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
<table>
<thead>
<tr>
<th>Year</th>
<th>Prediction</th>
</tr>
</thead>
<tbody>
<tr>
<td>1876</td>
<td>“This ‘telephone’ has too many shortcomings to be seriously considered as a means of communication” <em>Western Union Memo</em></td>
</tr>
<tr>
<td>1895</td>
<td>“Heavier-than-air flying machines are impossible” <em>Lord Kelvin, President Royal Society</em></td>
</tr>
<tr>
<td>1920</td>
<td>“The wireless music box (radio) has no imaginable commercial value” <em>David Sarnoff’s Associates in response to his urgings for investments in the radio</em></td>
</tr>
<tr>
<td>1943</td>
<td>“I think there’s a world market for maybe five computers” <em>Thomas Watson, Chairman IBM</em></td>
</tr>
<tr>
<td>1949</td>
<td>“Computers in the future may weigh no more than 1.5 tons” <em>Popular Mechanics forecasting the relentless march of science.</em></td>
</tr>
<tr>
<td>1977</td>
<td>“There is no reason anyone would want a computer in their home” <em>Ken Olson, President, Chairman and Founder of Digital Equipment</em></td>
</tr>
</tbody>
</table>
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

Octane Barrel Capacity of FCC

New Reactor Concepts
Improved Reaction Systems
Octane Catalysts
Extended Riser
Zeolite Catalysts
Amorphous Catalysts

Octane Barrel Capacity of FCC

Theoretical Octane Barrels

Octane Barrels / 100 Barrels Feed


4,800 5,000 5,200 5,400 5,600 5,800 6,000 6,200

4,800 5,000 5,200 5,400 5,600 5,800 6,000 6,200
Trends in the Processing Industries

- Energy & Feedstocks
- Environmental Constraints
- Product Quality
- Sustainability
- Profitability
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 $\Delta T$, less volume
- Monolith catalysts – lower $\Delta T$, better mass tfr
- Micro-channel reactors – better mass tfr
- HiGee fractionation – better mass tfr

Increasing Commercial Acceptance
Process Intensification Potential

Propane Dehydrogenation

<table>
<thead>
<tr>
<th>Relative Intensity</th>
<th>Process Geometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>CURRENT</td>
<td>NO HYDRAULIC LIMITATION</td>
</tr>
<tr>
<td>3</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>ISO-THERMAL</td>
</tr>
<tr>
<td></td>
<td>22</td>
</tr>
<tr>
<td></td>
<td>CRUSHED CATALYST</td>
</tr>
<tr>
<td></td>
<td>36</td>
</tr>
<tr>
<td></td>
<td>LESS ATTENUATION</td>
</tr>
<tr>
<td></td>
<td>60</td>
</tr>
<tr>
<td>IDEAL PT CLUSTERS</td>
<td></td>
</tr>
</tbody>
</table>

Ideal PT Clusters
Trends in the Processing Industries

- Energy & Feedstocks
- Environmental Constraints
- Sustainability
- Product Quality
- Profitability

uop
### Replacing HF Alkylation

**Waste generated for world scale alkylate plant:**

<table>
<thead>
<tr>
<th>Material</th>
<th>Amount, MM lbs/yr</th>
<th>Cost, MM$/yr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alumina</td>
<td>9.8</td>
<td>5.9</td>
</tr>
<tr>
<td>KOH</td>
<td>3.9</td>
<td>2.0</td>
</tr>
<tr>
<td>Lime</td>
<td>5.9</td>
<td>1.9</td>
</tr>
<tr>
<td>HF Acid Makeup</td>
<td>33.2</td>
<td>23.4</td>
</tr>
<tr>
<td><strong>TOTAL</strong></td>
<td><strong>52.8</strong></td>
<td><strong>33.2</strong></td>
</tr>
</tbody>
</table>

- New solid acid catalyst, new reactor
  - Inherent safety, Lower waste
  - Lower capital
Trends in the Processing Industries

- Energy & Feedstocks
- Environmental Constraints
- Sustainability
- Profitability
- Product Quality
Availability of Oil?

Meadows, 1992, p. 133
WRI, 1996
Evolution of Price of Brent Crude Oil

IPE Brent Crude Oil Closing Price (begin July 1988)

IPE Brent Crude - Daily Closing in 12 previous months

copyright oilenergy.com, 2004
Evolution of Quality of Processed Crude Oil
Natural Gas as a Feedstock

**Indirect Conversion**
- Fischer-Tropsch
- MeOH + MTG
- Steam Reform / WGS
- MeOH Synthesis
- MeOH + MTO

**Direct Conversion**
- Combustion
- Cracking
- Aromatization
- Oxyhalogenation
- Coupling
- Direct POX

*Demonstrated or Existing*  *To Be Developed / Demonstrated*
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 $10^{18}$)

<table>
<thead>
<tr>
<th>H$_2$ Quantity</th>
<th>6x$10^{12}$ Nm$^3$ per year</th>
</tr>
</thead>
<tbody>
<tr>
<td>New Plants</td>
<td>7000 @ 100,000 Nm$^3$ per hour each</td>
</tr>
<tr>
<td>Asset Investment*</td>
<td>$1-3$ trillion ($10^{12}$)</td>
</tr>
</tbody>
</table>

* Includes H2 delivery assets
Evolution of Hydrogen Roadmap

<table>
<thead>
<tr>
<th>H₂ Function</th>
<th>Short Term</th>
<th>Medium Term</th>
<th>Long Term</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuel Quality Improvement</td>
<td>Fuel Enhancement</td>
<td>Primary Fuel</td>
<td></td>
</tr>
</tbody>
</table>


5 years | Time 10 - 20 years | >20 years

Central Distributed


Renewables

UOP 4221-46
A Polymer Electrolyte Membrane (PEM) Fuel Cell is a Reactive Membrane Process

- Anode Reaction: \[ H_2 \rightarrow 2H^+ + 2e^- \]
- Cathode Reaction: \[ \frac{1}{2} O_2 + 2H^+ + 2e^- \rightarrow H_2O \]
The MEA is a Membrane with Dispersed Pt Catalyst on Both Sides

Cross-Section of PEM Fuel Cell

- **Waste Gas**
- **O₂ / H₂O**
- **H₂ / H₂O**
- Gas Diffusion Electrode
- Electrocatalyst Layer
- Proton Exchange Membrane

- **H⁺**
- **e⁻**
- **Gas Diffusion Electrode**
- **Gas Diffusion Electrode**

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.
Higher current density is good, as this means less MEA area and lower cost.
But higher potential is also good, as this means higher efficiency
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

At low current density V decreases rapidly due to kinetics of ionization & polarization of double layer.
Fuel Cell i-V Curve

At medium current density, the potential (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, \( V = V_o - \eta_\Omega - \eta_{CT} - \eta_{MT} \)

\[ \eta_\Omega = i R_{int} \]

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

\[ i_o = nF k_1 C_R \exp \left( -\frac{U^0 - \alpha nF \Delta \varphi}{RT} \right) \]

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

\[ i_L = \frac{D nF C_b}{\delta} \]
**Fuel Cell Theory**

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\[
i_L = \frac{D nF C_b}{\delta}
\]

Depends on electrical resistance of membrane, electrodes, catalyst/electrode junctions, etc.
**Fuel Cell Theory**

Cell voltage, \( V = V_0 - \eta_\Omega - \eta_{CT} - \eta_{MT} \)

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Depends on intrinsic kinetics of charge transfer at the electrocatalyst
**Fuel Cell Theory**

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

\[
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\]

Depends on double layer polarization at the electrode/membrane interface.
Fuel Cell Theory

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Depends on mass transfer properties of electrocatalyst and stack design
Fuel Cell Theory

Cell voltage, \( V = V_0 - \eta_\Omega - \eta_{CT} - \eta_{MT} \)

\[
\eta_\Omega = i \mathcal{R}_{int}
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\eta_{CT} = - \frac{RT}{\alpha nF} \ln i_o + \frac{RT}{\alpha nF} \ln i
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\[
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\]

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

- 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

- Energy & Feedstocks
- Environmental Constraints
- Product Quality
- Profitability

Sustainability
A new set of criteria
Outline

- Future Directions
- Fundamentals
  - Molecular level
  - Reactions and Catalysis
  - Reactor Selection and Design
  - Process Design and Optimization
- Conclusions
Knowledge Flow in Technology Delivery

Layer 1: Molecular Insight

Layer 2: Reaction Level

Layer 3: Reactor Design

Layer 4: Process Design and Optimization
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.

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
**TSR methodology**

Catalyst Volume Mapped By Varying Space-Time

Conversion

Rate = \( F \times \frac{dX}{dV} \)

--> Rate = \( F \times \frac{dX}{d\tau} \)
TSR: Experimental Protocol

Temperature

Flow Rate

Time
Many Pilot Plant Runs vs Single TSR Experiment

Feed

Fractional Catalyst Volume

Conversion

Product

Space Time, sec.

Reactor Inlet Temperature, K

0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
700
750
800
850
900
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°C

- Oscillating Reactor
  - Frequency related to mass
Typical TEOM Data
Reactors to suit every need

- **FCC**
- **Fixed-Fluid Bed; MTO**
- **Cyclic Fixed Bed axial Flow; Detal**
- **Circulating Liquid Riser; SCA**
- **Fixed Bed axial Flow; Hydrocracking**

Reaction Kinetics Time Constant

- **m-seconds**
- **seconds**
- **minutes**
- **hours**

Catalyst Deactivation Time Constant

- **Seconds**
- **Minutes**
- **Hours**
- **Days**
- **Months**
- **Years**
Alkylene Flow Scheme

Alkylene Reactor

Fractionation Section

LPG

Alkylate

Feeder Treatment

Feed Treatment

Olefin Feed

Reactivation Wash Zone

$iC_4/H_2$

Fractionation Section

Reactivation Vessel

H$_2$

Reactivation Wash Zone

Isobutane Recycle
Simulated Flow Field for Alkylene Riser with Olefin Injection

Incorporated Alkylene kinetics to study the effect of poor mixing
Scale up of olefin injection?

Olefin Vol. Fraction

Diameter 1
Nozzle inlet velocity 1

Olefin Vol. Fraction

Diameter 2
Nozzle inlet velocity 2
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

LAB Complex PEP Dividing Wall Column
MTBE revamp

- **C₄ olefins**
- **Methanol**
- **Reactors section**
- **Recovery section**
- **Unreacted C₄ hydrocarbons**
- **MTBE**

Flowchart showing the process of MTBE revamp with the main steps being the conversion of C₄ olefins using methanol in the reactor section, followed by recovery and recycle of methanol.
MTBE revamp to InAlk with resin

C₄ olefins

Recycle oxygenate

Oxygenate recovery section

Unreacted C₄ to Direct Alkylation or Fleximer

Packing or trays

Olefinic product

H₂

Light ends

Alkylate product

Water

Olefin saturation section

Unreacted C₄ to Direct Alkylation or Fleximer

Olefinic product

Olefin saturation section

Olefin saturation section

Reactor section

Recycle oxygenate

Oxygenate recovery section

Unreacted C₄ to Direct Alkylation or Fleximer

Packing or trays

Olefinic product

H₂

Light ends

Alkylate product

Water
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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