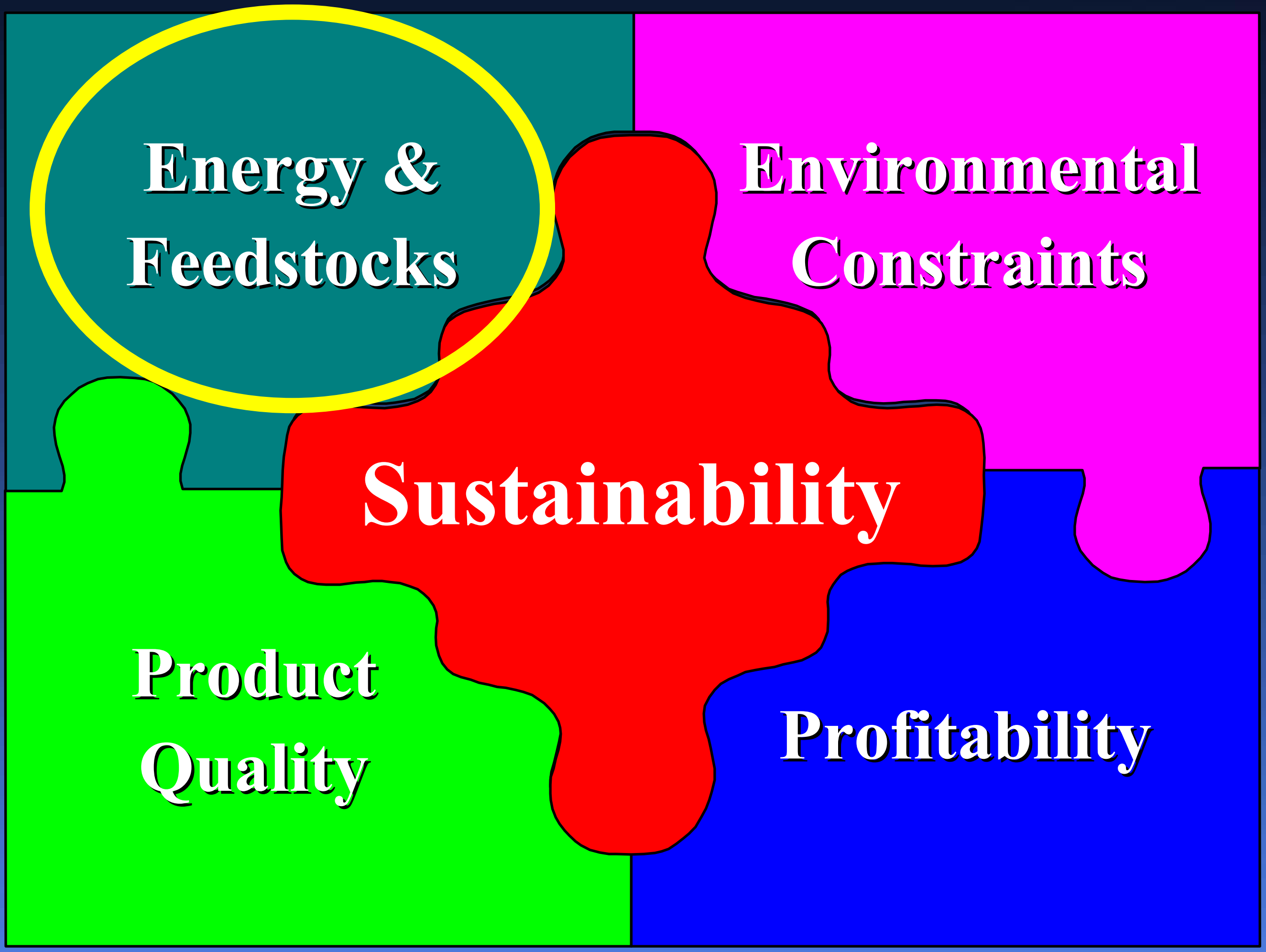
- Waste generated for world scale alkylate plant:

Material	Amount, MM lbs/yr	Cost, MM$/yr
Alumina	9.8	5.9
KOH	3.9	2.0
Lime	5.9	1.9
HF Acid Makeup	33.2	23.4
TOTAL	52.8	33.2

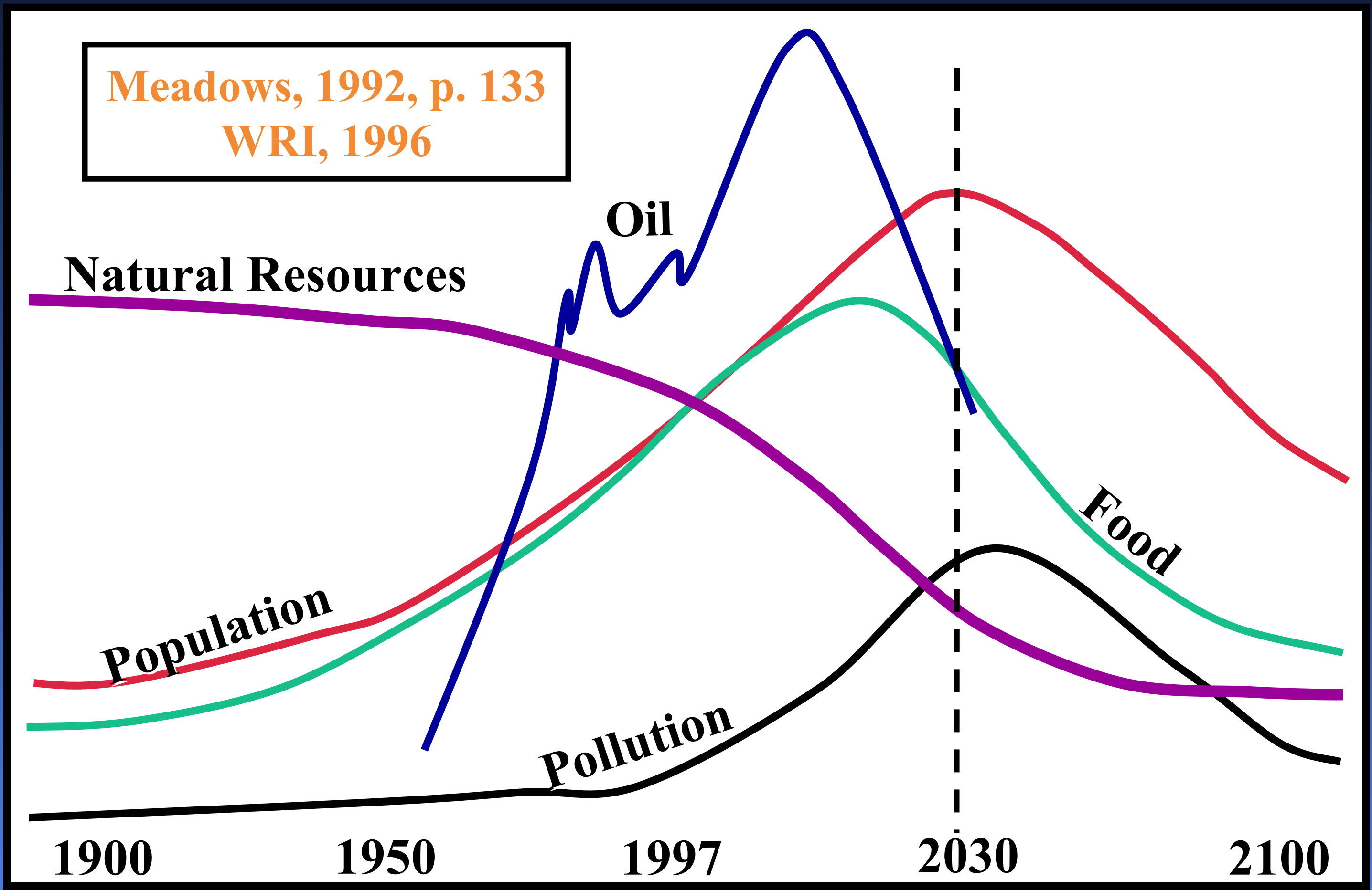


- New solid acid catalyst, new reactor
  - **Inherent safety, Lower waste**
  - **Lower capital**

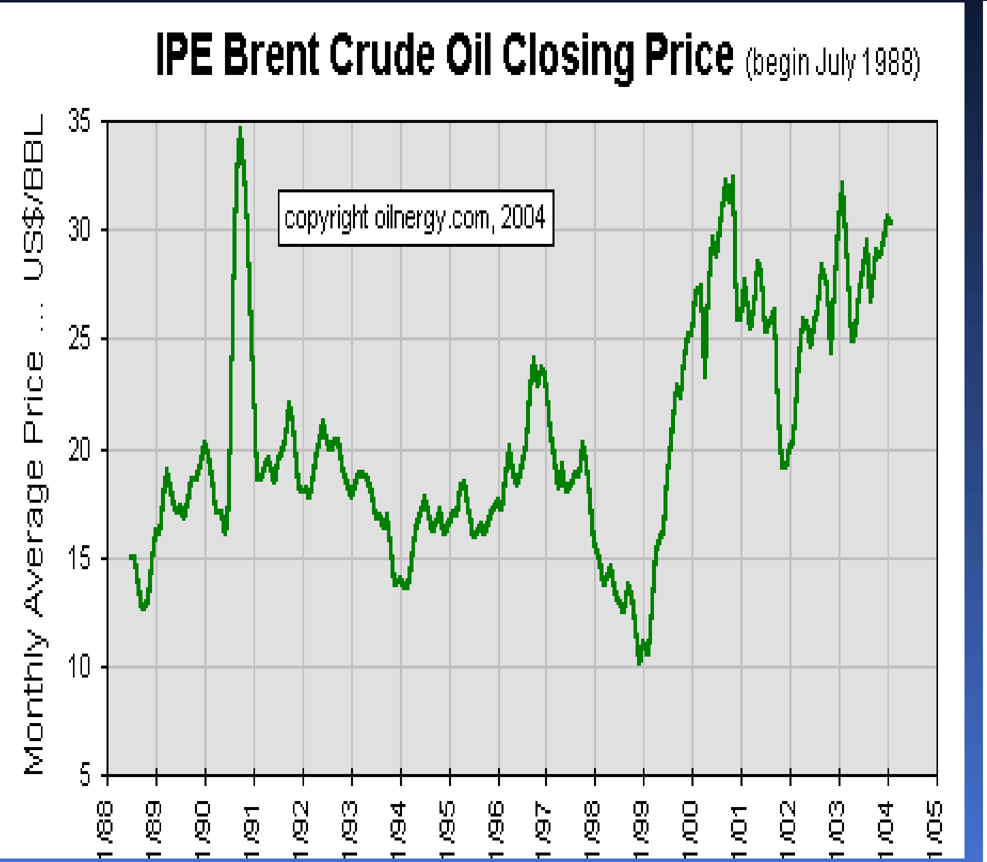
Trends in the Processing Industries

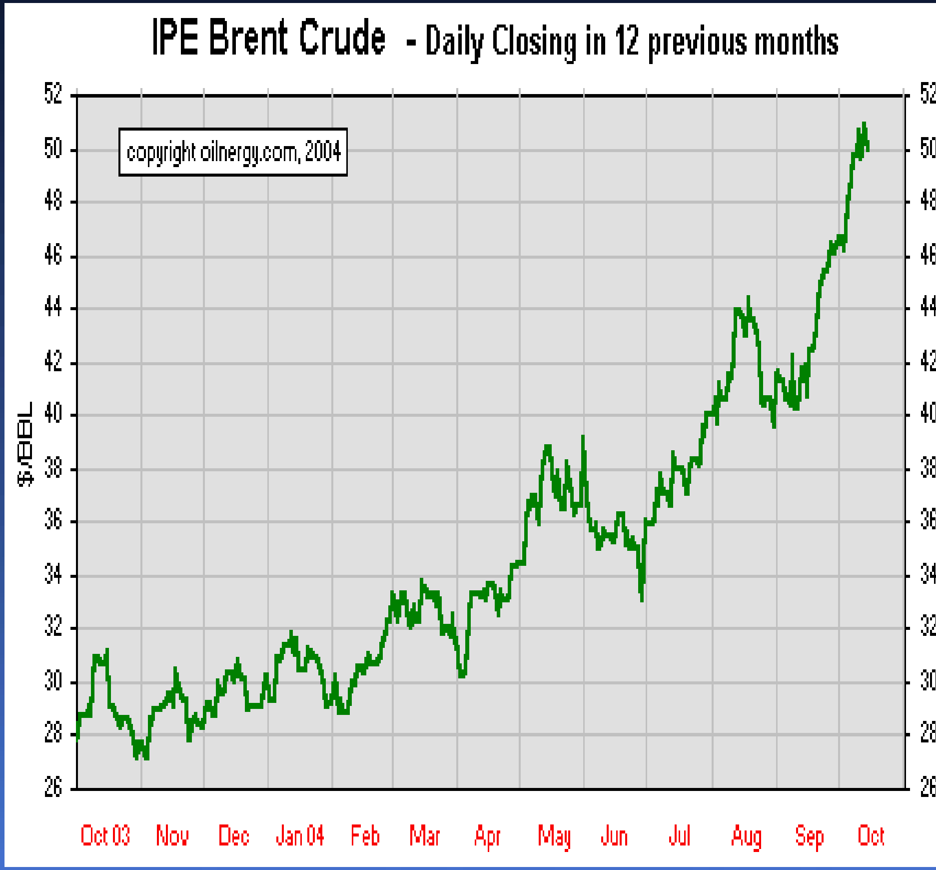


Availability of Oil ?

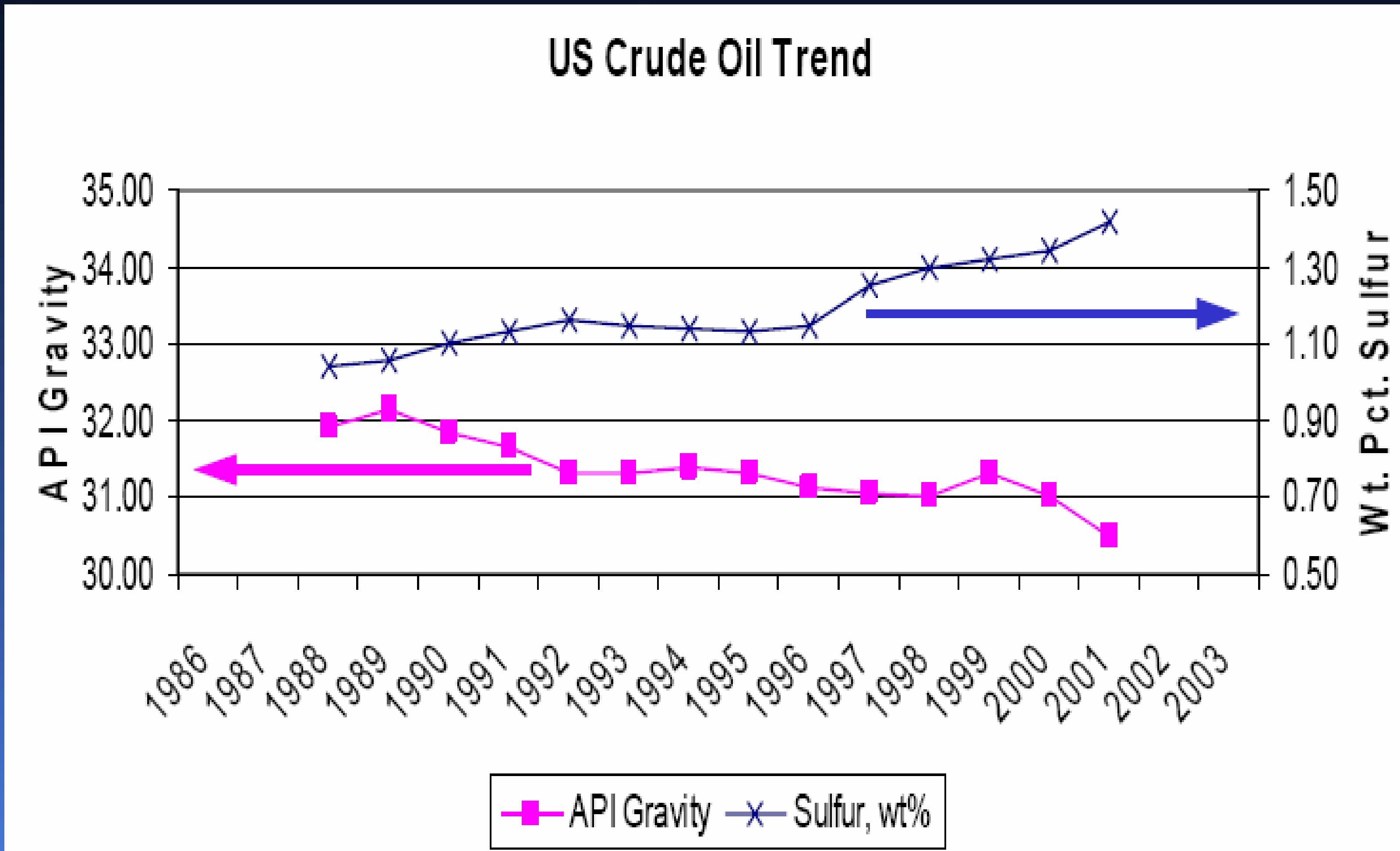


Evolution of Price of Brent Crude Oil

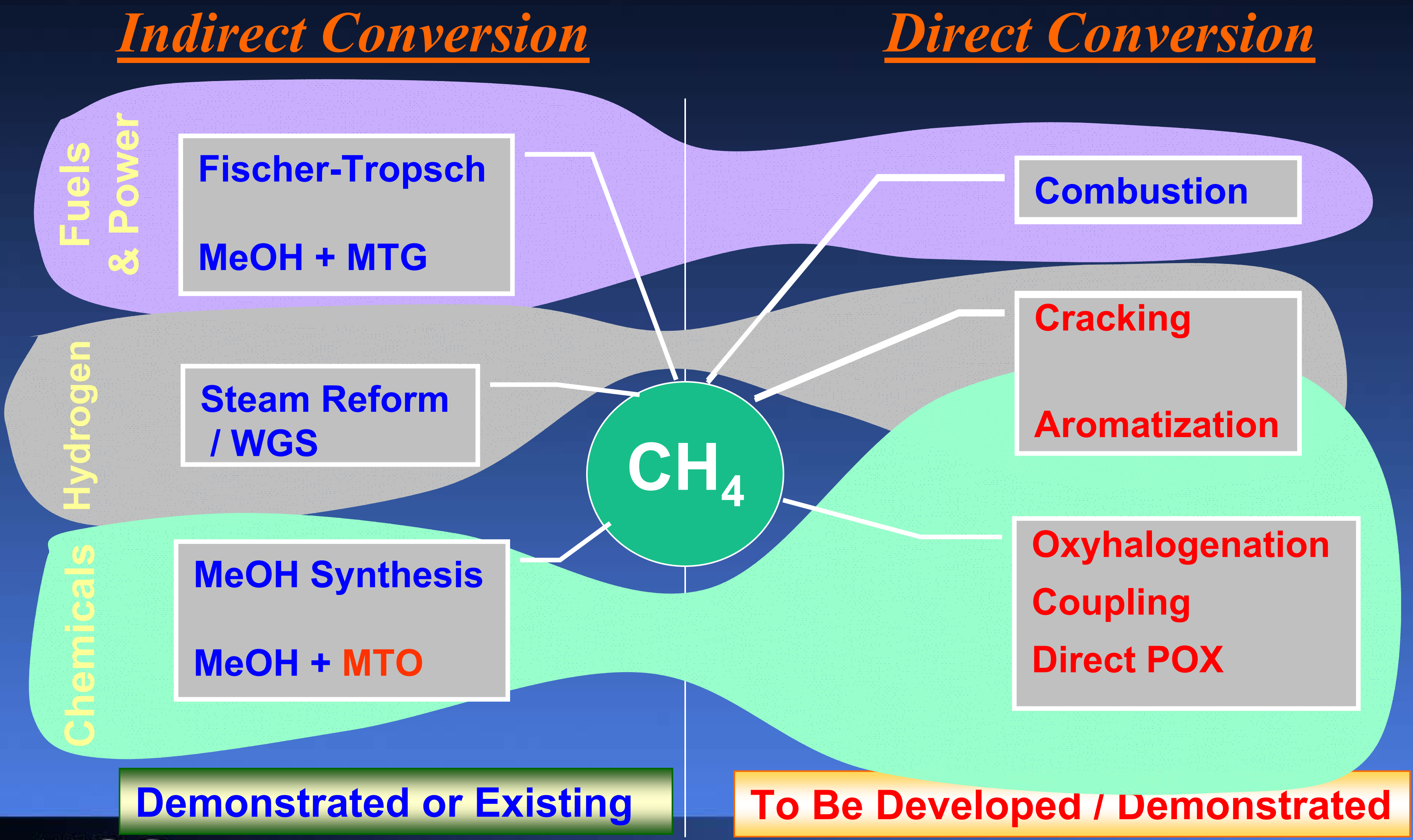




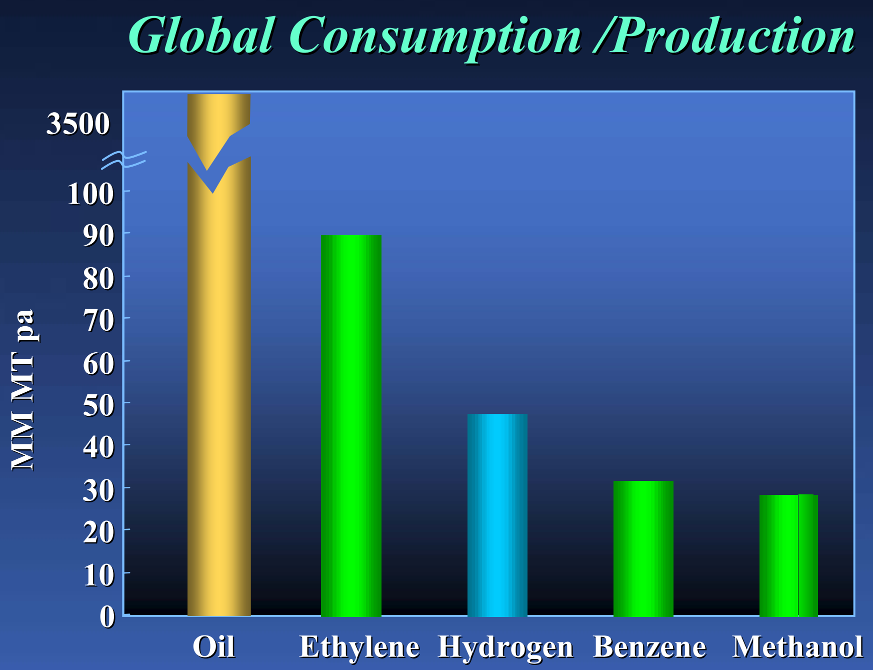
Evolution of Quality of Processed Crude Oil

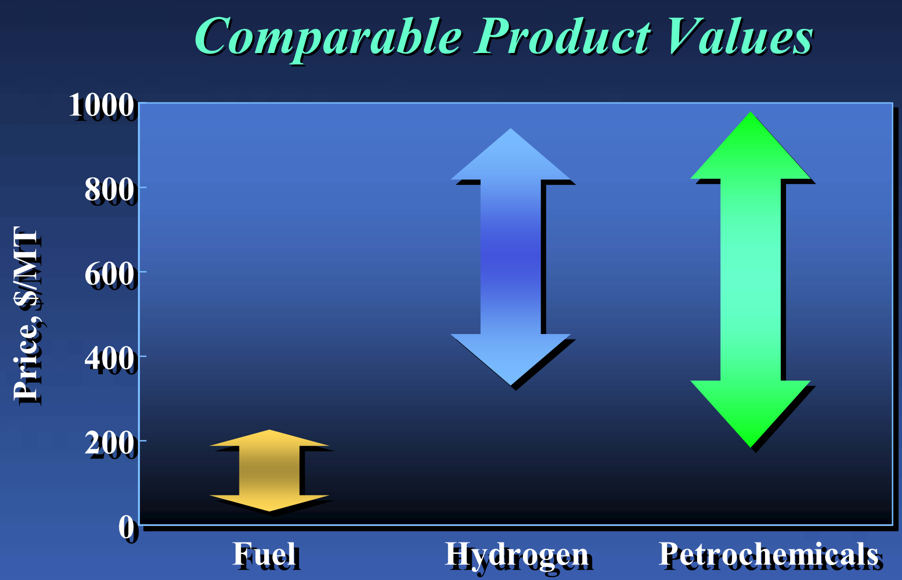


Natural Gas as a Feedstock



Hydrogen as a fuel ?





Hydrogen currently looks like a petrochemical in scale and value

Hydrogen as a fuel in 2025 entails :

Assume 10% World Energy Demand (based on 2025) Equivalent to 68 EJ (exa joules -10^{18})

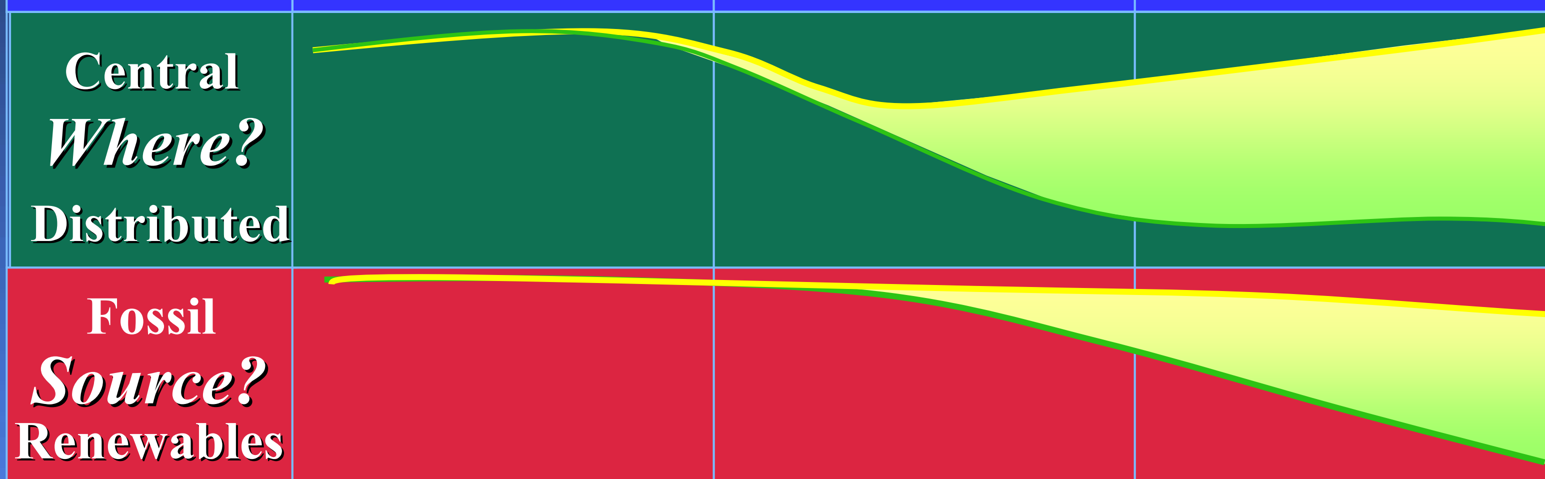
H_2 Quantity	$6x10^{12}$ Nm^3 per year
New Plants	7000 @ 100,000 Nm^3 per hour each
Asset Investment*	\$1-3 trillion (10^{12})

* Includes H2 delivery assets

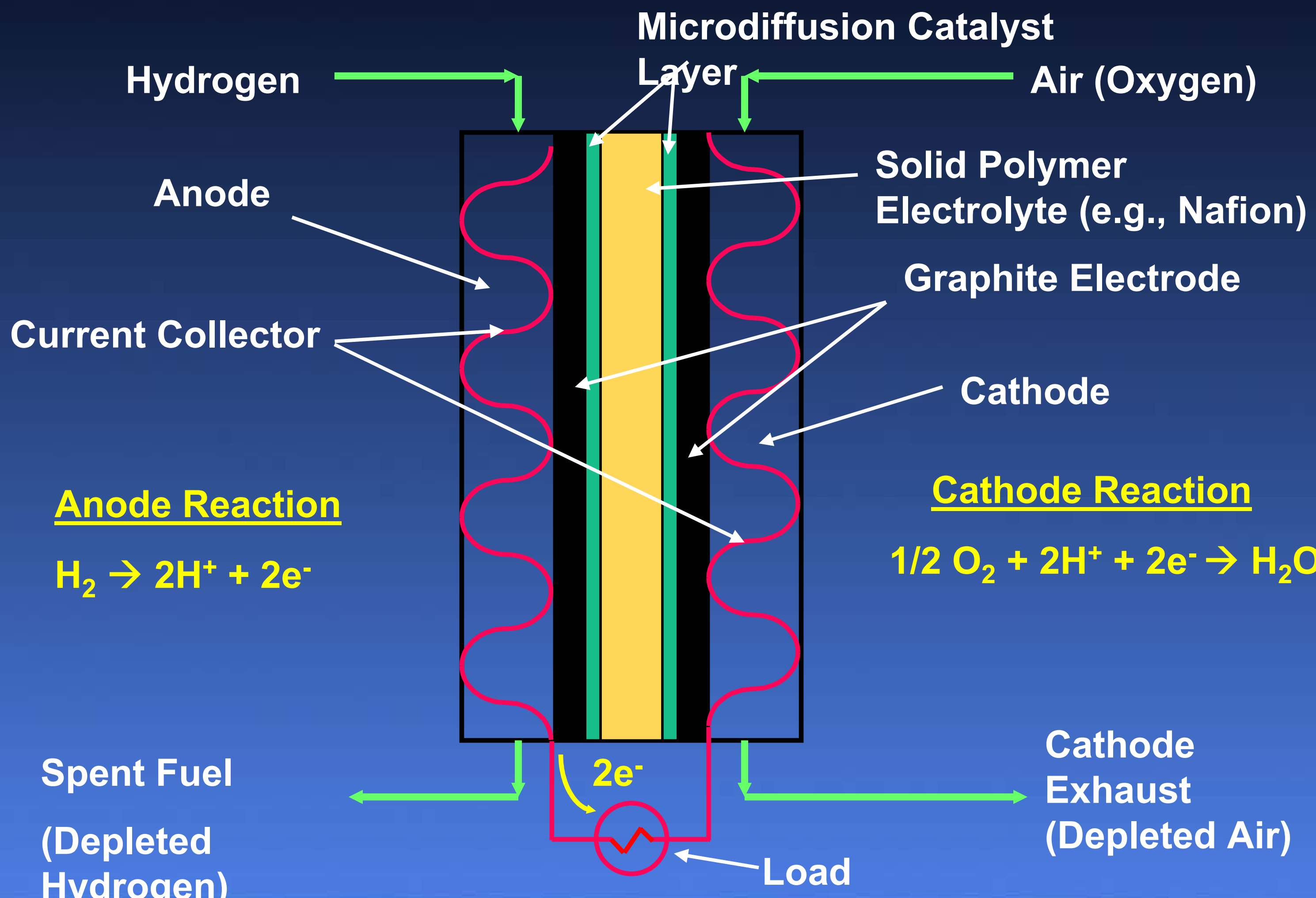
Evolution of Hydrogen Roadmap

Time →

	5 years	10 - 20 years	>20 years
	Short Term	**Medium Term**	**Long Term**
H_2 Function	Fuel Quality Improvement	Fuel Enhancement	Primary Fuel



A Polymer Electrolyte Membrane (PEM) Fuel Cell is a Reactive Membrane Process



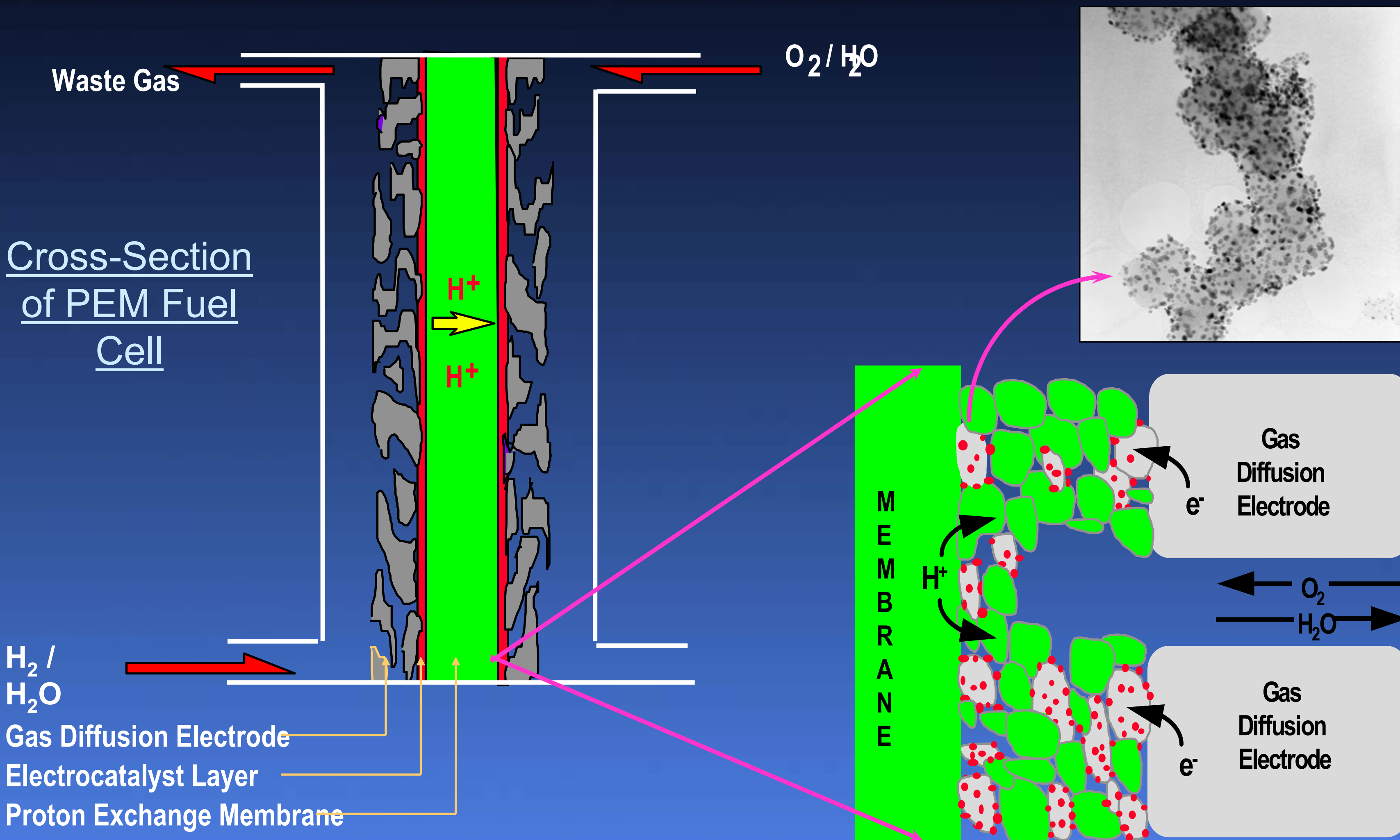
Anode Reaction

$H_2 \rightarrow 2H^+ + 2e^-$

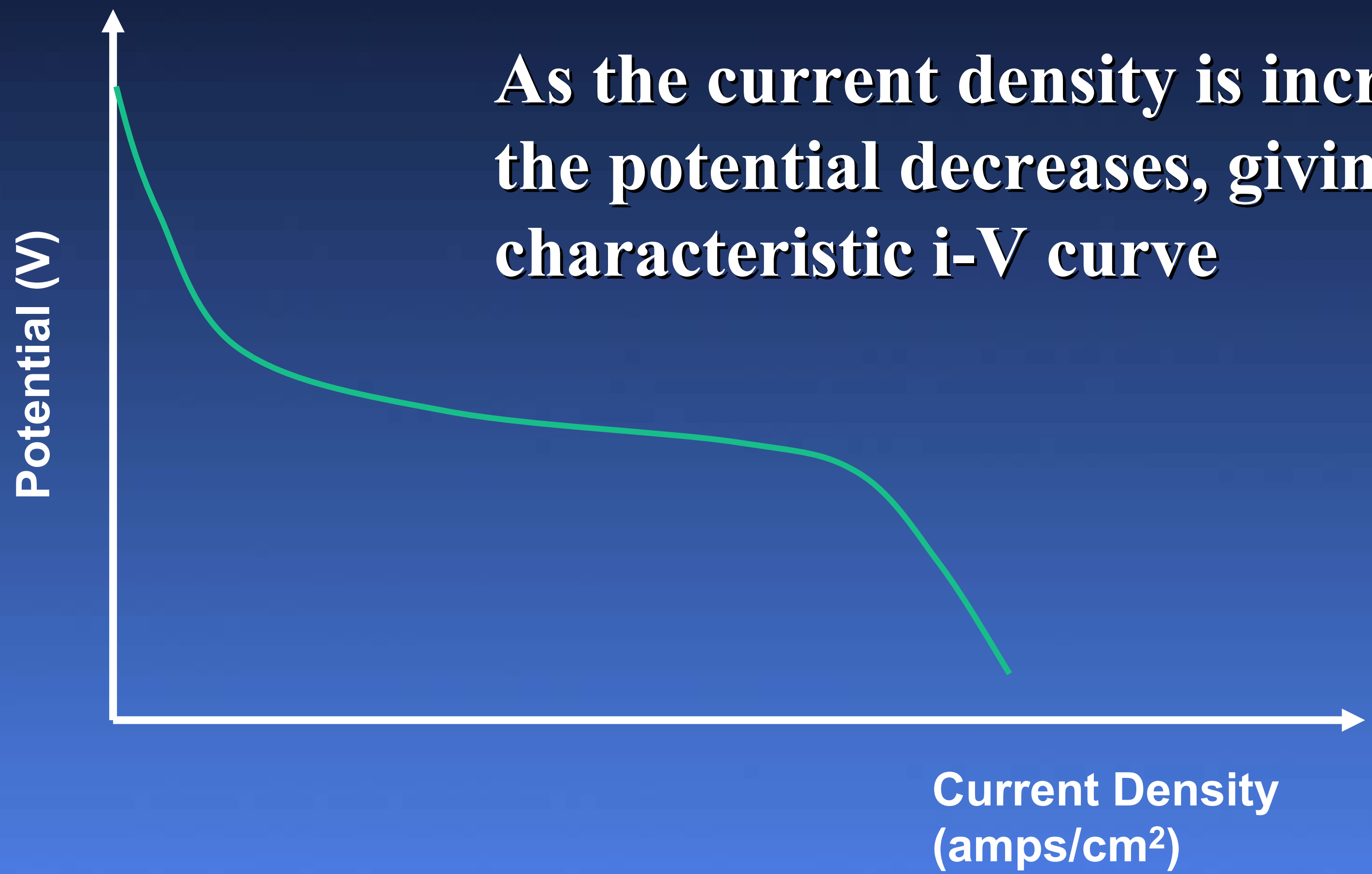
Cathode Reaction

$1/2\ O_2 + 2H^+ + 2e^- \rightarrow H_2O$

The MEA is a Membrane with Dispersed Pt Catalyst on Both Sides



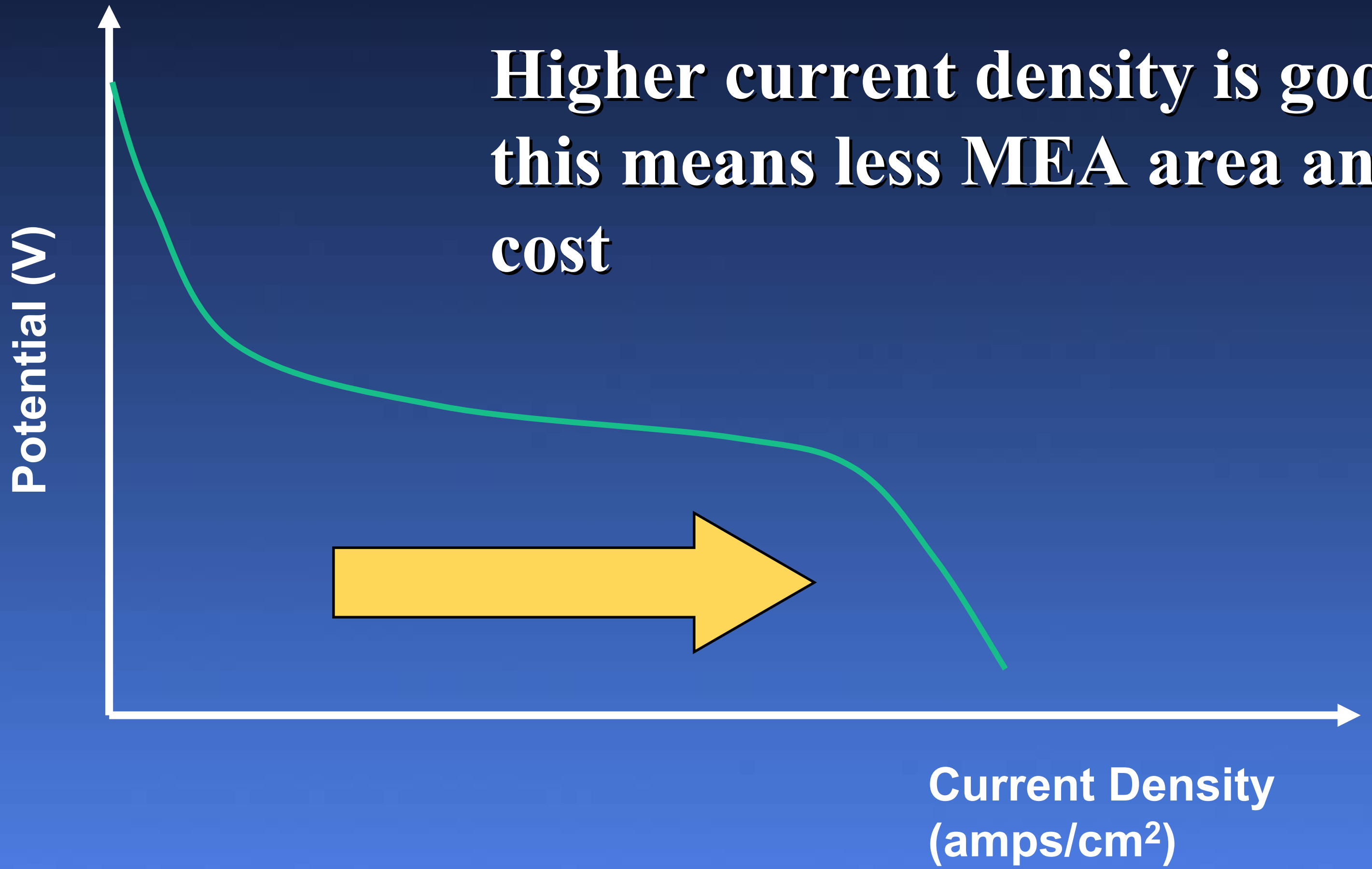
Fuel Cell i-V Curve



As the current density is increased the potential decreases, giving a characteristic i-V curve

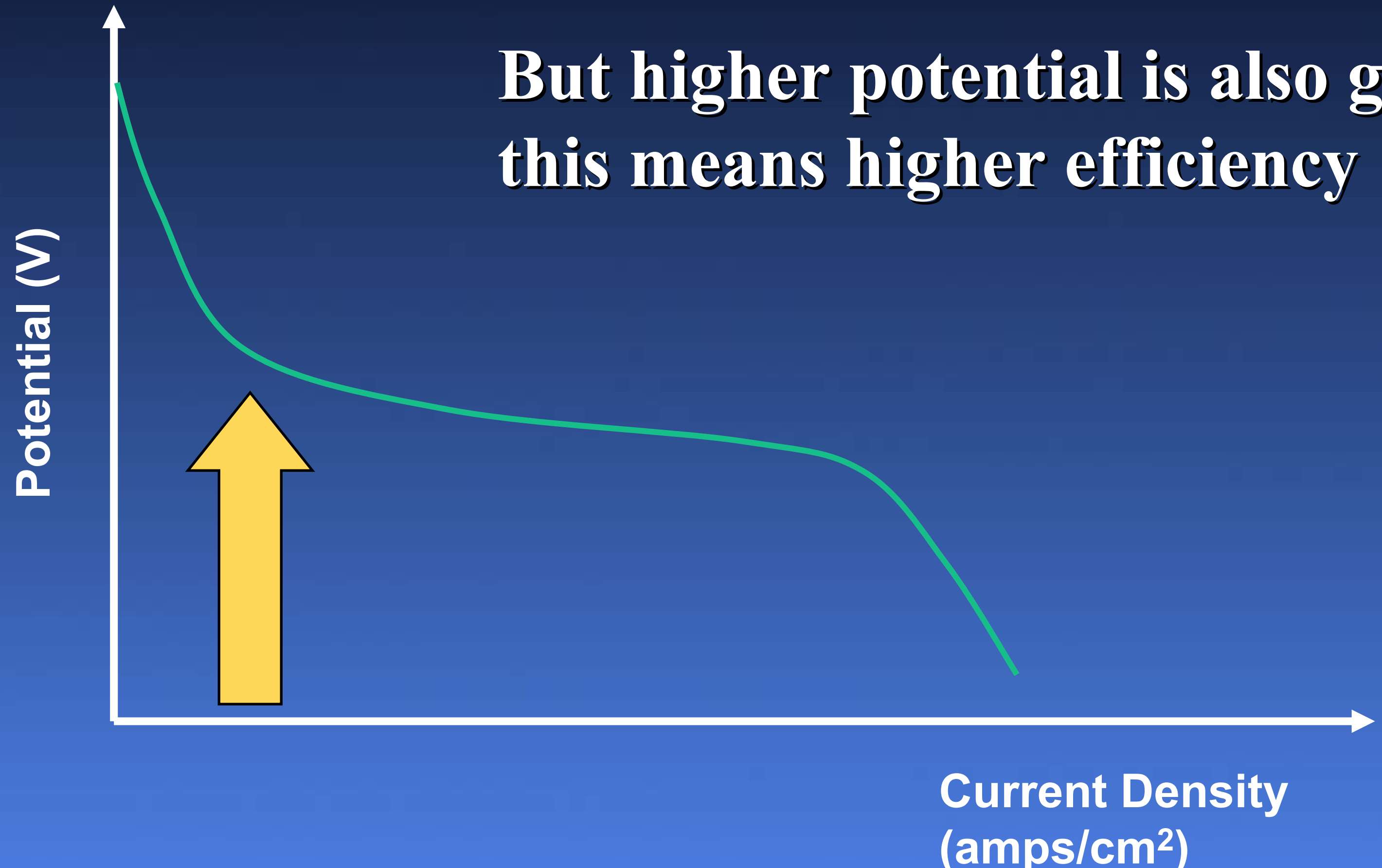
Fuel Cell i-V Curve

Higher current density is good, as this means less MEA area and lower cost

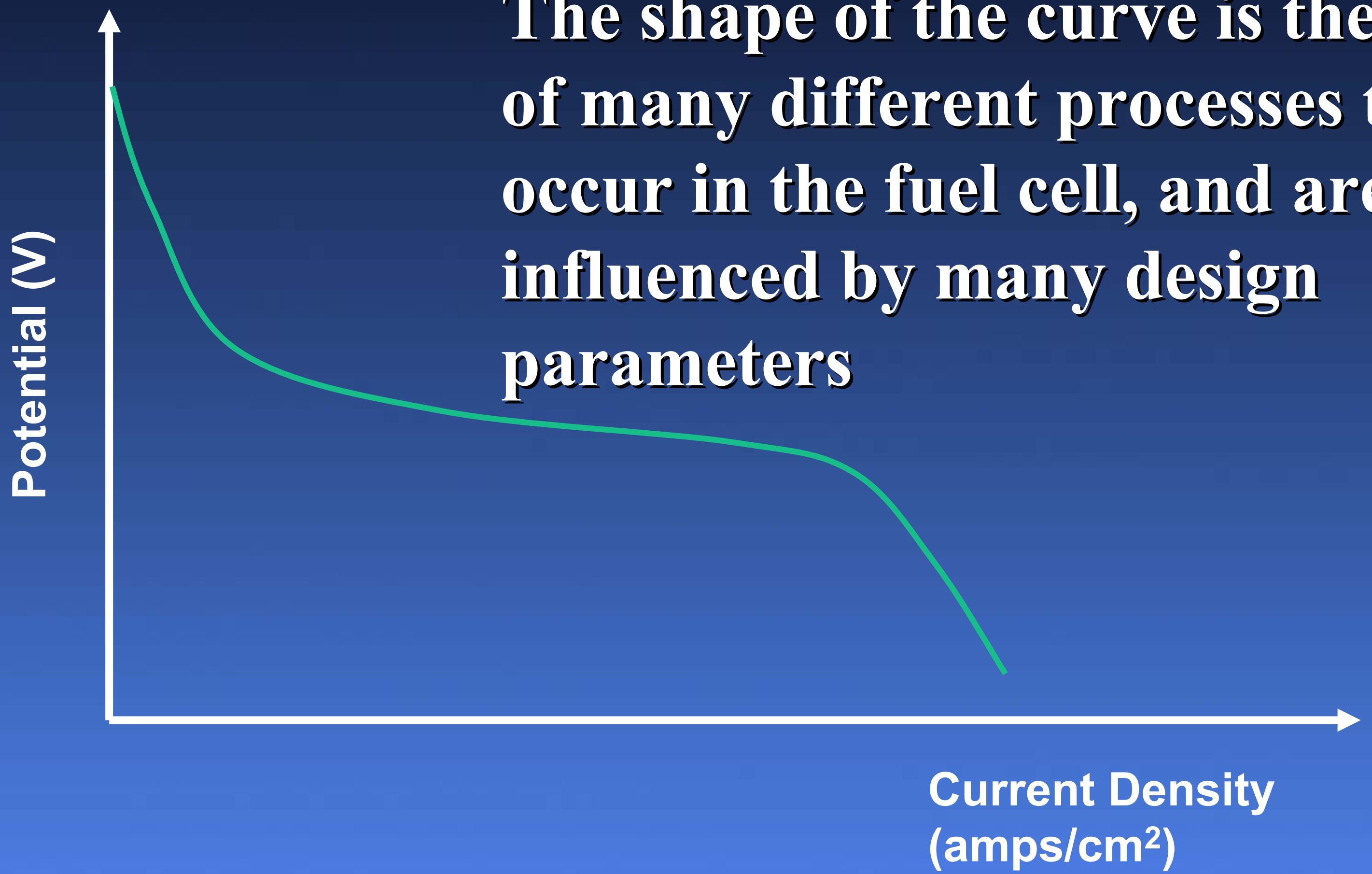


Fuel Cell i-V Curve

But higher potential is also good, as this means higher efficiency

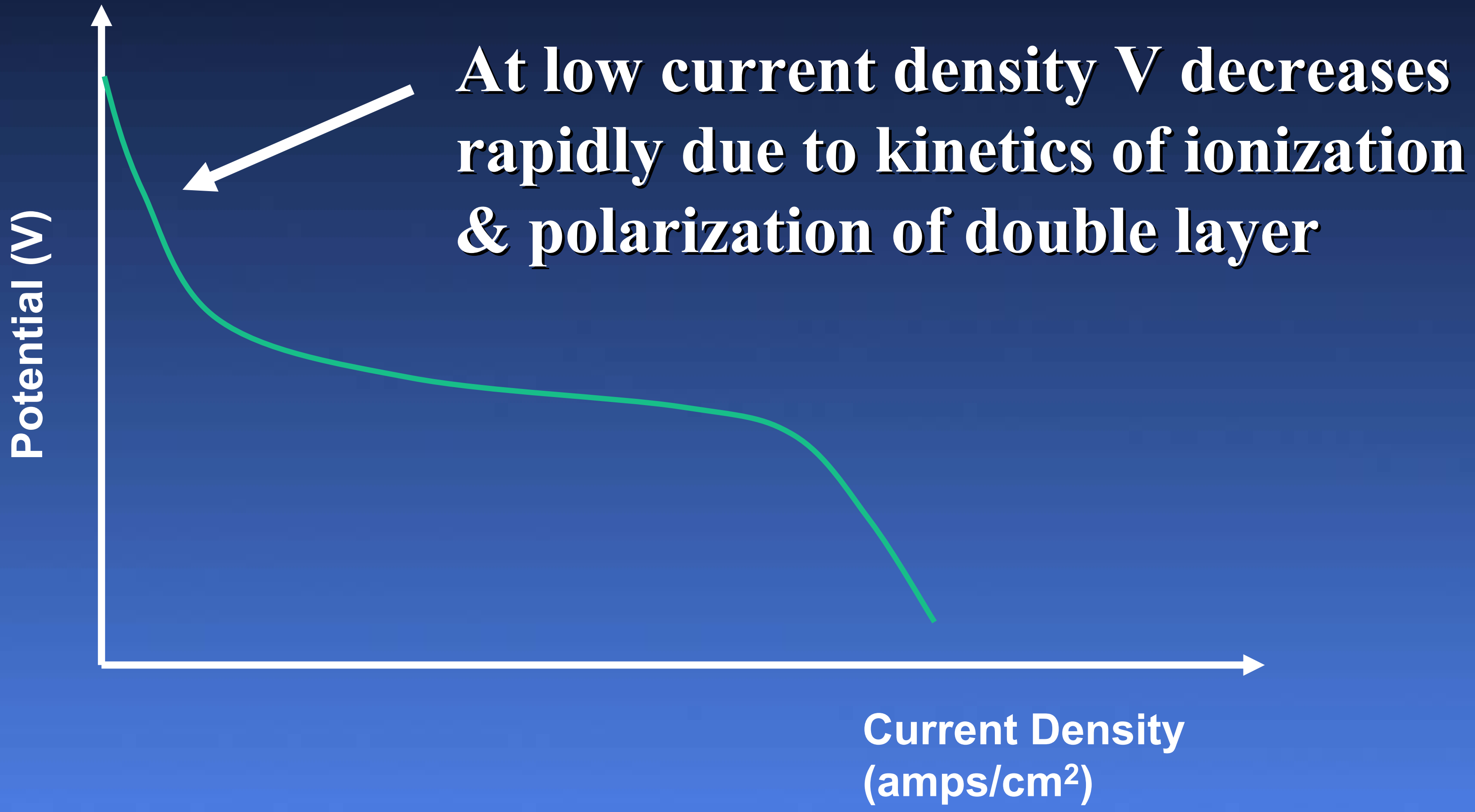


Fuel Cell i-V Curve



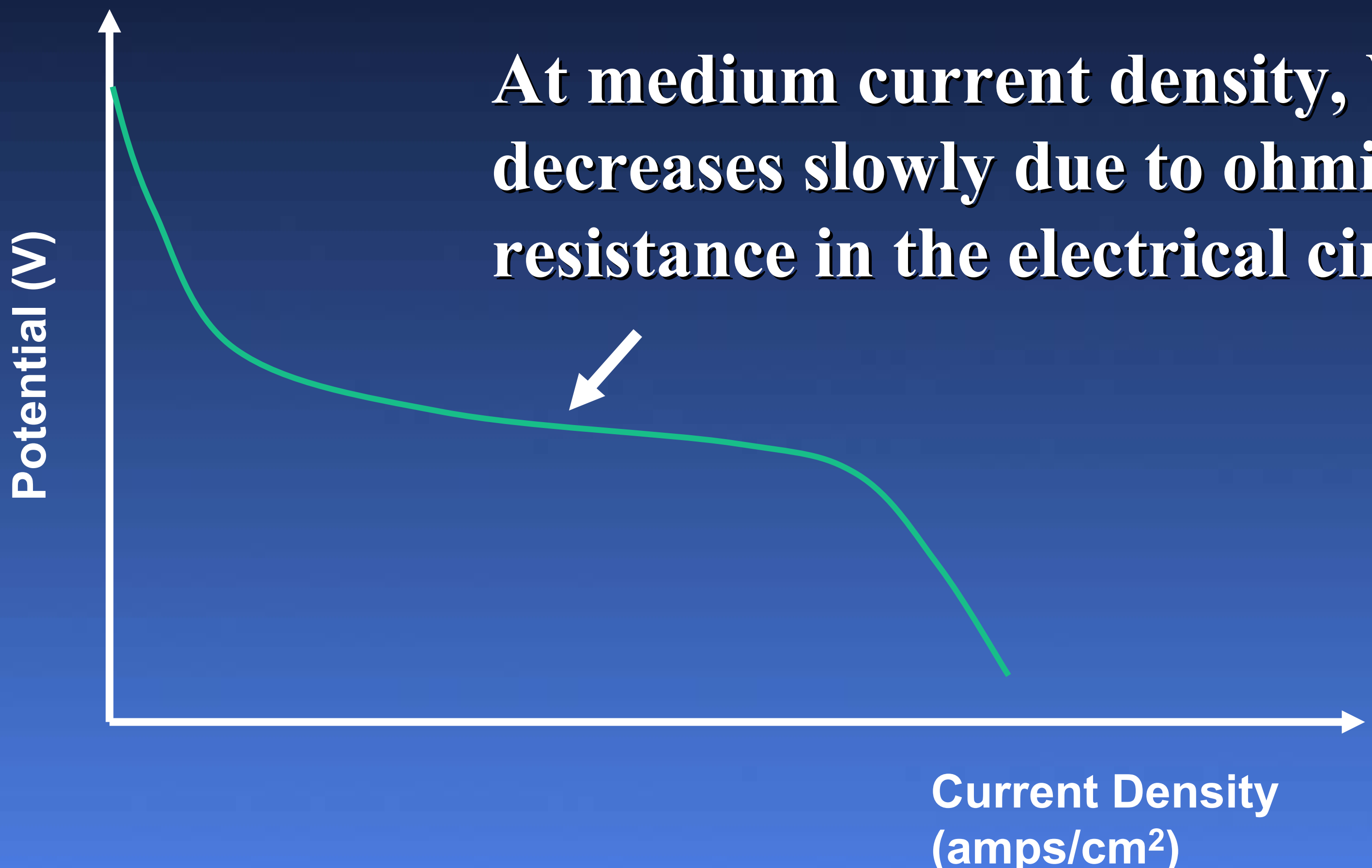
The shape of the curve is the result of many different processes that occur in the fuel cell, and are influenced by many design parameters

Fuel Cell i-V Curve



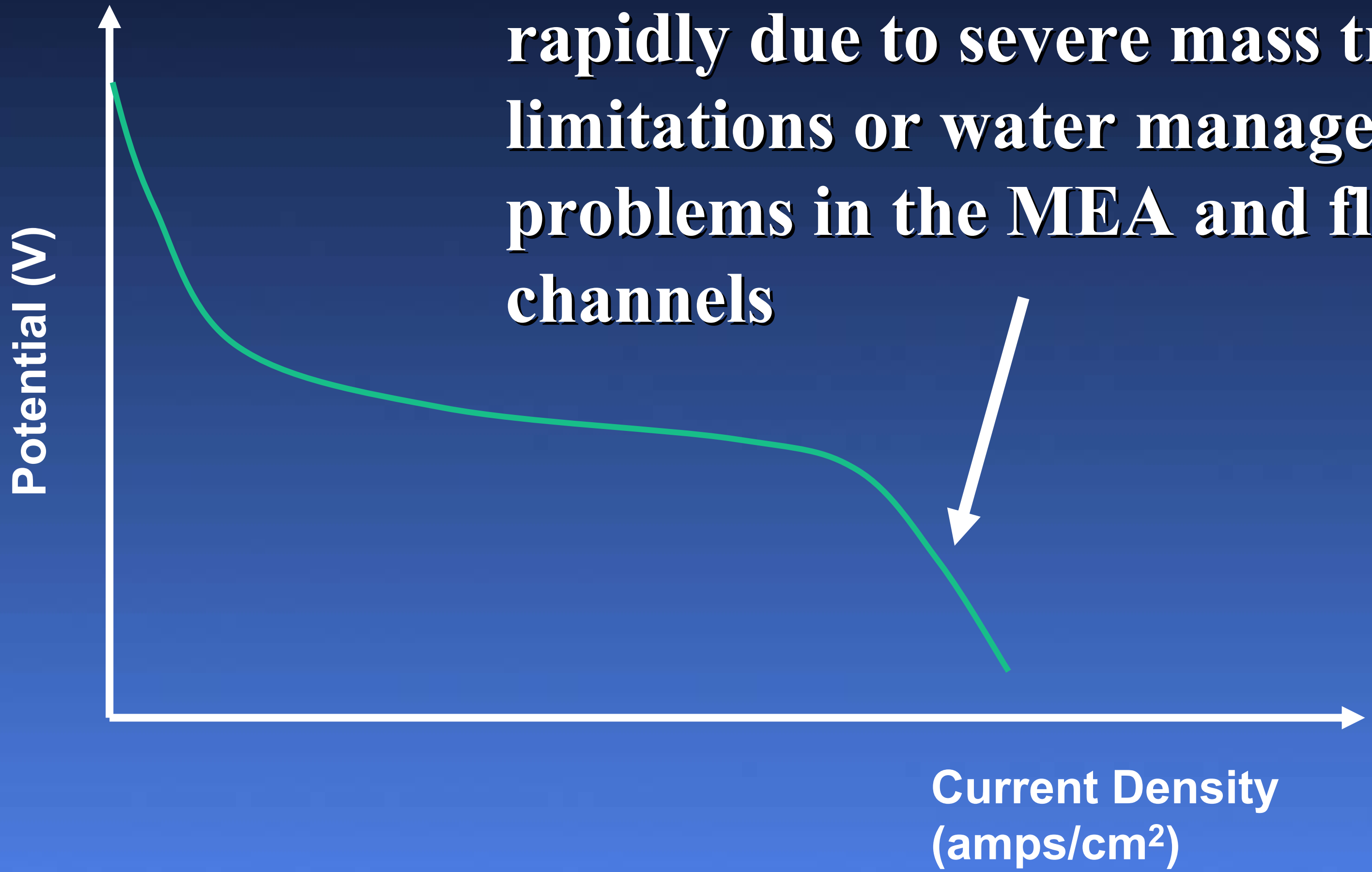
Fuel Cell i-V Curve

At medium current density, V decreases slowly due to ohmic resistance in the electrical circuit



Fuel Cell i-V Curve

At high current density, V decreases rapidly due to severe mass transfer limitations or water management problems in the MEA and flow channels



Fuel Cell Theory

Cell voltage, $V = V_o - \eta_{\Omega} - \eta_{CT} - \eta_{MT}$

$$\eta_{\Omega} = i\,\Re_{int}$$

$$\eta_{CT} = -\frac{RT}{\alpha nF}\ln i_o + \frac{RT}{\alpha nF}\ln i$$

$$i_o = nF\,k_1 C_R \exp\left(\frac{-U_a^o - \alpha nF\,\Delta\varphi}{RT}\right)$$

$$\eta_{MT} = \frac{RT}{\alpha\, n\, F}\ln\left(1 - \frac{i}{i_L}\right)$$

$$i_L = \frac{D\,nF\,C_b}{\delta}$$

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Fuel Cell Theory

Cell voltage, $V = V_o - \eta_\Omega - \eta_{CT} - \eta_{MT}$

$$\eta_\Omega = i\,\Re_{int}$$

Depends on electrical resistance of membrane, electrodes, catalyst/electrode junctions, etc.

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Depends on intrinsic kinetics of charge transfer at the electrocatalyst

$$\eta_{MT} = \frac{RT}{\alpha n F} \ln\left(1 - \frac{i}{i_L}\right)$$

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Depends on double layer polarization at the electrode/ membrane interface

$$\eta_{MT} = \frac{RT}{\alpha\, n\, F} \ln\left(1 - \frac{i}{i_L} \right)$$

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$$i_L = \frac{D\, nF\, C_b}{\delta}$$

Depends on mass transfer properties of electrocatalyst and stack design

Fuel Cell Theory

Cell voltage, $V = V_o - \eta_{\Omega} - \eta_{CT} - \eta_{MT}$

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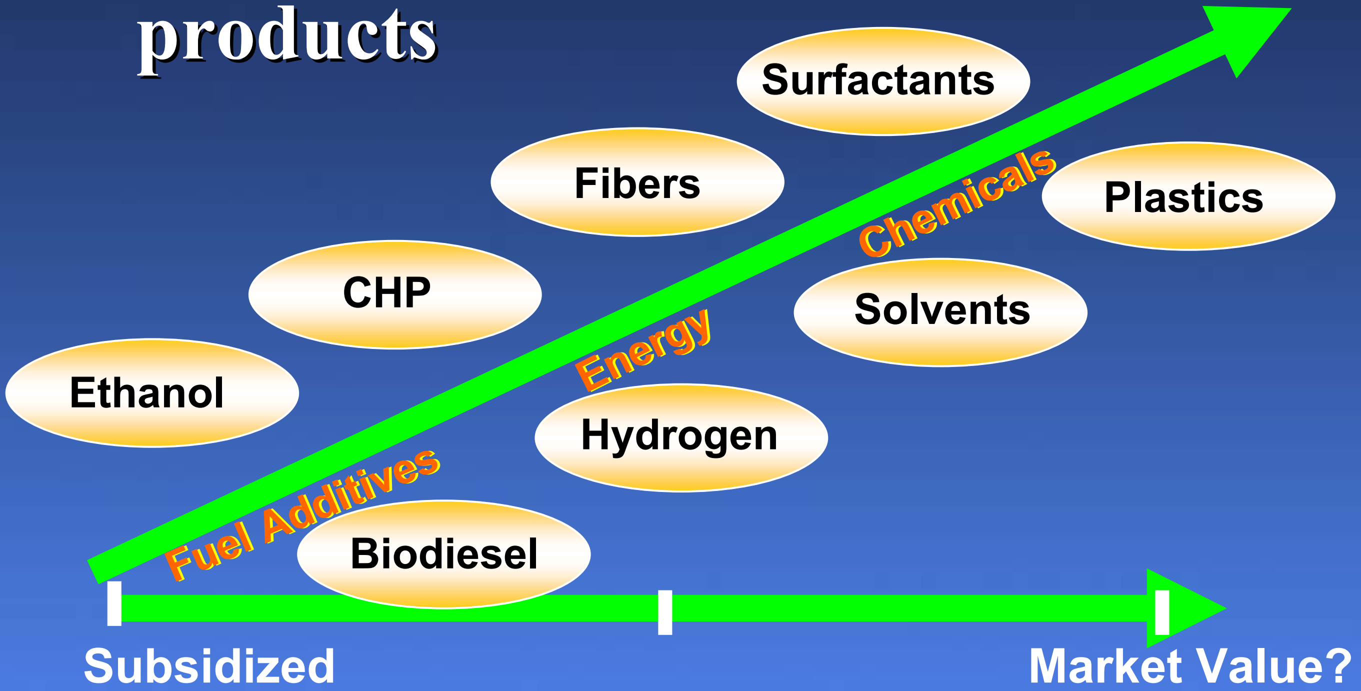
$$\eta_{MT} = \frac{RT}{\alpha n F}\ln\left(1 - \frac{i}{i_L}\right)$$

$$i_L = \frac{D\,nF\,C_b}{\delta}$$

All of these depend on temperature and concentration profiles in the electrocatalyst, hence “reactor design’

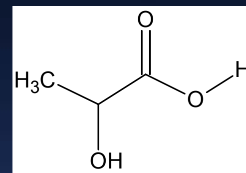
Renewable Feedstocks

- Biofuels subsidized
  - Drive EtOH cost down
  - Value from by-products
- Market Value with higher value added products



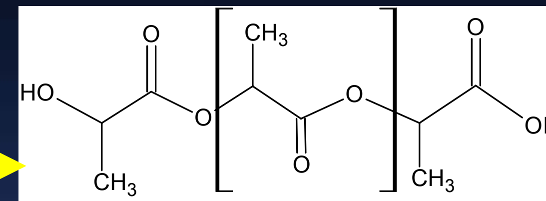
Example: Cargill-Dow Natureworks™ PLA

Corn Starch (or other biomass) → **1. Hydrolysis (enzymatic) 2. Fermentation** →



Lactic Acid

→ **Polymerization** →

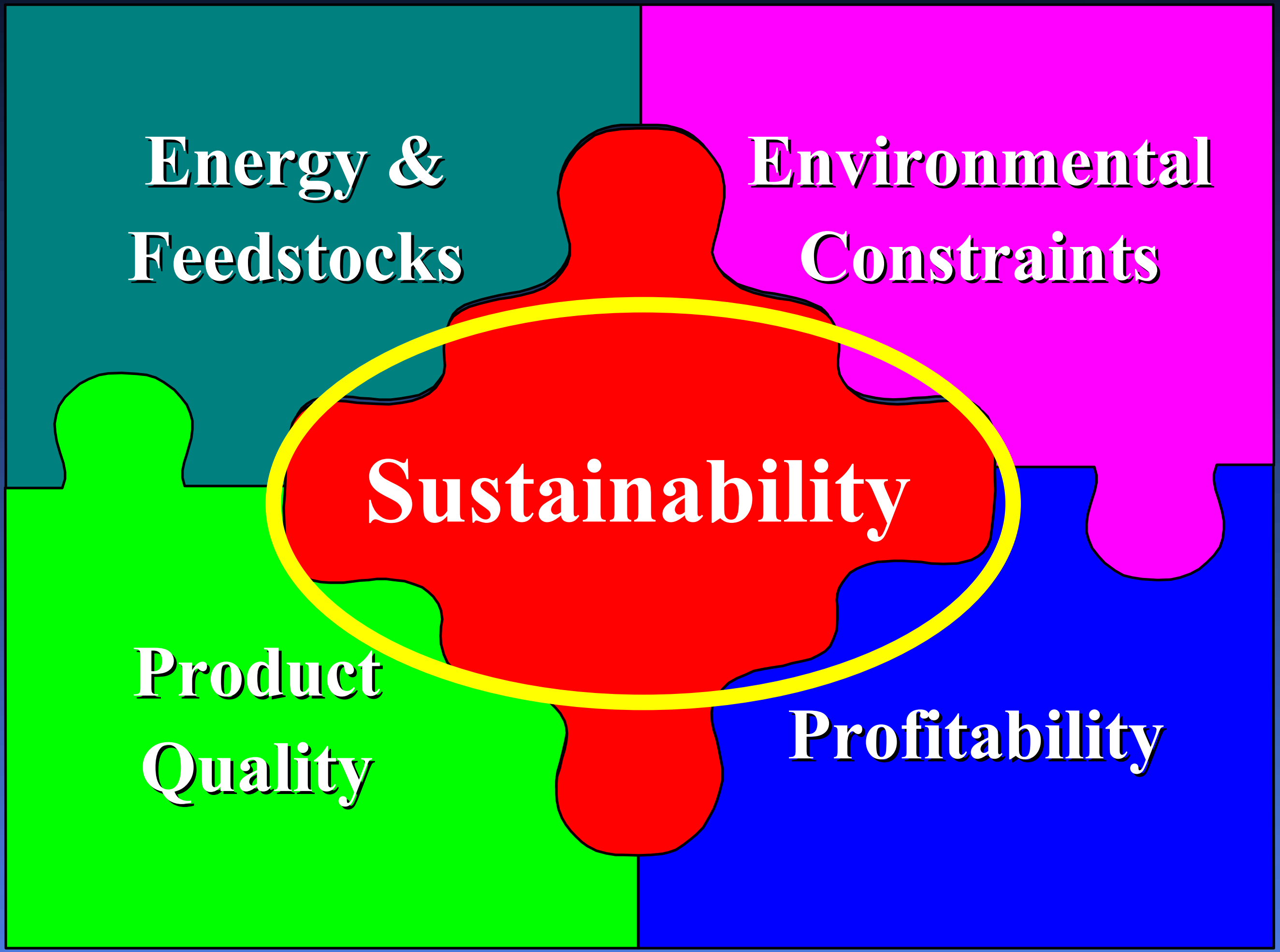


Polylactic Acid (PLA)

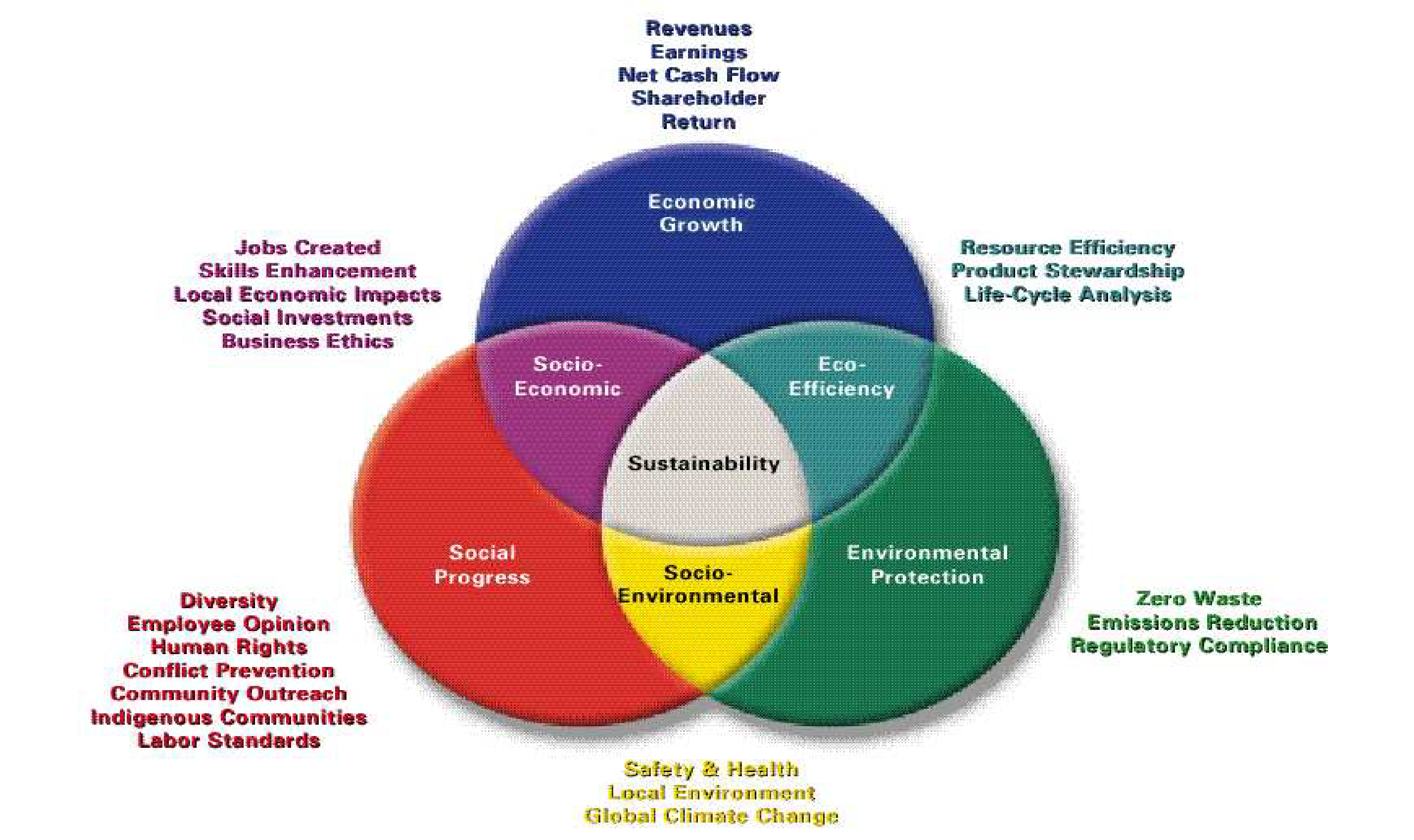
Cargill Dow Dedicates PLA Refinery April 2002

- 100% Annually Renewable Carbon Source
  - ✓ Life-Cycle Analysis (compared with petroleum derived polymer)
    - 20-50% net fossil fuel reduction
    - 15–60% reduction in greenhouse gases
- 140,000 kmta production plant started in 2002 (Blair, NE)
- 85+ Development Agreements

Trends in the Processing Industries



A new set of criteria

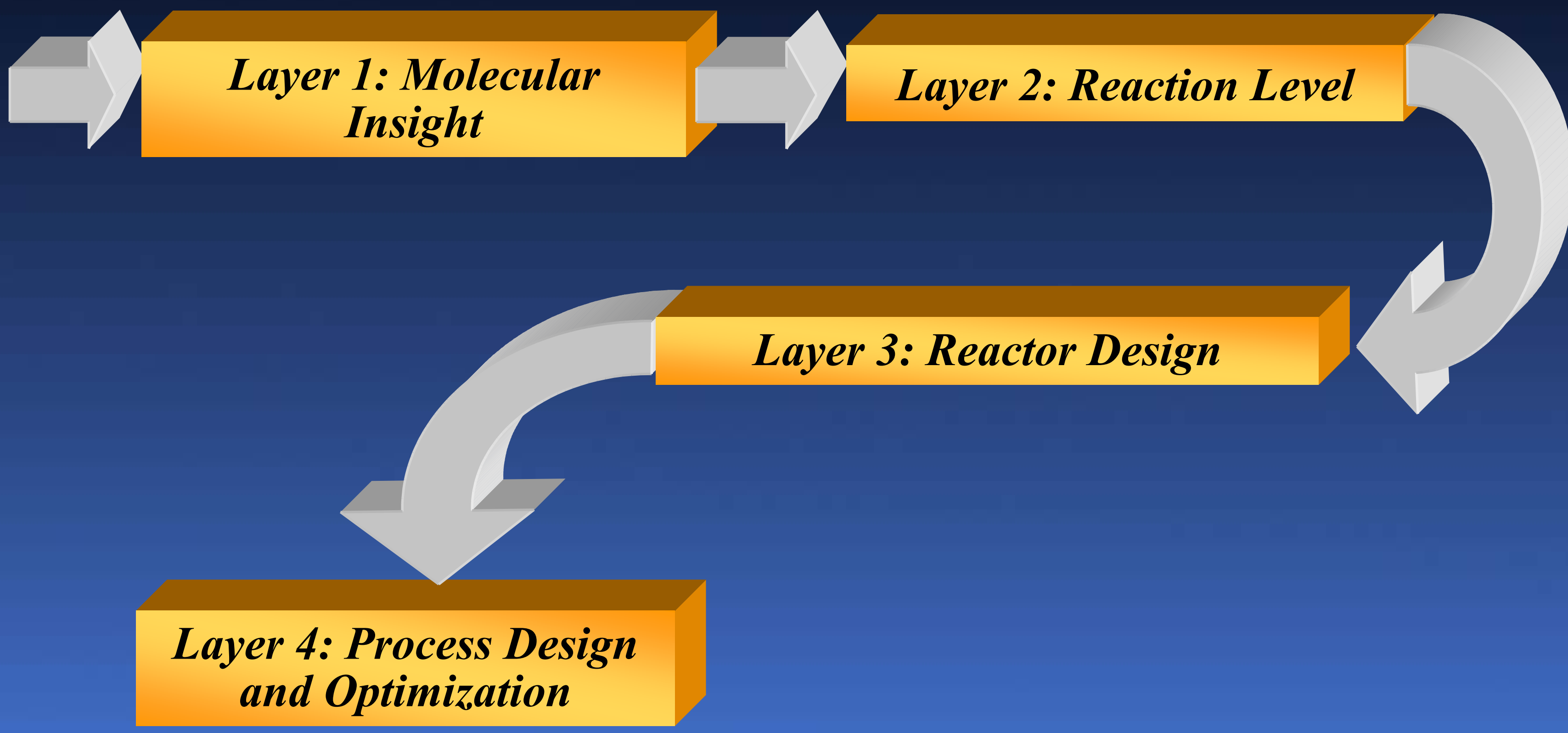


From Conoco's Sustainable Growth Report, May 2001

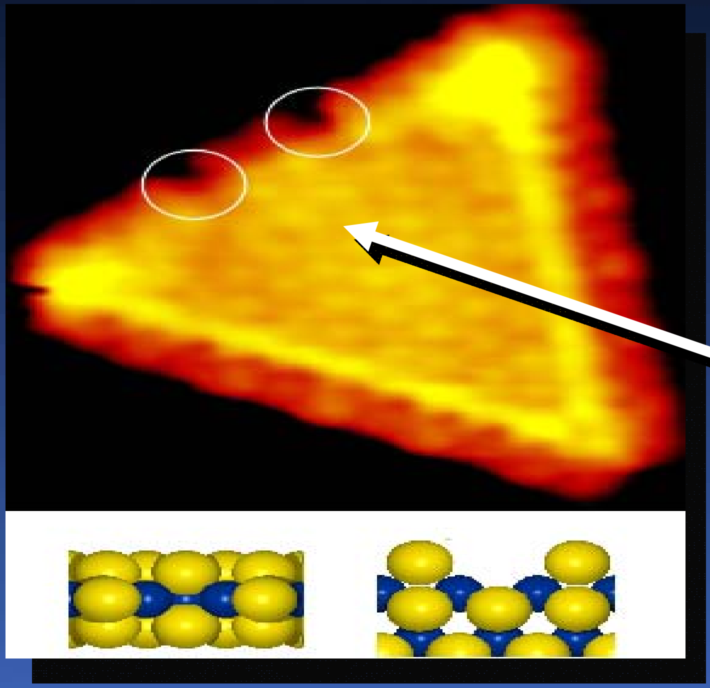
Outline

- Future Directions
- Fundamentals
  - Molecular level
  - Reactions and Catalysis
  - Reactor Selection and Design
  - Process Design and Optimization
- Conclusions

Knowledge Flow in Technology Delivery



Use of Computational Chemistry and STEM to Identify Active Sites



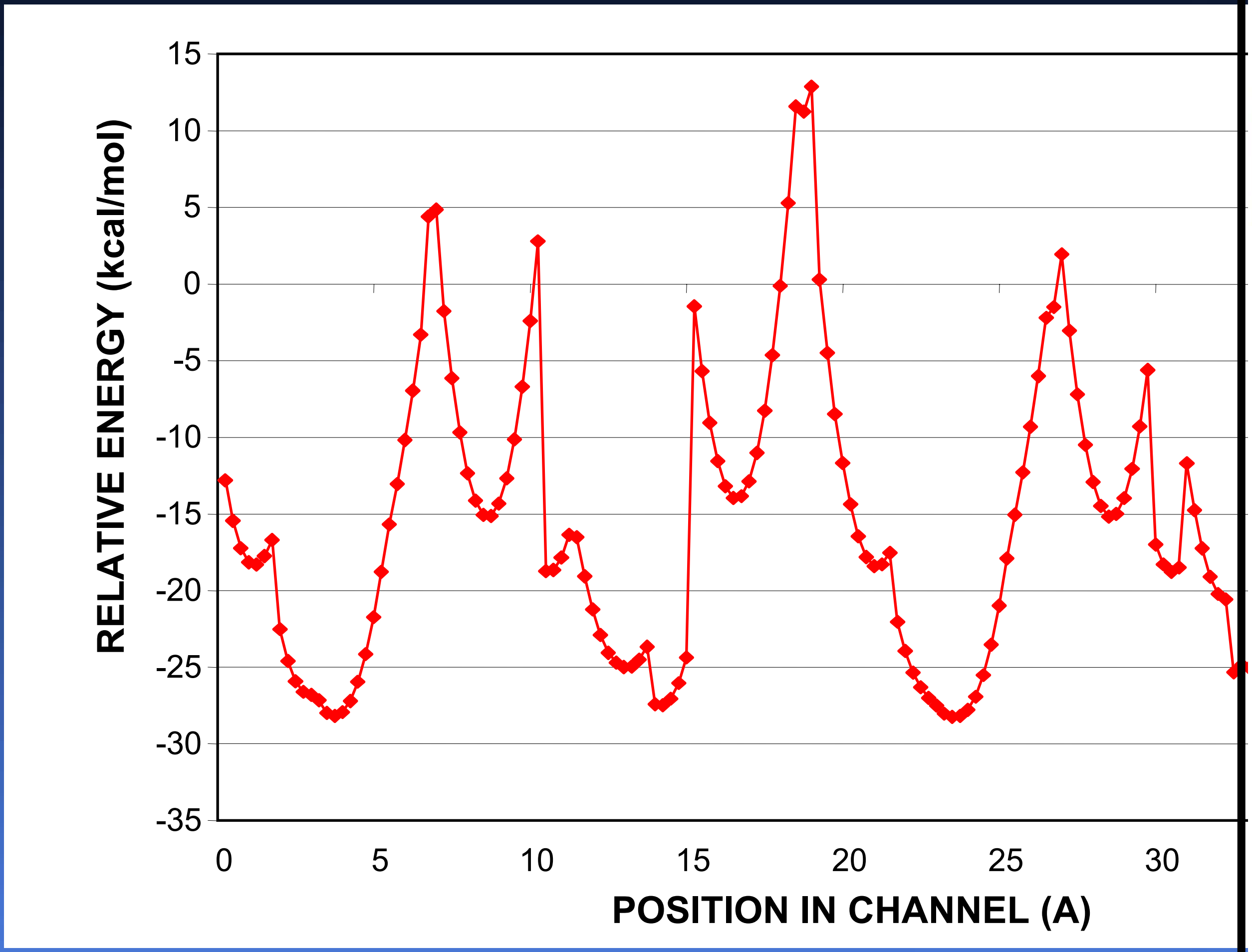
HDS activity is believed to take place on MoS_2 cluster edges. However, their coordination should make them inert ?

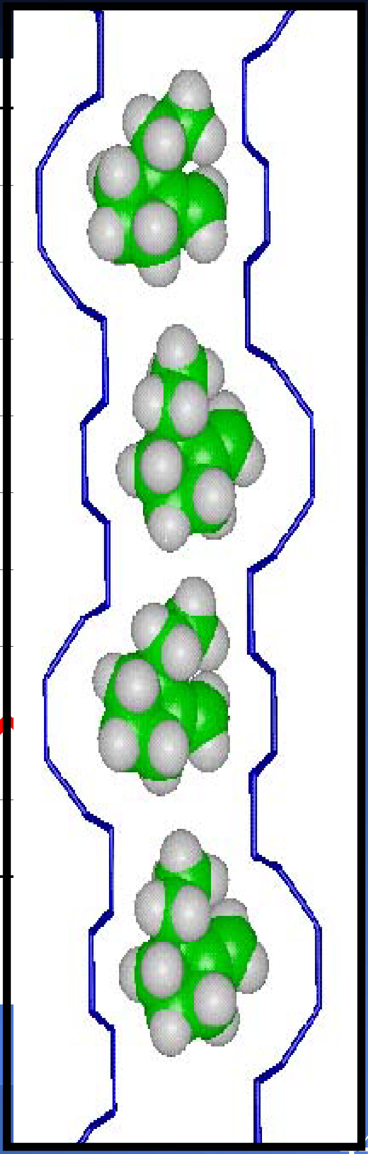
MoS_2 cluster reorganizes in the presence of atomic hydrogen, leading to sulfur vacancies, which are believed to be the active sites for HDS

The advent of DFT methods, fast computers and in-situ visualization techniques aids in understanding catalysis and designing next generation catalysts

S. Helveg et al., Phys. Rev. Lett., 84, 951 (2000)

Molecular Mechanics to Model Potential Energy Surface for Diffusion in Microporous Materials





Reaction Level : Temperature Scanning Reactor (TSR)

- Integral Microreactor
- Non-Steady-State Operation
- Special Methodology to Extract Reaction Rates
- Wide Range of Process Variables Studied in One Experiment

Original method revised substantially to allow for direct translation to conventional PP data

Source : Wojciechowski et al., USP 5593892, 5521095 and 5340745

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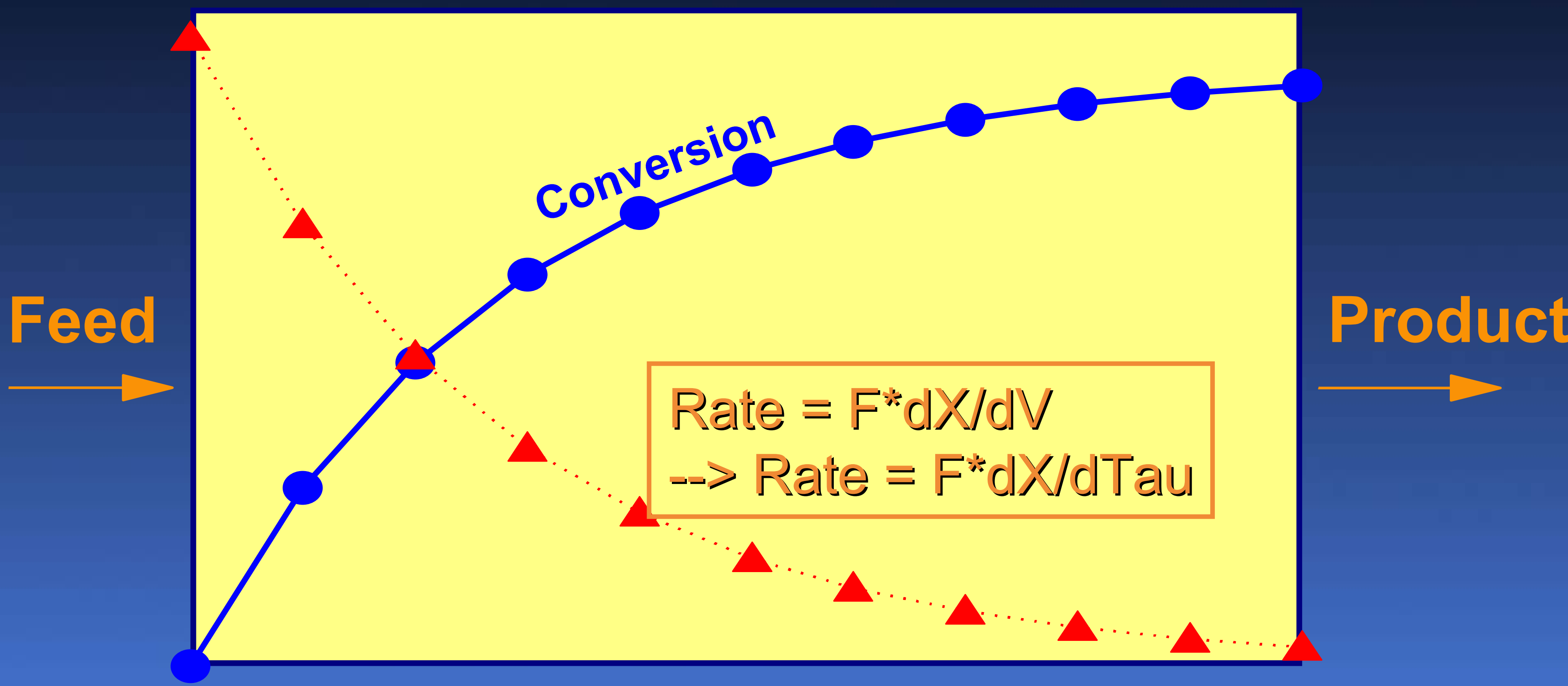
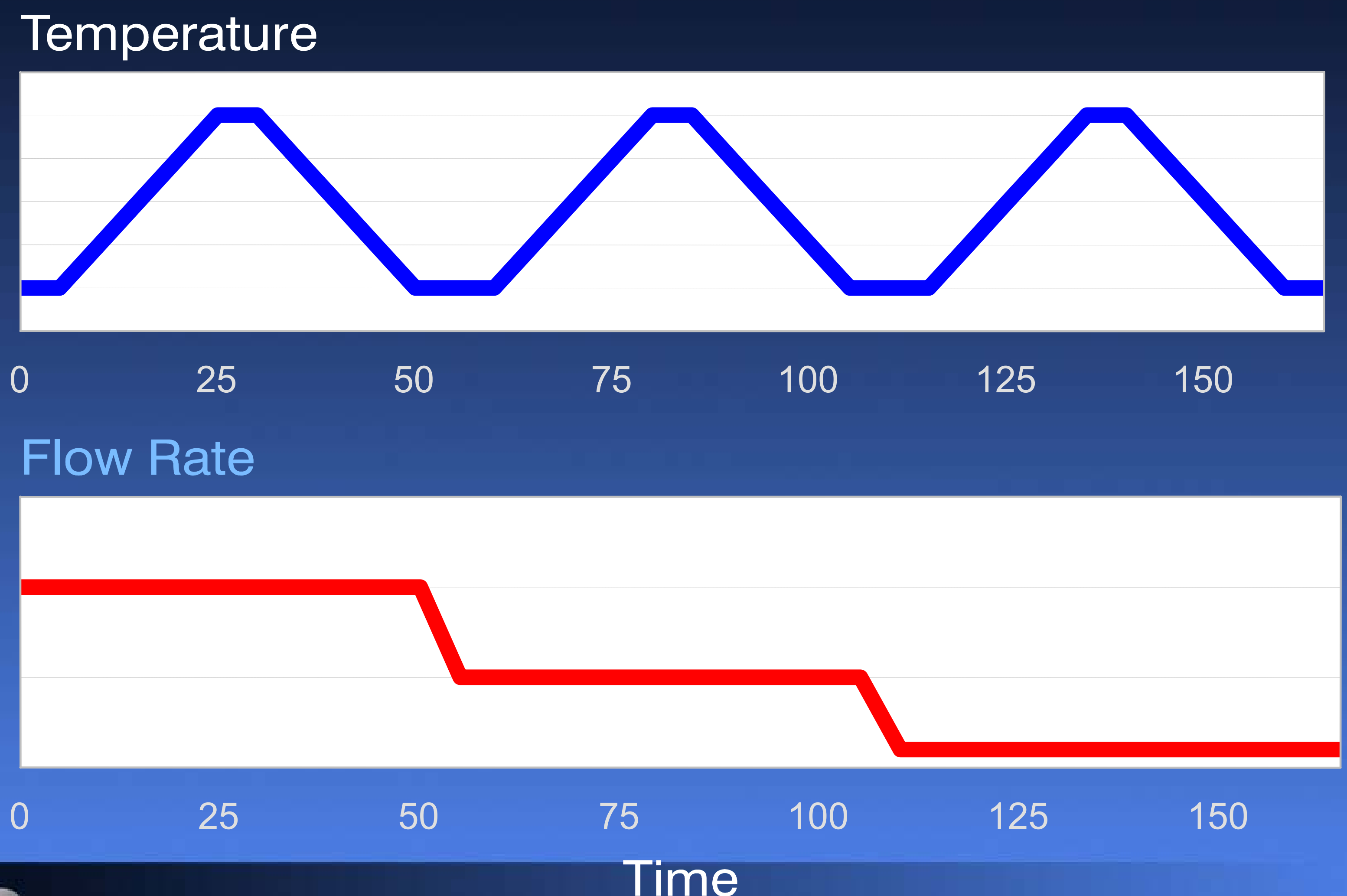
TSR methodology

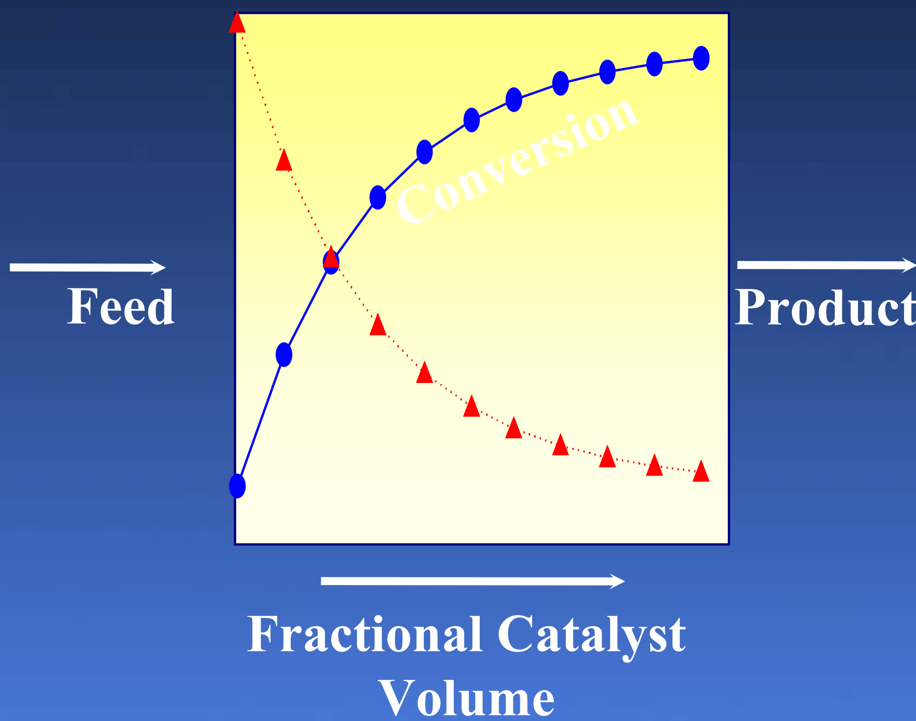


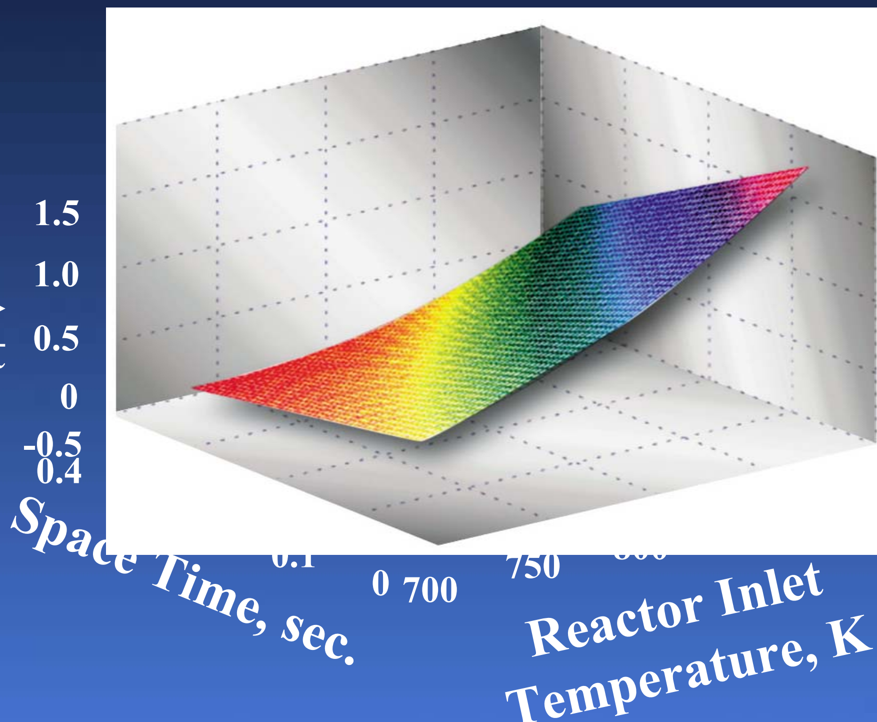
Catalyst Volume Mapped By Varying Space-Time

TSR : Experimental Protocol

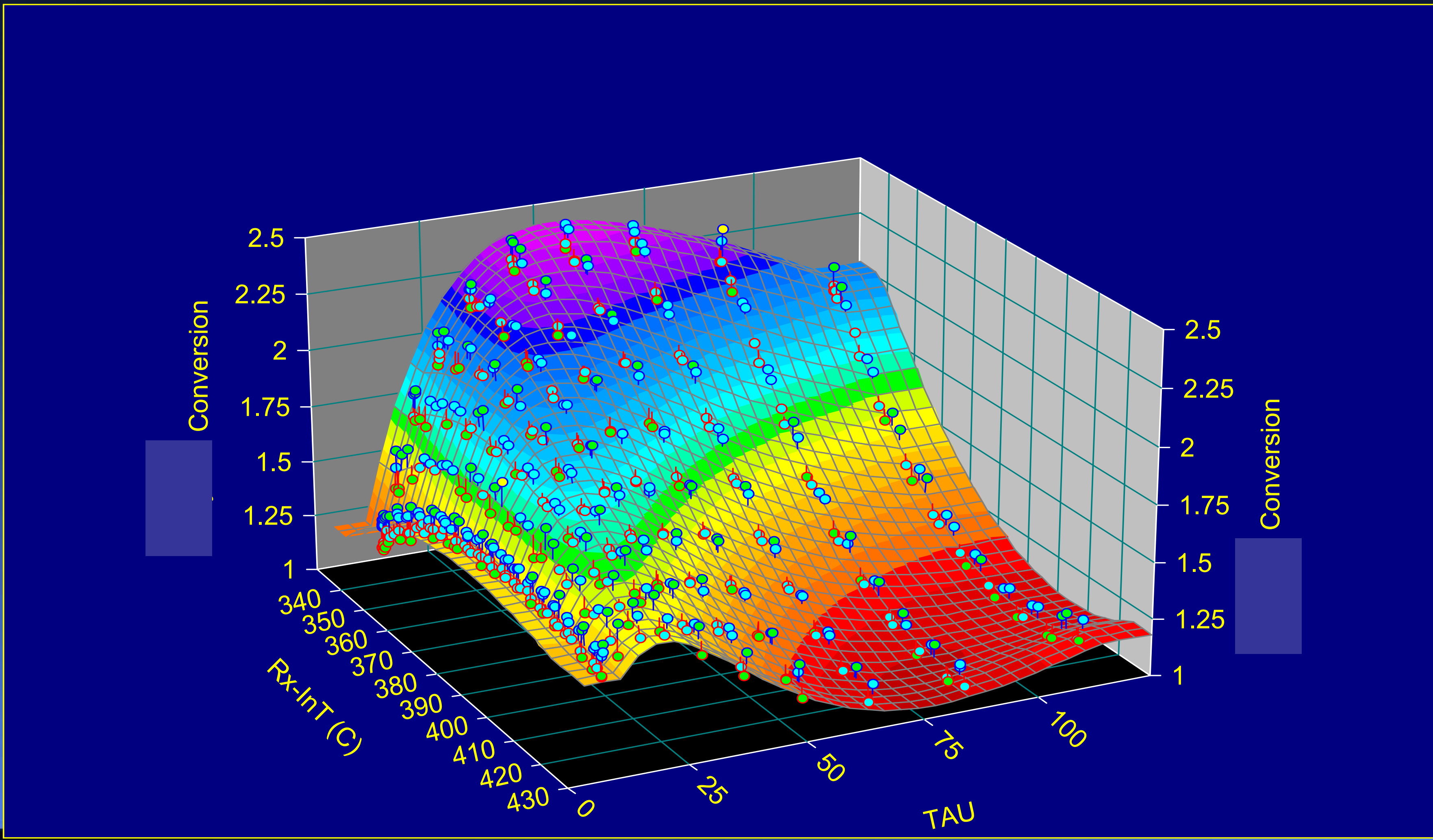


Many Pilot Plant Runs vs Single TSR Experiment

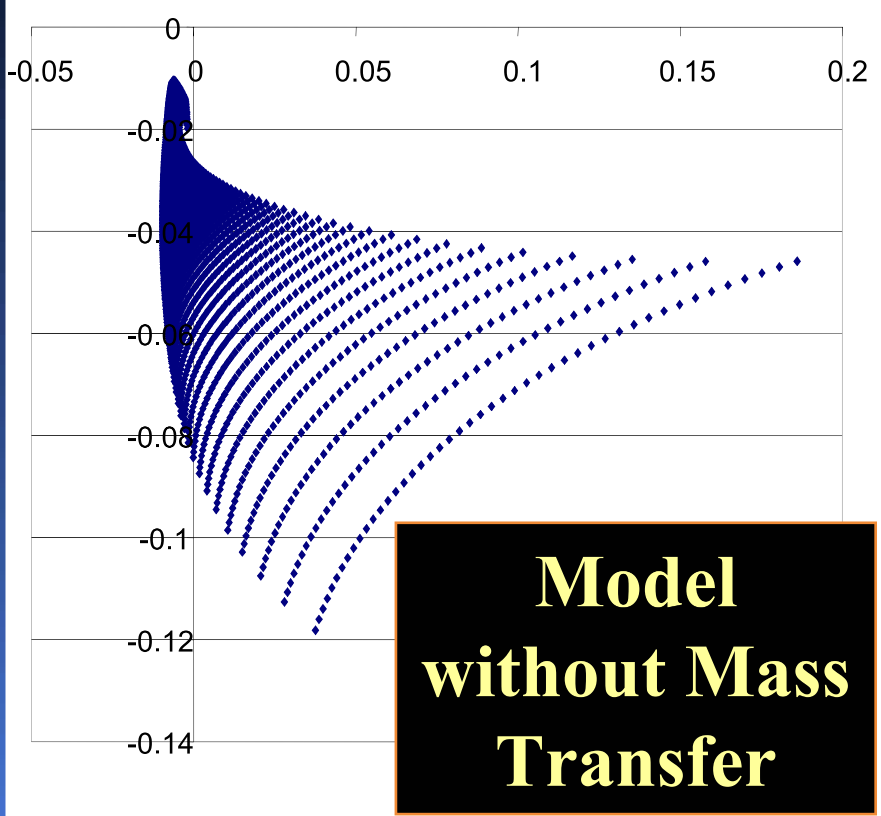


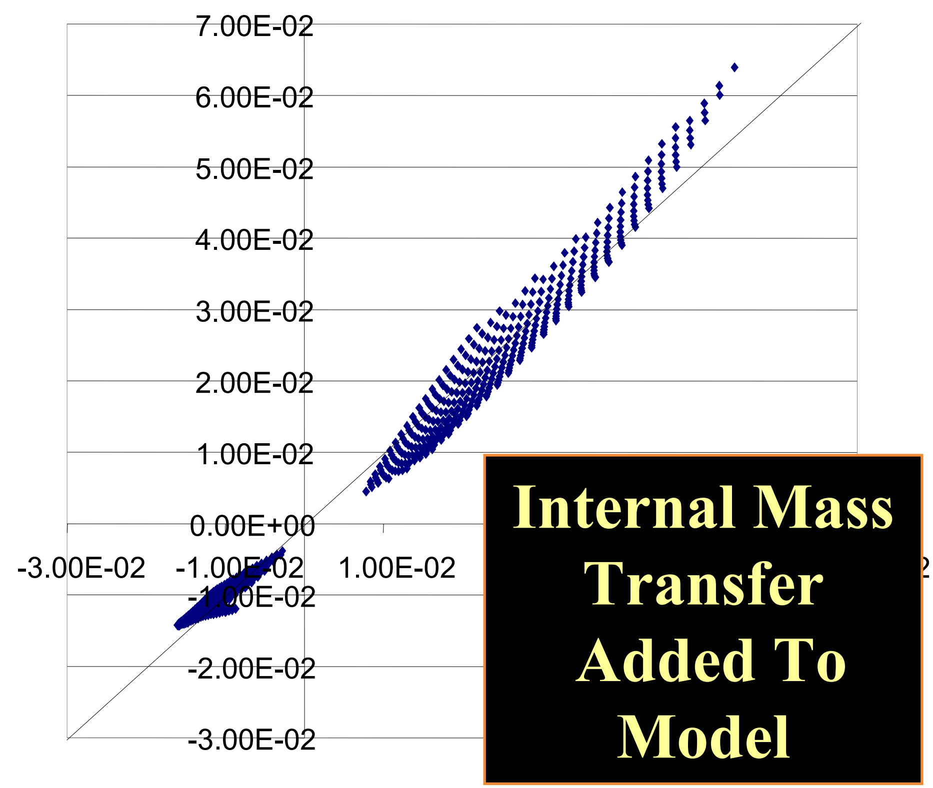


Conversion vs T and Tau



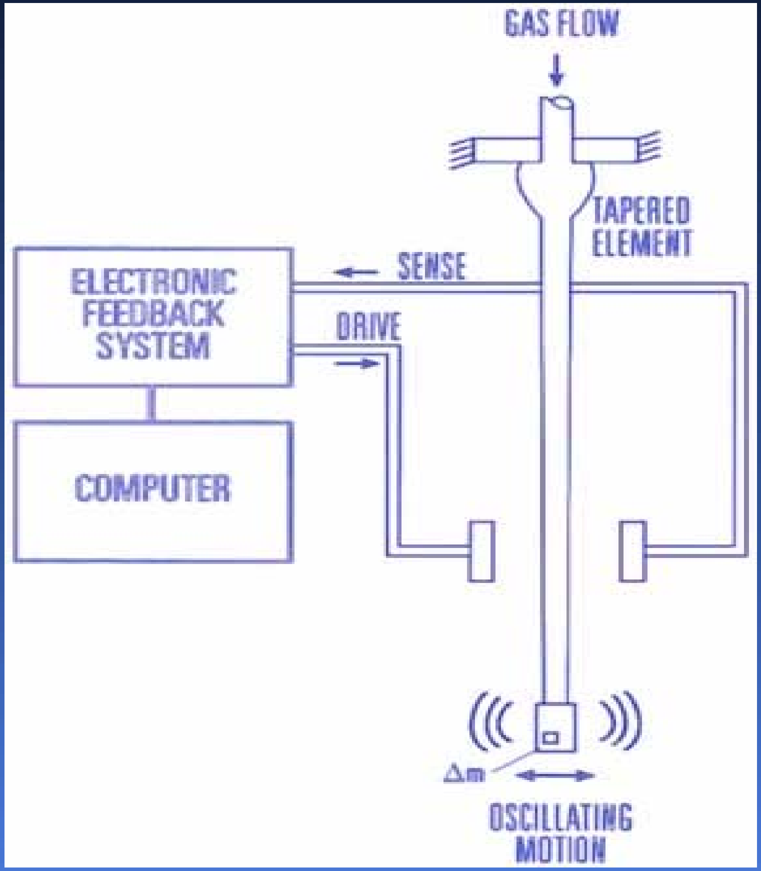
Typical Parity Plots for TSR data





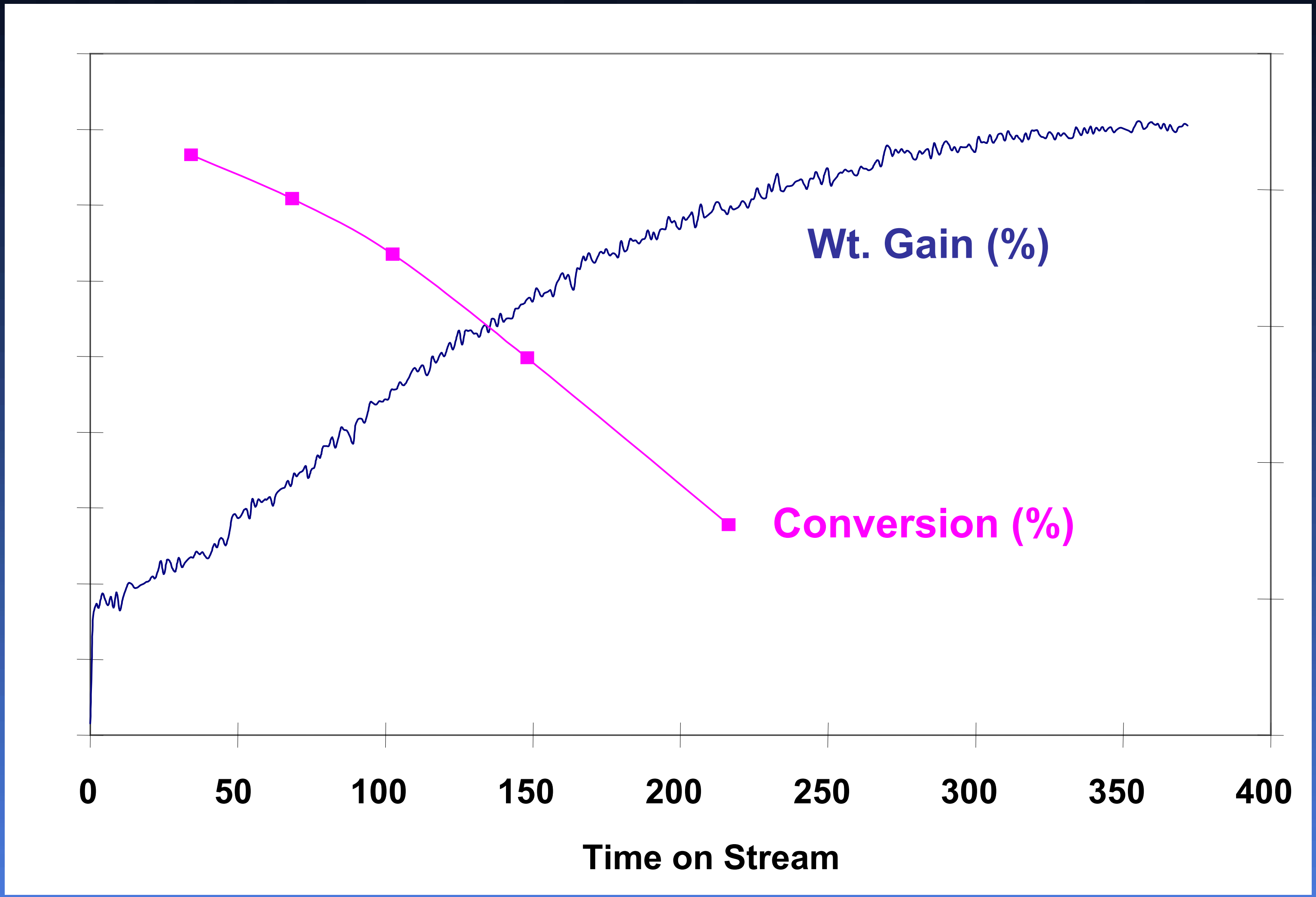
1400 data points

Studying Deactivation : TEOM

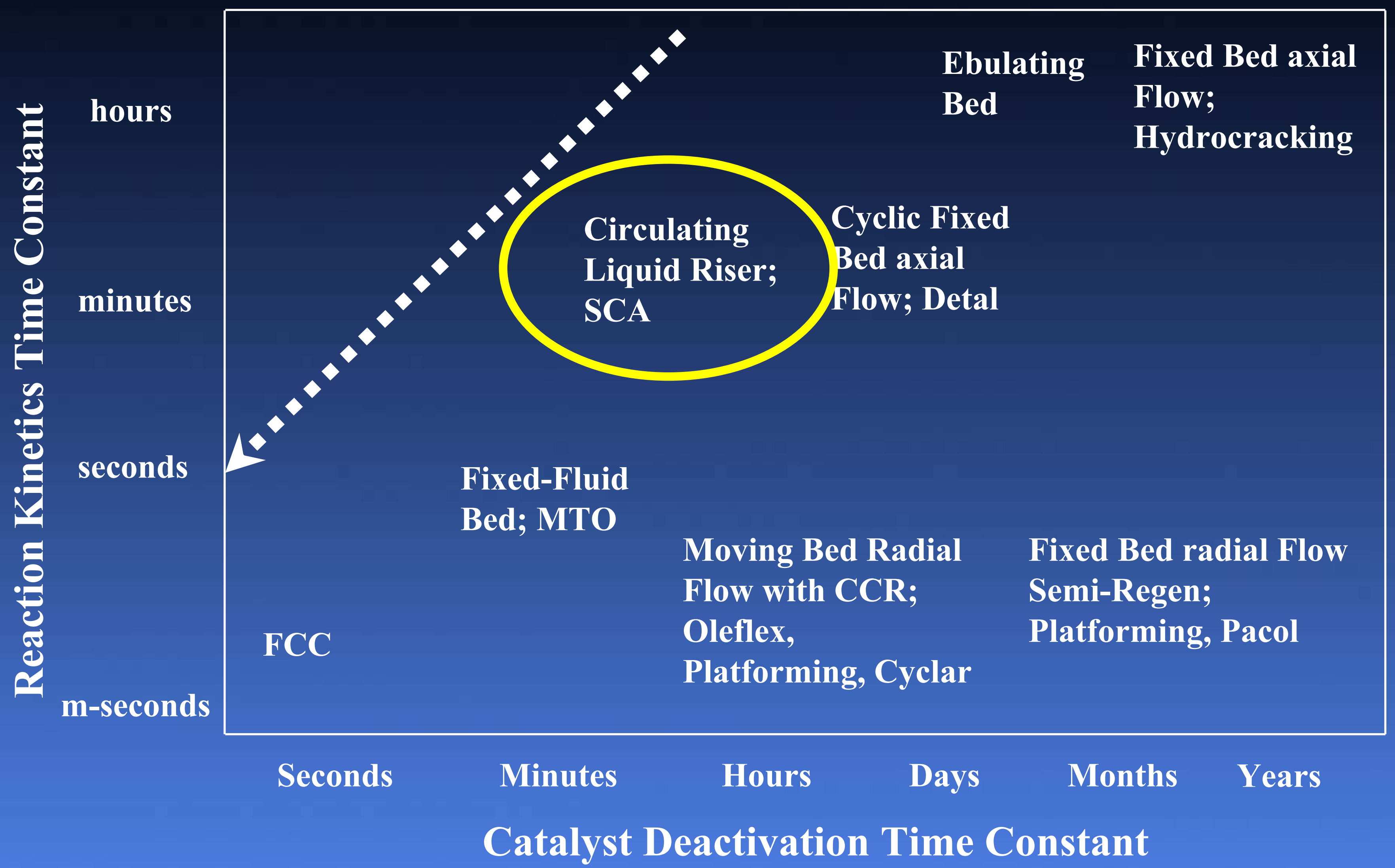


- Measure conversion, selectivity,and mass changes at process conditions
  - 800 psig
  - 600^{o}C
- Oscillating Reactor
  - Frequency related to mass

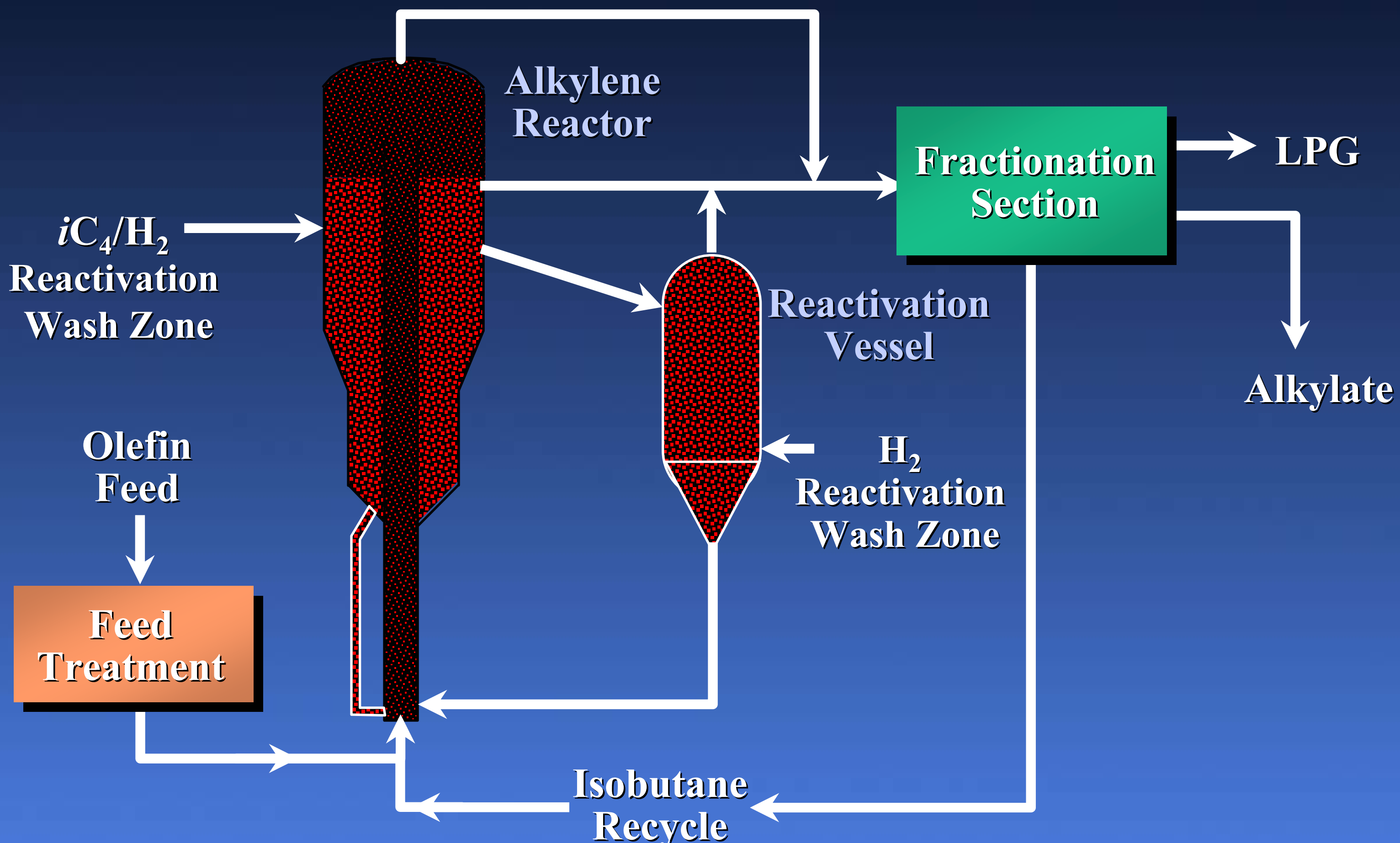
Typical TEOM Data



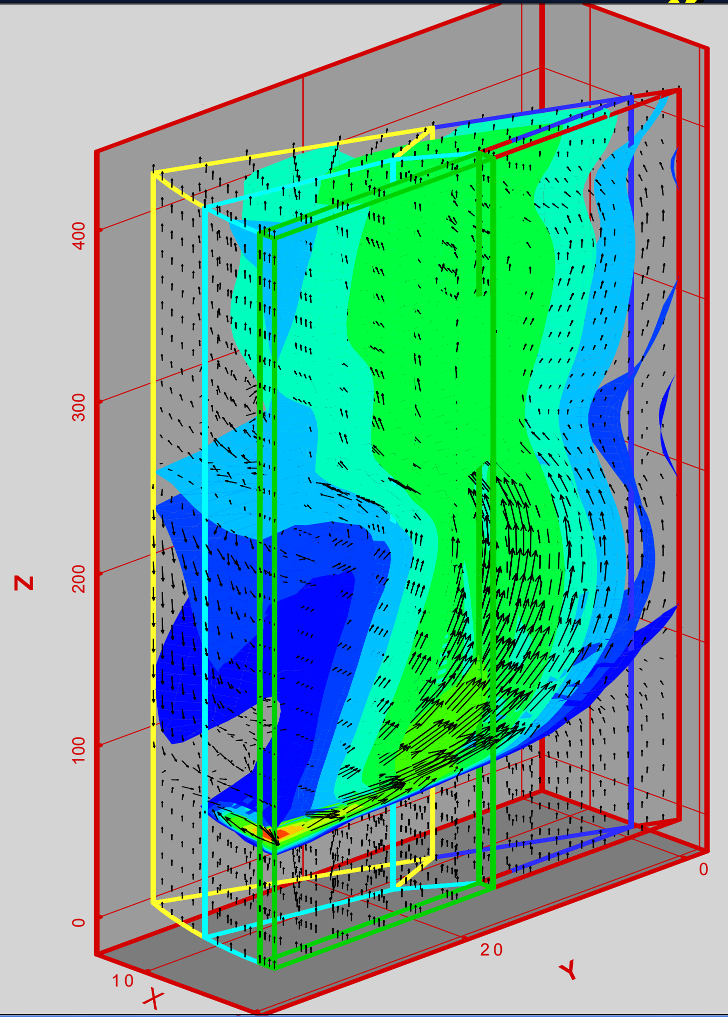
Reactors to suit every need



Alkylene Flow Scheme

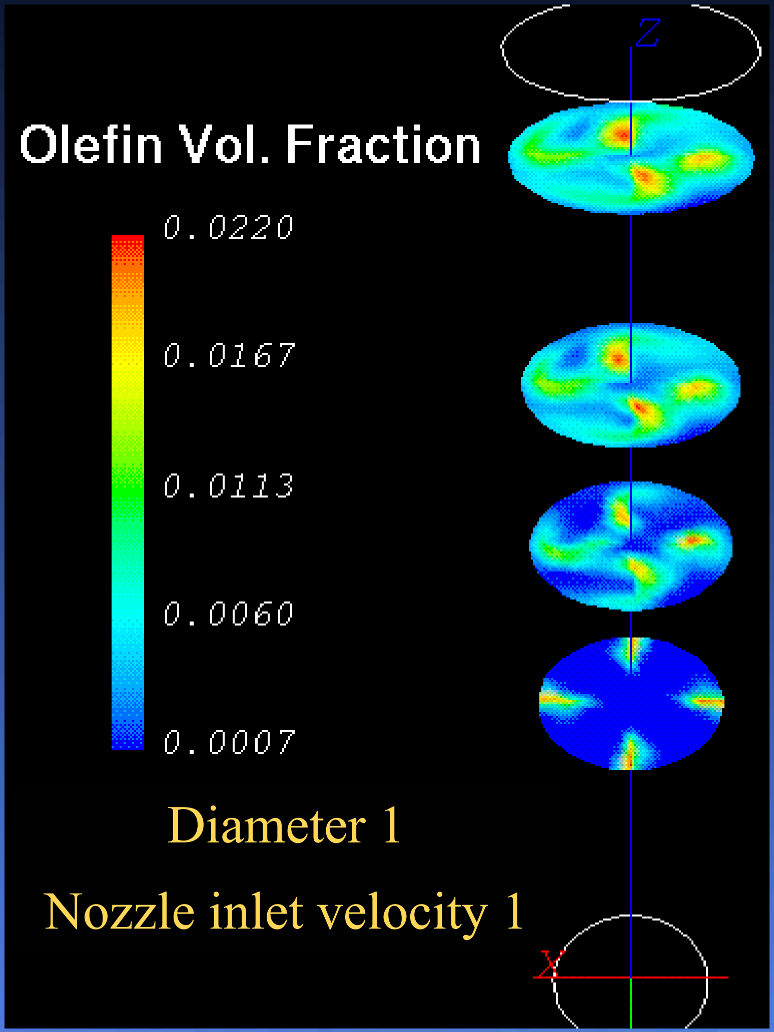


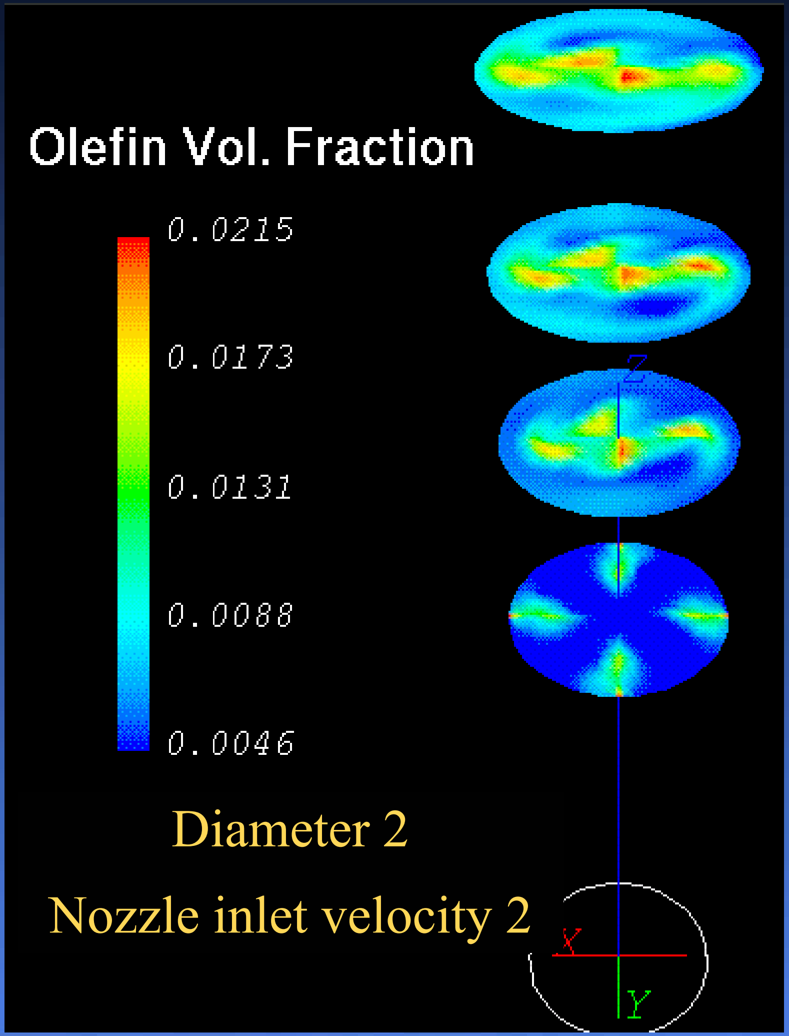
Simulated Flow Field for Alkylene Riser with Olefin Injection



Incorporated Alkylene kinetics to study the effect of poor mixing

Scale up of olefin injection ?

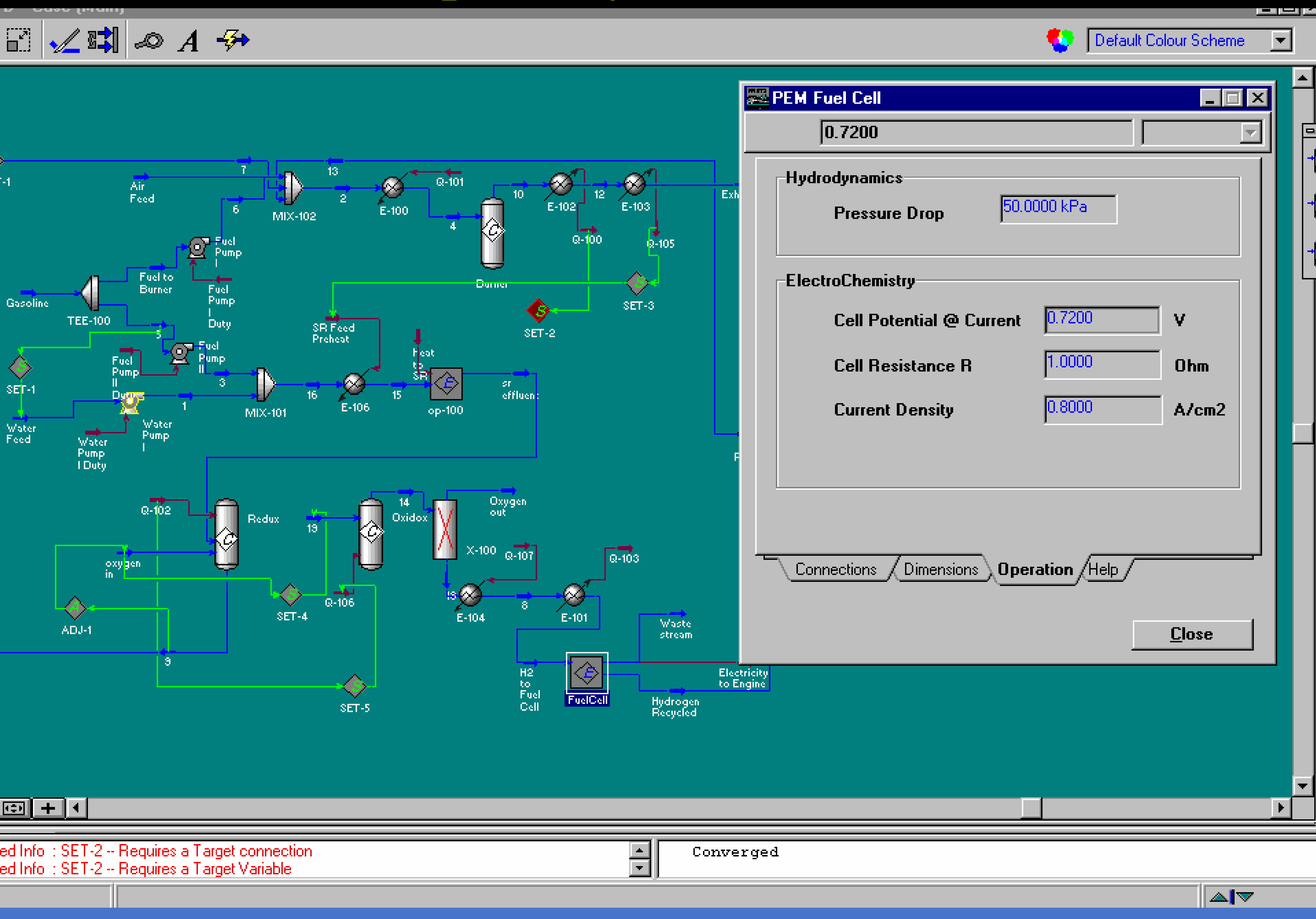




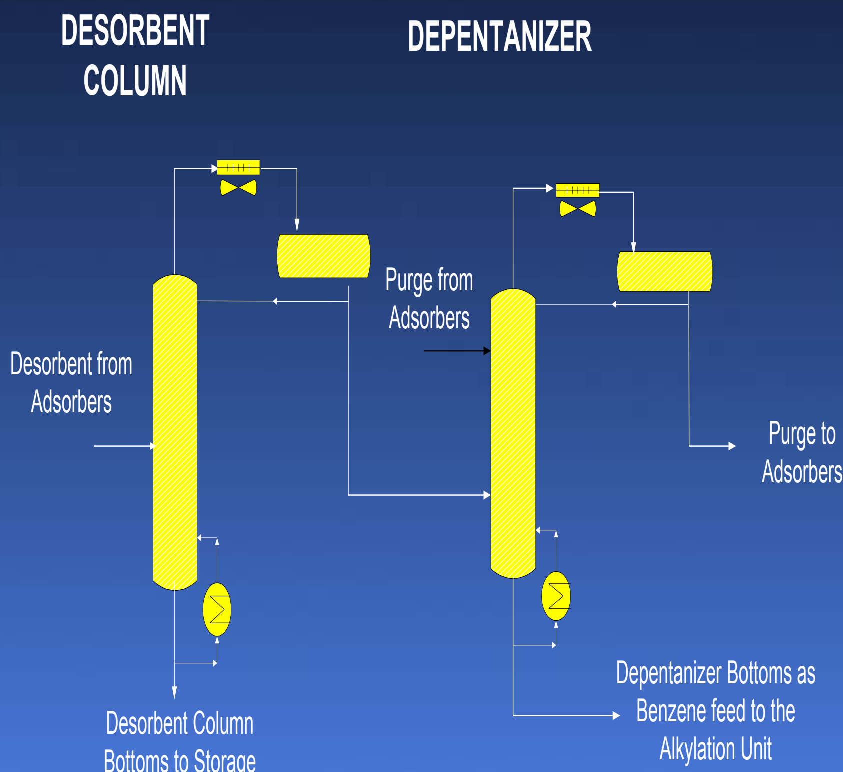
Alkylene modeling cont'd

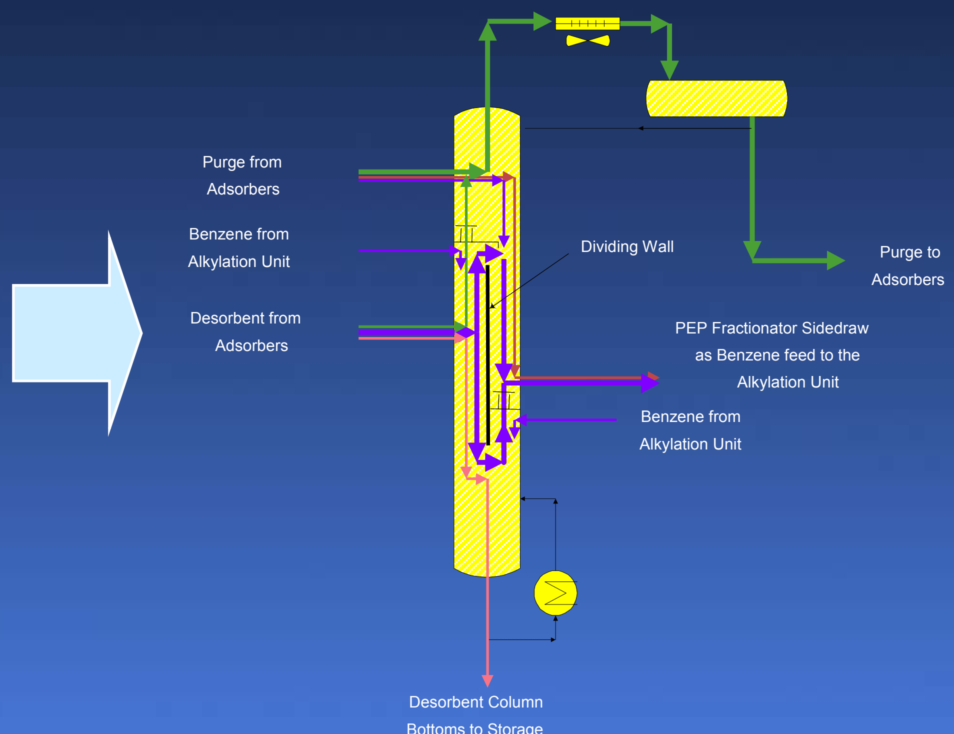
- Additional work on
  - Catalyst residence time in injection zones
  - Geometrical studies for disengagement vessel
  - Alkylate flushing from disengaged catalyst

Process Level : Proprietary Extensions in Flowsheets

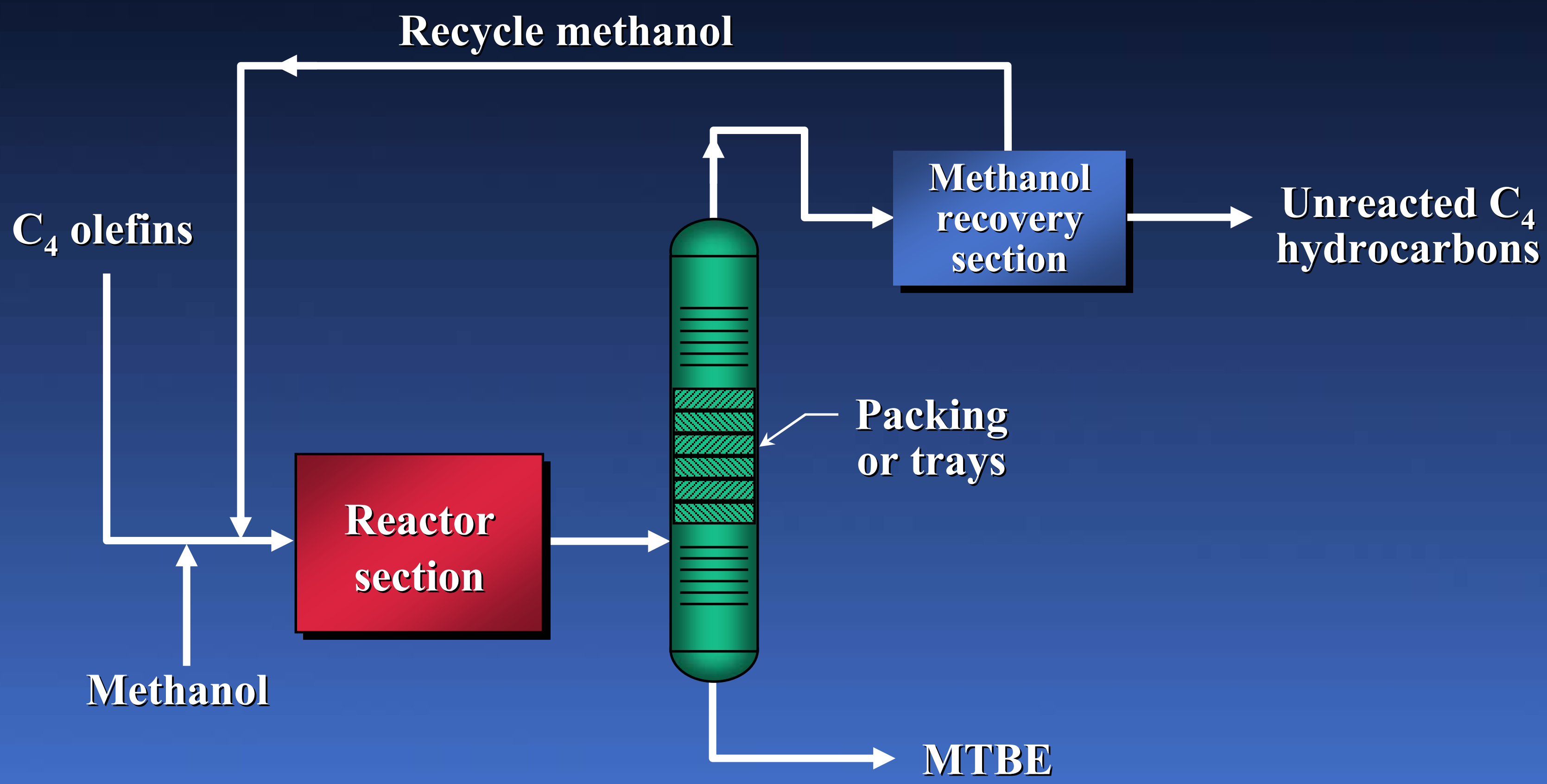


Overall Process Design: Separations

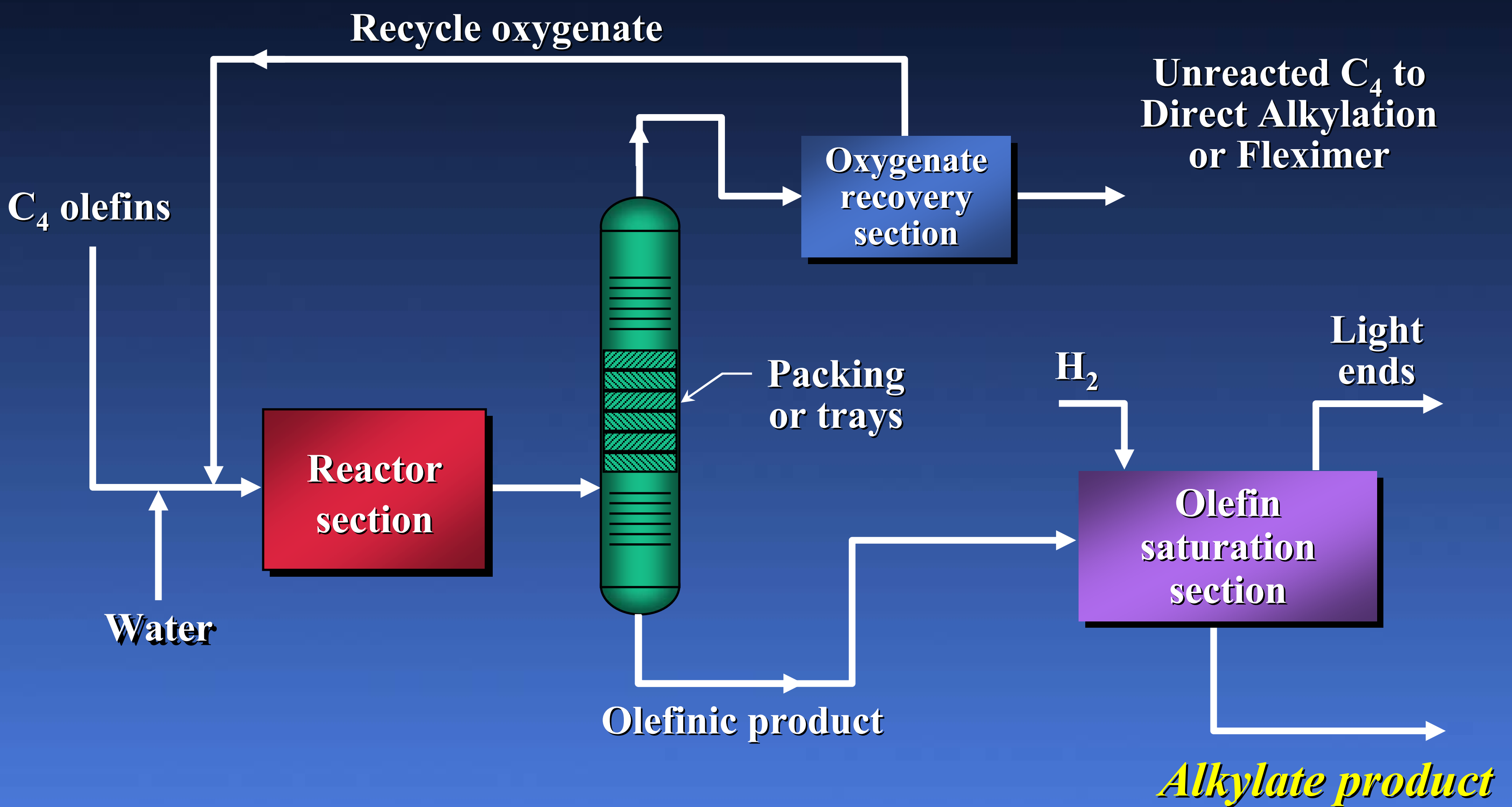




MTBE revamp


Recycle methanol
C_4 olefins
Methanol recovery section
Unreacted C_4 hydrocarbons
Packing or trays
Reactor section
Methanol
MTBE

MTBE revamp to InAlk with resin



Outline

- Future Directions
- Fundamentals
- Conclusions

Conclusions

- A new era in the processing industry
  - Gradual, rather than abrupt change over
  - New feed-stocks and new requirements require a new wave of innovation.
- Fundamentals
  - Almost established as the basis of technology development today
  - Critical for rapid innovation and optimization in the future

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