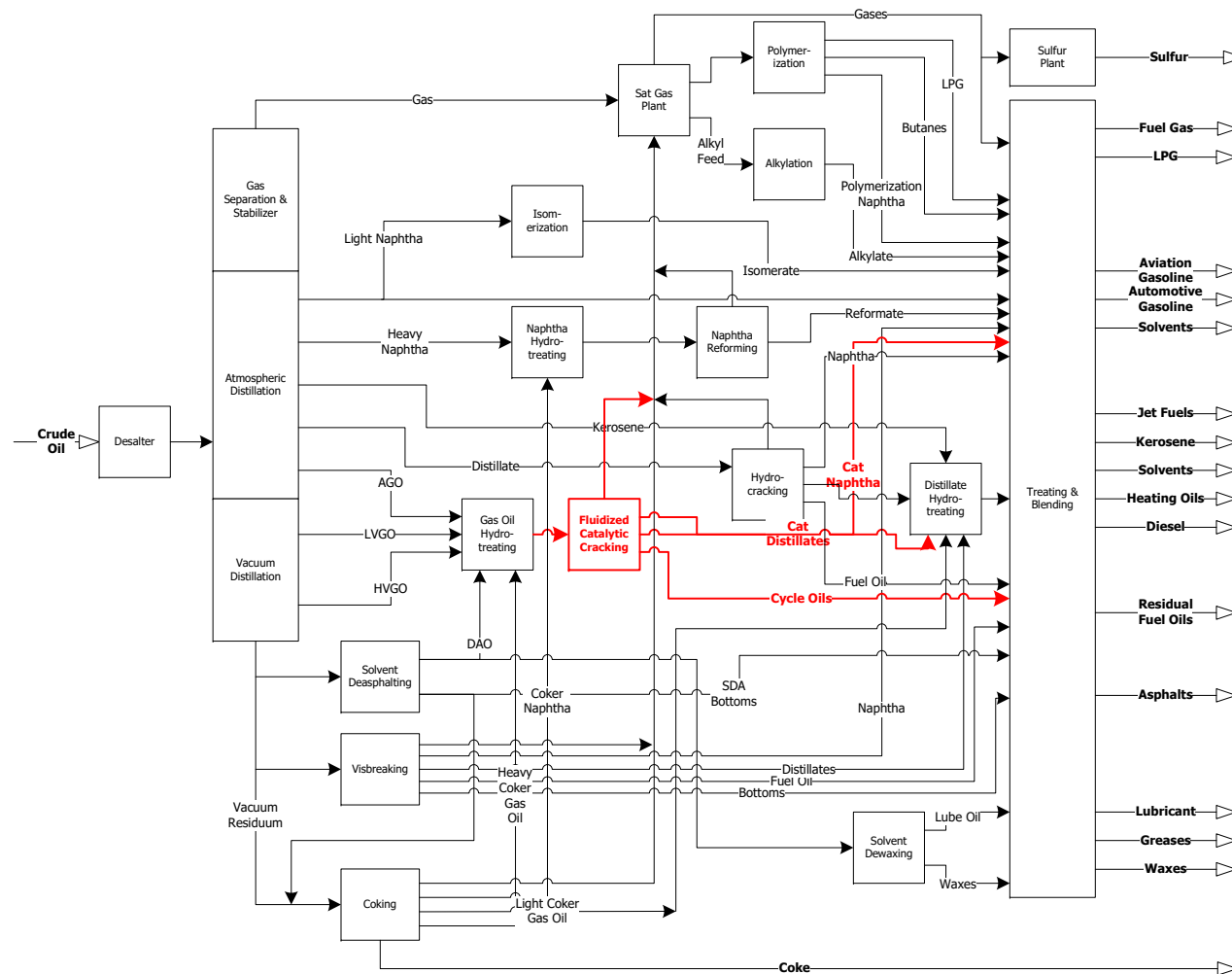


Fluidized Catalytic Cracking

Chapter 6





Overview of Catalytic Cracking

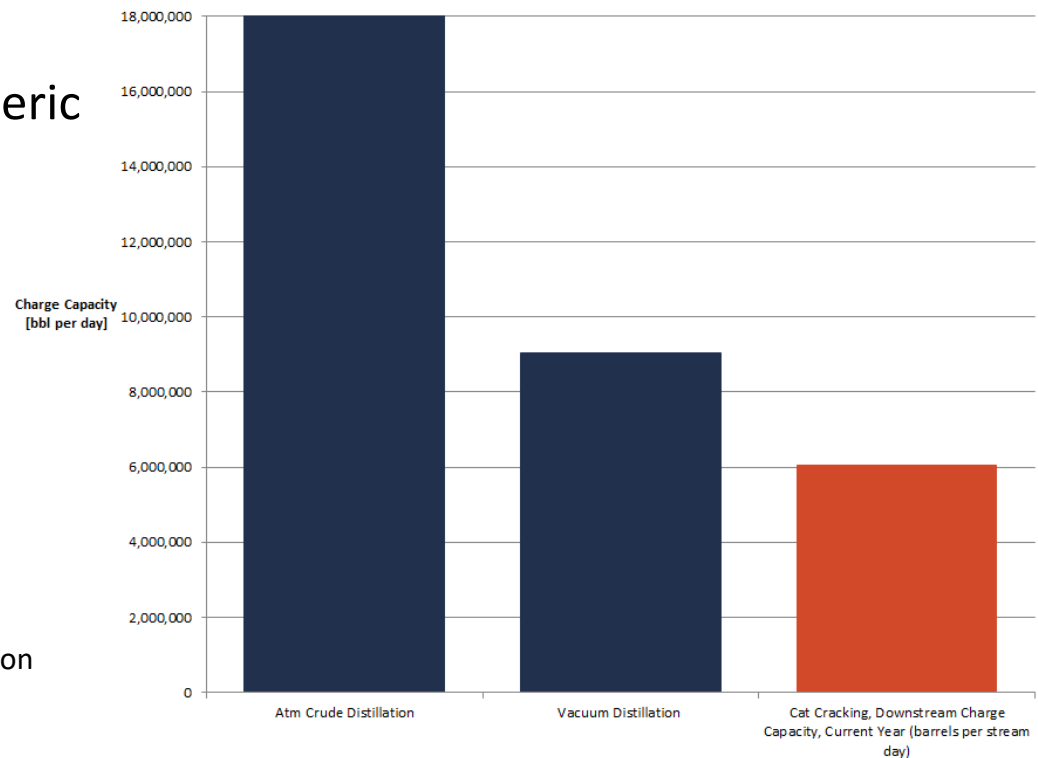
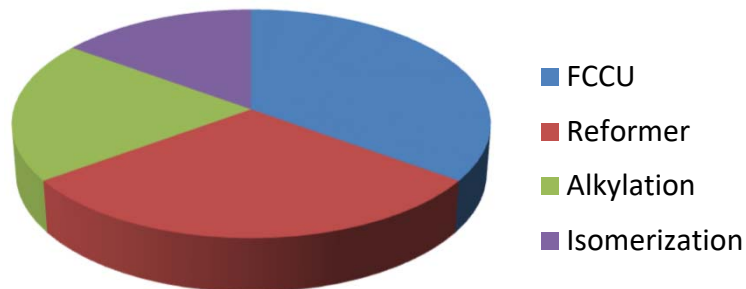
FCC “heart” of a modern US refinery

- Nearly every major fuels refinery has an FCCU

One of the most important & sophisticated contributions to petroleum refining technology

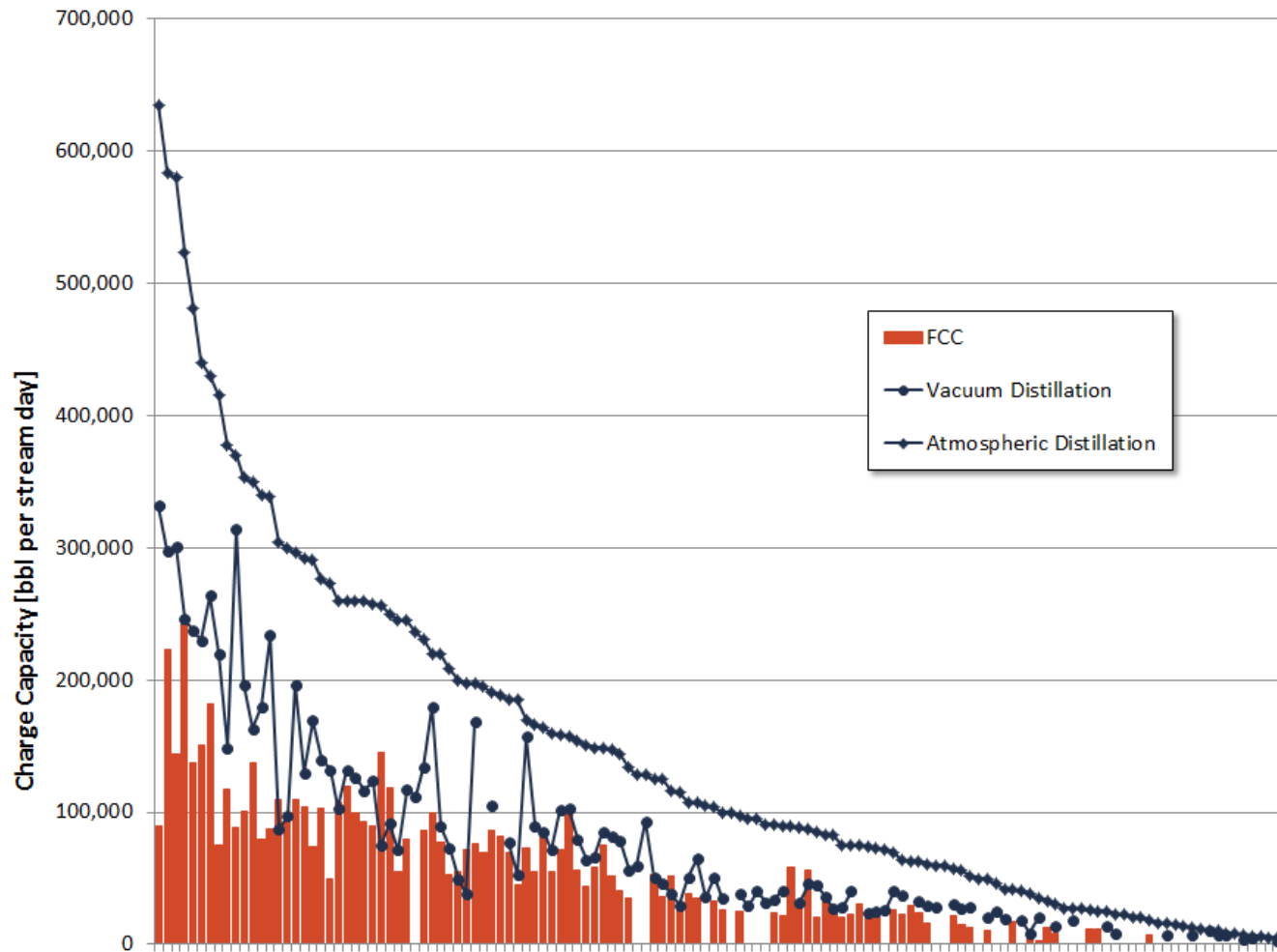
Capacity usually 1/3 of atmospheric crude distillation capacity

Contributes the highest volume to the gasoline pool



EIA, Jan. 1, 2017 database, published June 2017
<http://www.eia.gov/petroleum/refinerycapacity/>

U.S. Refinery Implementation



EIA, Jan. 1, 2017 database, published June 2017

<http://www.eia.gov/petroleum/refinerycapacity/>

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Purpose

Catalytically crack carbon-carbon bonds in gas oils

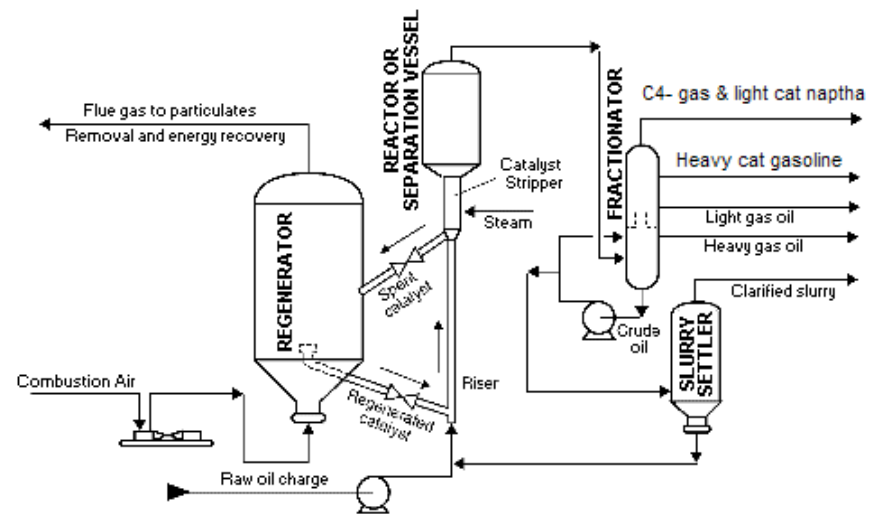
- Fine catalyst in fluidized bed reactor allows for immediate regeneration
- Lowers average molecular weight & produces
- high yields of fuel products
- Produces olefins

Attractive feed characteristics

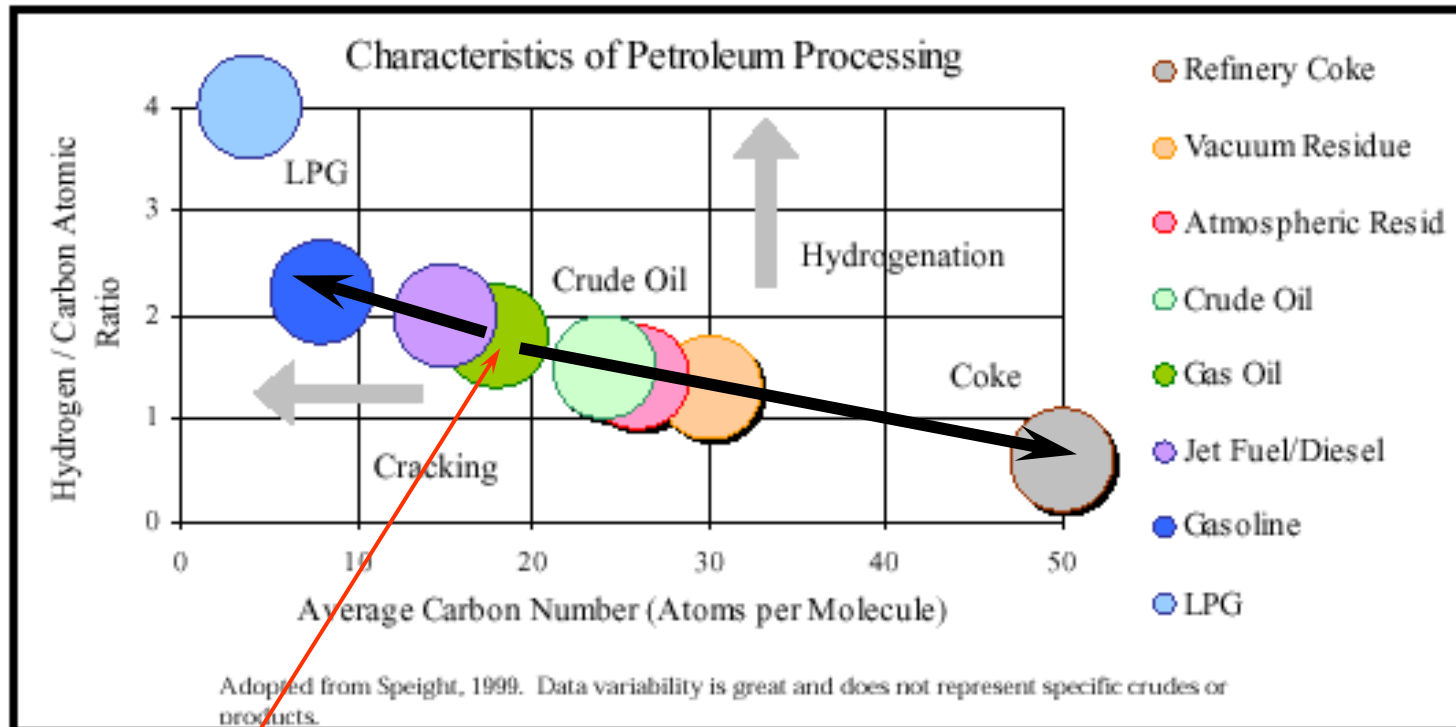
- Small concentrations of contaminants
 - Poison the catalyst
- Small concentrations of heavy aromatics
 - Side chains break off leaving cores to deposit as coke on catalyst
 - Must be intentionally designed for heavy resid feeds

Products may be further processed

- Further hydrotreated
- Olefins used as feedstock to alkylation process



Characteristics of Petroleum Products



Large conversion to light products requires some coke formation

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

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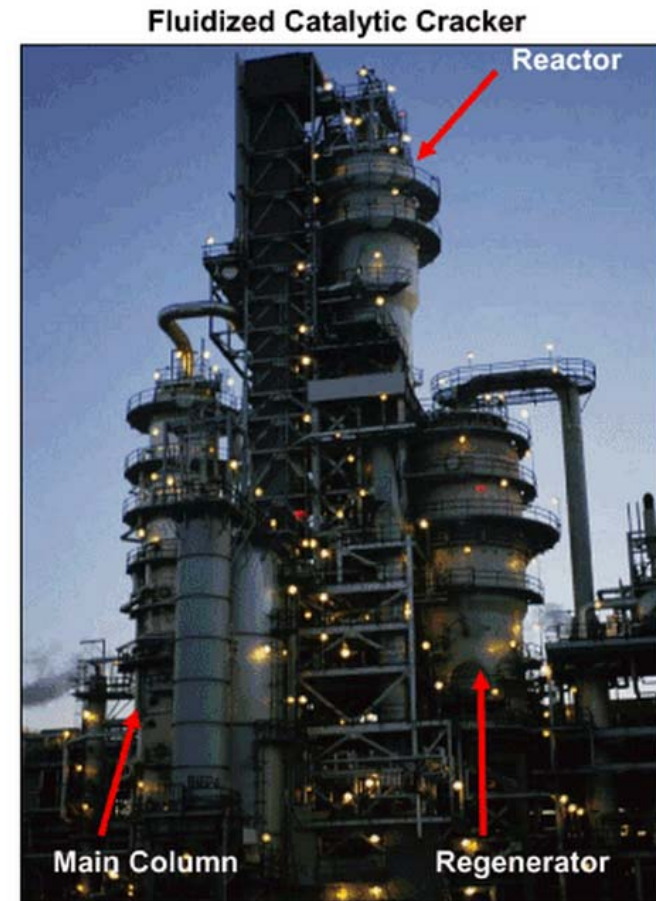
Fluid Catalytic Cracker



<http://flowexpertblog.com/2013/09/05/fccu-in-todays-refineries/>

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"Benecia Refinery Tour," Valero Energy Corp., July 9, 2007

<http://www.seinfo.com/dsvrp.uEe6.d.htm#1stPage>

Typical FCC Complex

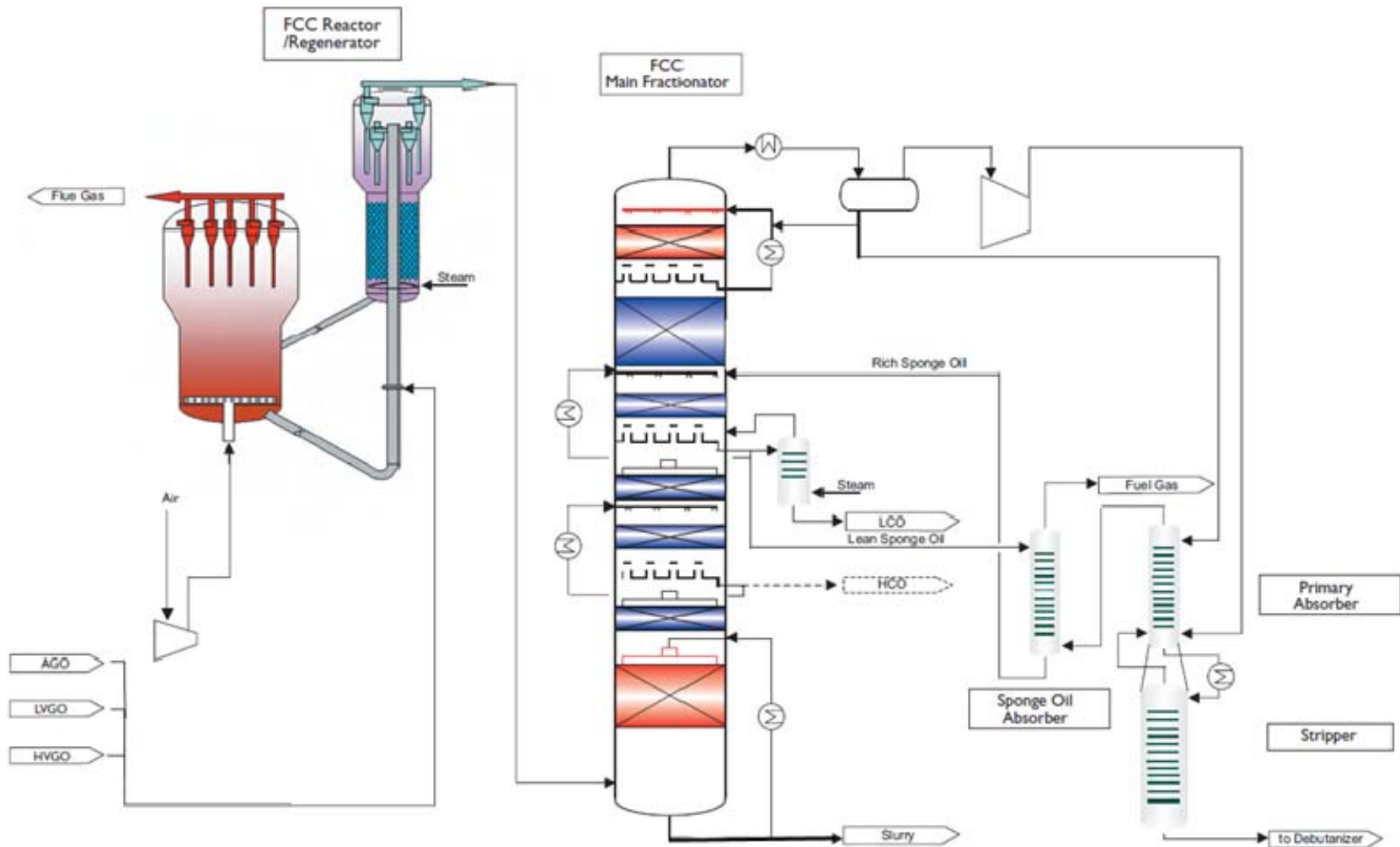
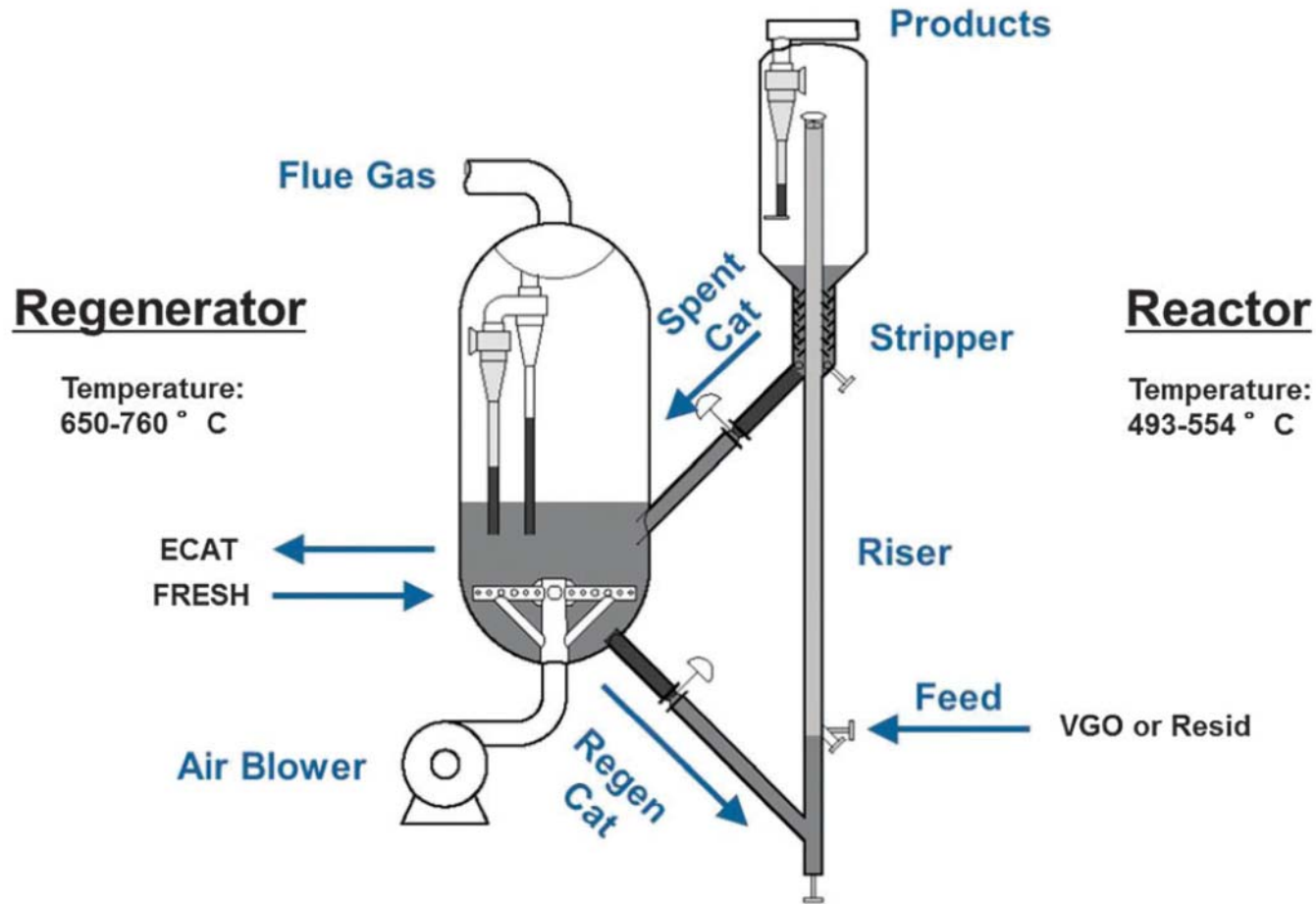


Figure modified from Koch-Glitsch Bulletin KGSS-1, Rev. 3-2010,
<http://www.koch-glitsch.com/Document%20Library/KGSS.pdf>

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FCC Riser/Regenerator Combination



"Fluid catalytic cracking: recent developments on the grand old lady of zeolite catalysis"
E.T.C. Vogt & B.M. Weckhuysen, *Chem Soc Rev*, 2015, 44, 7342-7370

History – Fixed, Moving, & Fluidized Bed Cracking

Cyclic fixed bed catalytic cracking commercialized in late 1930s

- 1st Houdry Process Corporation catalyst cracker started up at Sun Oil's Paulsboro, New Jersey, refinery in June 1936
- Three fixed bed reactors & processed 2,000 barrels/day
- Other adoptees: Sun, Gulf, Sinclair, Standard Oil of Ohio, & The Texas Company

Sun & Houdry started developing moving bed process in 1936

- 1st commercial 20,000-barrel/day unit commissioned at Magnolia's Beaumont Refinery in 1943

Fluidized bed catalytic cracking

- Up-flow dense phase particulate solid process credited to W.K. Lewis, MIT
- Early adopters: 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

Dilute phase — riser reactor design

- Molecular sieve based catalysts – 1960s
- Significantly higher cracking activity & gasoline yields – lower carbon on catalyst
- Plug flow – drastically reduced residence time & 90% feed conversions

FCC Feedstocks

Chemical species considerations

- Aromatic rings typically condense to coke
 - Feedstock can be hydrotreated to reduce the aromatic content
 - 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 to reduce poisons

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, low-sulfur products

- If feedstock not hydrotreated then the products must be separately hydrotreated to meet ultra low sulfur specs

FCC Products

Primary goal – make gasoline & diesel, minimize heavy fuel oil production

- “Cat gasoline” contributes largest volume to the gasoline pool
 - Front-end rich in olefins, back-end aromatics
 - Does not contain much C-6 & C-7 olefins – very reactive & form lighter olefins & aromatics

Coke production relatively small but very important

- Burned in regenerator & provides heat for cracking reactions
- Largest single source of CO₂ in refinery

Light ends high in olefins

- Good for chemical feedstock
- Can recover refinery grade propylene
- Propylene, butylene, & C₅ olefins can be alkylated for higher yields of high-octane gasoline

Cat kerosene & jet fuel – rarely made

- Low cetane number because of aromatics – lowers quality diesel pool
- Poor cold properties

Gas oils – “cycle oils”

- Essentially same boiling range as 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 shot coke problems

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 (per the text book) defined relative to what remains in the original feedstock boiling range:

$$\begin{aligned}\% \text{ Product Yield} &= 100 \times (\text{Product Volume}) / (\text{Feed Volume}) \\ \text{Conversion} &= 100\% - (\% \text{ Cycle Oil Yield})\end{aligned}$$

FCCU Yield Example

Product Yields from FCCU

Conversion = 72.0 vol%

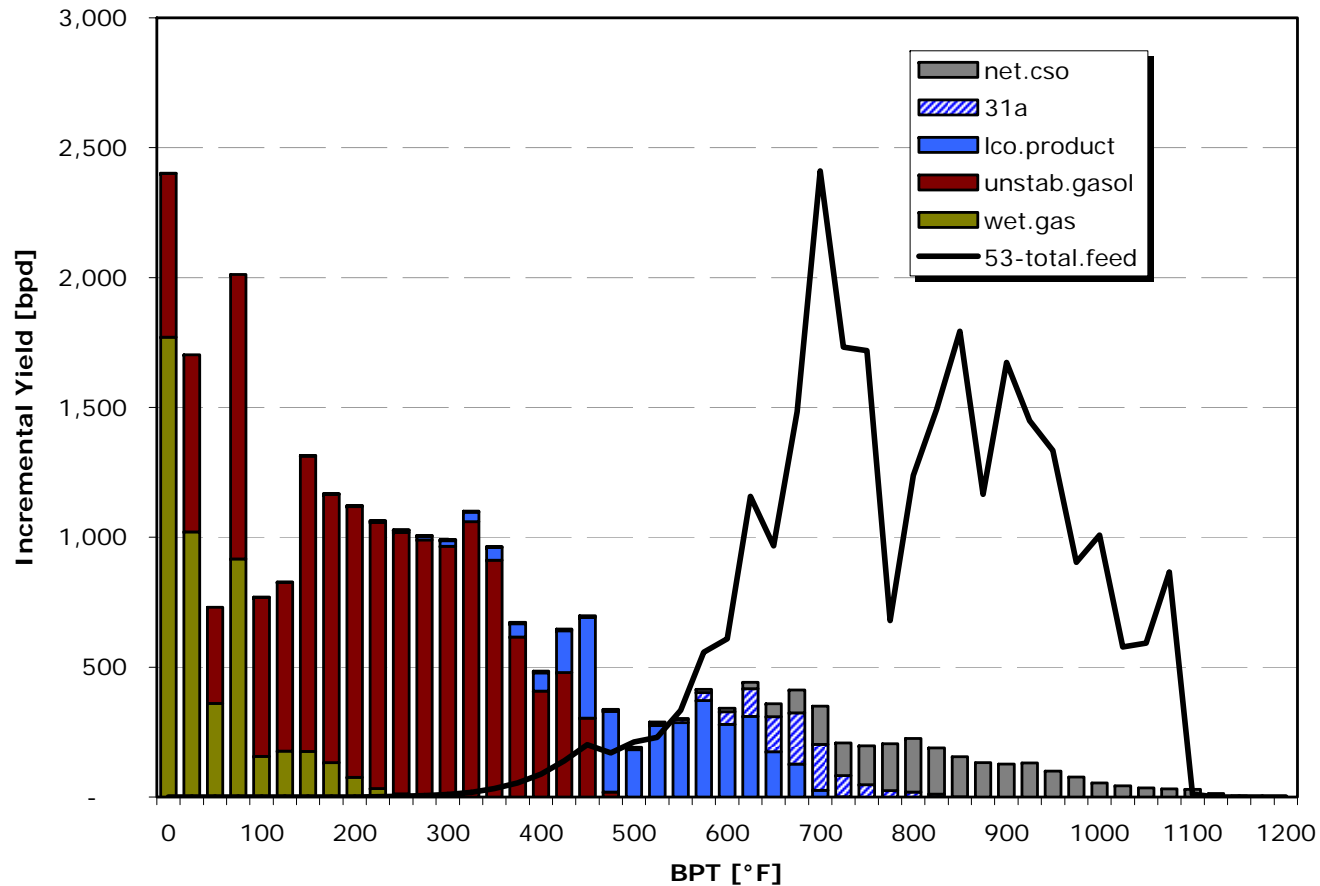
Fraction			Yields		Standard Densities			Watson K Factor	Sulfur Distribution		
	bbl/day	lb/day	vol%	wt%	*API	SpGr	lb/gal		Content	Recovery	
									wt%	lb/day	wt%
FCCU Feed (Total Gas Oil)	25,000	7,915,013	100.0%	100.0%	25.0	0.9042	7.538	12.00	0.50	39,575	
Light gases (C2-)		389,994		4.93%					2.5%	9,846	24.9%
Propane (C3)	639	113,468	2.56%	1.43%	147.6	0.5070	4.227		2.7%	3,027	7.6%
Propylene (C3=)	1,451	264,749	5.80%	3.34%	140.1	0.5210	4.344		1.1%	3,027	7.6%
Iso-butane (IC4)	1,397	275,362	5.59%	3.48%	119.9	0.5629	4.693		1.1%	3,027	7.6%
n-butane (NC4)	491	100,375	1.96%	1.27%	110.8	0.5840	4.869		3.0%	3,027	7.6%
Butylenes (C4=)	1,902	400,492	7.61%	5.06%	103.8	0.6013	5.013		0.8%	3,027	7.6%
Gasoline (C5+)	14,263	3,732,025	57.05%	47.15%	57.9	0.7473	6.230		0.1%	2,010	5.1%
Light Cycle Oil (LCO)	5,300	1,630,520	21.20%	20.60%	29.6	0.8786	7.325		0.4%	6,095	15.4%
Heavy Cycle Oil (HCO)	1,700	620,576	6.80%	7.84%	4.2	1.0425	8.692		1.0%	6,095	15.4%
Coke		387,452		4.90%					0.1%	396	1.0%
Total	27,143	7,915,013	108.57%	100.00%						39,575	100.0%
Cycle Oils	7,000	2,251,096	28.00%	28.44%	22.6	0.9184	7.657			12,189	30.8%
Total LPG	5,880	1,154,446	23.52%	14.59%						15,134	38.2%

	Yields [vol%]	
	Unnormalized	Normalized
Propane (C3)	2.92%	2.56%
Propylene (C3=)	6.63%	5.80%
Iso-butane (IC4)	6.38%	5.59%
n-butane (NC4)	2.24%	1.96%
Butylenes (C4=)	8.69%	7.61%
Total	26.87%	23.52%

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Boiling Point Ranges for Products



Based on example problem in:
Refinery Process Modeling, A Practical Guide to Steady State Modeling of Petroleum Processes, 1st ed.
 Gerald Kaes, Athens Printing Company, 02004

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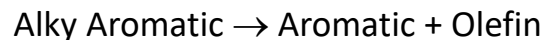
Catalytic Cracking Catalysts & Chemistry

Composites – zeolite dispersed in amorphous matrix

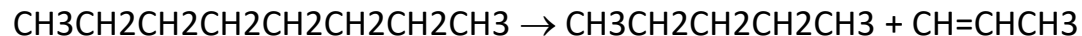
- Zeolite – 10-50 wt % – provides activity, stability, & selectivity
- Matrix – 50-90% – provides desirable physical properties & some catalytic activity

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

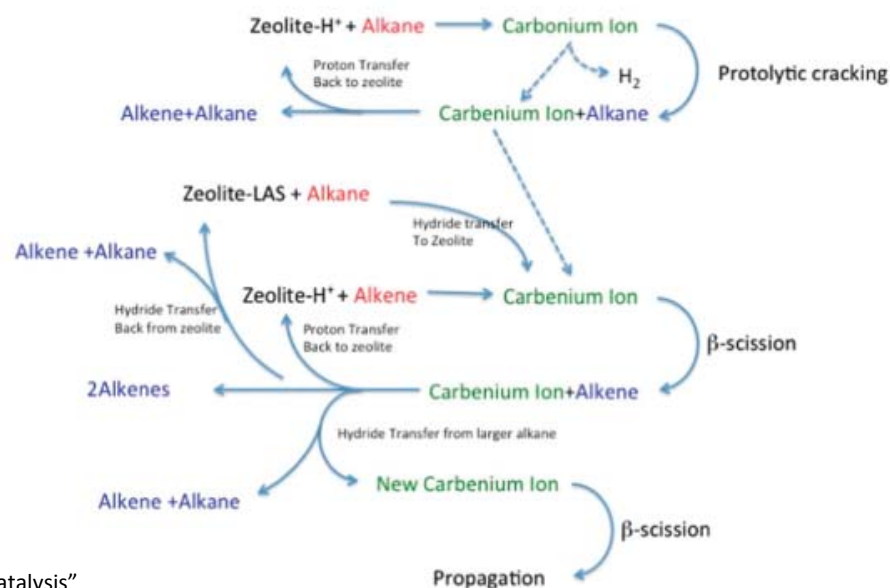
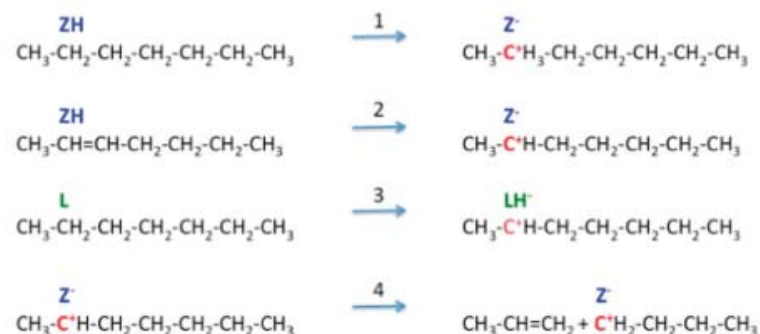
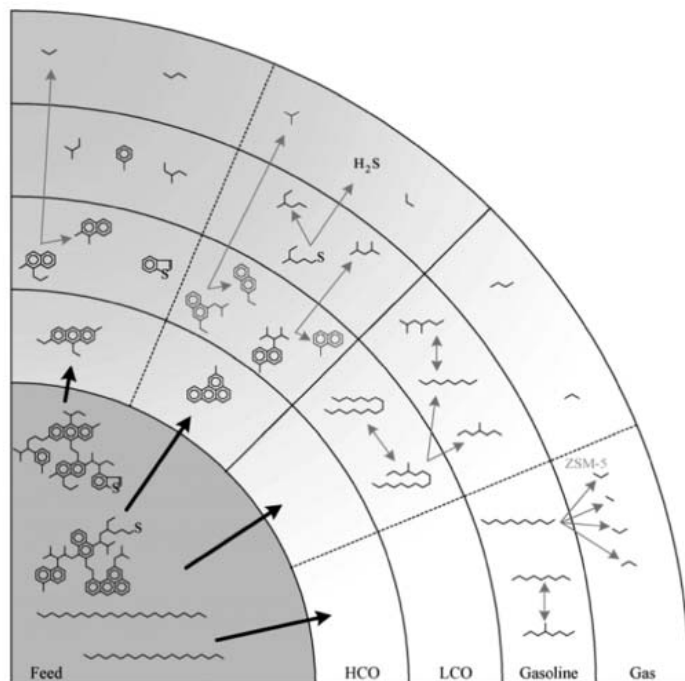


- Example



- 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

Complex System of Chemical Reactions



“Fluid catalytic cracking: recent developments on the grand old lady of zeolite catalysis”
E.T.C. Vogt & B.M. Weckhuysen, *Chem Soc Rev*, 2015, 44, 7342-7370

Catalysts & Chemistry

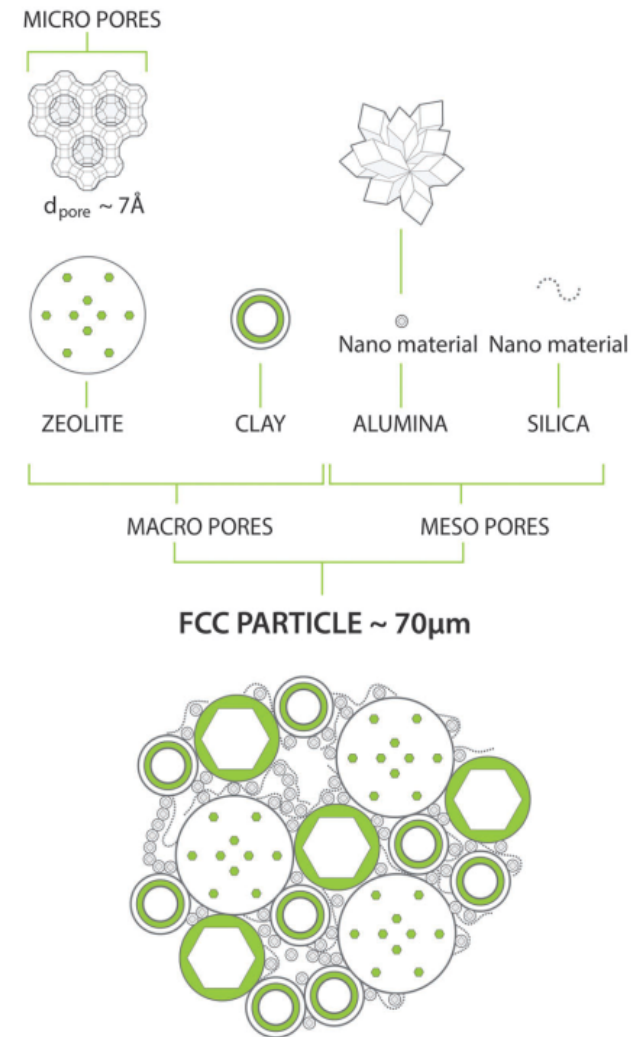
FCC catalysts consists of a number of components to meet demands of FCC system

- High activity, selectivity, & accessibility; coke selectivity
 - High gasoline & low coke yields
- Good fluidization properties & attrition resistance
 - 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
- Hydrothermal stability
- Metals tolerance

Main active component is a zeolite

- Internal porous structure with acid sites to crack larger molecules to desired size range

"Fluid catalytic cracking: recent developments on the grand old lady of zeolite catalysis"
E.T.C. Vogt & B.M. Weckhuysen, *Chem Soc Rev*, 2015, 44, 7342-7370



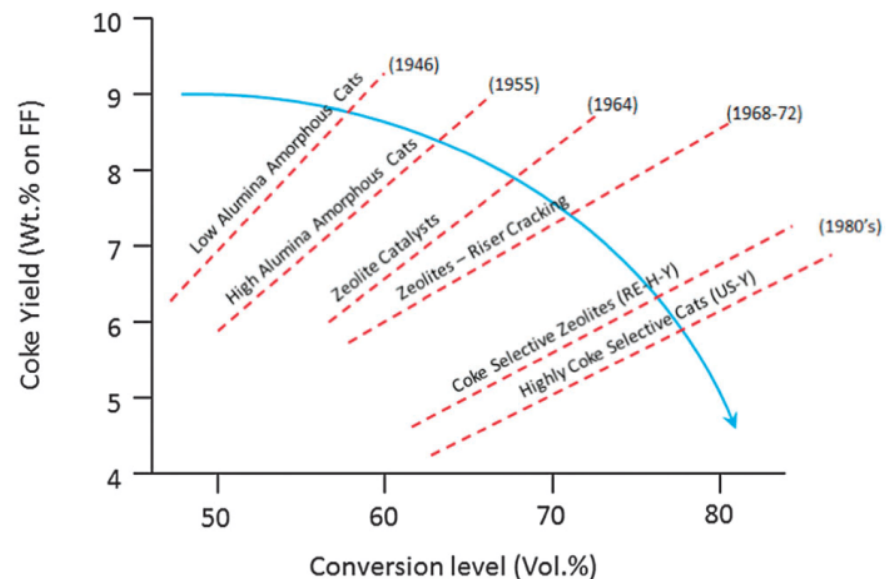
Catalysts & Chemistry

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 tailored to maximize a particular product
 - Focus used to be on gasoline...
 - now more likely diesel yield or ...
 - increased olefin production
- Additives
 - Bottoms cracking
 - ZSM-5 for increased C3 production
 - CO combustion promoters in regenerator

FCC catalyst cost

- Generally the 2nd highest operating expense, after crude oil purchases
- May pay upwards of \$3,000 per ton



"Fluid catalytic cracking: recent developments on the grand old lady of zeolite catalysis"
E.T.C. Vogt & B.M. Weckhuysen, *Chem Soc Rev*, 2015, 44, 7342-7370

Yields are catalyst dependent

As Produced Yields, volume %	Base	HDXtra	
Gasoline	56.9	51.5	
LCO	20.7	30.9	+ 10.2%
CSO	5.7	5.1	
Corrected LCO (430–650°F) vol %	16.8	20.8	+ 4%

Table 1: FCC unit yield data of first commercial trial of HDXtra at Frontier, El Dorado, KS

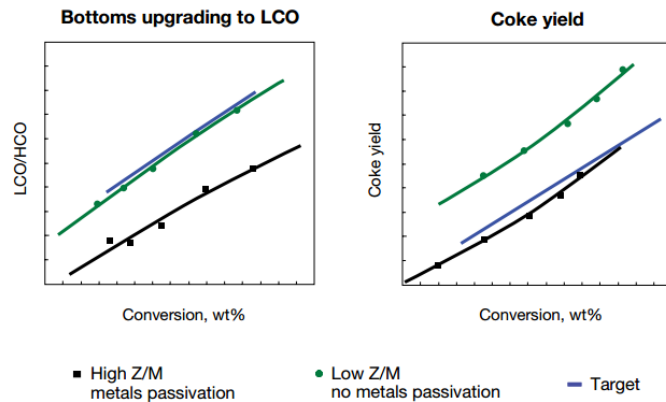


Figure 5: Defining the project objective for the development of Stamina

New Resid Fluid Catalytic Cracking (FCC) Catalyst Technology for Maximum Distillates Yield Demonstrated in Big West Oil's Salt Lake City Refinery, BASF Technical Note

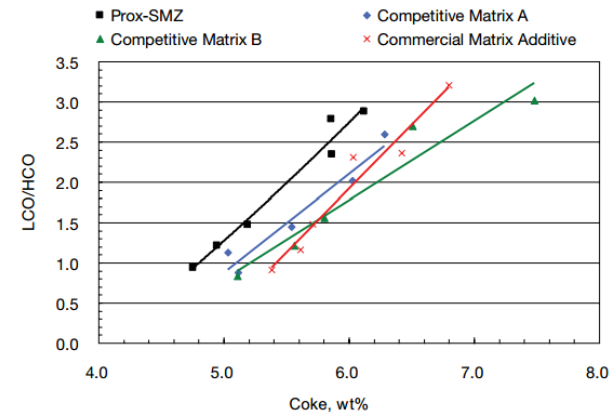


Figure 3: Bottoms upgrading of commercial FCC catalyst matrix materials in comparison to the novel Prox-SMZ matrix.

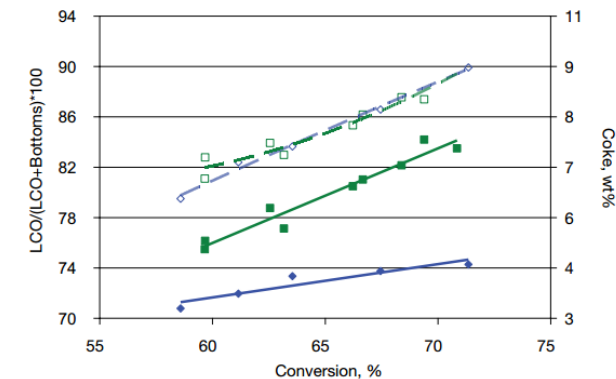


Figure 6: Comparison of the coke yield and the LCO selectivity of Flex-Tec and Stamina

Operating Conditions & Design Features

Designed to provide balance of reactor & regenerator capabilities

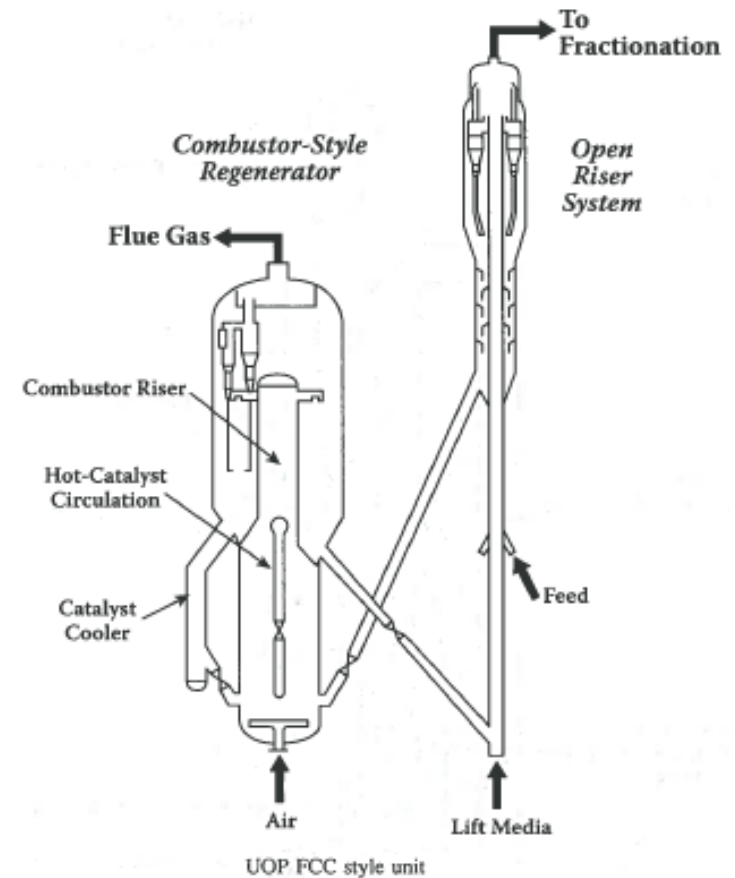
Usually operate to one or more mechanical limits

- 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.
- Important design point: quick, even, & complete mixing of feed with catalyst
 - Licensors have proprietary feed injection nozzle systems to accomplish this
 - Atomize feed for rapid vaporization
 - Can improve performance of an existing unit



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

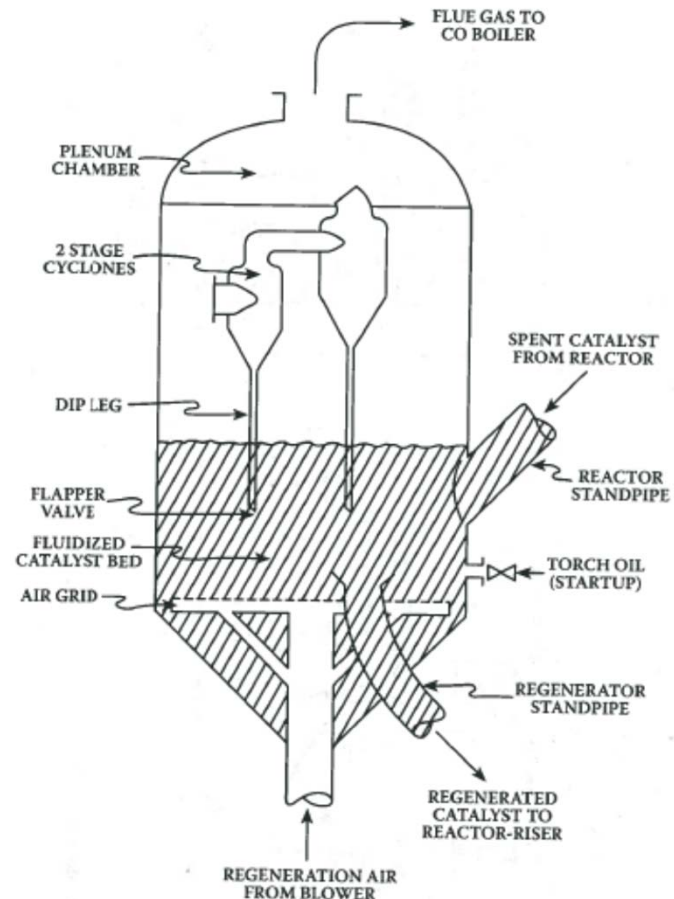
FCC Riser/Regenerator Combination

Cyclones

- Gas/solid separation in cyclones
 - Increased cross sectional area decreases gas velocity.
 - Normally 2 stage cyclones.
- Rapid separation to prevent “over cracking.”

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.

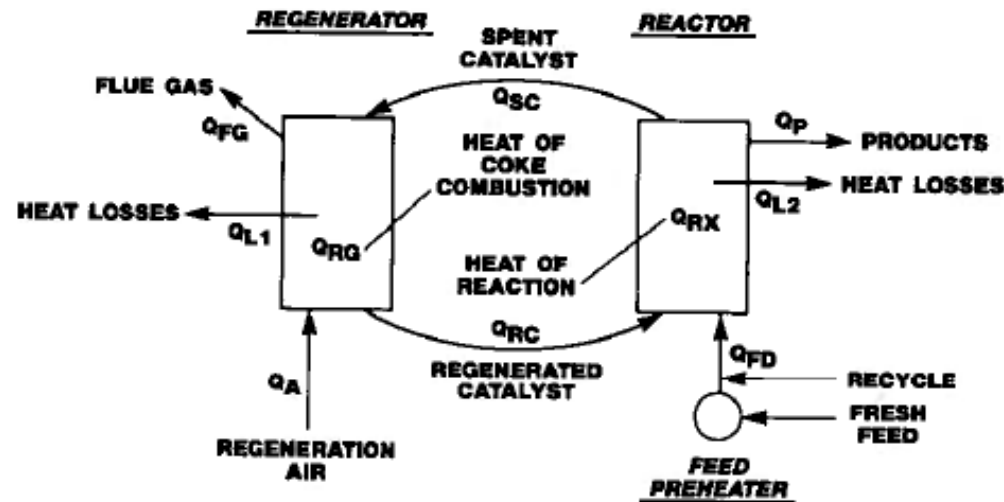


Petroleum Refining Technology & Economics – 5th Ed.
by James Gary, Glenn Handwerk, & Mark Kaiser, CRC Press, 2007

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.



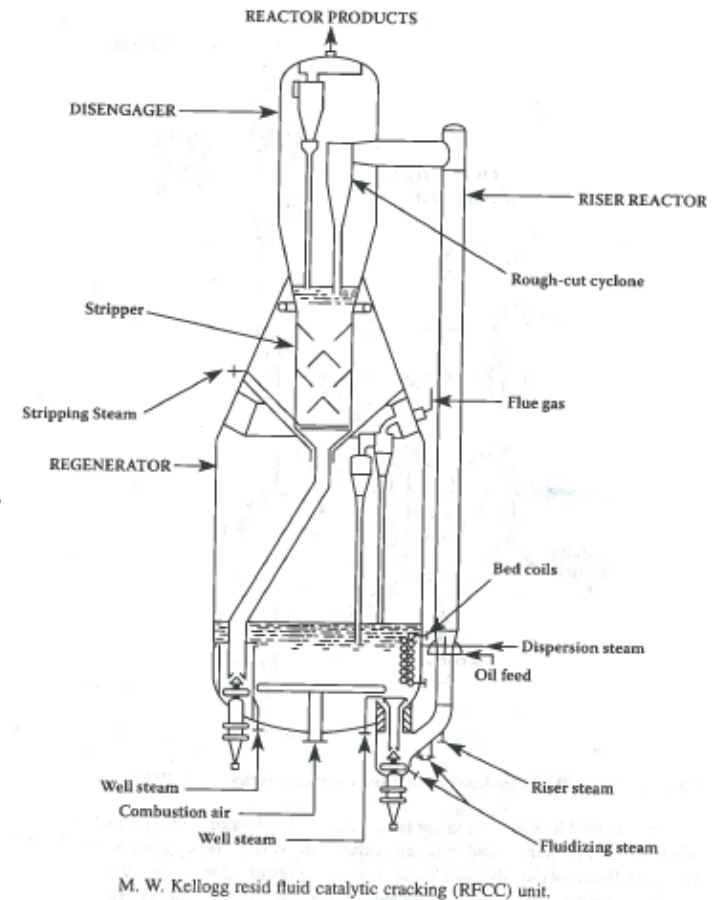
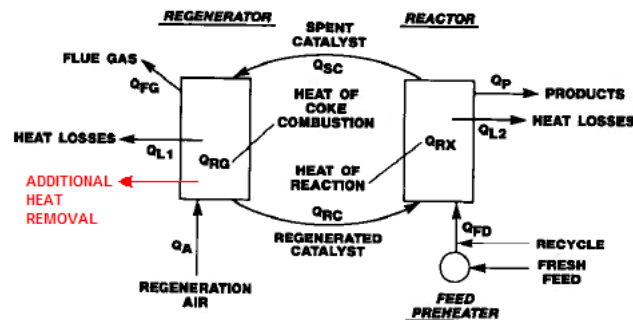
Resid Catalytic Cracking

Economics favoring direct cracking of heavier crudes & resids

- Instead of normal 5-8% coke yield can reach 15% with resid feeds

Requires heat removal in regenerator

- “Catalyst coolers” on regenerator to
 - Produces high-pressure steam
 - Specially designed vertical shell & tube heat exchangers
- Proprietary specialized mechanical designs available with technology license



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

Summary

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Summary

Heart of a gasoline-oriented refinery

Catalytically cracks feedstocks that are too heavy to blend into the diesel pool

- Special designs required to crack resids

Extremely active catalyst systems

- Deactivate with coke in the matter of seconds
- Requires the use of fluidized bed systems to regenerate catalyst
- The heat liberated from burning off the coke provides the heat to drive the cracking reactions

Supplemental Slides

Updated: July 5, 2017

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FCC vs. Hydrocracker Installed Cost

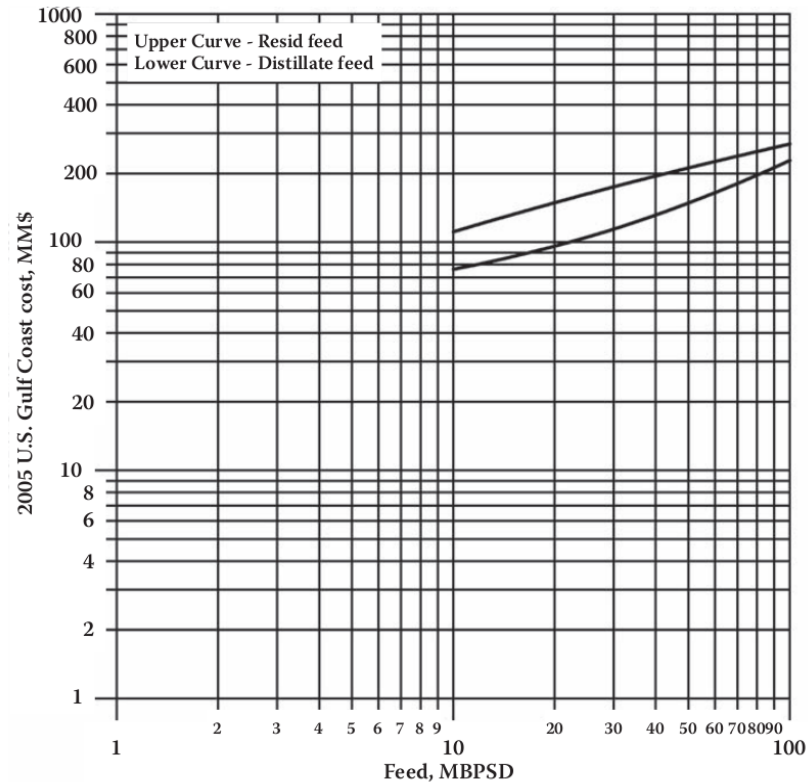


FIGURE 6.28 Fluid catalytic cracking units investment cost: 2005 U.S. Gulf Coast (see Table 6.5).

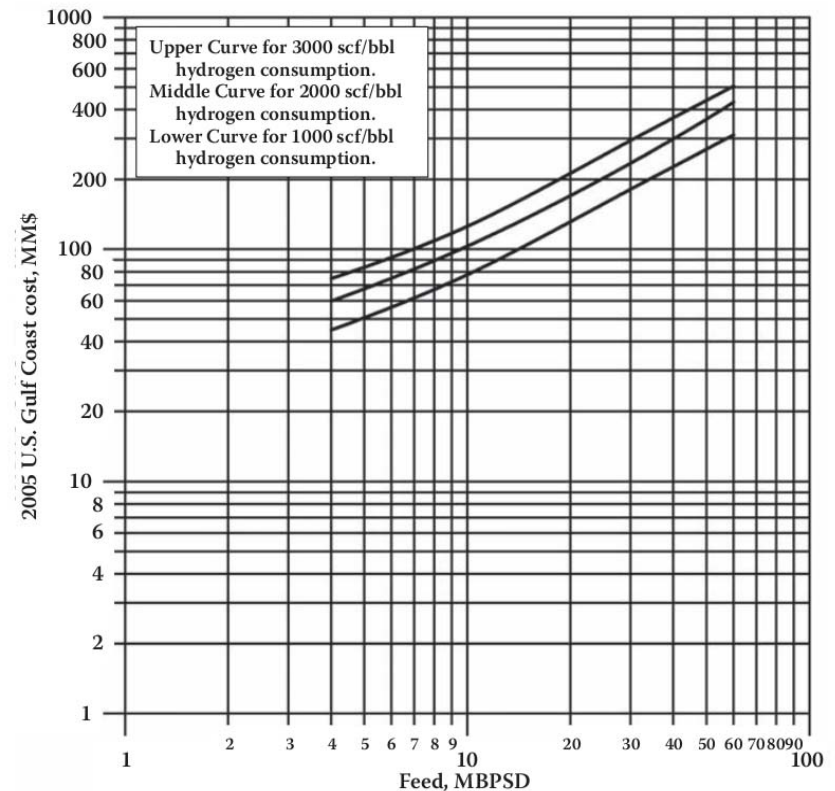


FIGURE 7.7 Catalytic hydrocracking unit investment cost: 2005 U.S. Gulf Coast (see Table 7.4).

FCCs tend to be less expensive than Hydrocrackers

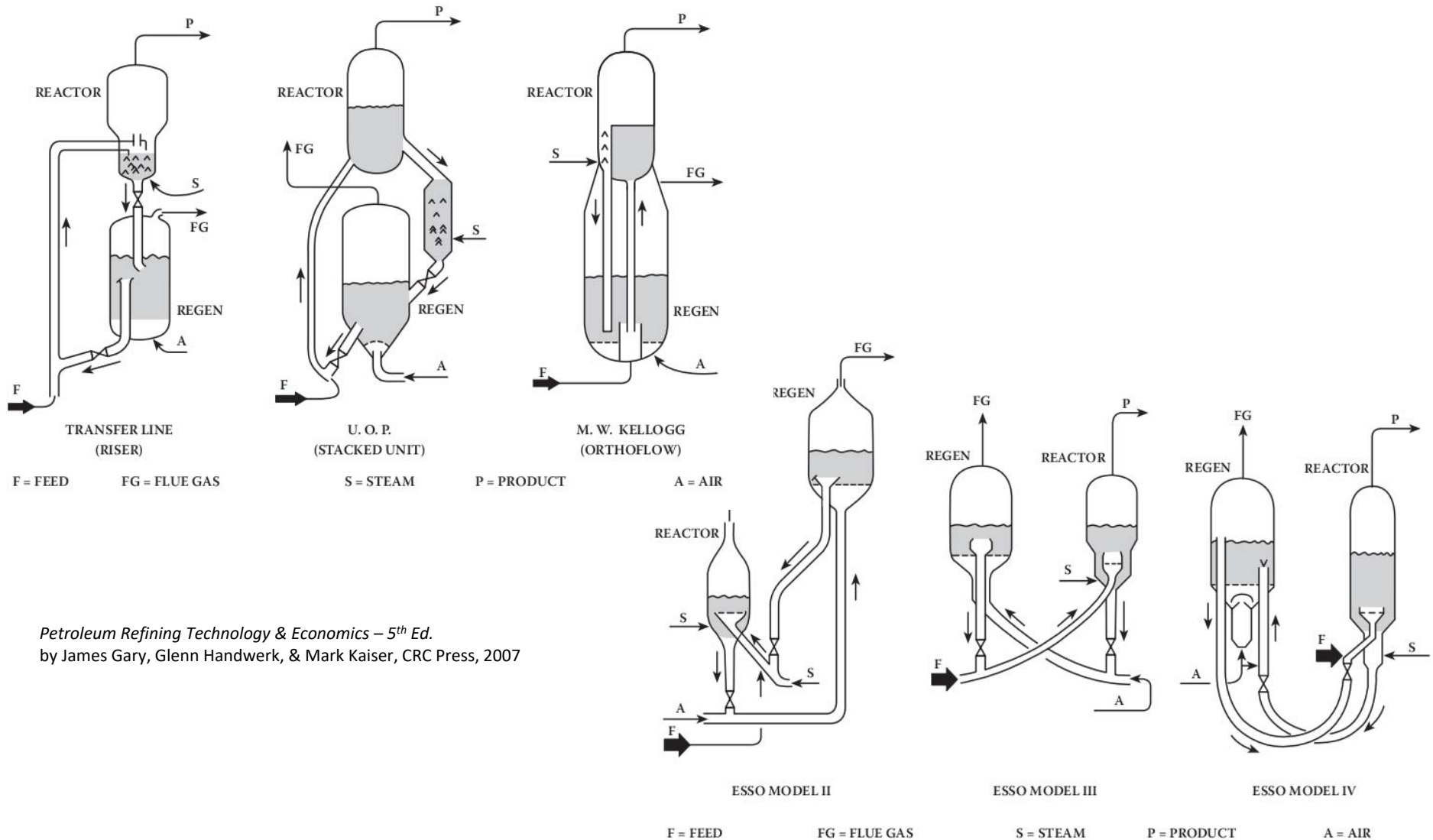
- 50,000 bpd distillate FCC – \$150 million installed cost
- 50,000 bpd @ 2000 scf/bbl – \$350 million installed cost

Petroleum Refining Technology & Economics, 5th ed.
Gary, Handwerk, & Kaiser
CRC Press, 2007

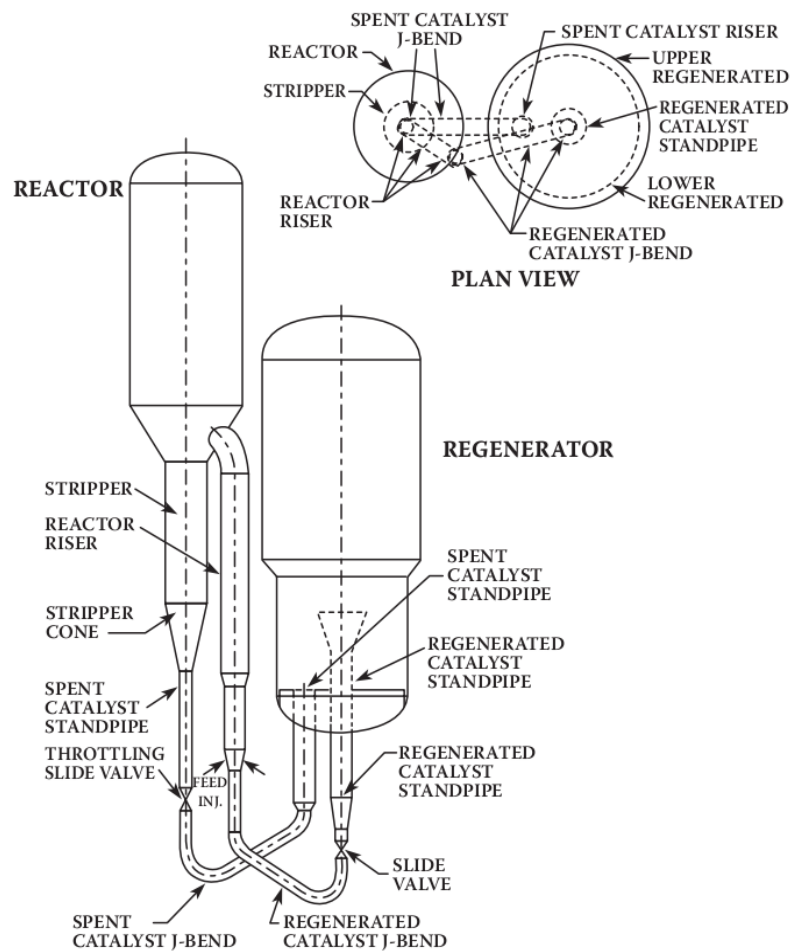
Fluidized Catalytic Cracking Technologies

Provider	Features
Axens	Resid cracking
ExxonMobil Research & Engineering	Fluid catalytic cracking
Haldor Topsoe A/S	Fluid catalytic cracking – pretreatment
KBR	Fluid catalytic cracking; FCC – high olefin content; resid cracking
Lummus Technology	Fluid catalytic cracking; FCC for maximum olefins
Shaw	Fluid catalytic cracking; deep catalytic cracking; resid cracking
Shell Global Solutions	Fluid catalytic cracking
UOP	Fluid catalytic cracking

Other FCC Configurations



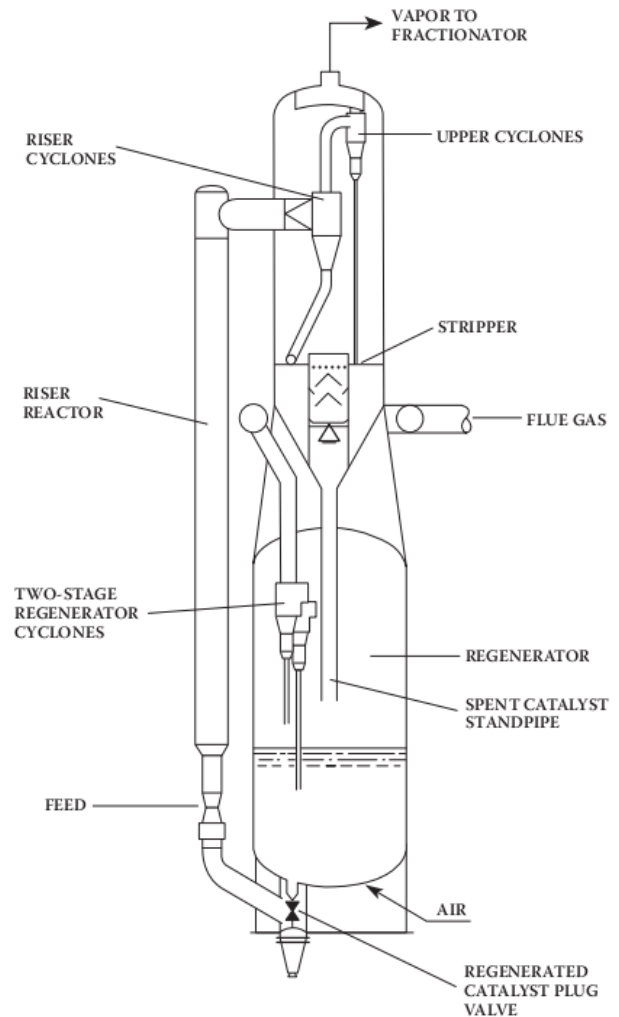
Petroleum Refining Technology & Economics – 5th Ed.
by James Gary, Glenn Handwerk, & Mark Kaiser, CRC Press, 2007



Exxon Flexicracking IIR FCC Unit

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

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M.W. Kellogg Design

Catalyst Considerations

Adjustment of active catalytic components (zeolite & active matrix) can achieve various refinery objectives

Considerations

- Bottoms Cracking
- Octane
- Coke selectivity
- ZSM-5 additive
- Resid cracking
- Additives
- FCC catalyst cost
 - Generally the 2nd highest operating expense, after crude oil purchases
 - May pay upwards of \$3,000 per ton

FCC Catalyst Selection Considerations, Hoyer, March 2015
http://www.refinerlink.com/blog/FCC_Catalyst_Selection_Considerations/

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Catalyst Considerations

Bottoms Cracking

- Large-pore matrix permits easy access of large molecules
- Large molecule cracking mechanisms
 - Matrix cracking
 - Most efficient upgrading into higher-valued gasoline & light cycle oil
 - Cracking on the external zeolite surface
 - Minimal bottoms upgrading, very small fraction of total zeolite surface
 - Thermal cracking
 - Nonselective – tends to produce to gas & coke

Octane

- Sodium content & amount of rare earth exchange effects degree of octane enhancement
- Trade offs
 - Increased FCC conversion & gasoline yield can be at the expense of octane number
 - Increased gasoline olefin content can improve RON
 - Increased branching & aromatic content improves MON

Catalyst Considerations

Coke selectivity

- A coke-selective catalyst reduces the regenerator temperature
 - Could allow for a higher reactor temperature to increase octane w/o exceeding regenerator temperature or air compressor limits

ZSM-5 additive

- Does not require complete catalyst change out – small amount, 1-5% of total catalyst
- Enhances gasoline octane
 - Selectively cracks straight chain paraffins & olefins (low-octane) to mainly C3 and C4 olefins.
 - Some olefins isomerized to more highly branched (high octane)
 - Does not affect aromatics or naphthenes (high octane)

Catalyst Considerations

Resid cracking

- No single optimum catalyst for all resid processing applications
- Allow for greater selectivity in products compared to thermal cracking
 - Must cope with high levels of coke precursors & metals in resid feeds
- Requires coke-selective & metals-resistant catalysts, metals passivators, and SO_x emission-reducing catalysts
- Feed's CCR issues w/o cat cooler
 - Increased CCR, increased regenerator temperature, decreased C/O ratio, & declining conversion

Additives

- Passivation agents to mitigate nickel and vanadium
- SO_x-reduction additives for regenerator emissions
- High-density fines used as fluidization aids.

Improving Cat Cracking Process Monitoring

Mass Balance

- Hydrocarbon balance – can you account for your process stream?
- Catalyst balance – Can you account for every pound of catalyst from injection to regenerator spent catalyst to slurry catalyst content?

Pressure Balance

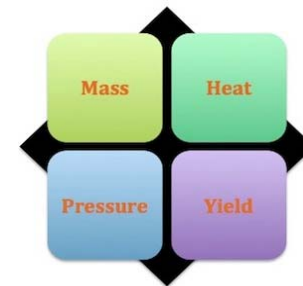
- Drives reliability & long-term safe operation
- Understand pressure profiles including: air blower, regenerator, reactor, & wet gas compressor
- Help troubleshoot mechanical issues –air grids & cyclones

Heat Balance

- Important for kinetic reactions of the plant as well as distillation and heat recover/integration in the unit

Yield Balance

- Understand the economic implications of the unit & help focus on key indicators
- Catalyst cost/usage impacts the operating expense of the Cat Cracker?
- Impact of feed quality variations on yields?



Ref: http://www.refinerlink.com/blog/Cat_Cracking_Process_Monitoring