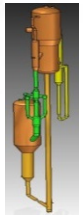
Naphtha Catalytic Cracking in FCC Units Past & Present ?



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May 4-8, 2015

REFCOMM GALVESTON

May 4-8, 2015

Purpose (Objective)

- To present and briefly discuss “light straight run” or paraffinic naphtha catalytic cracking in FCC’s

Contents - Covering 3 Points

Why Naphtha Cracking ?

- Feedstock Availability
- How to Crack Naphtha ?
- Past & Present (Future) Experiences

Naphtha Sources ?

p-Naphtha Sources (no olefins)

- LSR, Natural Gas Condensates, Hydrocracker, Hydrotreater, others ?

• Olefinic Naphtha Sources

- Cracked FCC, Coker, Visbreaker, others ?

Light Crude Properties

US Crudes *				
Property		Bakken	WTI	Lite La Sweet
API Gravity	Degrees	>41	40	35.8
Sulfur	Wt.%	<0.2	0.33	0.36
Yield Volume %				
Light Ends	C1-C4	3	1.5	1.8
Naphtha	**C5-330°F**	**30**	**29.8**	**17.2**
Kerosene	**330-450°F**	**15**	**14.9**	**14.6**
Diesel	450-680°F	25	23.5	33.8
VGO	680-1000°F	22	22.7	25.1
Resid	1000+°F	5	7.5	7.6

Heavy Feeds - Easier to Crack !!

Light Feeds - Hard to Crack !!

Why Naphtha / Condensate ? Supply !

- Lighter Crudes for Refinery Feedstocks are Increasing
  - Fracking for Shale Gas and Shale Oil
- Condensates from Natural Gas
- Lighter Crudes Produce More Naphtha
- Increasing Demand for Diesel not Gasoline
- Petrochemicals - Steam Cracking (Feedstock)
  - Ethylene Demand is Growing Faster than Propylene
  - Shifts from Naphtha, Gasoils to Ethane

"Somewhat decoupling" of naphtha pricing from crude

What to Do with Excess Naphtha Supply ??

Dispose It

- Burn it (Fuel)
- Export it for Steam Cracking ???
- Diluent for TAR Sands Production
- Re-inject into Existing Wells

Convert It

- Reformer or Isomerize it
- Crack it
  - Steam Crackers
  - Catalytically Crack It !

Petrochemicals Opportunities

Main Building Blocks ← Produced by Steam Cracking
Ethane & Liquid Feeds
Naphtha Reformers

- Olefins - Two Main Blocks
  - Ethylene
  - Propylene ← Secondary Source Produced by FCC's
  - Butylenes ← Co-monomer & ALKY Feedstock
- Aromatics
  - Benzene
  - Paraxylene (other xylenes too)

* High Olefins - FCC (HOFCC) produces C3= and byproducts of other light olefins and aromatics

Typical Cracking Yields by Process Type

Wt.%	FCC	R2P*	DCC*	HS-FCC*	SC* (C2)	NCC*
Ethylene	1-2	1-2	2-6	3-4	45-50	7.1
Propylene	3-5	10-12	15-25	16-20	1-3	16.8
Butylenes	6-8	12-14	13-17	13-16	1-2	8.6
Gasoline	45-55	28-35	22-40	30-40	1-3	48.5

R2P - Resid to Propylene
DCC & HS-FCC - HOFCC Types
SC – Steam Cracking Ethane
NCC- Naphtha Catalytic Cracking
NCC- Published Data

How to Crack Naphtha?

Cracking Mechanisms

Thermal Cracking

- Non-catalytic Free Radical Chain Formation
- Randomly Ruptures Chemical Bonds

Catalytic Cracking

- Carbenium Ion Formation
- Selectively Opens Chemical Bonds
- Hydrogen Transfer, Isomerization

- Both Form Coke from Condensation

Naphtha Cracking

Steam Cracking - Thermal

- Not Selective to Propylene makes Ethylene (P/E Ratio)
  - P/E Ratio of 0.55-0.68 (Naphtha & Gasoil Cracking)
- Steam Cracker capacities are world class size > 1000 KTA

Naphtha Cracking - Catalytic

- Propylene Selective not Ethylene
- P/E Ratio of 1.0 to 2.4
- Naphtha FCC capacities 20 MBPD == 64 KTA of ethylene

SC 20 MBPD = 264 KTA

Steam Cracking Yields

Propylene/Ethylene(P/E) Ratio indicates propylene selectivity

Typical light olefin yields for steam cracking			
Feedstock	Ethylene, wt%	Propylene, wt%	P/E
Ethane	80	3	0.04 (0.0375)
Propane	44	15	0.34
Naphtha	30	16	0.53
Gas oil	23	15	0.65

Table 1

How to Crack Naphtha ?

Lighter Feedstock

- More Heat for Cracking (Higher Heat of Reaction)

Higher Severities

- Higher Reactor Temperatures
- Higher Cat/Oil Ratios
- Increase Residence Times
- Higher Cat Activity
- Different Catalyst Formulations*

How to Crack Naphtha ?

Existing Units Previous Experience

(Difficult)

Naphtha Feed Injection

- Mix with Current Feed Injection
- Below Current Feed Injection Elevation
- Into the Reactor Bed (Bed Cracking)

All Have Issues

Exiting Units Previous Experience

Mix with Current Feed Injection

- Increase Cat/Oil (Acts Heat Sink)
- Increase Severity / Conversion **

  (For All Injection Locations)**

Concerns

- Cat Circulation
- Delta Coke Issues
- Octane Loss !!

Exiting Units Previous Experience

Below Current Feed Injection Elevation

- Hottest Regen Cat Temperature
- Increase Cat/Oil (Acts Heat Sink)
- Claims of Gasoline Sulfur Reduction

Concerns

- Poor Naphtha and Catalyst Mixing
- Potential Coking
- Fresh Feed Catalyst Mixing *
- Inadequate Rx. Residence Times

Exiting Units Previous Experience

Into the Reactor Bed (Bed Cracking)

- Increases Residence Time
- Lower Cracking Temperatures
- Non Selective Cracking of Heavy Feed

Concerns

- Units Operate with Bed Cracking ?
- Method of Injection

How to Crack Naphtha ?

Hardware Changes Revamp / Grassroot Designs

- More Heat for Cracking (Higher Heat of Reaction)
- 2ND Reaction Zone (Riser/Down flow)
- Bed Cracking

Catalyst Changes

- Different FCC & Additive Ratios
- New Catalyst Systems (Grassroots)

Conclusions
Naphtha Catalytic Cracking in FCC Units

- p-Naphtha Supply Sources are Available Both Domestically & Globally
- Crack it! Requires Higher Severities, Rx Temp, C/O, Increase Residence Time, Bed Cracking
- Minimize 450°F+ Content with the Naphtha Feed in the Reaction Zone (Segregate from Heavy Feed)
- Revamps to Existing FCC's Utilizing a Second Reaction Zone are Feasible (HOFCC's Technology)
- Cracked Products for Petrochemicals and Alky

Useful References

- "Different Process Schemes for Converting Light Straight Run and Fluid Catalytic Naphthas in a FCC Unit for Maximum Propylene Production " Corma , A. and others, Applied Catalysts, 2004
- "Naphtha Catalytic Cracking for Propylene Production "Dean, C.F. Petroleum Technology Quarter, Processing Shale Feedstocks 2013
- "Optimize Olefins and Aromatics Production", C.F Dean and W.S. Letzsch, Hydrocarbon Processing, November, 2014
- "Development of Comprehensive Naphtha Catalytic Cracking Kinetic Model" Longstaff, Daniel. Energy & Fuels ACS, 2012
- "Maximizing The Many Individual Products From A Catalytic Cracker Part I", W.S. Letzsch and C.F Dean, Hydrocarbon Processing, July, 2014

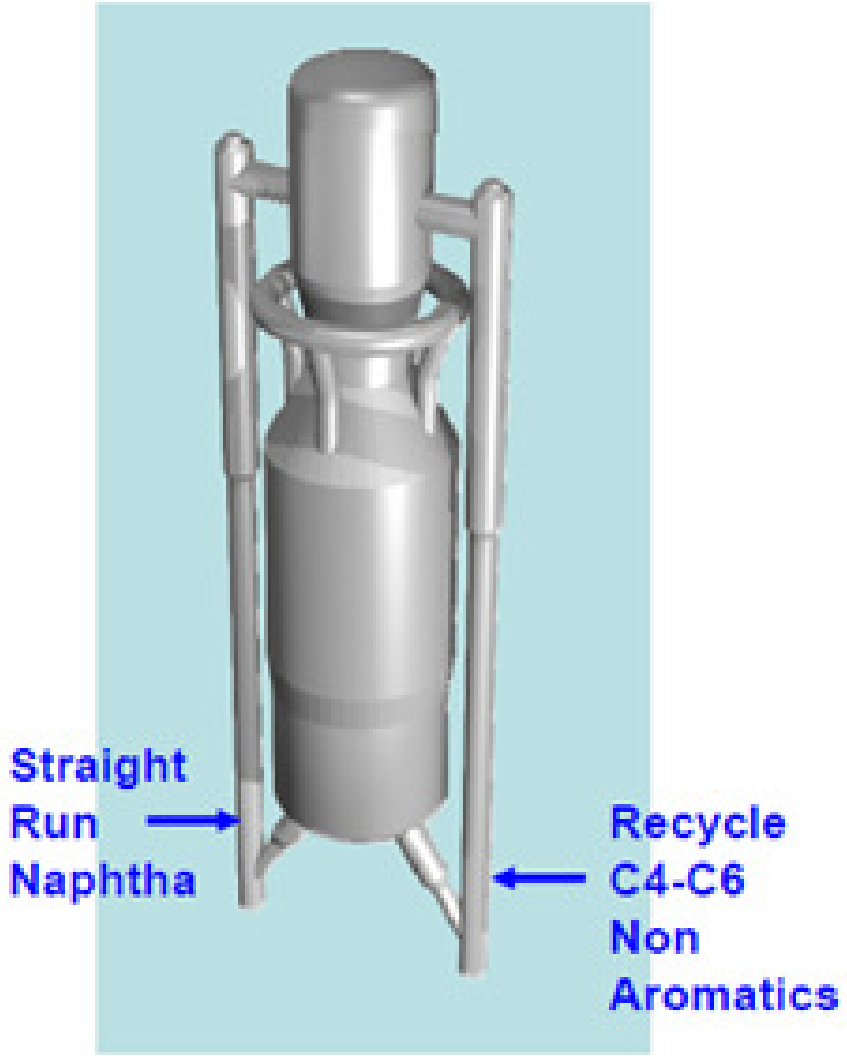
THANK YOU

The End

Questions - Comments ???

Follow-up Discussions?

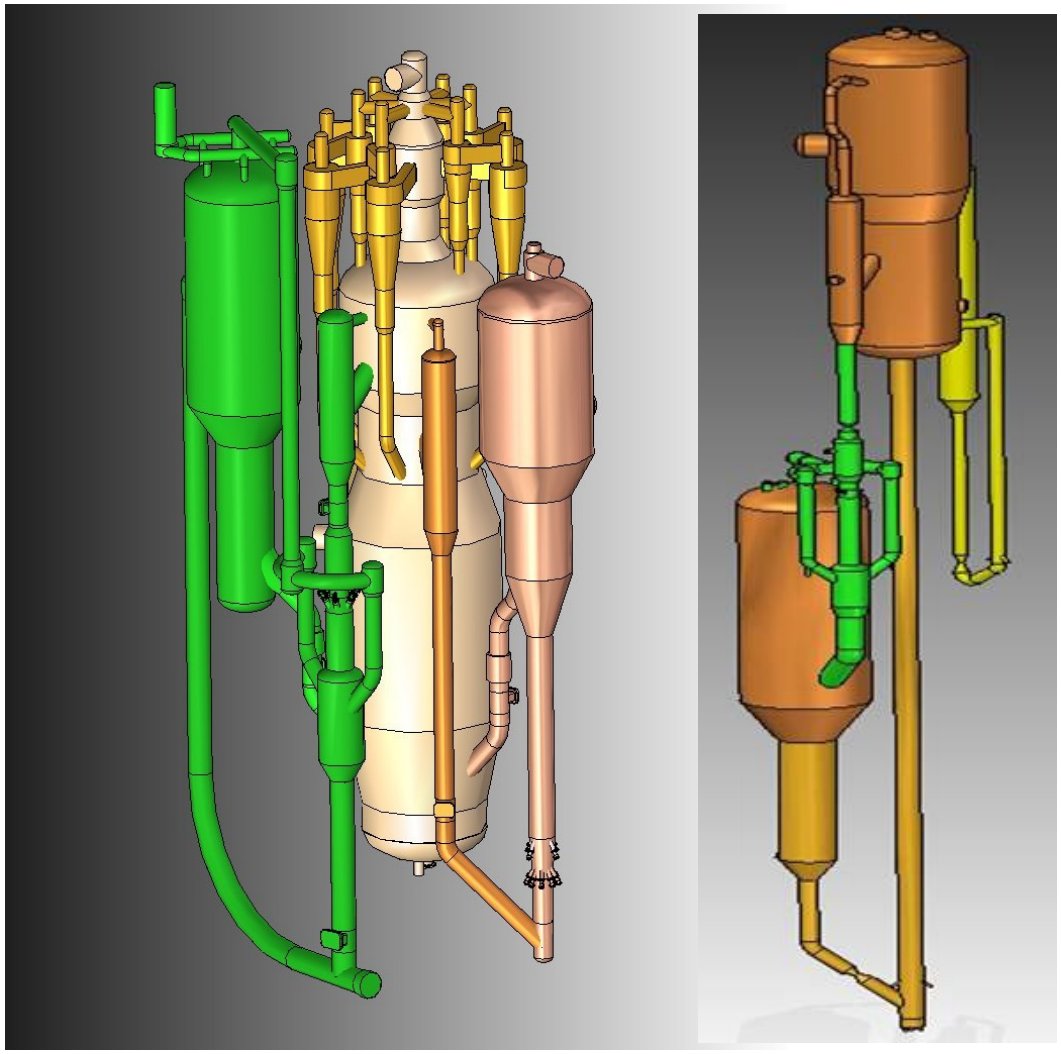
Advanced Catalytic Olefins (ACO)



- Proprietary KBR proven FCC technology
- P/E ratio ≅ 1
- Proprietary SK Corporation Catalyst
- Dual Risers
  - Fresh Naphtha
  - Recycle

HS-FCC Naphtha Process

- Retrofit Type to existing FCCU
- Standalone Unit



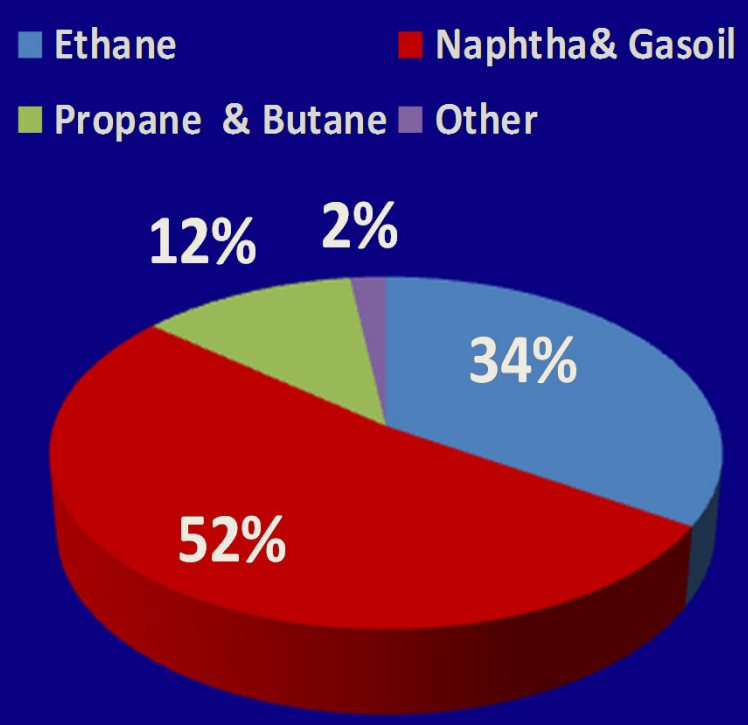
Aromatics Potential Sources

	Steam Cracker Gasoline	CCR Reformate	HOFCC Petrochemical Naphtha
BTX Content wt.%	85	56-80	59
Benzene	56	7-10	6
Toluene	19	19-28	22
Total C8's	9-11	30-42	31

HOFCC naphtha needs further treating ,etc. to meet Petrochemical Grade

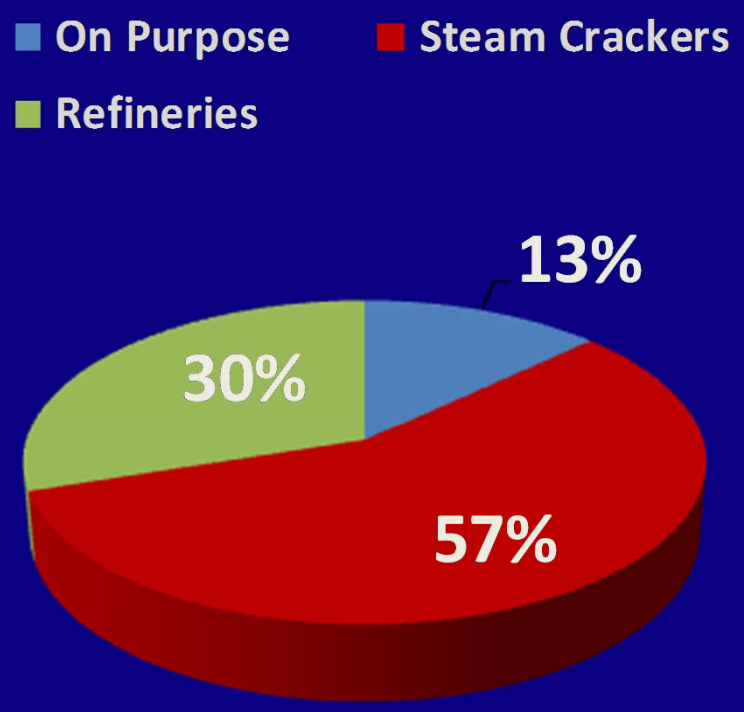
Ethylene & Propylene Supply Sources

Ethylene Supply Sources



127 Million Tons (US) 2011*

Propylene Supply Sources



79 Million Tons (US) 2011*

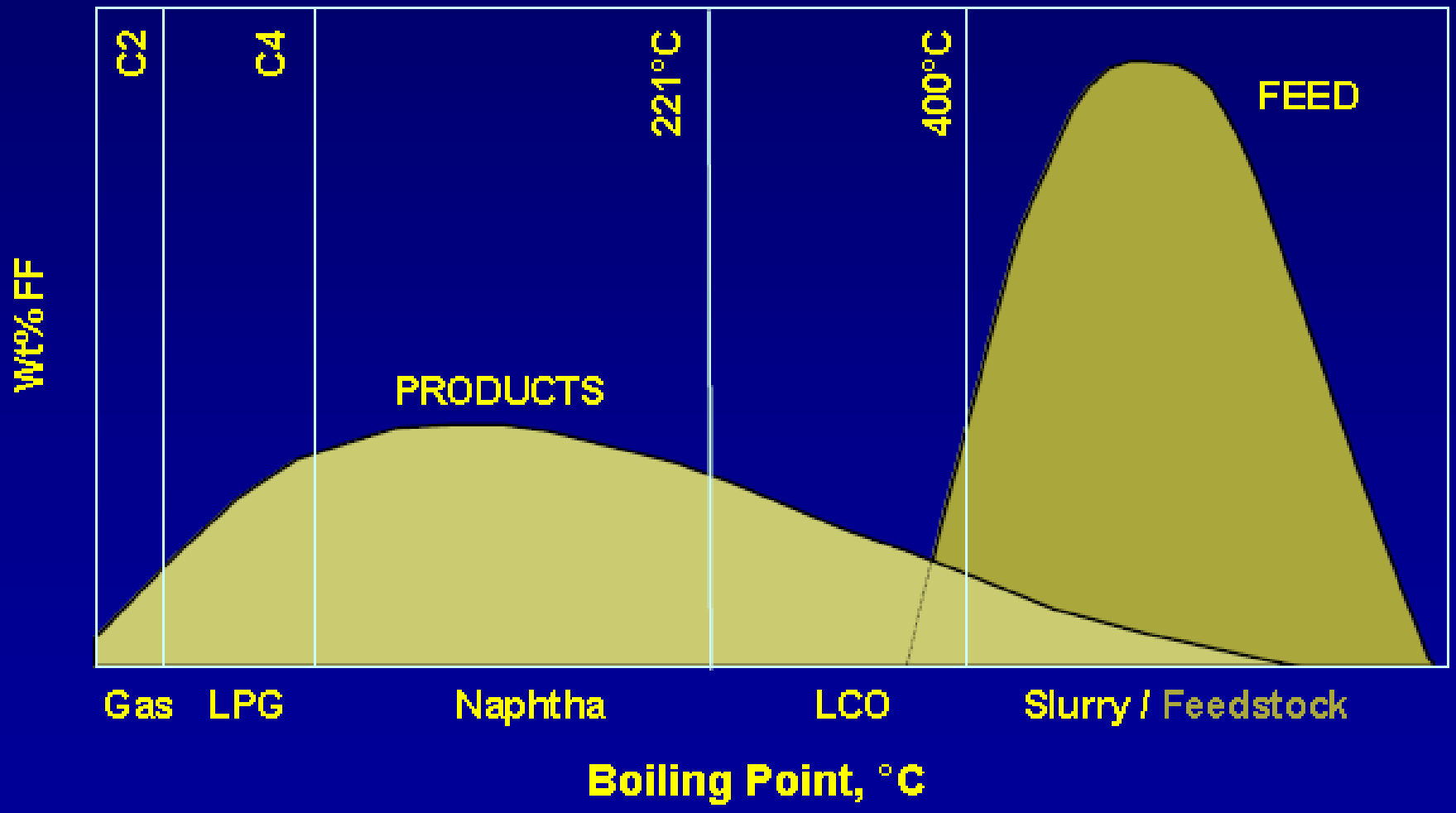
Data Courtesy of IHS CMAI

Light Crudes & Condensates

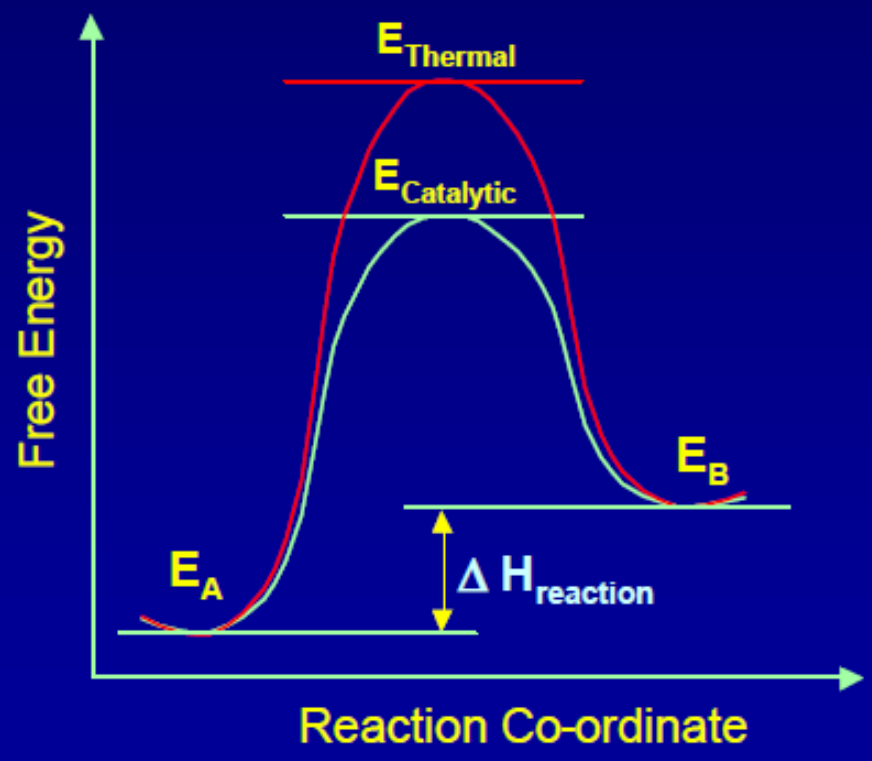
- Will be split into Light and Heavy fractions
  - Distillate Cut for Diesel and Jet/Kero
  - Bottoms – GO + Heavy tails for FCC Feed
- LPG

- Naphtha to Petrochemicals not fuels/gasoline*

Boiling Range Distribution of FCC Feed and Products



Principles of Catalysis



- Catalysts Lower Activation Energies of Forward & Backwards Reactions, Increasing the Rates of Both
- The Heat of Reaction is Unchanged by the Catalyst
- The Position of Thermodynamic Equilibrium is Unchanged by the Catalyst
- Non-Equilibrium Distributions Occur Under Kinetic Controlled Conditions

Summary of Cracking Reactions

Paraffin	→	Paraffin + Olefin
Naphthene	→	Olefin
Alkylaromatic	→	Alkylaromatic + Olefin
Olefin	→	Olefin + Olefin

- Relative Cracking Rates:
  Olefin > Alkylaromatic side chain > Paraffin > Naphthene
- Olefins most readily form carbocations
- Aromatic side-chains readily undergo cracking reactions, however, aromatic rings do not crack

Summary of Cracking Reactions

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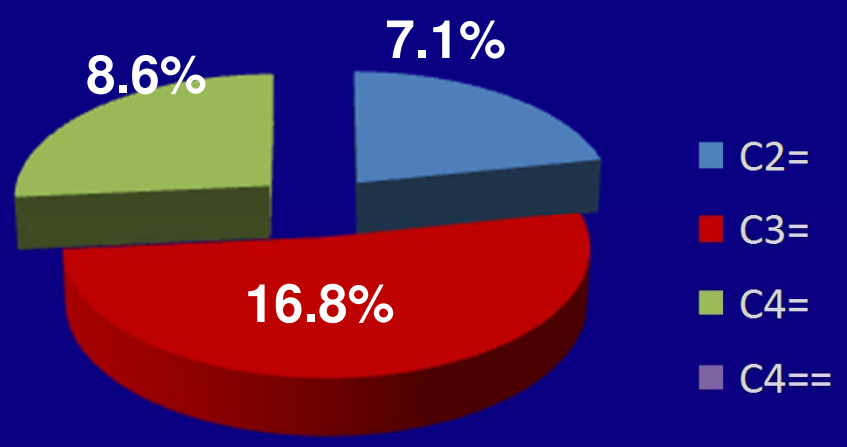
Full Range Naphtha Yields Olefins wt%

Catalytic Cracking

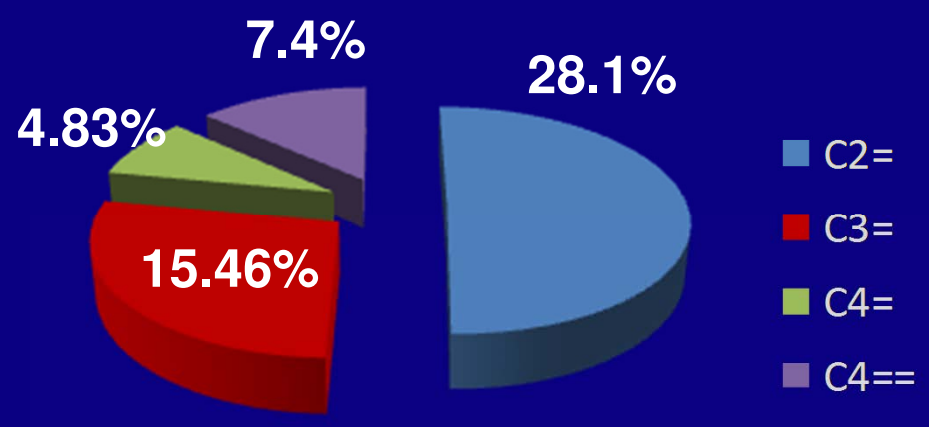
Downer Reactor



P/E of 2.4

Steam Cracking

Furnace Reactor



P/E of 0.55

Naphtha Downer vs Steam Cracker Yields