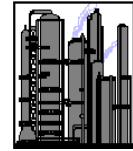


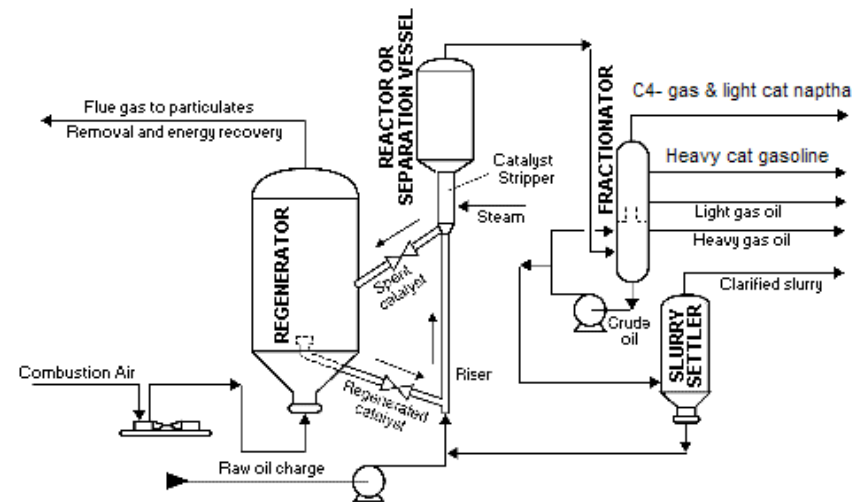
Catalytic Cracking

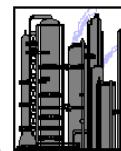
Chapter 6



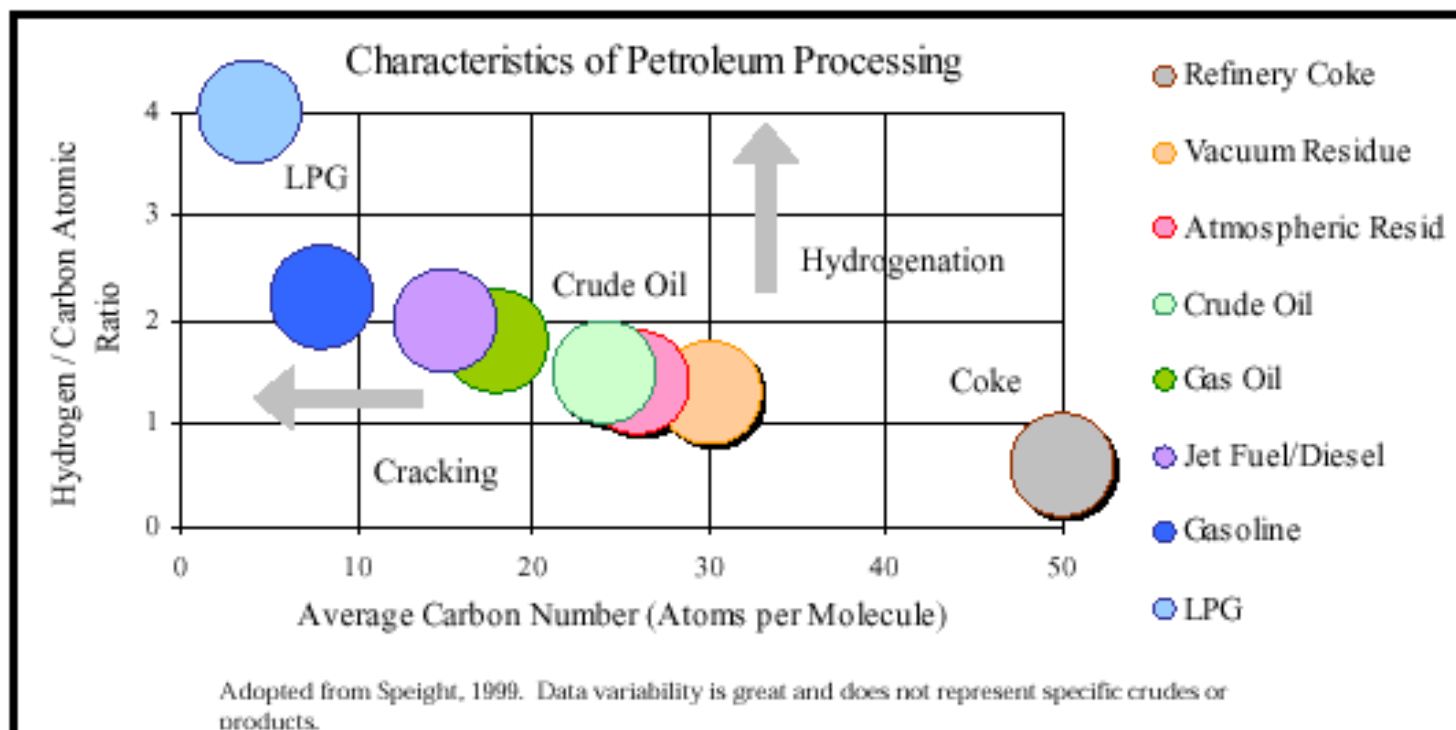
Purpose

- ▶ Catalytically crack carbon-carbon bonds in gas oils
 - Fine catalyst in fluidized bed reactor allows for immediate regeneration
 - Lowers average molecular weight & produces high yields of fuel products
 - Produces olefins
- ▶ Attractive feed characteristics
 - Small concentrations of contaminants
 - Poison the catalyst
 - Small concentrations of heavy aromatics
 - Side chains break off leaving cores to deposit as coke on catalyst
 - Must be intentionally designed for heavy resid feeds
- ▶ Products may be further processed
 - Further hydrocracked
 - Alkylated to improve gasoline anti-knock properties

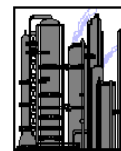




Characteristics of Petroleum Products



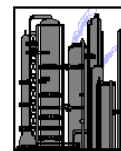
Refining Overview – Petroleum Processes & Products,
by Freeman Self, Ed Ekholm, & Keith Bowers, AIChE CD-ROM, 2000



Overview of Catalytic Cracking

- ▶ FCC “heart” of a modern US refinery
 - Nearly every major fuels refinery has an FCCU
- ▶ One of the most important & sophisticated contributions to petroleum refining technology
- ▶ Capacity usually 35% to 40% of the crude distillation capacity
- ▶ Contributes the highest volume to the gasoline pool

FCCU	35 vol%
Reformer	30 vol%
Alkylation	20 vol%
Isomerization	15 vol%

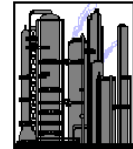


U.S. Refinery Implementation

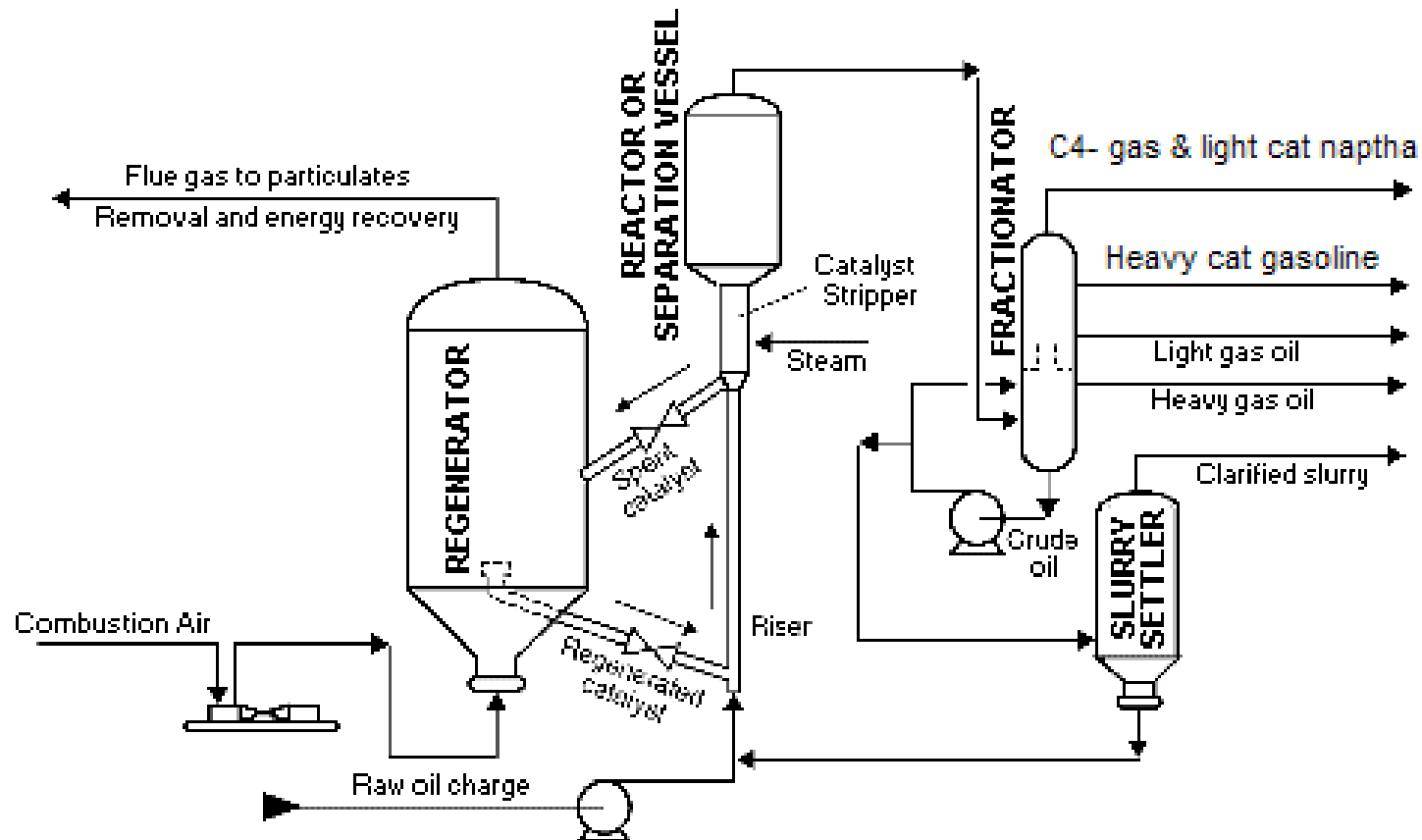
Company	State	Site	Atmospheric Crude Distillation Capacity (barrels per stream day)	Vacuum Distillation Downstream Charge Capacity, Current Year (barrels per stream day)	Cat Cracking: Fresh Feed Downstream Charge Capacity, Current Year (barrels per stream day)	Cat Cracking: Recycled Feed Downstream Charge Capacity, Current Year (barrels per stream day)
ExxonMobil Refining	Louisiana	BATON ROUGE	524,000	242,500	242,000	0
ExxonMobil Refining	Texas	BAYTOWN	596,400	288,600	215,500	8,000
BP	Texas	TEXAS CITY	475,000	237,000	175,000	8,000
BP	Indiana	WHITING	420,000	247,000	165,000	4,000
PDVSA	Louisiana	LAKE CHARLES	440,000	235,000	147,000	3,000
Hovensa LLC	Virgin Islands	KINGSHILL	525,000	225,000	149,000	0
ConocoPhillips	New Jersey	LINDEN	250,000	75,000	145,000	0
Sunoco	Pennsylvania	PHILADELPHIA	355,000	163,200	138,500	0
Marathon Petroleum	Louisiana	GARYVILLE	275,000	142,000	131,000	0
Motiva Enterprises	Louisiana	NORCO	250,000	95,000	120,000	0



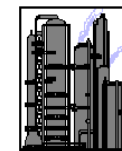
Top 10 combined Cat Cracking



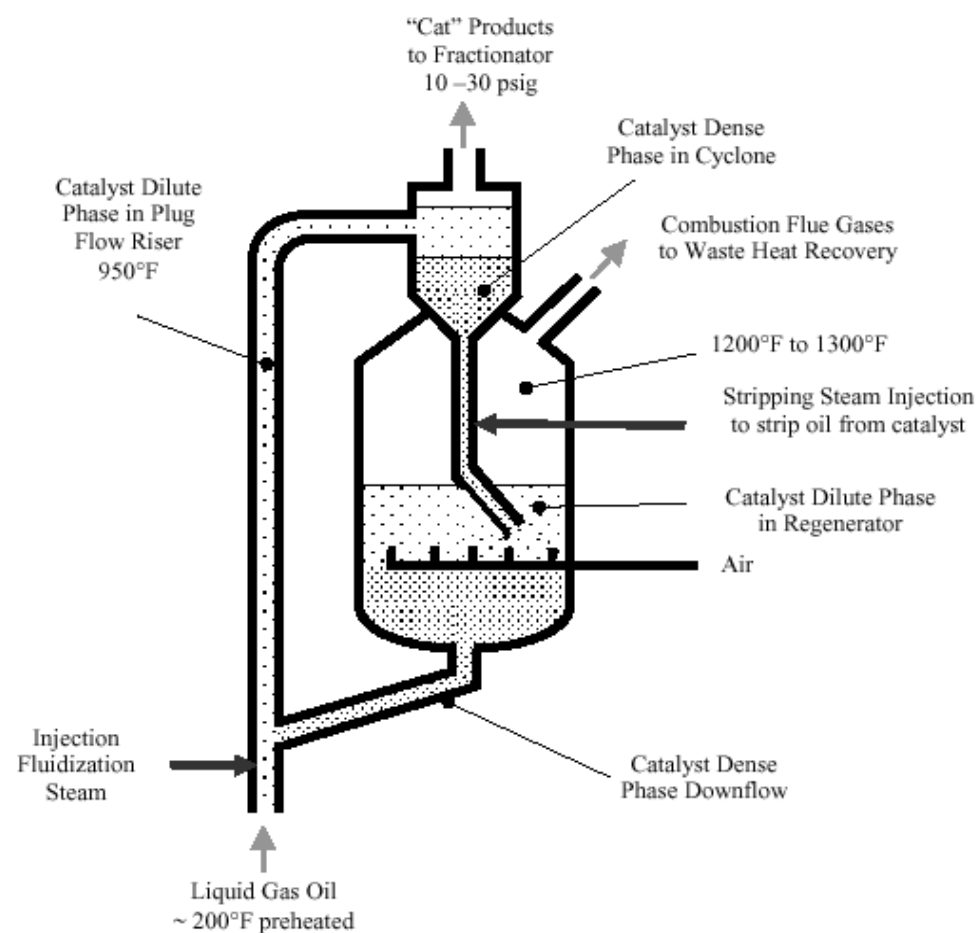
FCC Complex



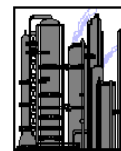
Modified from http://www.osha.gov/dts/osta/otm/otm_iv/otm_iv_2.html



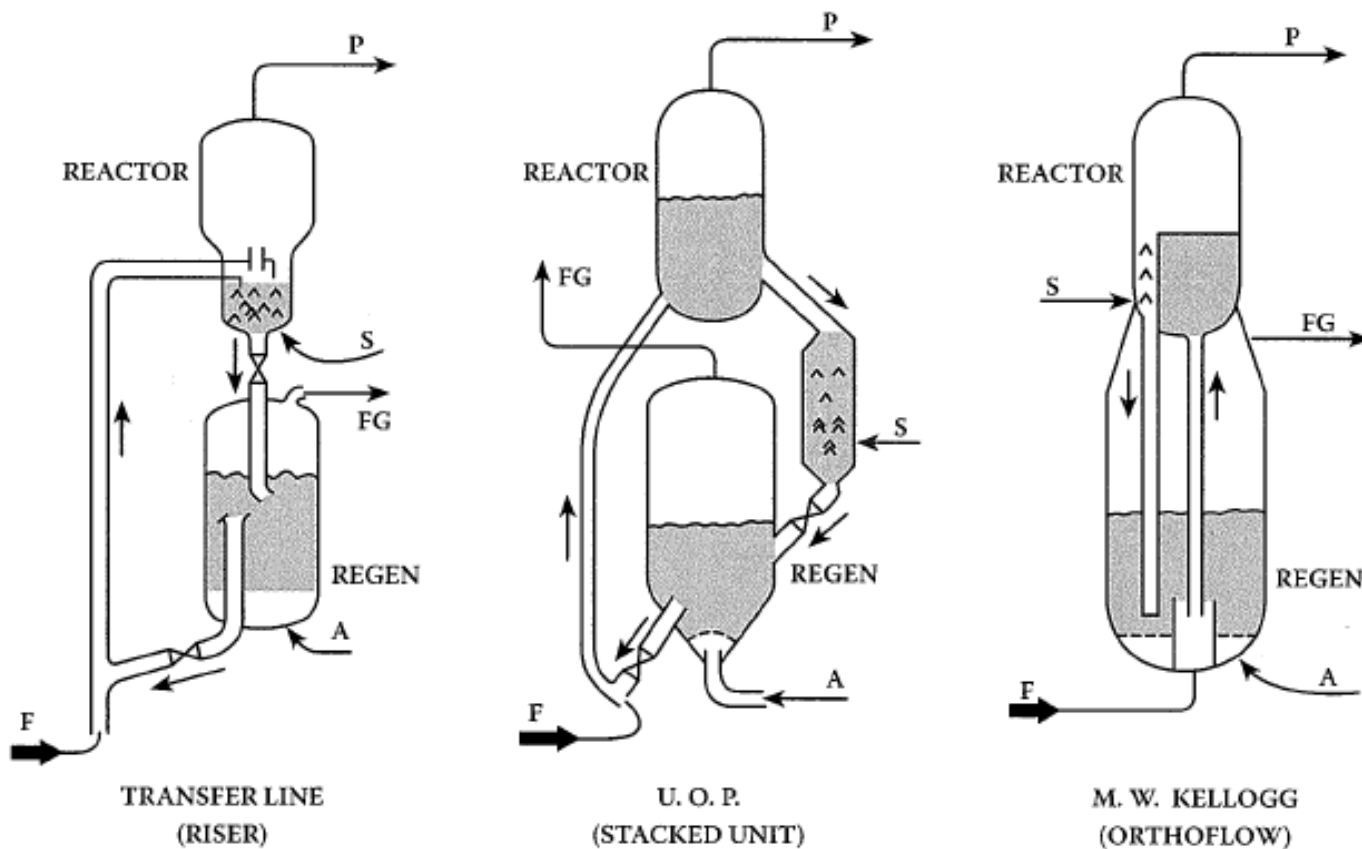
FCC Riser/Regenerator Combination



Refining Overview – Petroleum Processes & Products,
by Freeman Self, Ed Ekholm, & Keith Bowers, AIChE CD-ROM, 2000



Other FCC Configurations

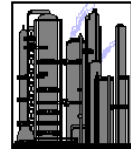


F = FEED FG = FLUE GAS S = STEAM P = PRODUCT A = AIR



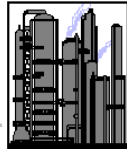
Petroleum Refining Technology & Economics – 5th Ed.
by James Gary, Glenn Handwerk, & Mark Kaiser, CRC Press, 2007

Fluidized Catalytic Cracking Technologies

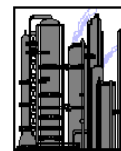


Provider	Features
Shaw	Deep catalytic cracking
ExxonMobile Research & Engineering	Fluid catalytic cracking
KBR	Fluid catalytic cracking
Lummus Technology	Fluid catalytic cracking
Shaw	Fluid catalytic cracking
Shell Global Solutions	Fluid catalytic cracking
UOP	Fluid catalytic cracking
Lummus Technology	Fluid catalytic cracking for maximum olefins
KBR	Fluid catalytic cracking, high olefin content
KBR	Fluid catalytic cracking, residual
Haldor Topsoe A/S	Fluid catalytic cracking -- pretreatment
Shaw	Resid cracking
Axens	Resid cracking

Early Fixed & Moving Bed Catalytic Cracking

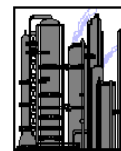


- ▶ Cyclic fixed bed catalytic cracking commercialized in late 1930s
 - Houdry Process Corporation formed in 1930
 - First Houdry catalyst cracker started up at Sun Oil's Paulsboro, New Jersey, refinery in June 1936
 - Three fixed bed reactors & processed 2,000 barrels/day
 - 12,000 barrels/day commercial unit went on stream at Sun's Marcus Hook Refinery in 1937
 - Other adoptees: Gulf, Sinclair, Standard Oil of Ohio, & The Texas Company
- ▶ Sun & Houdry Process Corporation started development on a moving bed process in 1936
 - Pilot Thermofor catalytic cracker was started in 1941
 - First commercial 20,000-barrel/day unit commissioned at Magnolia's Beaumont Refinery in 1943



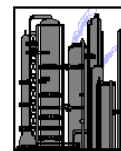
Fluidized Catalytic Cracking

- ▶ Up-flow dense phase particulate solid process credited to W.K. Lewis, MIT
- ▶ Originally developed as the Winkler coal gasification process
 - Standard Oil of New Jersey, Standard Oil of Indiana, M.W. Kellogg, Shell Oil, The Texas Company, & others
- ▶ Dense phase – back mixed reactor
 - Model I FCCU at Standard Oil of New Jersey’s Baton Rouge Refinery, 1942
 - Model II dominated catalytic cracking during early years
 - Designed before first Model I operating
- ▶ Dilute phase — riser reactor design
 - Catalysts based on molecular sieve – 1960s
 - Significantly higher cracking activity & gasoline yields – lower carbon on catalyst
 - Plug flow – drastically reduced residence time & 90% feed conversions



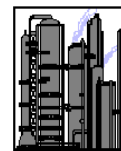
Feeds for Catalytic Cracking

- ▶ Aromatic rings typically condense to coke
 - No hydrogen added to reduce coke formation
 - Amount of coke formed correlates to carbon residue of feed
 - Feeds normally 3-7 wt% CCR
- ▶ Catalysts sensitive to heteroatom poisoning
 - Sulfur & metals (nickel, vanadium, & iron)
 - Feeds may be hydrotreated
- ▶ Atmospheric & vacuum gas oils are primary feeds
 - Could be routed to the hydrocracker for diesel production
 - Not as expensive a process as hydrocracking
 - Dictated by capacities & of gasoline/diesel economics
- ▶ Hydrotreated feed results in cleaner products, not high in sulfur



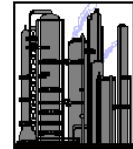
FCC Products

- ▶ Primary goal to make gasoline & diesel while minimizing production of heavy fuel oil
 - “Cat gasoline” contributes largest volume to the gasoline pool
 - Front end rich in olefins
 - Back end highly aromatic with some olefins
 - Does not contain much C-6 & C-7 olefins – very reactive & form lighter olefins & aromatics
- ▶ Coke production small but very important
 - Burned in regenerator & provides heat for cracking reactions
- ▶ Light ends contain large amounts of olefins
 - Good for chemical feedstock
 - Can recover chemical grade propylene & ethylene
 - Propylene, butylene, & C₅ olefins can be alkylated for higher yields of high-octane gasoline

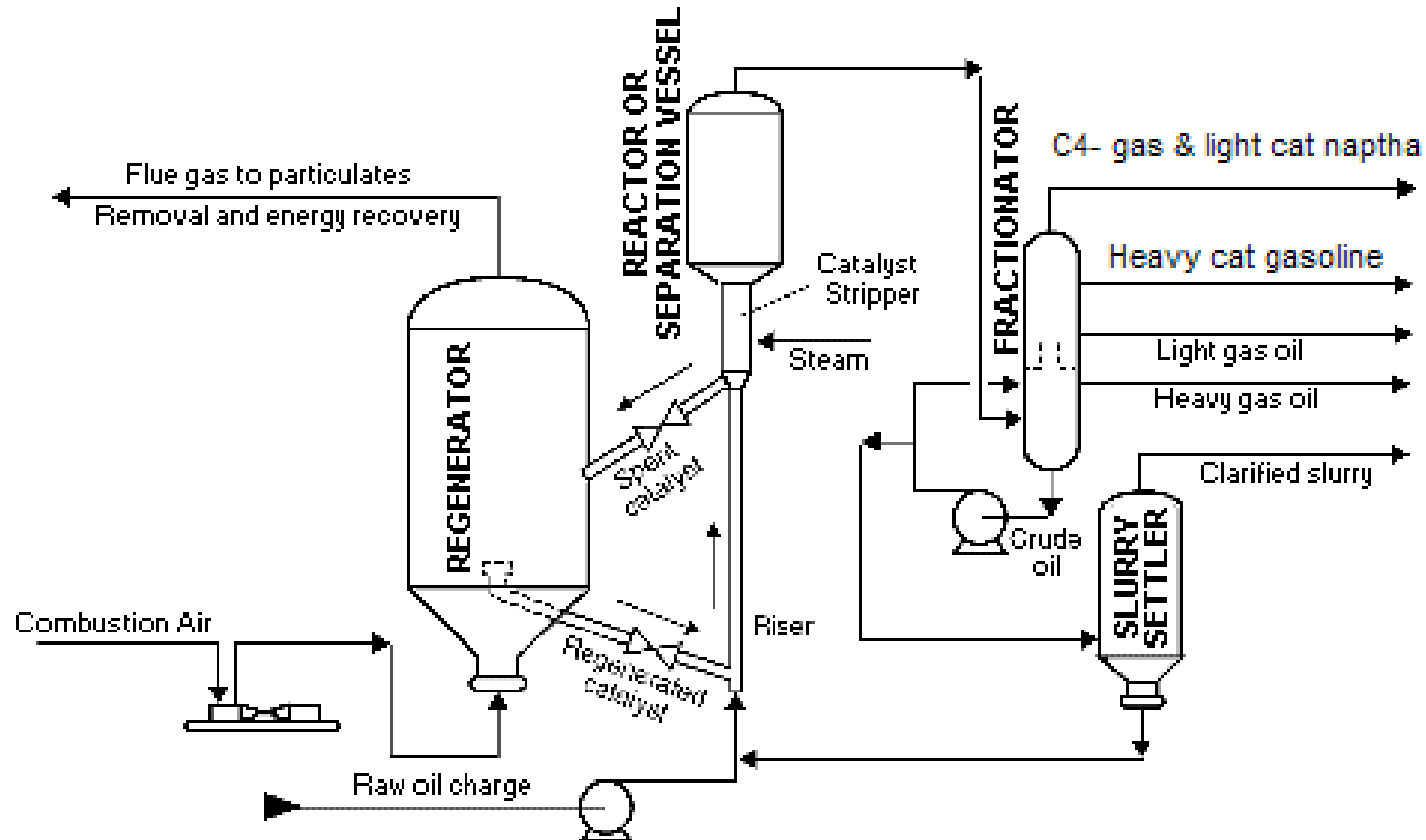


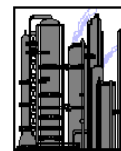
FCC Products

- ▶ Cat kerosene & jet fuel
 - Low centane number because of aromatics – lowers quality diesel pool
- ▶ Gas oils – “cycle oils”
 - Same boiling range as initial gas oil feedstock
- ▶ “Slurry”
 - Heavy residue from process
 - High in sulfur, small ring & polynuclear aromatics, & catalyst fines
 - Usually has high viscosity
 - Disposition
 - Blended into the heavy fuel oil (“Bunker Fuel Oil” or Marine Fuel Oil)
 - Hydrocracked
 - Blended into coker feed – can help mitigate problems with shot coke production



FCC Products

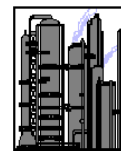




Product Yields

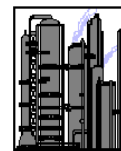
- ▶ Produces high yields of liquids & small amounts of gas & coke
 - Mass liquid yields are usually 90%-93%; liquid volume yields are often more than 100% (volume swell)
 - (Rule of thumb) Remaining mass yield split between gas & coke
- ▶ ***The yield pattern is determined by complex interaction of feed characteristics & reactor conditions that determine severity of operation***
 - Rough yield estimation charts given in text pp. 117-130 pp. 144-156
- ▶ Conversion defined relative to what remains in the original feedstock boiling range

$$\text{Conversion} = 100\% - (\text{Gas Oil Yield})$$



Use of Yield Charts

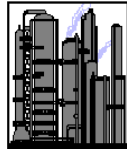
		Vol%		Wt%		Density	
Fuel Gas				6.19			
LPG	C3	6.20	6.21		Ratio		Pure
	C3=		6.21		Ratio		Pure
	IC4		6.22		Ratio		Pure
	NC4		6.22		Ratio		Pure
	C4=s		6.22		Ratio		Pure
Gasoline		6.23		Ratio		6.27	
Cycle Oils	LCO	100% - Conv	△	△	△	Ratio	Ratio
	HCO		6.24/25		Ratio		6.27
Coke				6.18			
Total				100%	100%		



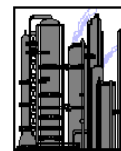
Catalytic Cracking Catalysts & Chemistry

- ▶ Zeolite catalysts
 - High activity
 - High gasoline & low coke yields
 - Good fluidization properties
 - Size between flour & grains of sand.
 - Balance between strength (so it doesn't break apart as it moves through system) but doesn't abrade the equipment internals.
 - » 70 tons/min typical circulation rate
- ▶ Acid site catalyzed cracking & hydrogen transfer via carbonium mechanism
 - Basic reaction — carbon-carbon scission of paraffins & cycloparaffins to form olefins & lower molecular weight paraffins & cycloparaffins
 - Paraffinic side chains can be cleaved from aromatic cores
 - Olefins exhibit carbon-carbon scission & isomerization with alkyl paraffins to form branched paraffins
 - Cycloparaffins will dehydrogenate (condense) to form aromatics
 - Small amount of aromatics & olefins will condense to ultimately form coke

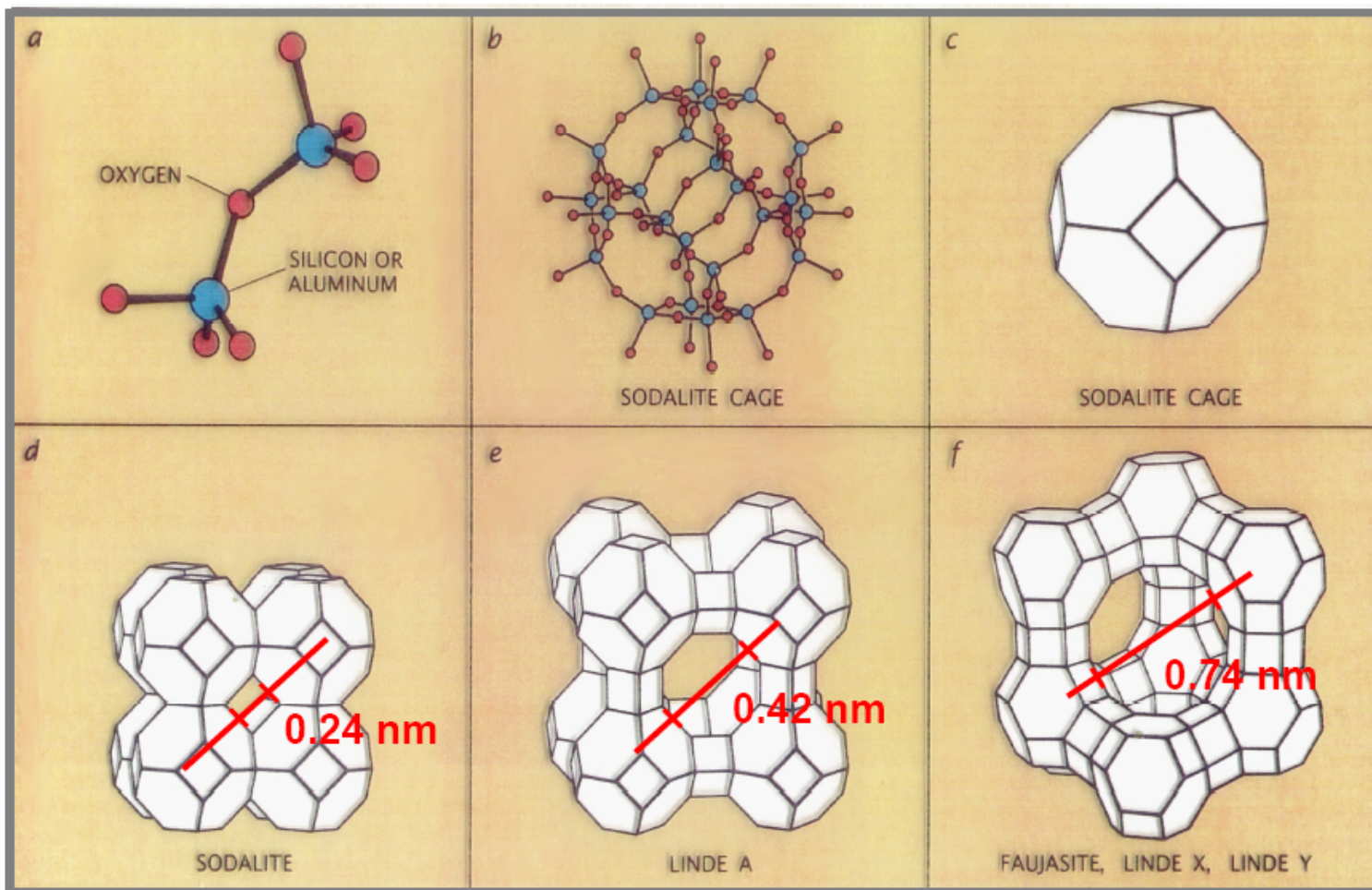
Catalytic Cracking Catalysts & Chemistry



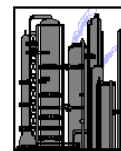
- ▶ Research continues by catalyst suppliers & licensors
 - Recognition that both crackability of feed & severity of operations are factors
 - Theoretical basis for cracking reactions lead to more precise catalyst formulation
 - Catalyst can be tailored to maximize gasoline or diesel yield or increase olefin production
 - Additives
 - Bottoms cracking
 - ZSM-5 for increased C₃ production
 - CO combustion promoters (in regenerator)



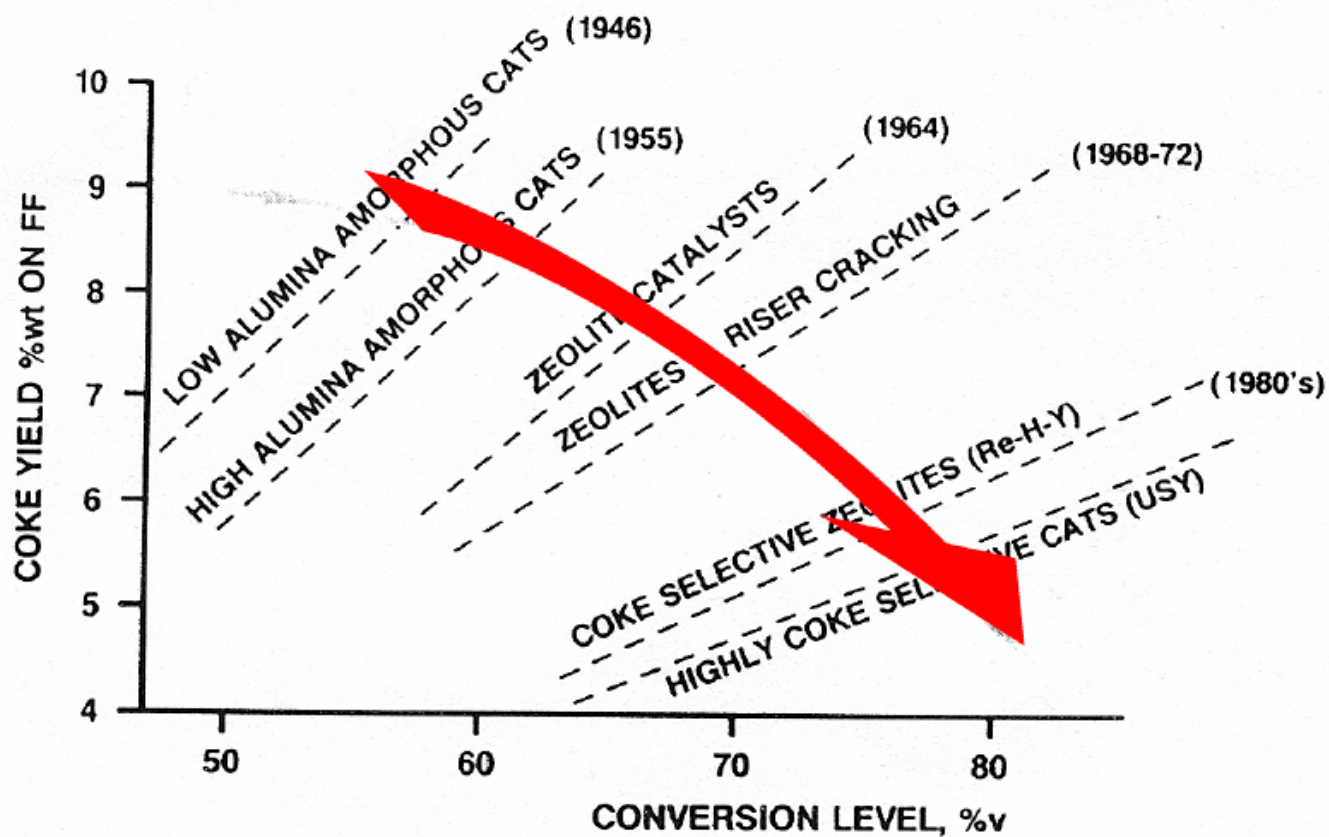
Zeolite Structure



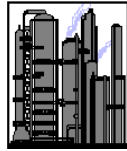
Ref: http://thor.tech.chemie.tu-muenchen.de/index.php?option=com_frontpage&Itemid=1



Trends in Catalysts

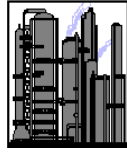


Operating Conditions & Design Features



- ▶ Designed to provide balance of reactor & regenerator capabilities
- ▶ Usually operate to one or more mechanical limits
 - Common limit is capacity to burn carbon from the catalyst
 - If air compressor capacity is limit, capacity may be increased at feasible capital cost
 - If regenerator metallurgy is limit, design changes can be formidable.
 - Regenerator cyclone velocity limit
 - Slide valve ΔP limit

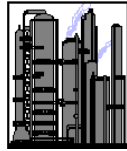
FCC Riser/Regenerator Combination



▶ Risers

- Inlet typically 1300°F, outlet 950 - 1000°F
- Increased reactor temperature to increase severity & conversion
 - May need to reverse to lower olefin content (gasoline formulation regulations)
- Reactor pressure controlled by the fractionator overhead gas compressor
 - Typically 10 to 30 psig
- High gas velocity fluidizes fine catalyst particles.
- Current designs have riser contact times typically 2 to 3 seconds.
 - Times less than 0.25 seconds reported
- Important design point: quick, even, & complete mixing of feed with catalyst
 - Licensors have proprietary feed injection nozzle systems to accomplish this
 - Want to atomize the feed so it vaporizes as quickly as possible
 - Can improve performance of an existing unit

FCC Riser/Regenerator Combination

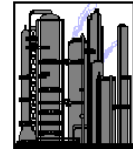


▶ Cyclones

- Gas/solid separation occurs in cyclone.
 - Increased cross sectional area decreases gas velocity.
- Rapid separation desired to prevent “over cracking.”
- Design norm – 2 stage cyclones.

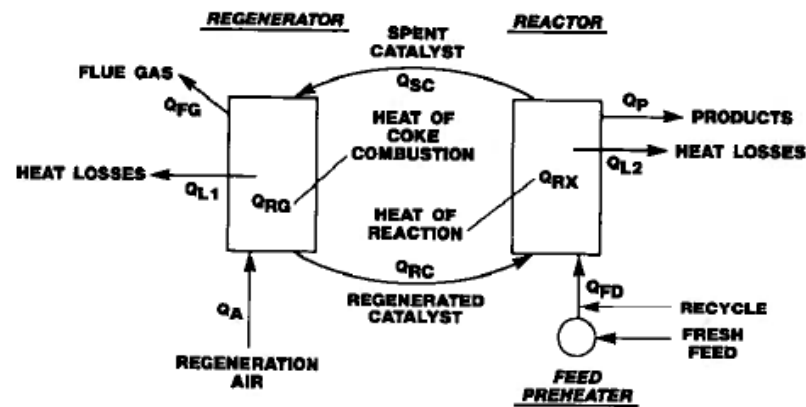
▶ Regenerators

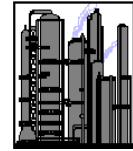
- Regenerators operate 1200 - 1500°F
 - Limited by metallurgy or catalyst concerns
- Temperature determines whether combustion gases primarily CO or CO₂
 - Partial Burn. Under 1300°F. High CO content. Outlet to CO boilers & HRSG (heat recovery/steam generation).
 - Full Burn. High temperatures produce very little CO. simpler waste heat recover systems.



FCC Riser/Regenerator Combination

- ▶ Heat balance
 - Reactor & regenerator operate in heat balance
 - More heat released in the regenerator, higher temperature of regenerated catalyst, & higher reactor temperatures.
 - Heat moved by catalyst circulation.





Resid Catalytic Cracking

- ▶ Economics favoring use of heavier crudes & direct cracking of resids
 - Instead of a normal 5-8% coke yield, it can reach 15% with resid feeds
- ▶ Requires heat removal equipment in the regenerator
 - External “catalyst coolers” on regenerator
 - Produces high-pressure steam
 - Specially designed vertical shell & tube heat exchangers
 - Proprietary specialized mechanical designs available with technology license

