Petrochemical Industry: 
Role of Innovations and Feedstock Availability

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and 
Lovraj Kumar Memorial Trust 

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Gurgaon, India on March 6, 2008

Vora International Process (VIP) Corp
Outline

- Introduction
- Technology Innovations and Feedstocks
  - Coal & Natural Gas
  - Aromatics
  - Olefins
- Summary

Vora International Process (VIP) Corp
Petrochemicals

There are three basic raw materials that make up major part of Petrochemical industry

1. Synthesis Gas from Coal or Natural Gas
   Hydrogen, Ammonia, Urea, Methanol, GTL/CTL and derivatives

2. Aromatics
   Benzene, Toluene and Xylenes (BTX) and its derivatives

3. Olefins
   Ethylene, Propylene and its derivatives
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Petrochemicals: Methane Derivatives

Coal Gasification

Natural Gas

LNG

Electricity

Steam Reforming, Partial Ox.

Synthesis Gas

FT

GTL Fuel

DME

Fuel

Ethylene Propylene

MTO

Liquid Fuel

MTG

Formaldehyde Acetic acid MTBE & Other Chemicals

Fuel

Methanol

Vora International Process (VIP) Corp
Coal & Natural Gas

- New investments and production for some products shifting where lower cost natural gas is available
- With high crude oil prices Coal is coming back
1. PT Bumi Resources interested coal liquefaction plant in Indonesia
2. Reliance Industries interested in CTL plant in India
3. Gail planning coal project in China
4. Yankuang Group’s CTL plant approved in China
5. China Coal to fund chemical projects from IPO
6. Sasol plans to build indirect CTL plant in China
7. Malaysia plans integrated gas-petrochemical project
8. Itera and Uralkhimost to build 600 KTA methanol plant in Russia
9. Shell proposes LNG/GTL project in Egypt
10. Mitsubishi gas Chemical kicks off 850 kta methanol plant in China
11. Dow invests in direct methane utilization technology

There are 5 to 10 weekly news items on coal and natural gas upgrading
Synthesis Gas :- Key to Conversion of Natural gas or Coal

- For Coal or natural gas to chemicals, synthesis gas is the key intermediate
- With continuous incremental improvements, basic technology is unchanged
Synthesis Gas :- Key to Conversion of Natural gas or Coal

Key Products:
- Methanol
- DME
- Gasoline
- MTBE
- Acetic Acid
- Formaldehyde
- MTG
- Linear paraffins
- Fisher-Tropsch GTL
- Hydrogen
- Ammonia
- Urea
- Ethylene, Propylene
- Wax
- Fuel
- Liquid Fuel
- Linear paraffins

Chemicals:
- Fuel
- Liquid Fuel
- Linear paraffins
- Fisher-Tropsch GTL
- Wax
- Linear paraffins
- Hydrogen
- Ammonia
- Urea
- Acetic Acid
- Formaldehyde
- MTBE
- Chemicals
Coal & Natural gas (Methane)

- Pre-1950s Coal based petrochemicals
  - In 1955 US Benzene production 70% from Coal and 30% from Petroleum

- Late 1950s - With Refining capacity increasing and development of catalytic reforming technology, naphtha becomes primary feedstock
# Methanol Plant Construction

<table>
<thead>
<tr>
<th></th>
<th>1980s</th>
<th>1990s</th>
<th>2000-2008</th>
</tr>
</thead>
<tbody>
<tr>
<td>NA-USA &amp; Canada</td>
<td>Venezuela</td>
<td>Trinidad &amp; Tobago</td>
<td></td>
</tr>
<tr>
<td>Russia-Siberia</td>
<td>Norway</td>
<td>Chile</td>
<td></td>
</tr>
<tr>
<td>Saudi Arabia</td>
<td>Iran</td>
<td>Iran</td>
<td></td>
</tr>
<tr>
<td>Malaysia</td>
<td>Qatar,</td>
<td>Qatar</td>
<td></td>
</tr>
<tr>
<td>Ukraine</td>
<td>Saudi Arabia</td>
<td>Oman</td>
<td></td>
</tr>
<tr>
<td>Libya</td>
<td>Trinidad</td>
<td>China-Coal</td>
<td></td>
</tr>
<tr>
<td>New Zealand</td>
<td>Libya</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Indonesia</td>
<td>Chile</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Indonesia</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Malaysia</td>
<td></td>
</tr>
</tbody>
</table>

- Pre 1980 production mostly in NA, WE and Japan
- Post 1980 new Construction mostly at advantaged natural gas sites
Methanol-Summary

- Industry shifted to locations where cost of natural gas is lower
- Single train production capacity increased from 2500 MTD to 5000 MTD, lowering cost of production per ton of methanol
- One or more new plants under design construction with capacity of up to 10000 MTD
Outline

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  - Coal & Natural Gas
  - Aromatics
  - Olefins
- Summary
Aromatics (BTX): Raw Material & Technology

- **1950s:** Development of liquid-liquid solvent extraction technology accelerates production and uses of BTX
  - 1952: Extraction by EG; Dow Chemical
  - 1960s: Extraction by Sulfolane; Shell

- **1960s:** Adsorptive separation of components, employing molecular sieves, by class and molecular shape developed
  - 1964: separation of normal paraffins from kerosene accelerated production of linear alkylbenzene (LAB)
  - Until 1970: paraxylene produced via Crystallization
  - 1971: Adsorptive Separation, UOP Parex Commercialized for pX production
## Petrochemicals: BTX Derivatives

<table>
<thead>
<tr>
<th>Benzene</th>
<th>Toluene</th>
<th>Xylene</th>
</tr>
</thead>
<tbody>
<tr>
<td>2007: 38 mm MTA</td>
<td>2007: 36 mm MTA</td>
<td>2007: 33 mm MTA</td>
</tr>
<tr>
<td>EB-Styrene</td>
<td>Toluene diisocynate</td>
<td>pX-PTA-Polyester</td>
</tr>
<tr>
<td>Cumene-Phenol-Phenolic resins</td>
<td>Motor Fuel-Octane Enhancement</td>
<td>oX-Phthalic anhydride</td>
</tr>
<tr>
<td>LAB</td>
<td>Solvent</td>
<td>mX-isophthalic acid</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>Conversion to Bz-pX</td>
<td></td>
</tr>
<tr>
<td>Cyclohexanol</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cyclohexanone</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Caprolectum-Nylon</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Adipicacid-Nylon</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- Bz: Benzene
- pX: Xylene
- oX/mX: Oxidation of Xylene
Aromatics (BTX)

- **Pre-1950s Coal based petrochemicals**
  - In 1955 US Benzene production 70 % from Coal and 30% from Petroleum

- **1950s - With Refining capacity increasing and development of catalytic reforming technology, naphtha becomes primary feedstock**

- **Two ways of deriving aromatics from naphtha**
  - Naphtha reforming
  - Pyrolysis of Naphtha
Worldwide \( p \)-Xylene Production Capacity

Increasing market share by adsorptive separation technology

Source: UOP
UOP Parex® Units
Increasing single train production Capacity
November 2006

- 77 Parex units had been brought on stream
- 14 Parex units under construction

Source: UOP
Benzene- Paraxylene Summary

- Sulfolane continues to be preferred solvent for aromatics extraction
- Adsorptive separation is preferred technology for paraxylene
- No radical shift foreseen in use of raw material or technology, Naphtha remains dominant raw material
Linear Alkylbenzene (LAB) 3.3 mm MTA production in 2007

- Kerosene → n-paraffins
  - Adsorptive separation

- n-paraffins → linear olefins + H2
  - Catalytic dehydrogenation

- Linear olefins + Benzene → LAB
  - HF Acid or Solid acid Catalysis
Continuous Renewal of LAB Technologies

Source: UOP
Linear Alkylbenzene (LAB) Summary

- Use of DDB began in 1940s, though superior in detergency, it is phased out due to poor biodegradability.

- All future growth of LAB is expected to use alkylation technology employing solid acid catalyst.

- Kerosene based paraffins may face competition from GTL based paraffins in future.
Outline

- Introduction

- Technology Innovations and Feedstocks
  - Coal & Natural Gas
  - Aromatics
  - Olefins

- Summary
## Petrochemicals: Olefins Derivatives

<table>
<thead>
<tr>
<th>Ethylene</th>
<th>Propylene</th>
<th>Butadiene</th>
</tr>
</thead>
<tbody>
<tr>
<td>2007: 120 mm MTA</td>
<td>2007: 70 mm MTA</td>
<td>2007: 10 mm MTA</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>Polypropylene</td>
<td>Polymers and copolymers with styrene and ACN</td>
</tr>
<tr>
<td>Ethylene Oxide-Ethylene glycols,</td>
<td>Acrylonitrile</td>
<td>ABS</td>
</tr>
<tr>
<td>Ethylene Oxide-Ethylene glycols,</td>
<td>Cumene-Phenol</td>
<td>nButene-MEK</td>
</tr>
<tr>
<td>EDC, VCM</td>
<td>Propylene Oxide</td>
<td>Isobutene-TBA</td>
</tr>
<tr>
<td>Vinyl acetate</td>
<td>Epichlorohydrin, Glycerol</td>
<td>Diisobutene, triisobutene &amp; polyisobutene</td>
</tr>
<tr>
<td>Ethyl alcohol acetaldehyde</td>
<td>Nonylphenol Tetramer</td>
<td>Isobutene-MTBE</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Motor Fuel Alkylate</td>
</tr>
</tbody>
</table>
**Ethylene: Raw Material & Technology**

<table>
<thead>
<tr>
<th>Raw Materials</th>
<th>Technology</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethane</td>
<td>Thermal Pyrolysis</td>
</tr>
<tr>
<td>Propane, butane</td>
<td></td>
</tr>
<tr>
<td>Naphtha, gas oil</td>
<td></td>
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</tbody>
</table>

Incremental innovations in thermal cracking and furnace design technology have allowed single train ethylene capacity to exceed 1 mm MT/Yr

Natural gas based or coal based Methanol to Olefins technology is on horizon
Ethylene

- Until 1980 primary production in NA, WE and Japan
- Choice of feedstock depended on region

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<thead>
<tr>
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</tr>
</thead>
<tbody>
<tr>
<td>Year</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C2-C4</td>
<td>65</td>
<td>75</td>
<td>70</td>
<td>4</td>
<td>8</td>
<td>10</td>
<td>2</td>
</tr>
<tr>
<td>Naphtha-GO</td>
<td>35</td>
<td>25</td>
<td>30</td>
<td>96</td>
<td>92</td>
<td>90</td>
<td>98</td>
</tr>
</tbody>
</table>

- NA more ethane based
- WE and Japan Naphtha based

- Expansion of ethylene production in ME promotes more ethane based crackers
## Middle east Ethylene Capacity

<table>
<thead>
<tr>
<th>Year</th>
<th>MTA</th>
</tr>
</thead>
<tbody>
<tr>
<td>2000</td>
<td>7</td>
</tr>
<tr>
<td>2004</td>
<td>11</td>
</tr>
<tr>
<td>2008</td>
<td>18</td>
</tr>
<tr>
<td>2012</td>
<td>35</td>
</tr>
</tbody>
</table>


- Ethylene produced from Ethane in ME has on average 250 to 400 $/MT production cost advantage over NA/WE Europe production.
Ethylene Supply – Global View

2006 Supply (Steam Crackers)

- Naphtha 52%
- Ethane 29%
- Propane 8%
- Butane 4%
- Gas Oil 5%
- Others 2%

Incremental Supply

- Non-ethane
- Ethane
- Current Base

Source: CMAI 2007

- Production from ethane crackers will increase
- Non-ethane sources of ethylene are needed to meet the demand
Propylene Supply – Global View

2006 Supply
(Polymer & Chemical Grades)

- PDH = Propane Dehydrogenation
- Metath. = Metathesis
- OC = Olefin Cracking
- MTO = Methanol-to-Olefins

On-purpose propylene = PDH + Metath. + OC + MTO

Substantially more propylene will come from “on-purpose propylene” technologies

Incremental Supply

- On-purpose propylene
- FCC Refineries
- Steam Crackers
- Current Base
- Demand

Source: CMAI 2007
PDH Capacity Growth

- Installed Capacity
- Size of New Units

Capacity, MM MTA

Unit Size, kMTA


UOP 4824D-06
Zeolite-catalyzed MeOH conversion

1975 – Mobil Oil discloses ZSM-5 catalyst for conversion of methanol to gasoline (MTG)

\[ 2 \text{CH}_3\text{OH} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{O-CH}_3 - \text{H}_2\text{O} \]

Isoparaffins
Aromatics
C\text{6+} olefins

C\text{2- C5} olefins

Chang, Silvestri, and Smith, US 3894103 and 3928483
Zeolite-catalyzed MeOH conversion

1977 – Mobil Oil discloses the use of various small pore zeolites for converting methanol to olefins (MTO)

– $C_2$–$C_4$ olefin concentration < 60% at 100% conversion
– Olefin fraction increases as conversion decreases

Chang, Lang, and Silvestri, US 4062905
Zeolite-catalyzed MeOH conversion

- 1982 – Edie Flanigen and her associates at Union Carbide announce discovery of silico aluminum phosphate molecular sieves. Flanigen and her group became part of UOP upon merger of CAPS Division of UCC with UOP
- SAPO-34 shows remarkable selectivity for conversion of methanol to light olefins
- \( C_2-C_4 \) olefin concentration < 85% at 100% conversion
Structures of SAPO-34 and ZSM-5

- **SAPO-34**
  - Structures of SAPO-34 and ZSM-5
  - Small Pore
  - Weak Acid Sites
  - Medium Pore
  - Strong Acid Sites

- **ZSM-5**
  - Structures of SAPO-34 and ZSM-5
  - Small Pore
  - Weak Acid Sites
  - Medium Pore
  - Strong Acid Sites

Source: UOP
Product Yields from MeOH: SAPO-34 and ZSM-5 Catalysts

SAPO-34 Catalyst: Once through C2= + C3= yield of 80%
ZSM-5 Catalyst: Once through C2= + C3= yield of 50%

Source: UOP
MTO Capacity Growth

- Installed Capacity
- Size of New Units

Capacity, MM MTA
Unit Size, kMTA

Ethylene-Propylene Summary

- ME becomes a major player: China, India growing as well
- Advantaged ethane supply in ME is limited
- Coal or natural gas based Methanol will be a new raw material source for ethylene and propylene
- Naphtha cracker and refinery FCC units will continue to be major source for propylene
- Advantaged propane feed stock will promote PDH at selective locations
- In future, natural gas based MTO projects at advantaged NG locations (ME, USSR..) may give tough competition to naphtha based projects.
Value of Products Produced from 1MM BTU of Natural Gas

Minimum of $4 per mmBTU differential is needed for NG to delivered LNG
## Stranded Gas Monetization Options

(for world-scale capacities with $2 to 6 billion investment)

<table>
<thead>
<tr>
<th>Monetization route</th>
<th>Worldscale economic capacity</th>
<th>Gas needed mm SCMD</th>
<th>30 Years Consumption billion SCM</th>
</tr>
</thead>
<tbody>
<tr>
<td>LNG</td>
<td>5 MM MTA LNG</td>
<td>22.2</td>
<td>222</td>
</tr>
<tr>
<td>GTL</td>
<td>100,000 BPD F-T Liquids</td>
<td>26.8</td>
<td>268</td>
</tr>
<tr>
<td>GTP</td>
<td>1,000,000 MTA PE + PP</td>
<td>7.5</td>
<td>75</td>
</tr>
</tbody>
</table>

LNG and GTL are suitable for only the largest gas fields
GTP can be implemented on many more gas fields
World’s gas fields by size

Number of Fields

% of world’s gas fields

- Large Fields = 13%

Total = 4,448 Fields

Source: Oil & Gas Journal
Why is Methanol Attractive?

- Readily synthesized on a large scale (current largest unit is 5000 MTD, 10,000 MTD under design)
- Transportable liquid fuel
- Has high energy density

<table>
<thead>
<tr>
<th></th>
<th>$H_2$ gas</th>
<th>Methane gas</th>
<th>DME gas</th>
<th>Methanol liquid</th>
<th>Naphtha liquid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kcal/M³</td>
<td>2400</td>
<td>8600</td>
<td>14200</td>
<td>3.97x10⁶</td>
<td>8.2x10⁶</td>
</tr>
<tr>
<td>@ 1 atm.</td>
<td>@ 25°C</td>
<td></td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

LNG Transportation Cost about $150-200/MT
Methanol Transportation Cost $10-20/MT
Advances in Methanol Technology

- Significant advances have taken place in mega methanol projects
  - First 5000 MTD methanol plant in operation in Trinidad since July 2004
  - 7500 MTD plant for Nigeria in design
  - 10 to 15000 MTD plants for Qatar in planning

- Cost of methanol production has come down significantly

\[
100 \$ / MT \text{ MeOH} = 229 \$ / MT \text{ HC Equiv.} \\
150 \$ / MT \text{ MeOH} = 343 \$ / MT \text{ HC Equiv.}
\]
## Methanol Plant Closure

<table>
<thead>
<tr>
<th>1990-2004</th>
<th>2005-2007 Closure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Japan 100%</td>
<td>Beaumont, USA 850</td>
</tr>
<tr>
<td>Norway 100%</td>
<td>Celanese, Bishop, USA 500</td>
</tr>
<tr>
<td>Korea 100%</td>
<td>Celanese, Clear Lake, USA 600</td>
</tr>
<tr>
<td>Italy 100%</td>
<td>Methanex, Kitimat, Canada 520</td>
</tr>
<tr>
<td>Spain 100%</td>
<td>Edmonton, Canada 800</td>
</tr>
<tr>
<td>France 100%</td>
<td>Pemex, Mexico 180</td>
</tr>
<tr>
<td>USA Part of it</td>
<td>Methanor, Netherland 1000</td>
</tr>
<tr>
<td>Canada Part of it</td>
<td>Methanex, New Zealand 700</td>
</tr>
<tr>
<td>Total</td>
<td>5150</td>
</tr>
</tbody>
</table>

Source: 2007 CMAI World Methanol Conf.
Why is Methanol Attractive?

- NG to LNG Delivered C efficiency about 85-90%
- NG to Methanol C efficiency about 70-80%
- LNG Transportation Cost about $150-200/MT
- Methanol Transportation Cost $10-20/MT
Gas to Polymer/Olefin Scenarios

Remote Gas Production

*Integrated GTP*
- Methanol Plant
- MTO Plant
- Polyolefin Plant

*Segregated GTP*
- Methanol Plant
- MTO Plant
- Polyolefin Plant

Polyolefin Markets
Patent Activity in USA

Syngas Conversion

- Syngas to MeOH
- Syngas to C2+ alcohol
- Syngas to FT Liquid
- MTO + MTG

# US Patents

Year

Overall Summary

- New application for production of light olefins will accelerate growth
- Significant Patent activity for Methanol to Olefins
- Though research continues in direct conversion of methane, no breakthrough on horizon
Overall Summary

- Time and time again, technology breakthrough has made major impact on industry.

- Industry always looks at availability of lower cost raw material or shifts to where they are

- No major changes expected in BTX or LAB production technologies

- As happened to the methanol industry, Olefins industry is poised for another change to come

- Natural gas based ethylene and propylene via MTO will dominate future new capacity

- Methanol will become a bigger and more important industry
Acknowledgement

My thanks to UOP and UOP colleagues for providing me updates on UOP processes
Q&A