Petrochemical Industry:
Role of Innovations and Feedstock Availability

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and
Lovraj Kumar Memorial Trust

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Outline

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

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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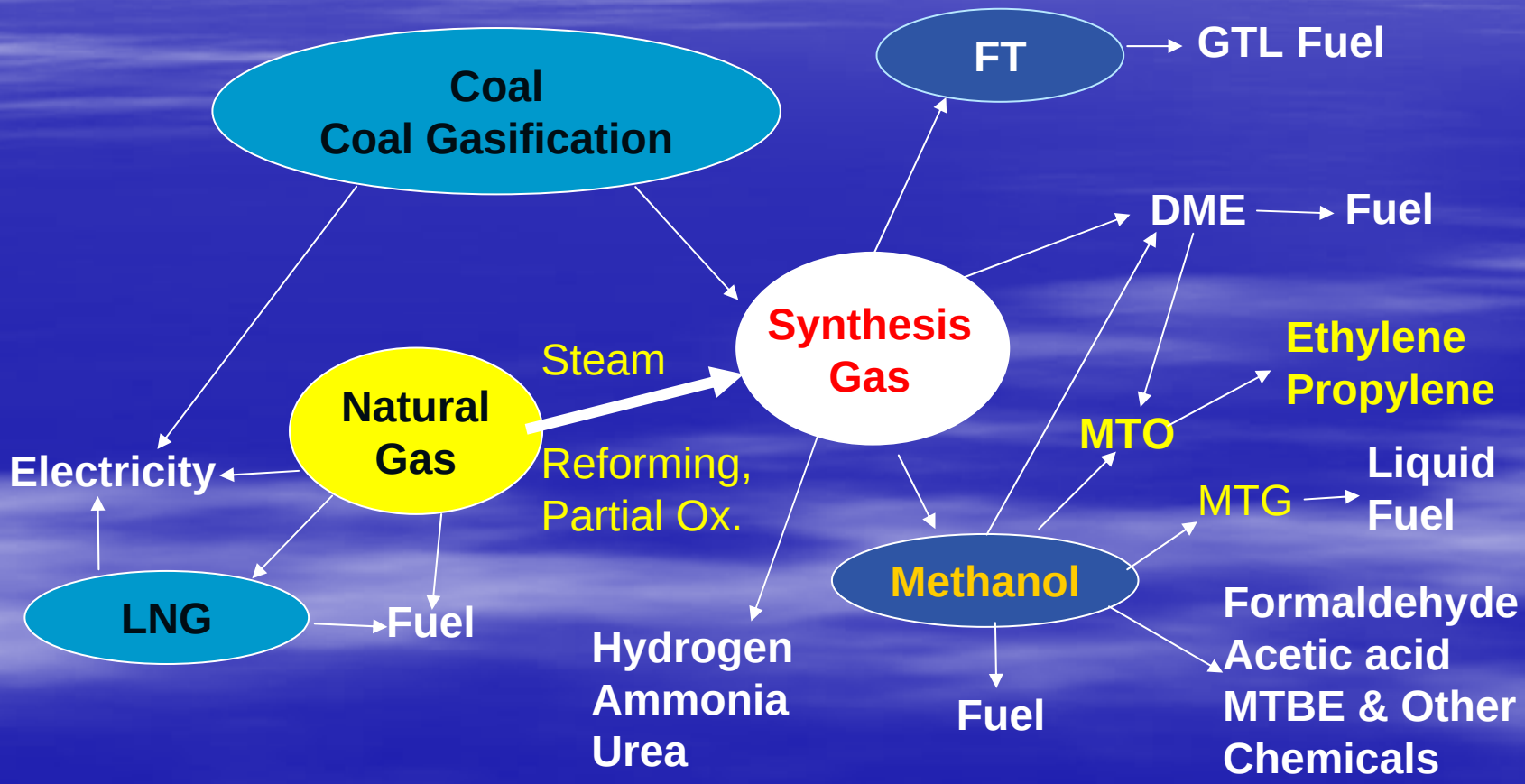
Petrochemicals:Methane Derivatives



Coal & 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

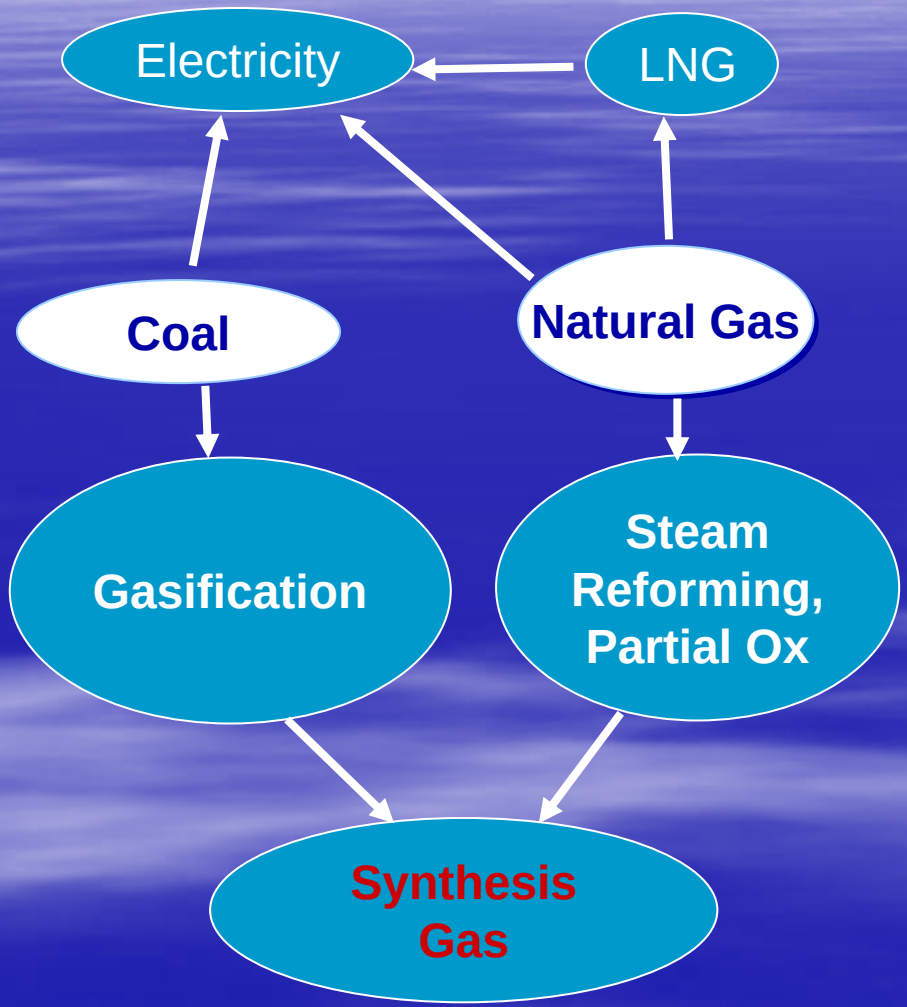
Alternative Feedstocks for petrochemicals and polymers

Vol. 2, Issue 2 January 28,2008, A weekly publication

1. PT Bumi Resources interested coal liquification 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 Uralkhimpst to build 600 KTA methanol plant in Rusiia
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

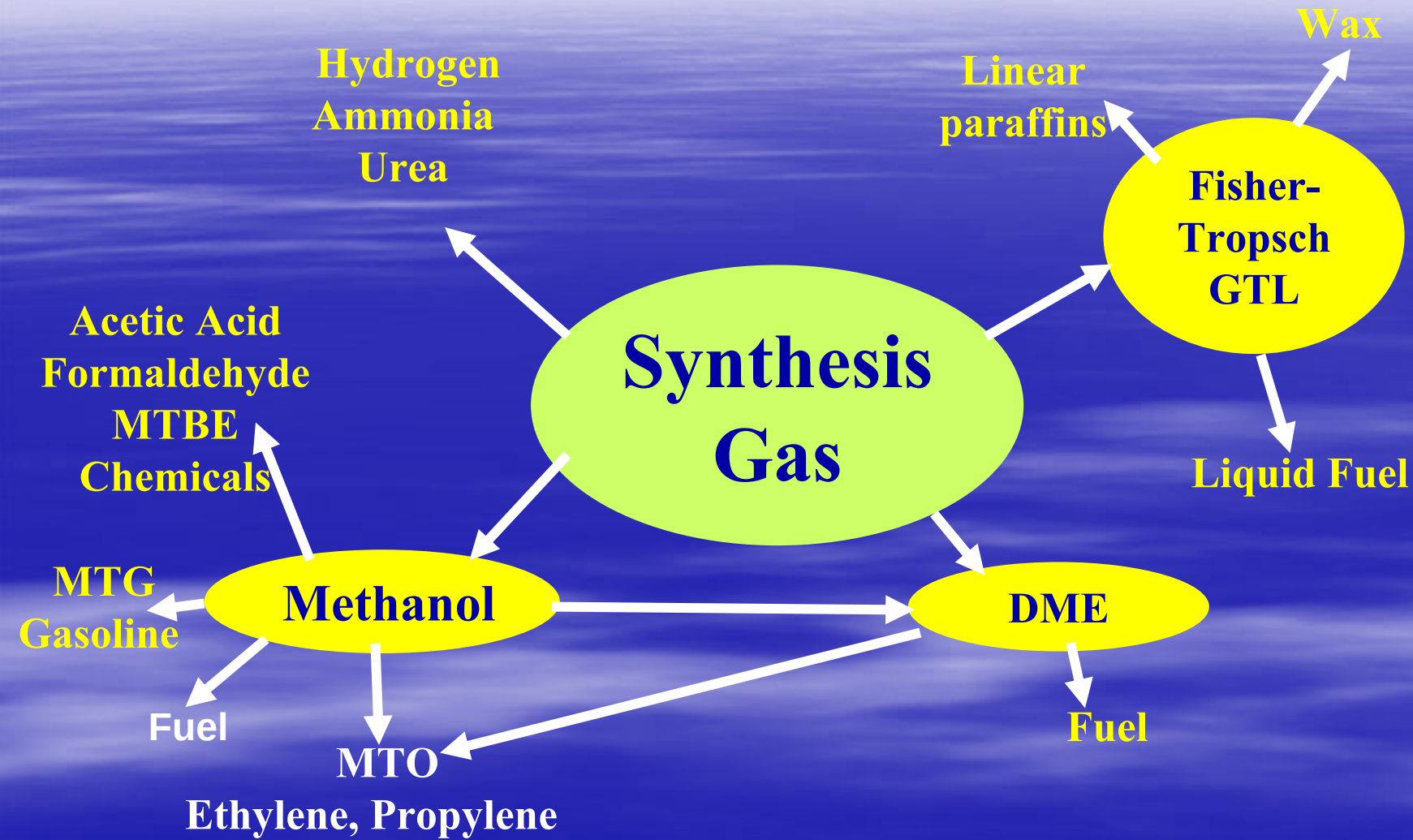
There are 5 to 10 weekly news items on coal and natural gas upgrading

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



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

1980s	1990s	2000-2008
NA-USA & Canada	Venezuela	Trinidad & Tobago
Russia-Siberia	Norway	Chile
Saudi Arabia	Iran	Iran
Malaysia	Qatar,	Qatar
Ukraine	Saudi Arabia	Oman
Libya	Trinidad	China-Coal
New Zealand	Libya	
Indonesia	Chile	
	Indonesia	
	Malaysia	

- **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

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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

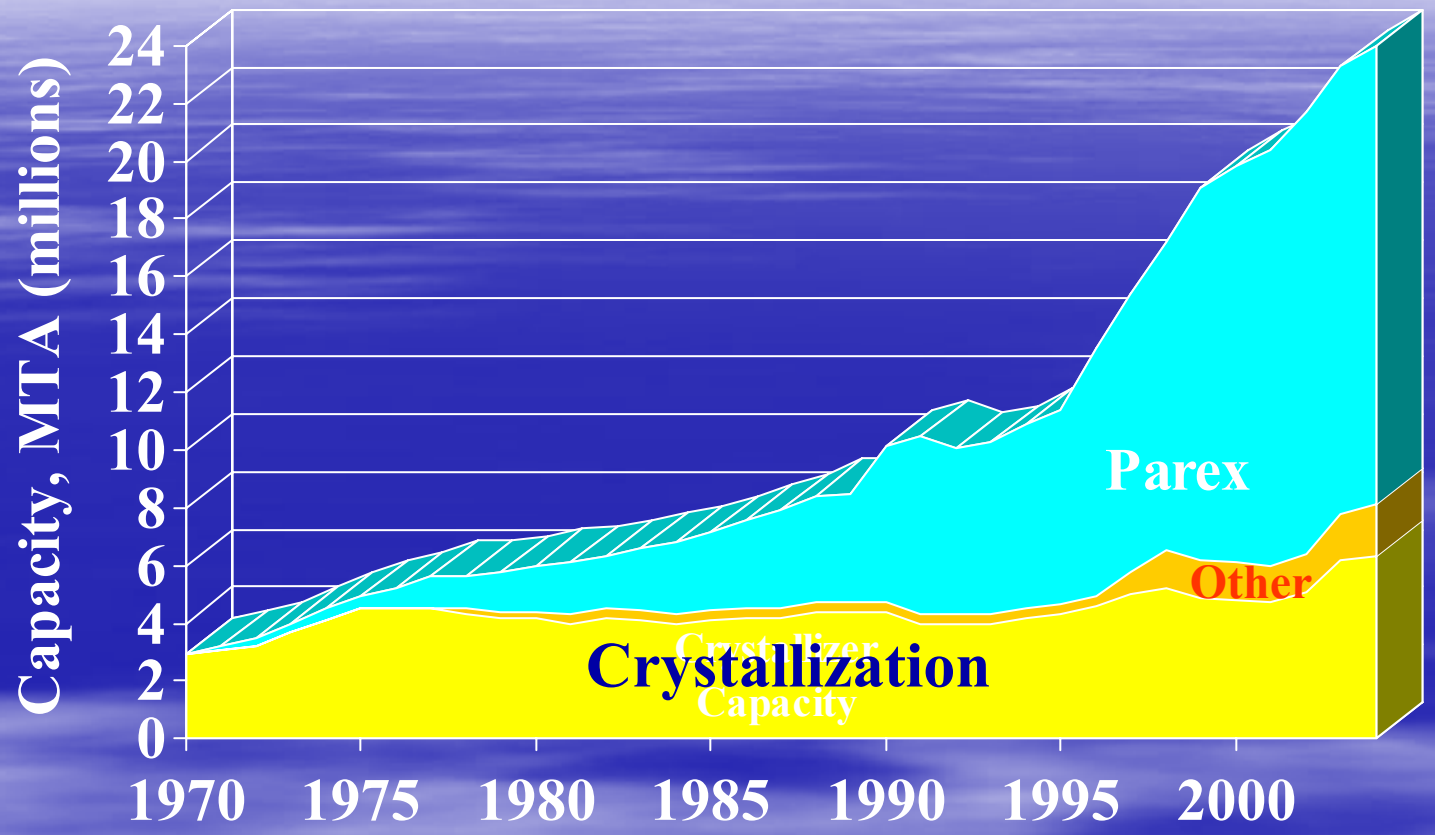
Petrochemicals:BTX Derivatives

Benzene 2007: 38 mm MTA	Toluene 2007: 36 mm MTA	Xylene 2007: 33 mm MTA
EB-Styrene	Toluene diisocynate	pX-PTA-Polyester
Cumene-Phenol-Phenolic resins	Motor Fuel-Octane Enhancement	oX-Phathalic anhydride
LAB	Solvent	mX-isophthalic acid
Cyclohexane	Conversion to Bz-pX	
Cyclohexnol Cyclohexanone		oX/mX Conversion to pX
Caprolectum-Nylon		
Adipicacid-Nylon		

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

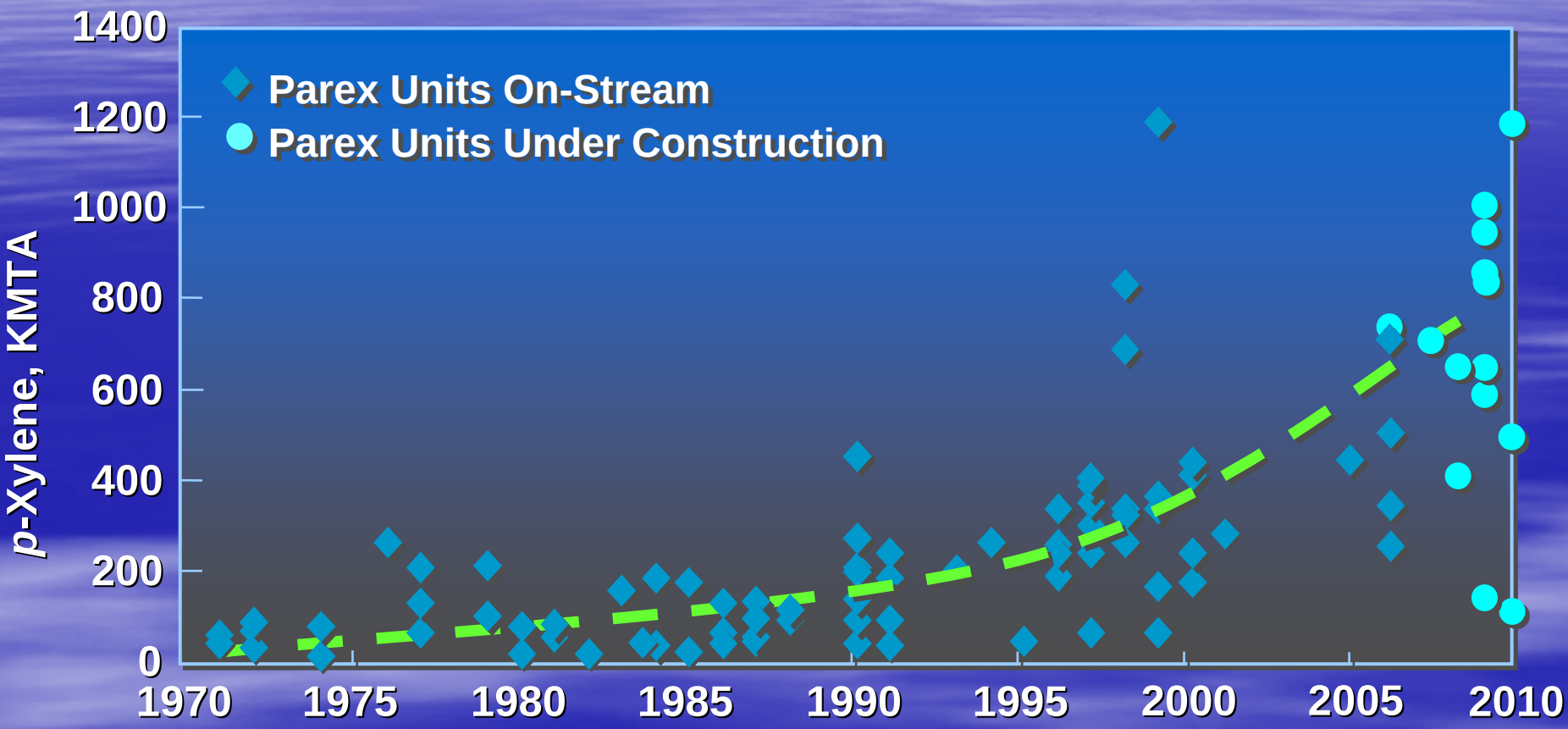
Worldwide *p*-Xylene Production Capacity



Increasing market share by adsorptive separation technology

Source: UOP

UOP Parex^{R} 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**

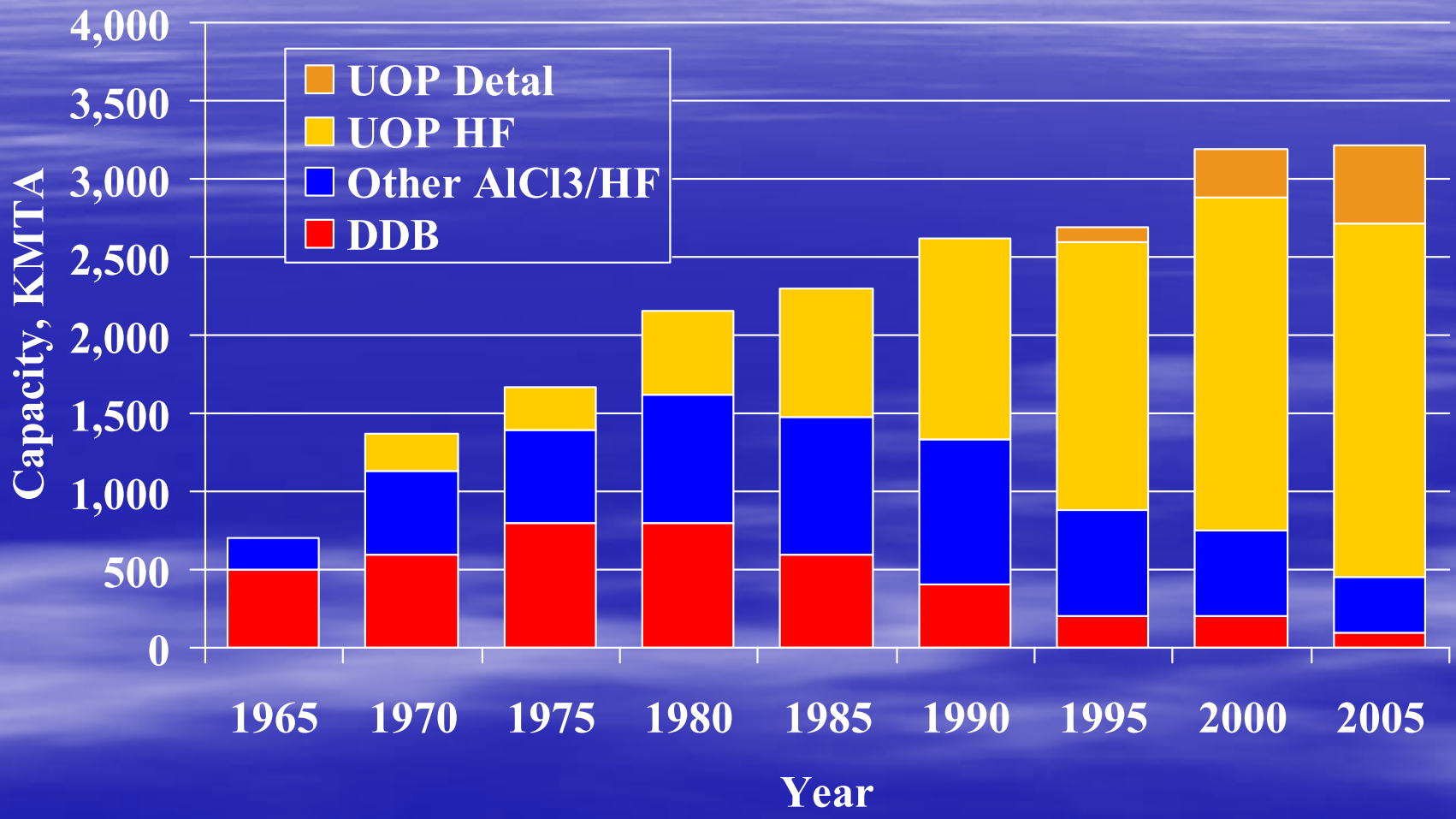
Linear Alkylbenzene (LAB)
3.3 mm MTA production in 2007

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**

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Petrochemicals:Olefins Derivatives

Ethylene 2007: 120 mm MTA	Propylene 2007: 70 mm MTA	Butadiene 2007: 10 mm MTA
Polyethylene	Polypropylene	**Polymers and copolymers with styrene and ACN**
EB-Styrene	Acrylonitrile	ABS
Ethylene Oxide-Ethylene glycols,	Cumene-Phenol	nButene-MEK
EDC, VCM	Propylene Oxide	Isobutene-TBA
Vinyl acetate	Epichlorohydrin, Glycerol	Diisobutene, triisobutene & polyisobutene
Ethyl alcohol acetaldehyde	Nonylphenol Tetramer	Isobutene-MTBE
		Motor Fuel Alkylate

Ethylene: Raw Material &Technology

Raw Materials

- **Ethane**
- **Propane, butane**
- **Naphtha, gas oil**

Technology

Thermal Pyrolysis

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**

Feedstock	USA			WE		Japan	
Year	79	91	06	79	91	79	91
C2-C4	65	75	70	4	8	10	2
Naphtha-GO	35	25	30	96	92	90	98

  - **NA more ethane based**
  - **WE and Japan Naphtha based**
- **Expansion of ethylene production in ME promotes more ethane based crackers**

Middle east Ethylene Capacity

Year	MTA
2000	7
2004	11
2008	18
2012	35

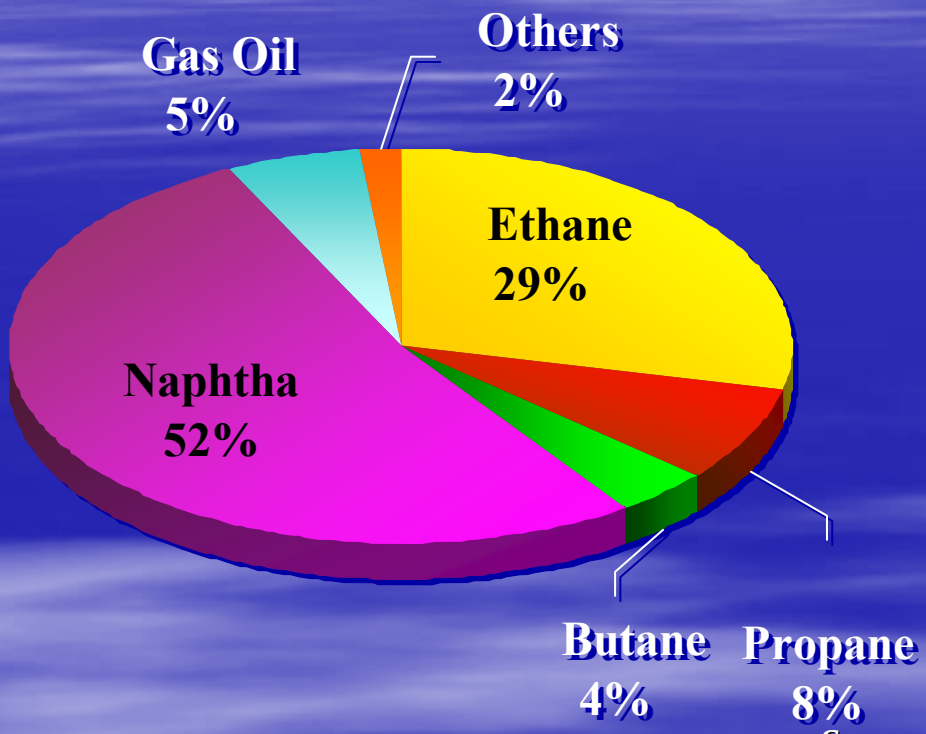
Source: CMAI- 2007 World Petroch. Conf.

- **Ethylene produced from Ethane in ME has on average 250 to 400 $/MT production cost advantage over NA/WE Europe production**

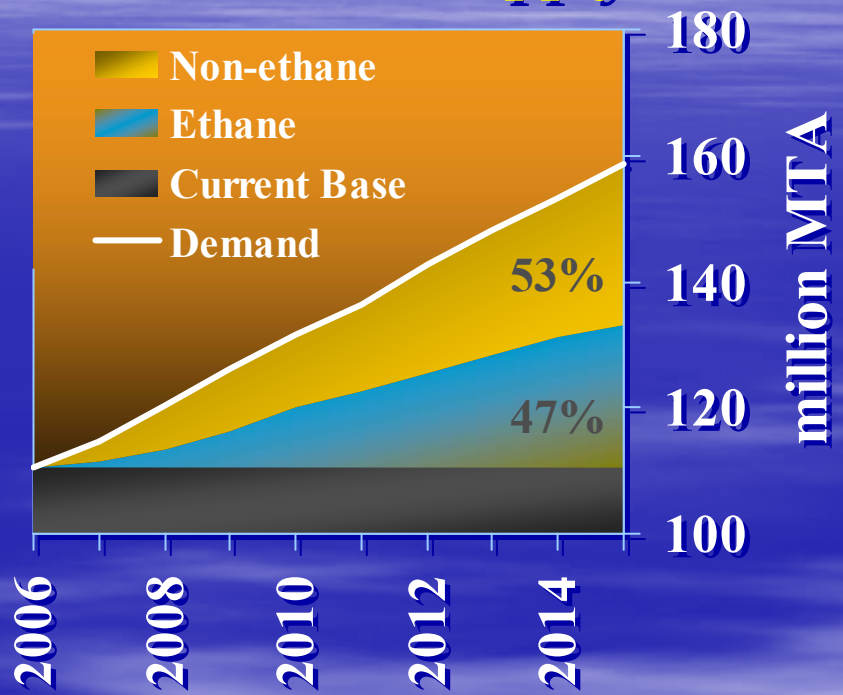
Ethylene Supply – Global View

2006 Supply

(Steam Crackers)



Incremental Supply



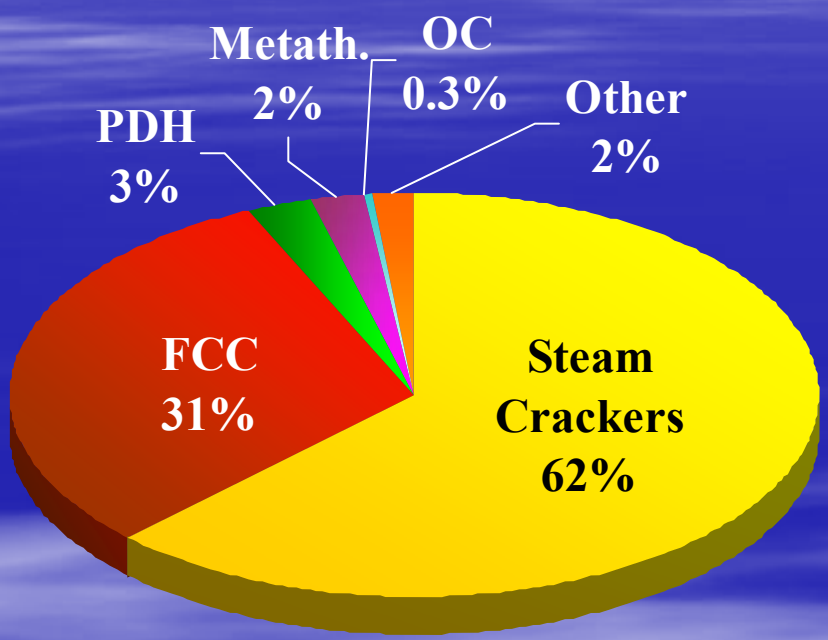
Source: CMAI 2007

- *Production from ethane crackers will increase*
- *Non-ethane sources of ethylene are needed to meet the demand*

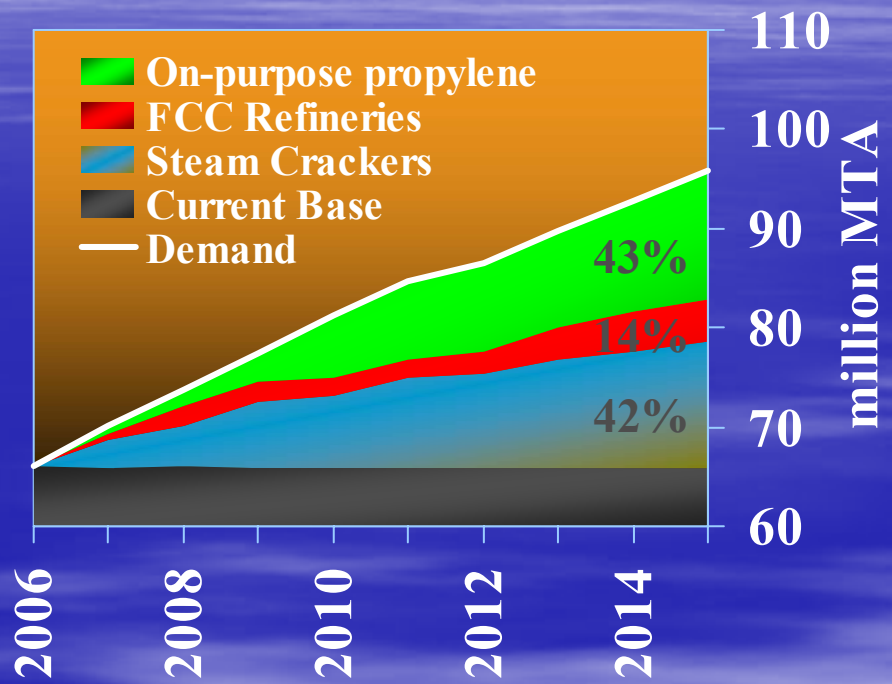
Propylene Supply – Global View

2006 Supply

(Polymer & Chemical Grades)



Incremental Supply

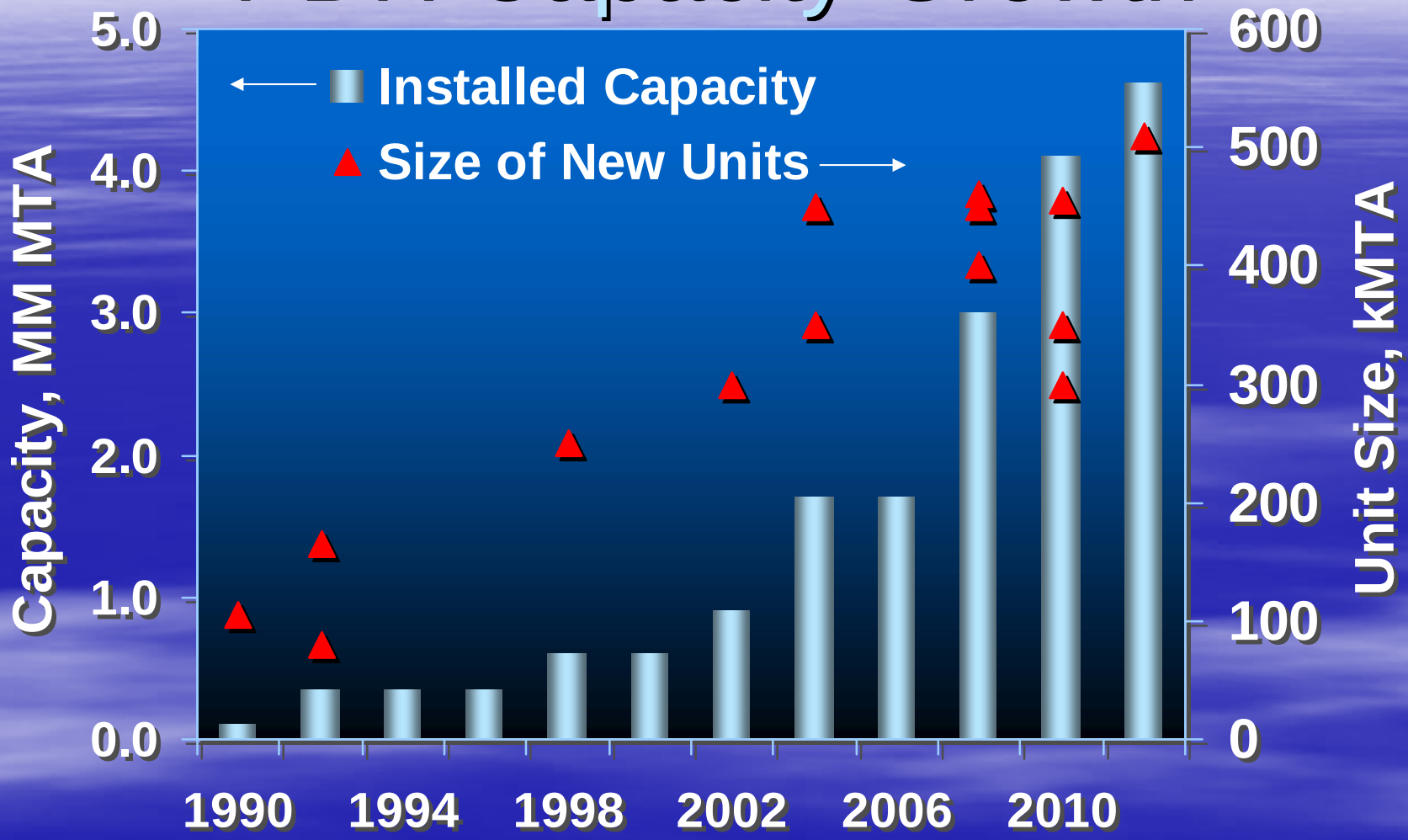


Source: CMAI 2007

Substantially more propylene will come from "on-purpose propylene" technologies

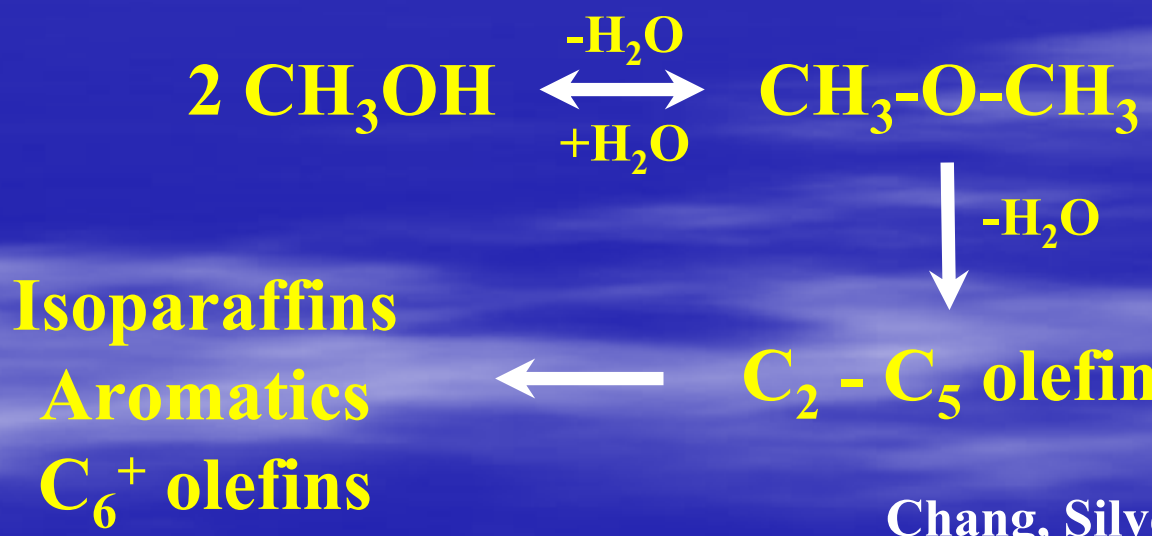
PDH = Propane Dehydrogenation, Metath. = Metathesis,
OC = Olefin Cracking, MTO = Methanol-to-Olefins
On-purpose propylene = PDH + Metath. + OC + MTO

PDH Capacity Growth



Zeolite-catalyzed MeOH conversion

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



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)

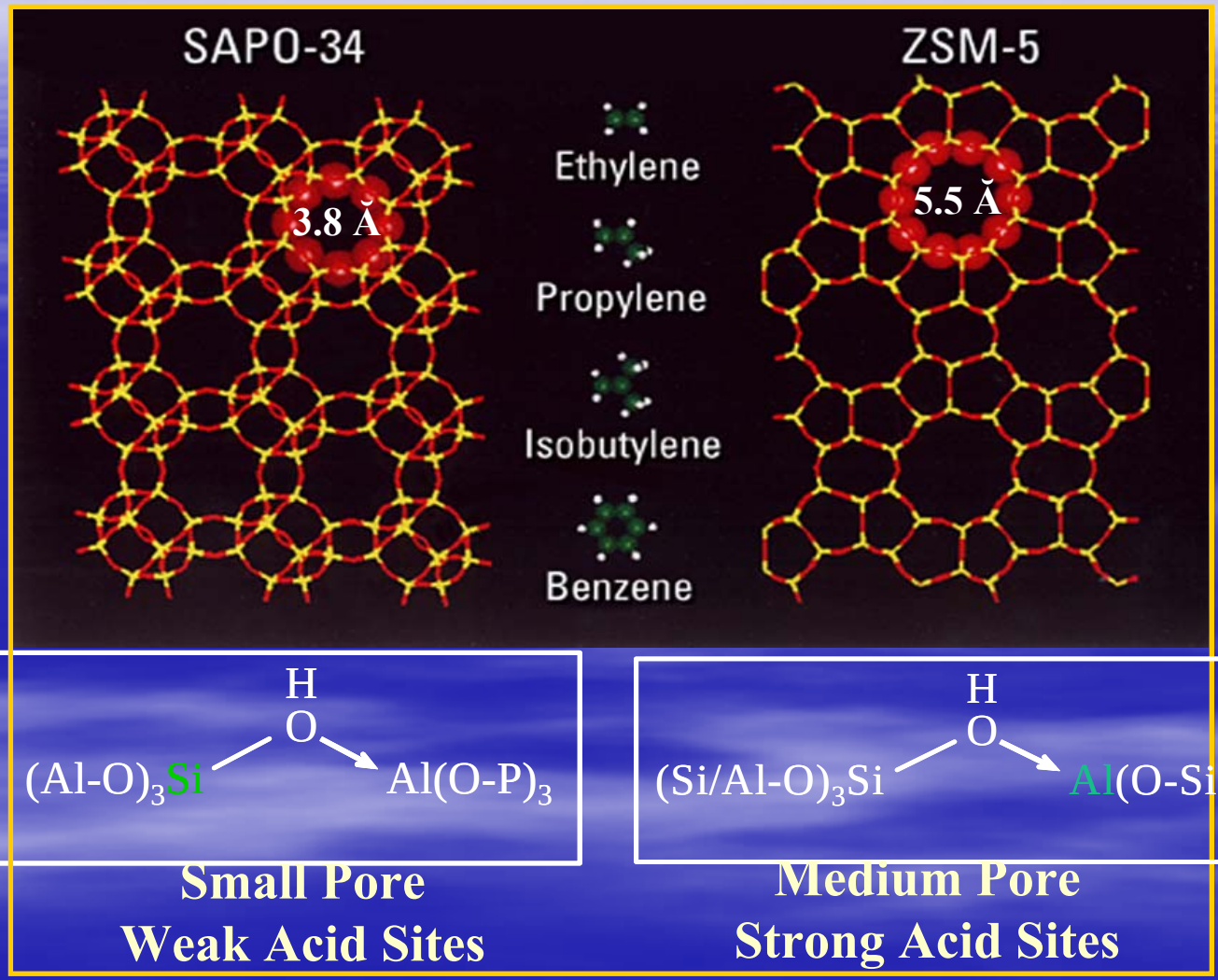
- C_2–C_4 olefin concentration < 60% at 100% conversion
- Olefin fraction increases as conversion decreases

Chang, Lang, and Silvestri, US 4062905

Zeolite-catalyzed MeOH conversion

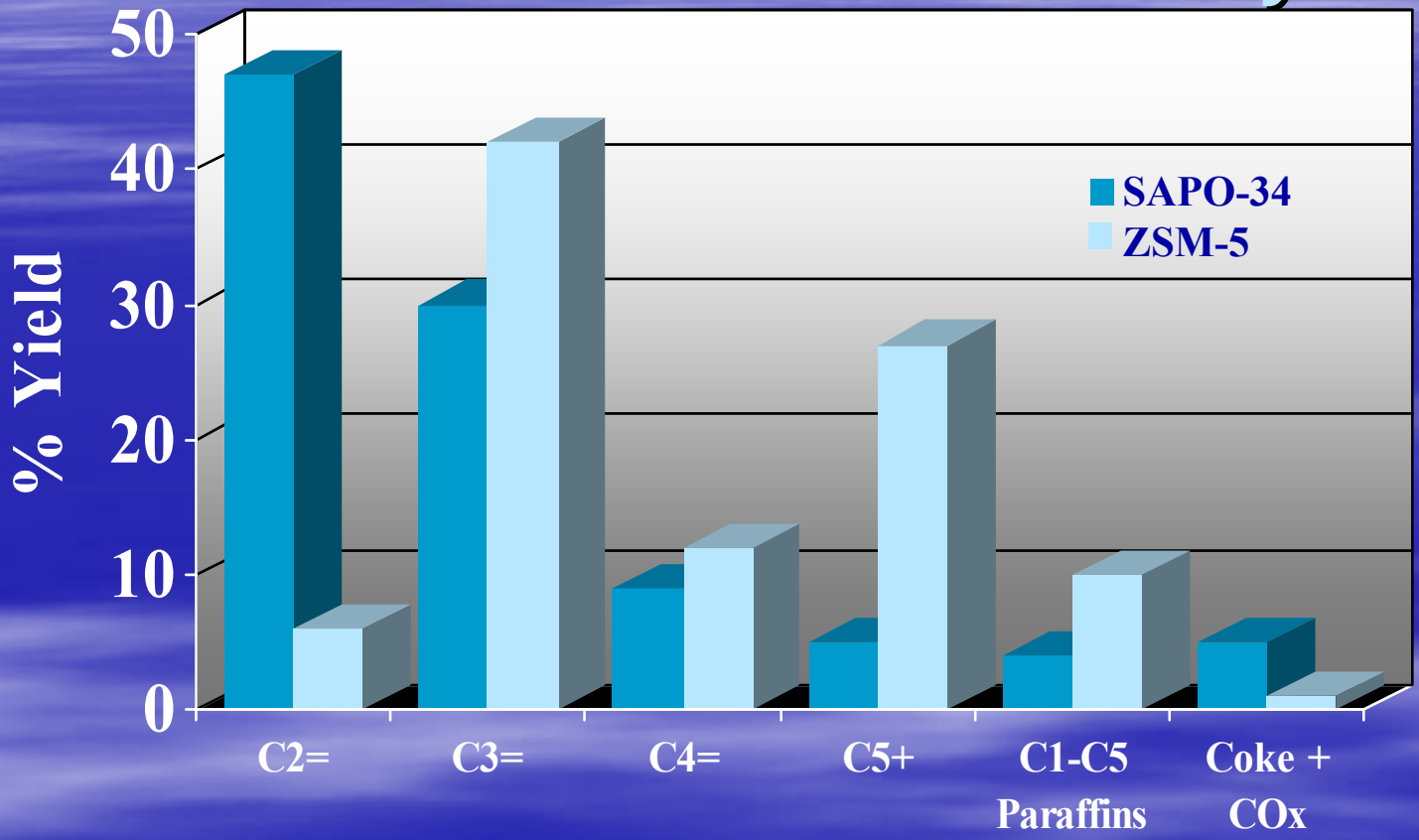
- 1982 – Edie Flanigen and her associates at Union Carbide announce discovery of silico aluminum phospate molecular sieves. Flanigen and her group became part of UOP upon merger of CAPS Division of UCC with UOP
- SAPO-34 shows remarkable selectivity for conversion of methanol to light olefins
- C_2–C_4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

Structures of SAPO-34 and ZSM-5



Source: UOP

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



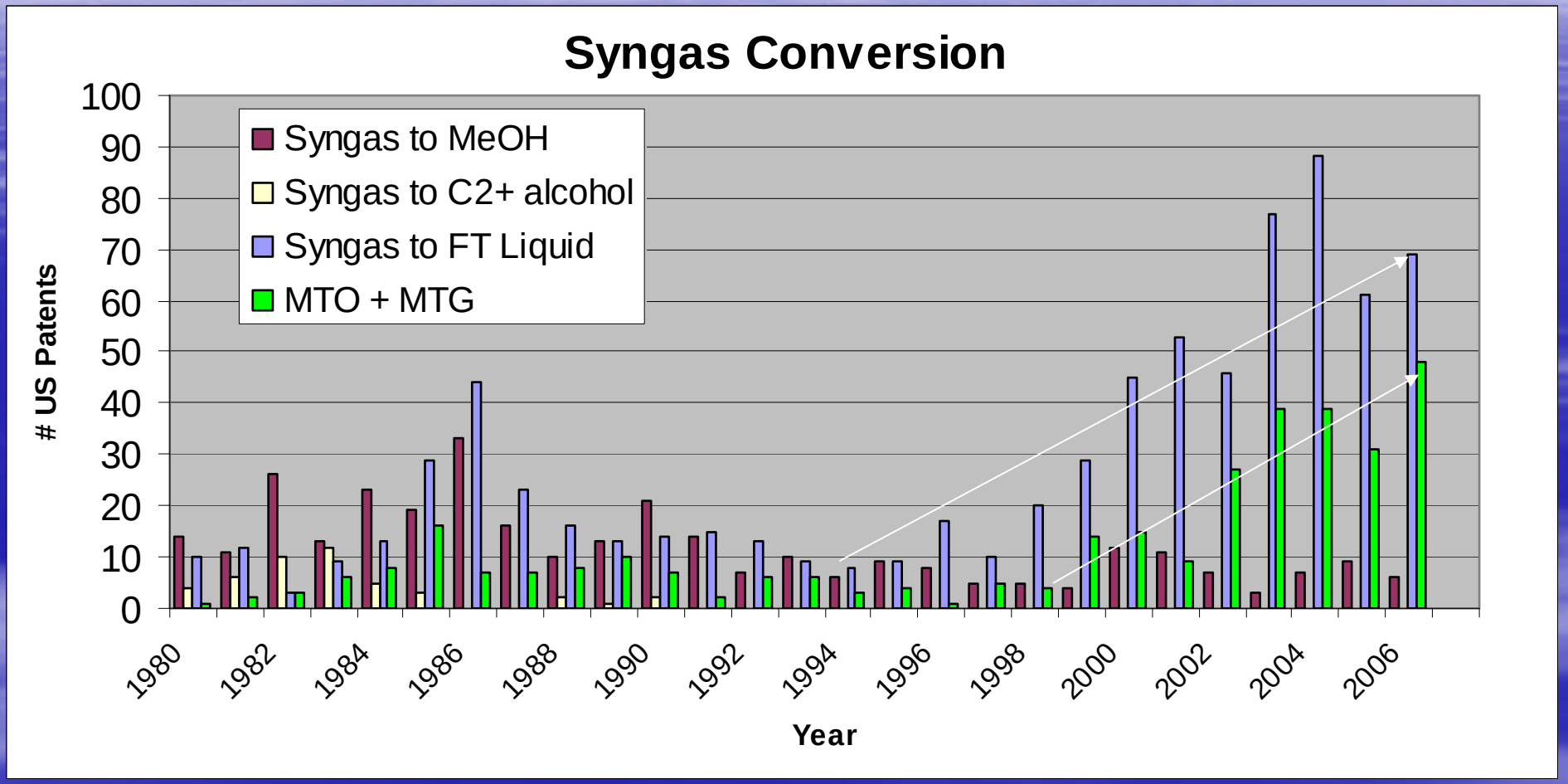
SAPO-34 Catalyst: Once through C2= + C3= yield of 80%

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

Source: UOP

MTO Capacity Growth

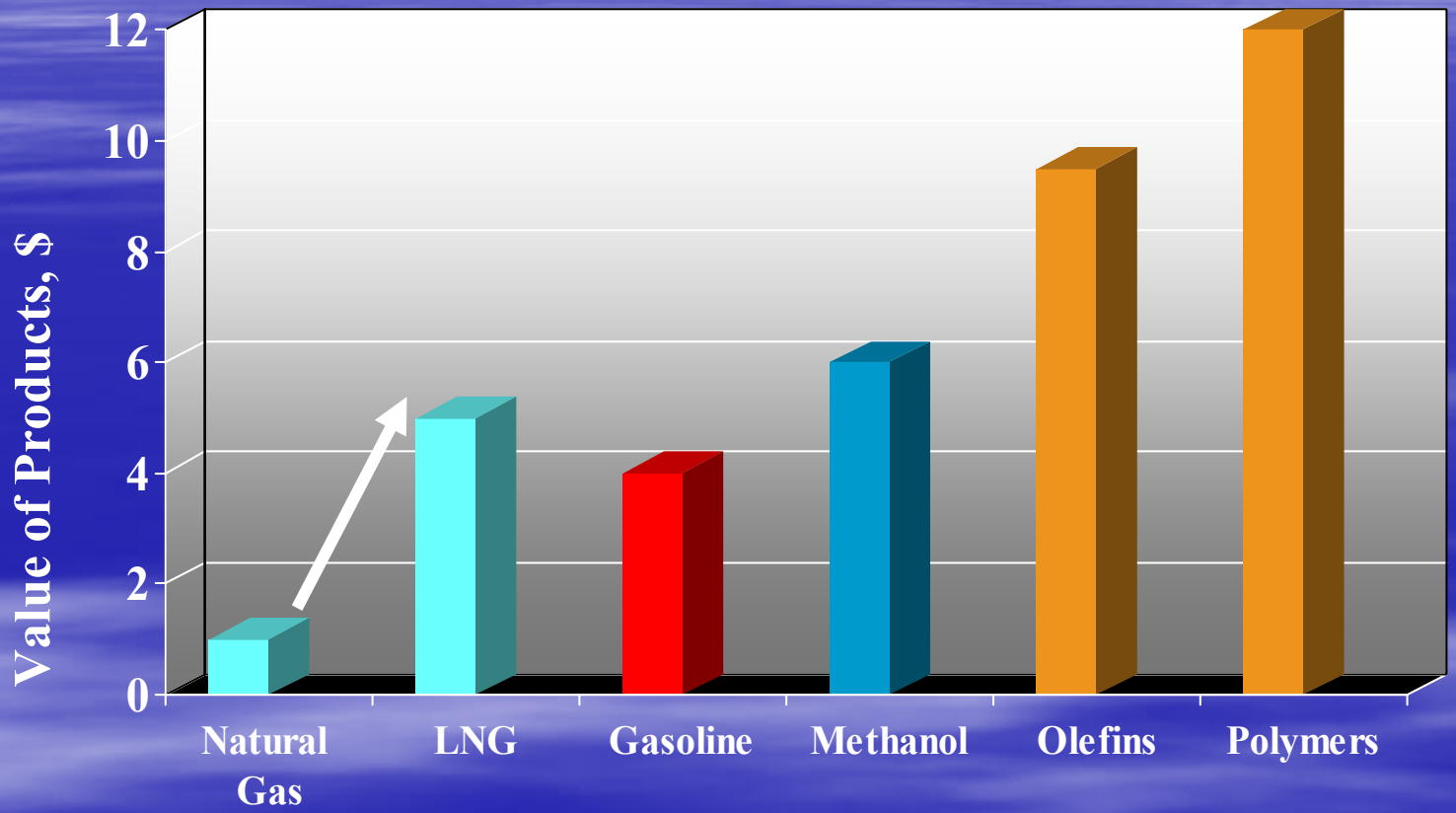
Patent Activity in USA



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

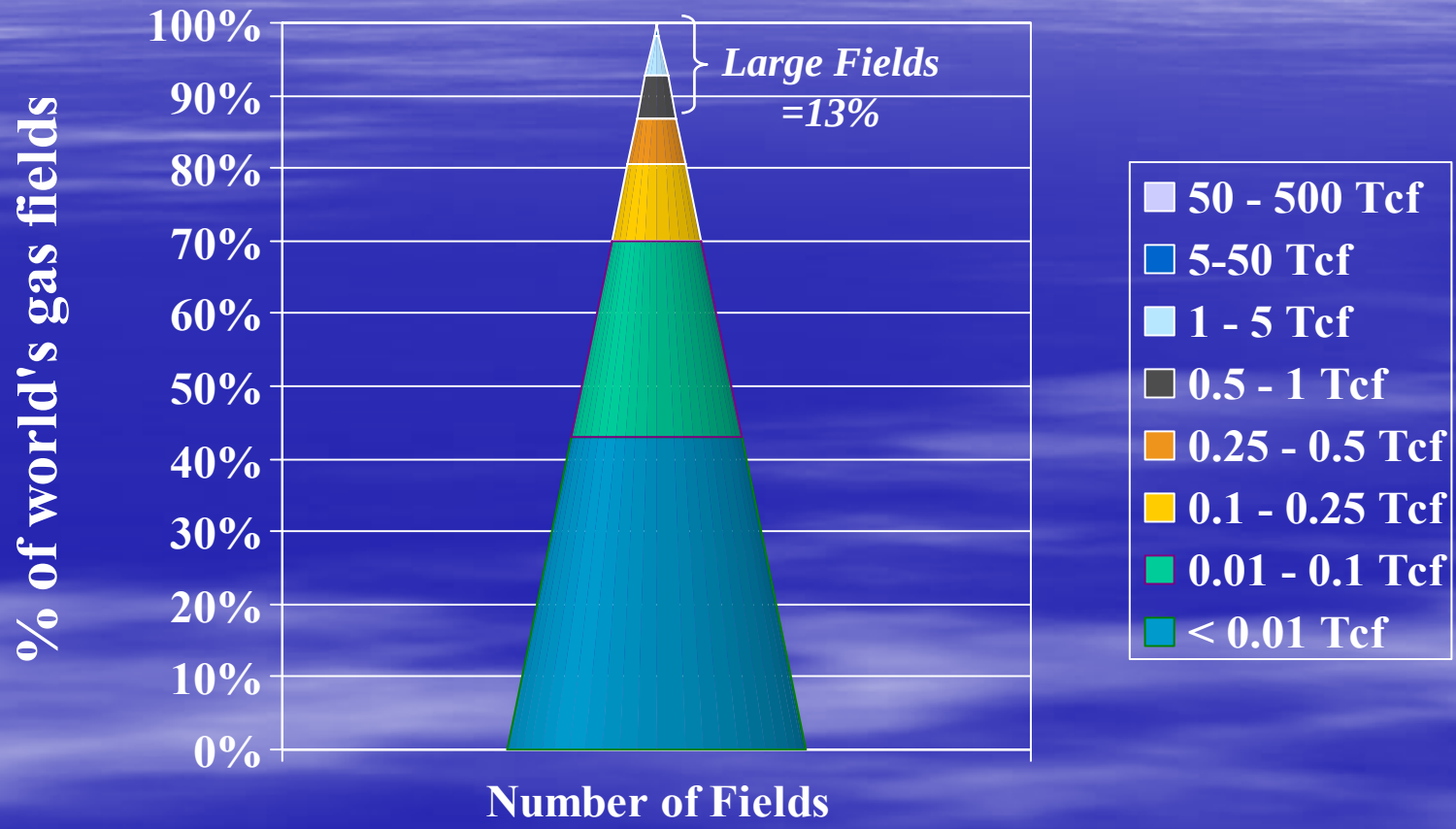
Stranded Gas Monetization Options

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

Monetization route	*Worldscale economic capacity*	*Gas needed mm SCMD*	*30 Years Consumption billion SCM*
LNG	**5 MM MTA LNG**	**22.2**	**222**
GTL	**100,000 BPD F-T Liquids**	**26.8**	**268**
GTP	**1,000,000 MTA PE + PP**	**7.5**	**75**

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



Total = 4,448 Fields

Source: Oil & Gas Journal

Why is Methanol Attractive?

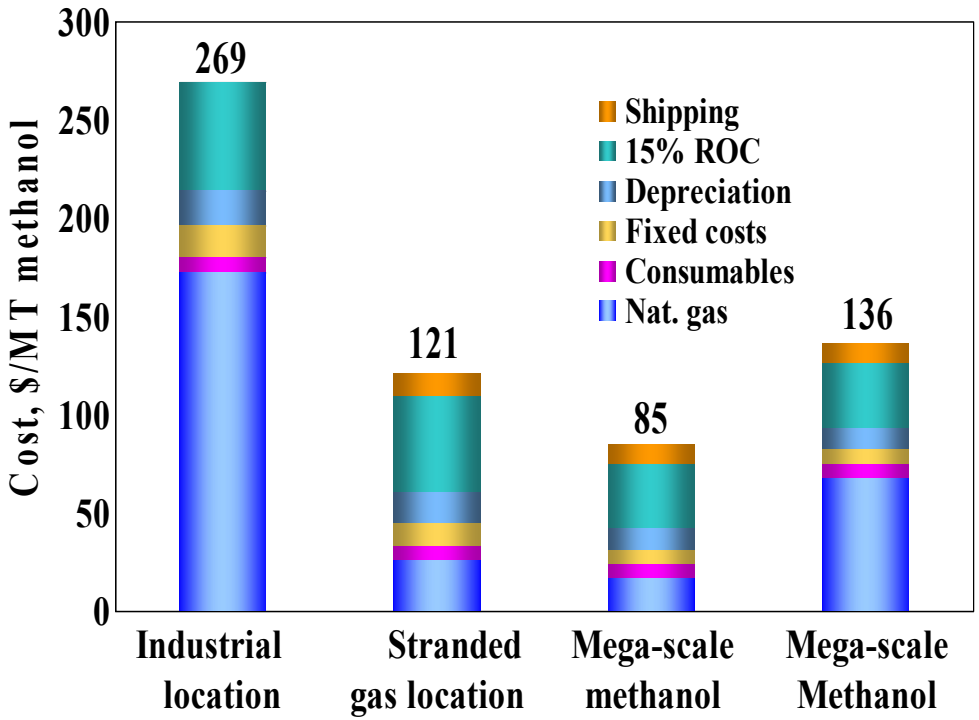
- Readily synthesized on a large scale (current largest unit is 5000 MTD, 10,000 MTD under design)
- Transportable liquid fuel
- Has high energy density

	H_2 gas	Methane gas	DME gas	Methanol liquid	Naphtha liquid
Kcal/M^3 @ 1 atm. 25C	2400	8600	14200	3.97×10^6	8.2×10^6

LNG Transportation Cost about $150-200MT
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



Nat. gas Price, $/MM Btu	$5.00	$0.75	$0.50	$2.00
Capacity, MT/D	1500	3000	7500	7500

100 $/MT MeOH = 229 $/MT HC Equiv.
150 $/MT MeOH = 343 $/MT HC Equiv.

Methanol Plant Closure

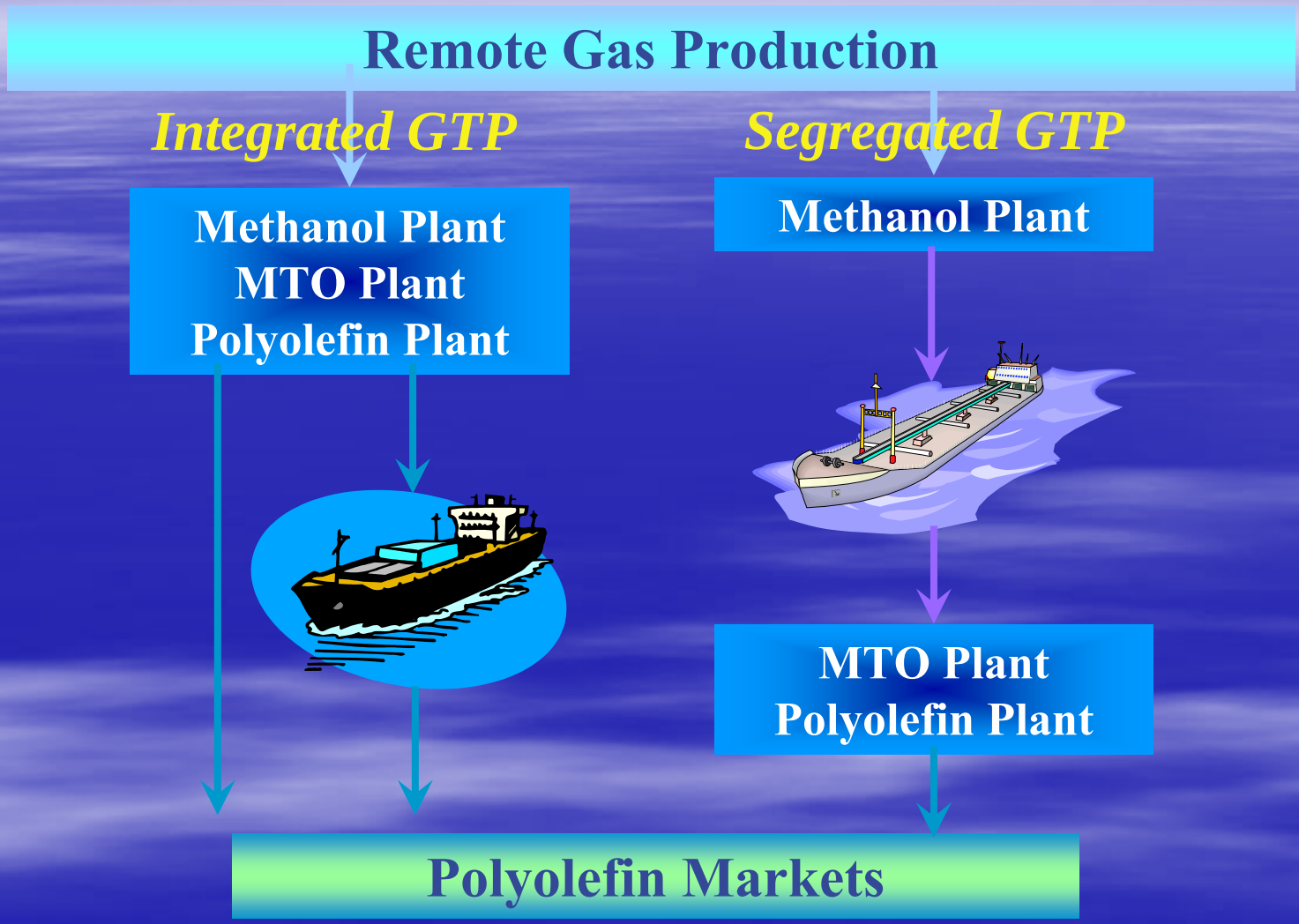
1990-2004	2005-2007 Closure	
Japan 100%	Beaumont, USA	850
Norway 100%	Celanese, Bishop, USA	500
Korea 100%	Celanese, Clear Lake, USA	600
Italy 100%	Methanex, Kitimat, Canada	520
Spain 100%	Edmonton, Canada	800
France 100%	Pemex, Mexico	180
USA Part of it	Methanor, Netherland	1000
Canada Part of it	Methanex,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

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 $150-200MT**
- **Methanol Transportation Cost $10-20/MT**

Gas to Polymer/Olefin Scenarios



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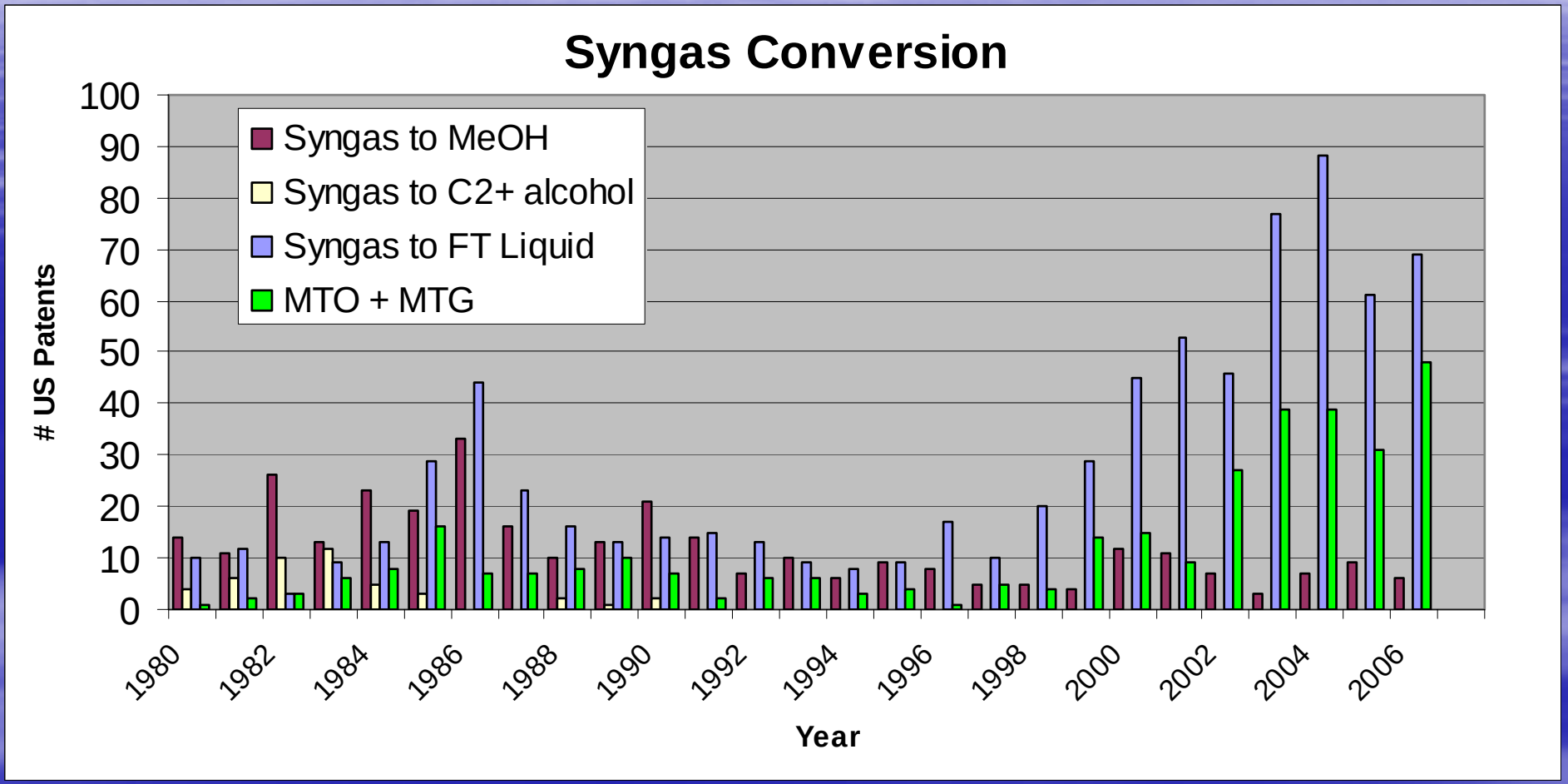

Overall Summary

- 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