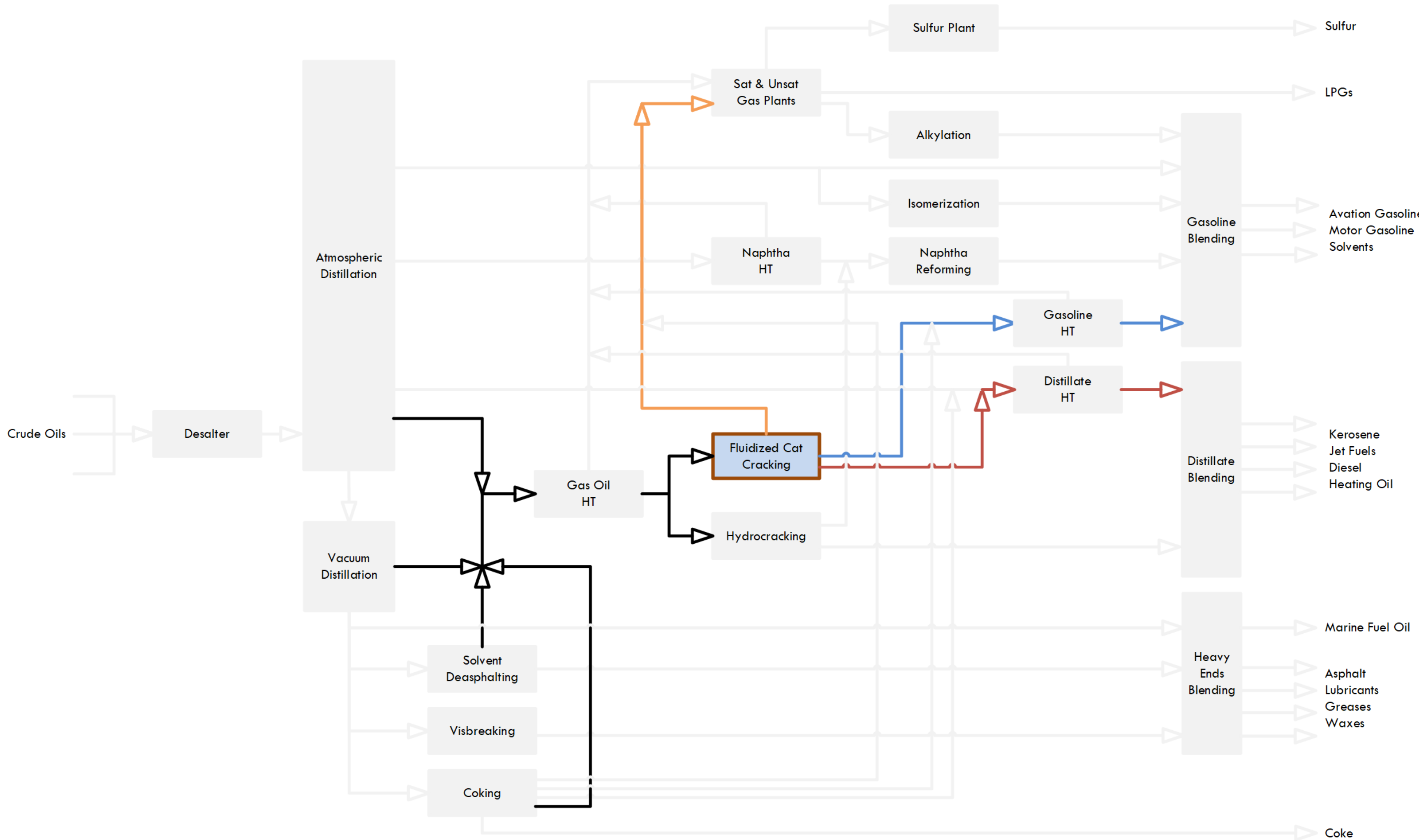
Fluidized Catalytic Cracking

Chapter 6

COLORADO SCHOOL OF MINES

Petroleum Refinery Block Flow Diagram



Updated: July 1, 2019

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Overview of Catalytic Cracking

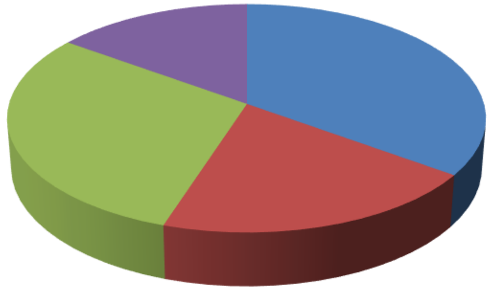
FCC "heart" of a modern US refinery

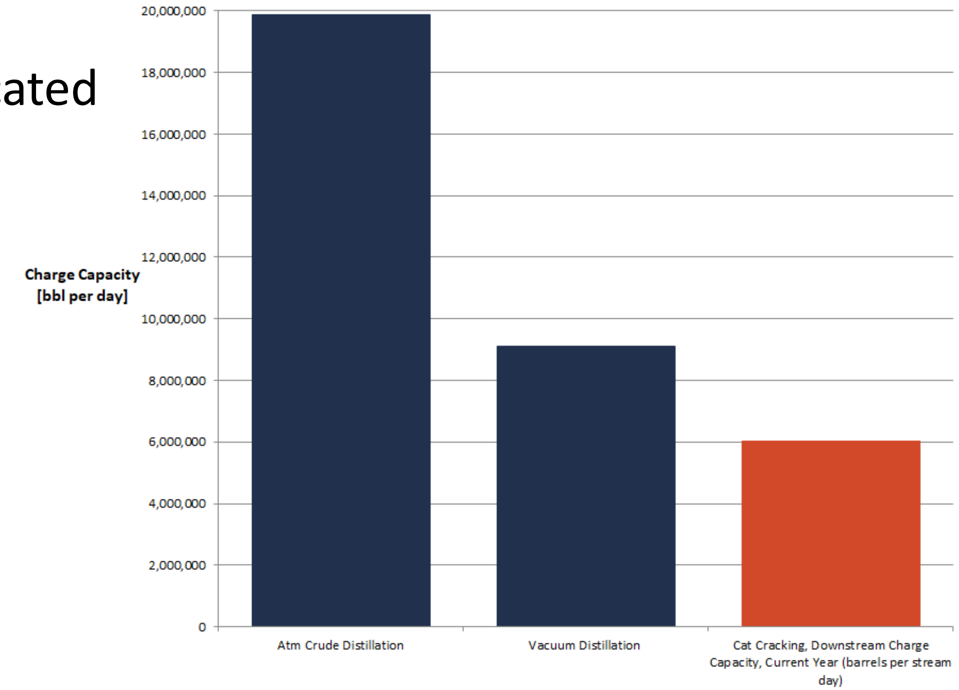
- Nearly every major fuels refinery has an FCCU

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

Capacity usually 1/3 of atmospheric crude distillation capacity

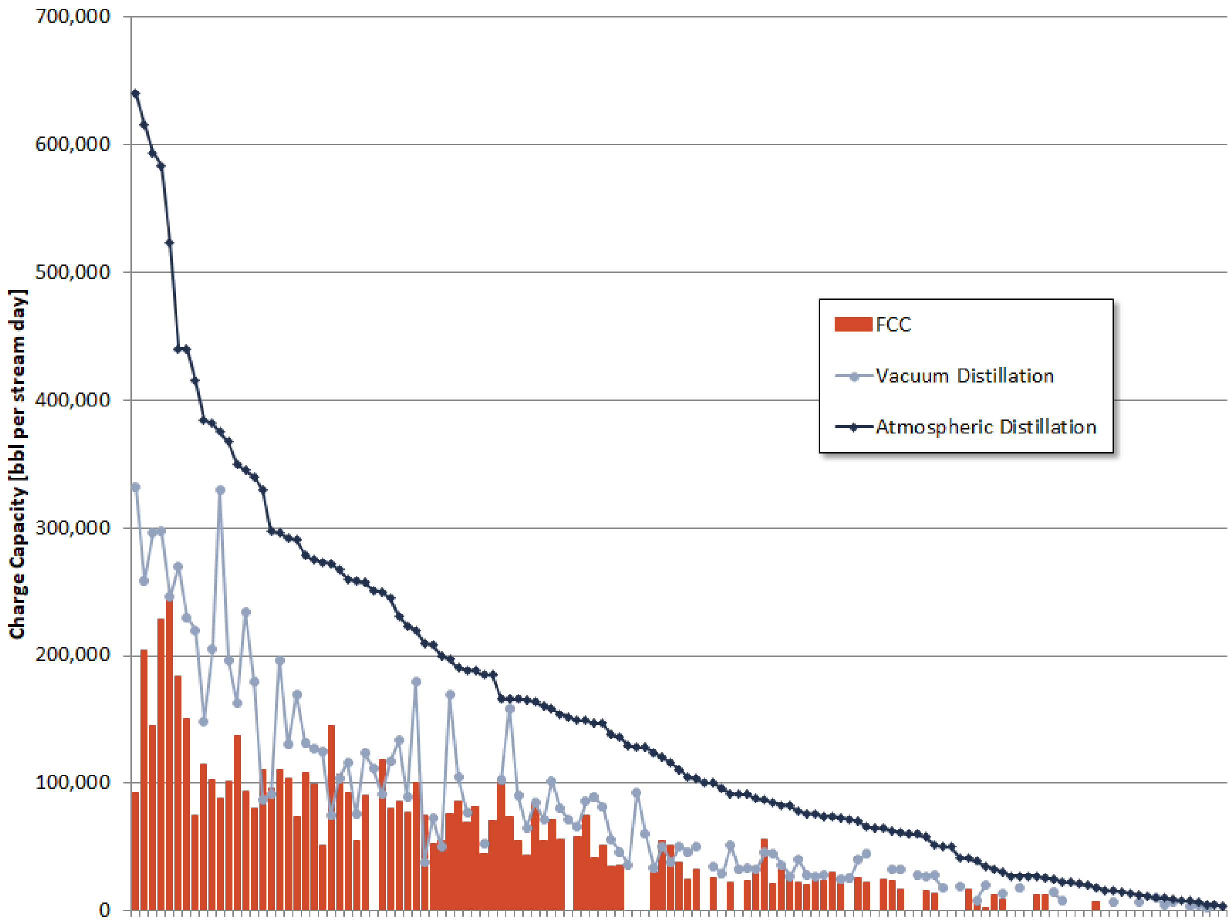
Contributes the highest volume to the gasoline pool





EIA, Jan. 1, 2019 database, published June 2019
http://www.eia.gov/petroleum/refinerycapacity/

U.S. Refinery Implementation



EIA, Jan. 1, 2019 database, published June 2019
http://www.eia.gov/petroleum/refinerycapacity/

Purpose

Catalytically crack carbon-carbon bonds in gas oils

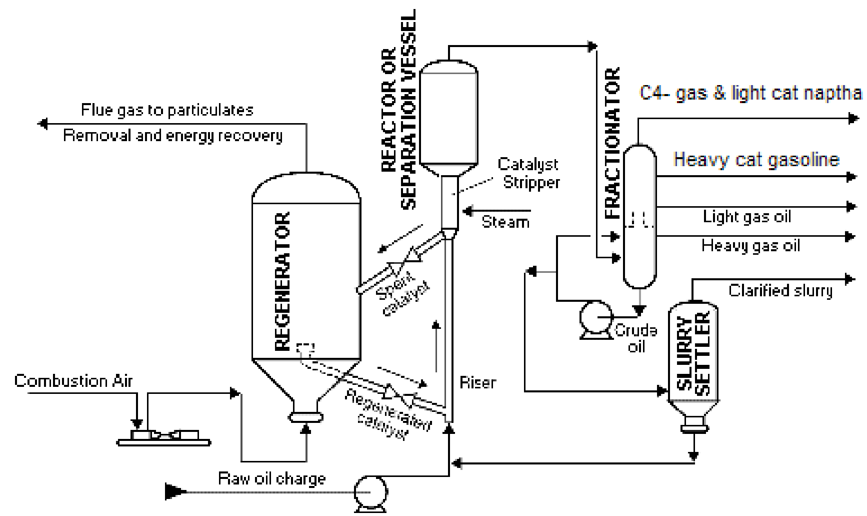
- Fine catalyst in fluidized bed reactor allows for immediate regeneration
- Lowers average molecular weight & produces
- high yields of fuel products
- Produces olefins

Attractive feed characteristics

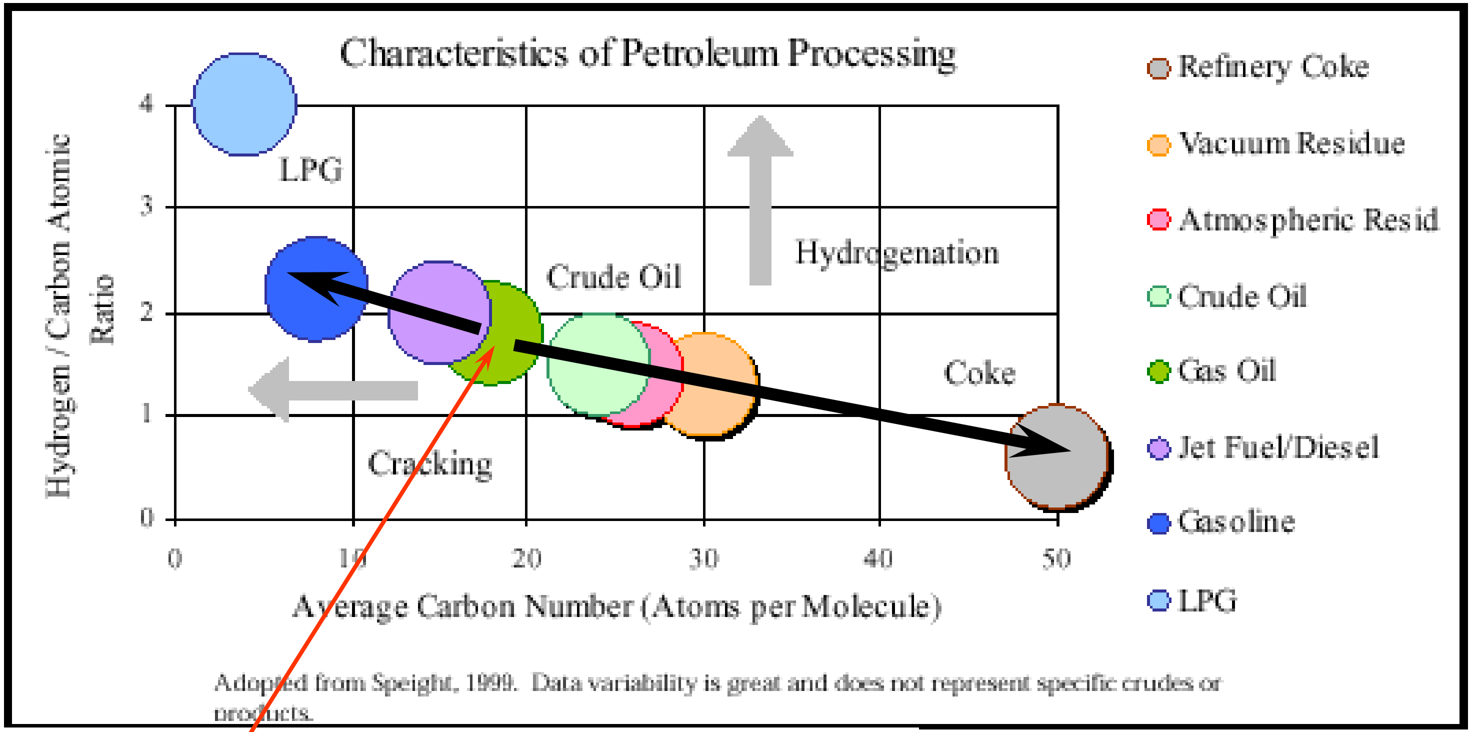
- Small concentrations of contaminants
  - Poison the catalyst
- Small concentrations of heavy aromatics
  - Side chains break off leaving cores to deposit as coke on catalyst
  - Must be intentionally designed for heavy resid feeds

Products may be further processed

- Further hydrotreated
- Olefins used as feedstock to alkylation process



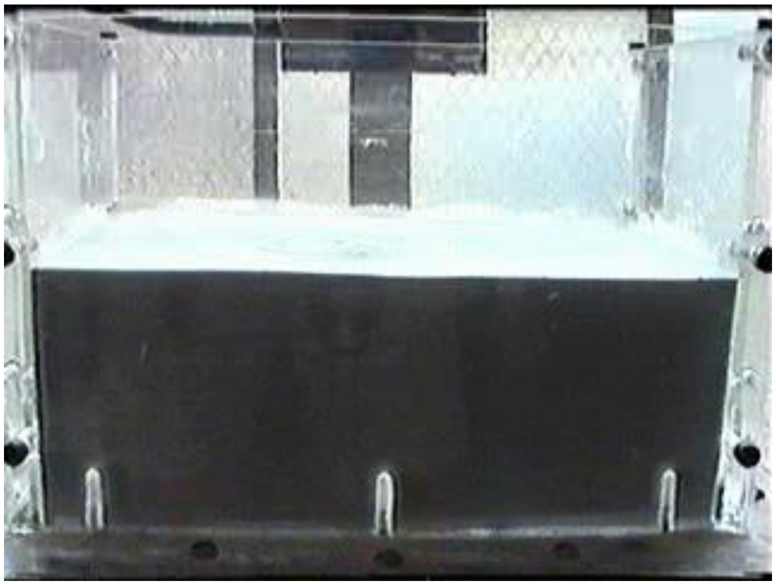
Characteristics of Petroleum Products



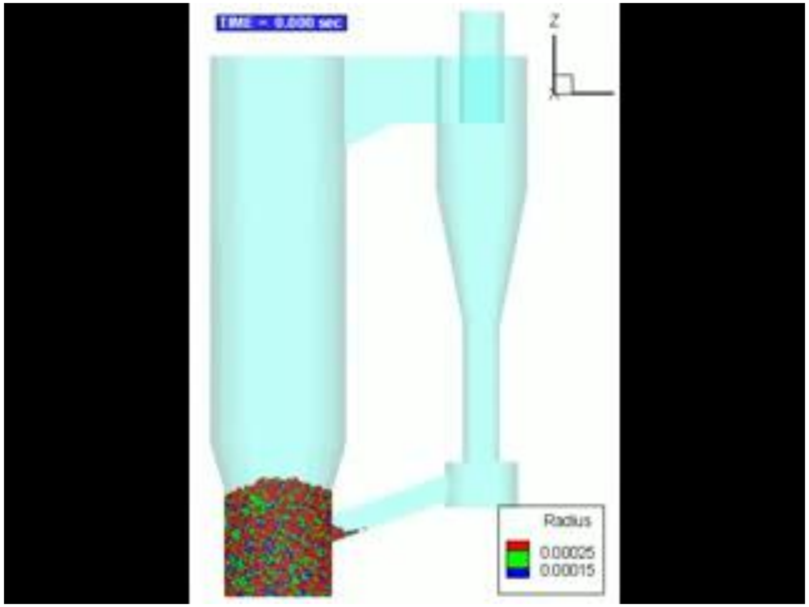
Large conversion to light products requires some coke formation

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

What is a fluidized bed?



https://www.youtube.com/watch?v=3BqVFGCUviY



http://www.youtube.com/watch?v=EB0r6A5VxFU

Fluid Catalytic Cracker

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

Fluidized Catalytic Cracker

"Benecia Refinery Tour," Valero Energy Corp., July 9, 2007
http://www.secinfo.com/dsvrp.uEe6.d.htm#1stPage

Typical FCC Complex

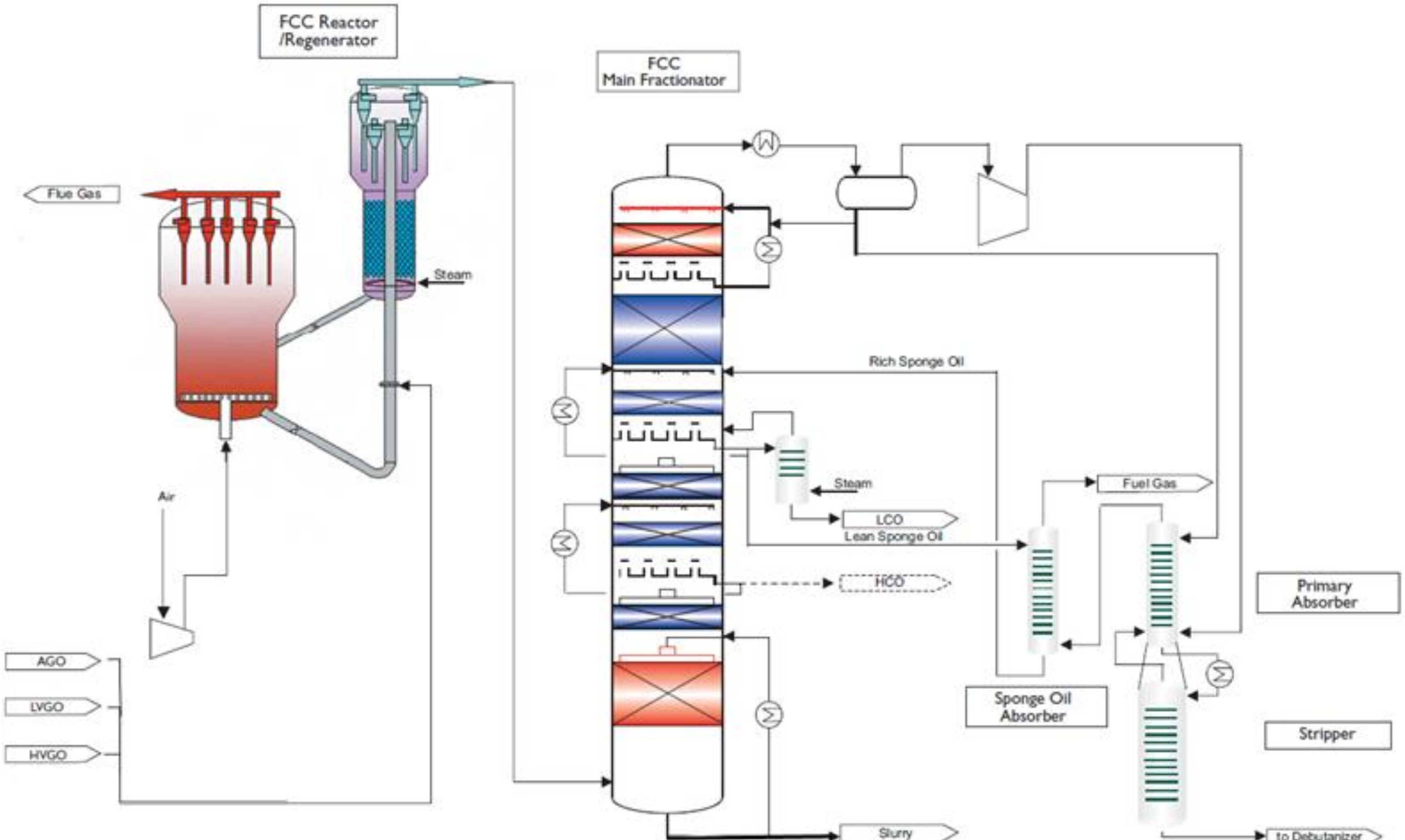
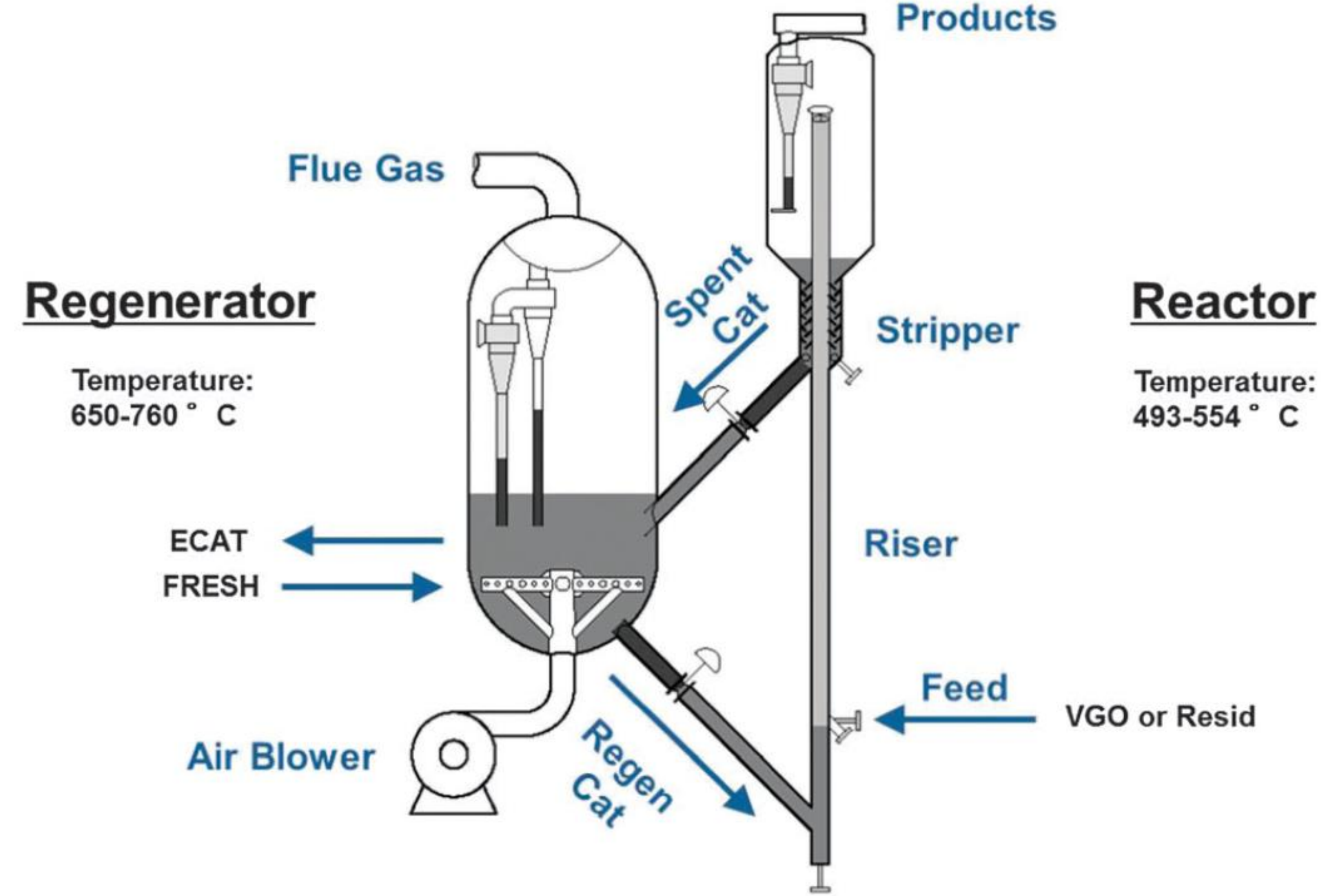


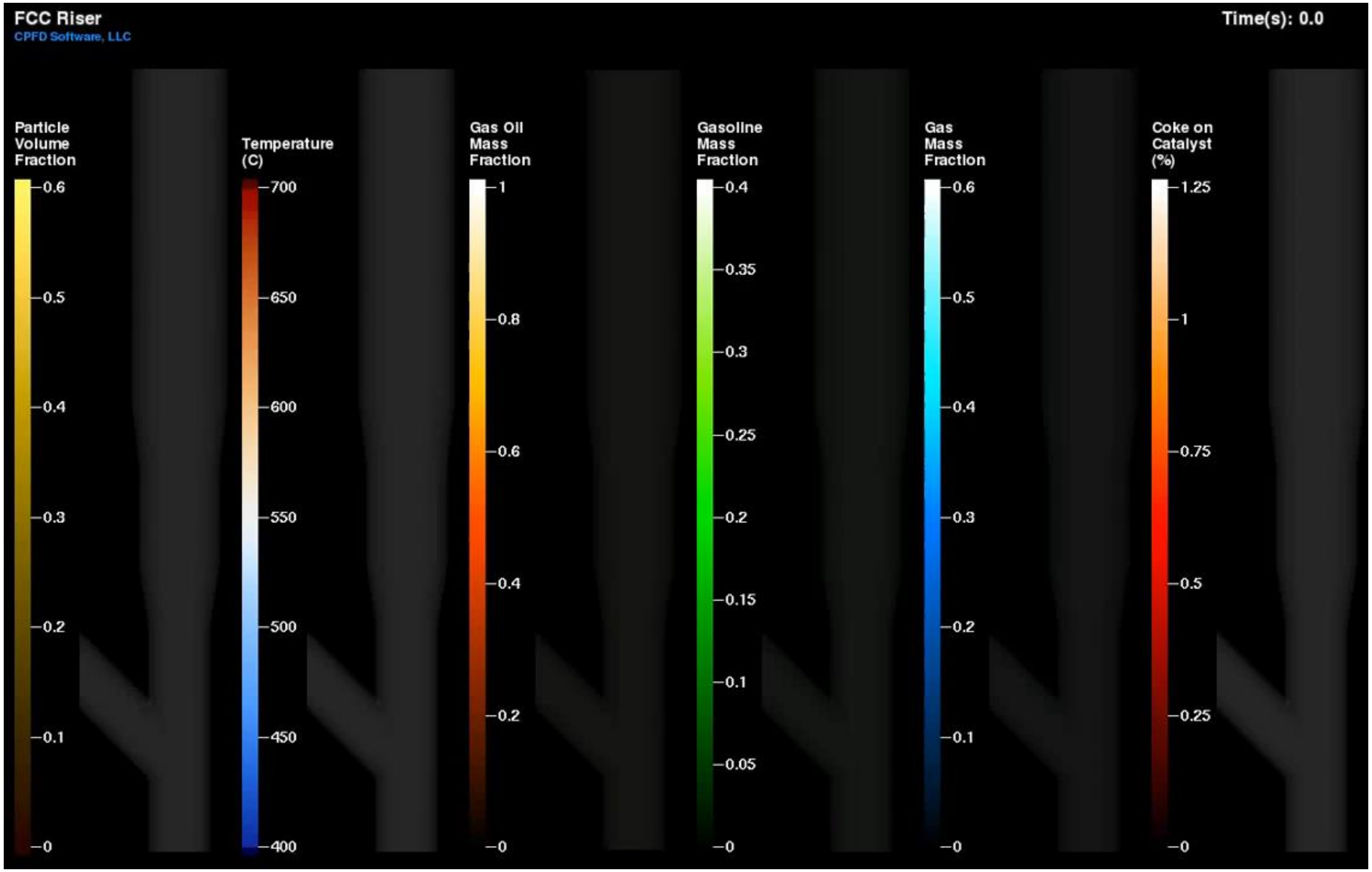
Figure modified from Koch-Glitsch Bulletin KGSS-1, Rev. 3-2010, http://www.koch-glitsch.com/Document%20Library/KGSS.pdf

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

CFD Simulation of an FCC Riser



https://www.youtube.com/watch?v=_781g72wCQM

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 CO_2 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:

$$\%\ \text{Product Yield} = 100 \times (\text{Product Volume}) / (\text{Feed Volume})$$

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

FCCU Yield Example

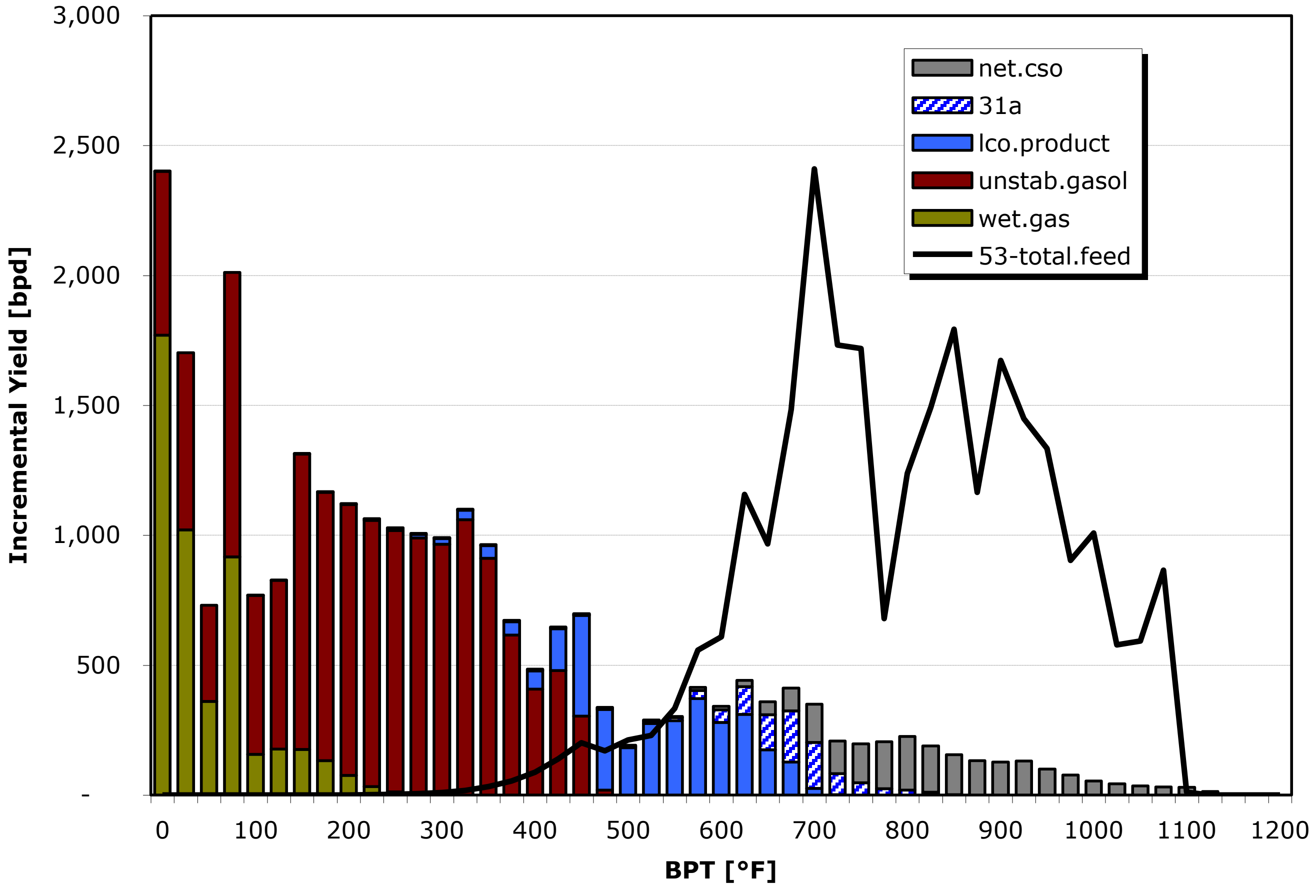
Product Yields from FCCU Using Gary et. al. Correlations

Conversion = 72.0 vol%

Fraction	bbl/day	lb/day	Yields vol%	Yields wt%	Standard Densities °API	Standard Densities SpGr	Standard Densities lb/gal	Watson K Factor	Sulfur Distribution Content wt%	Sulfur Distribution Content lb/day	Sulfur Distribution Recovery wt%
FCCU Feed (Total Gas Oil)	25,000	7,915,013	100.0%	100.0%	25.00	0.9042	7.538	12.00	0.50	39,575	
Light gases (C2-)		389,994		4.93%					3.90%	15,193	38.4%
Propane (C3)	639	113,468	2.56%	1.43%	147.6	0.5070	4.227		0%	0	
Propylene (C3=)	1,451	264,749	5.80%	3.34%	140.1	0.5210	4.344		0%	0	
Iso-butane (IC4)	1,397	275,362	5.59%	3.48%	119.9	0.5629	4.693		0%	0	
n-butane (NC4)	491	100,375	1.96%	1.27%	110.8	0.5840	4.869		0%	0	
Butylenes (C4=)	1,902	400,492	7.61%	5.06%	103.8	0.6013	5.013		0%	0	
Gasoline (C5+)	14,263	3,732,025	57.05%	47.15%	57.9	0.7473	6.230		0.06%	2,079	5.3%
Light Cycle Oil (LCO)	5,300	1,630,520	21.20%	20.60%	29.6	0.8786	7.325		0.43%	6,986	17.7%
Heavy Cycle Oil (HCO)	1,700	620,576	6.80%	7.84%	4.2	1.0425	8.692		0.86%	5,318	13.4%
Coke		387,452		4.90%					2.58%	9,998	25.3%
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		0.55%	12,304	31.1%
Total LPG	5,880	1,154,446	23.52%	14.59%					0%	0	0.0%

	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%

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

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

$$\text{Paraffin} \rightarrow \text{Paraffin} + \text{Olefin}$$

$$\text{Alkyl Napthene} \rightarrow \text{Naphthene} + \text{Olefin}$$

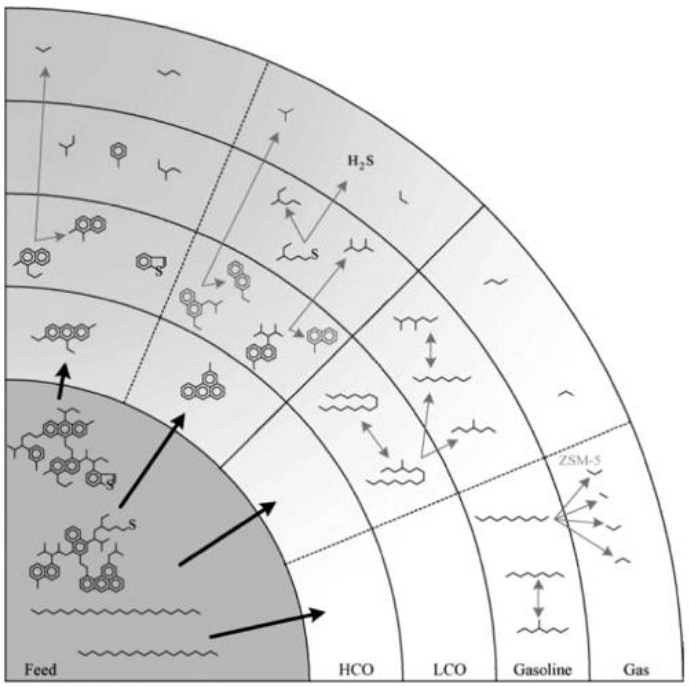
$$\text{Alky Aromatic} \rightarrow \text{Aromatic} + \text{Olefin}$$

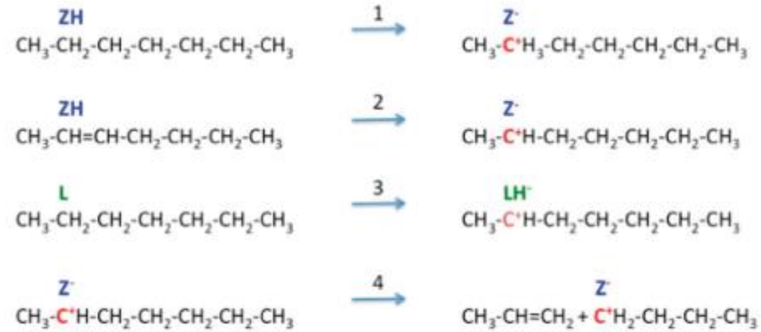
- Example

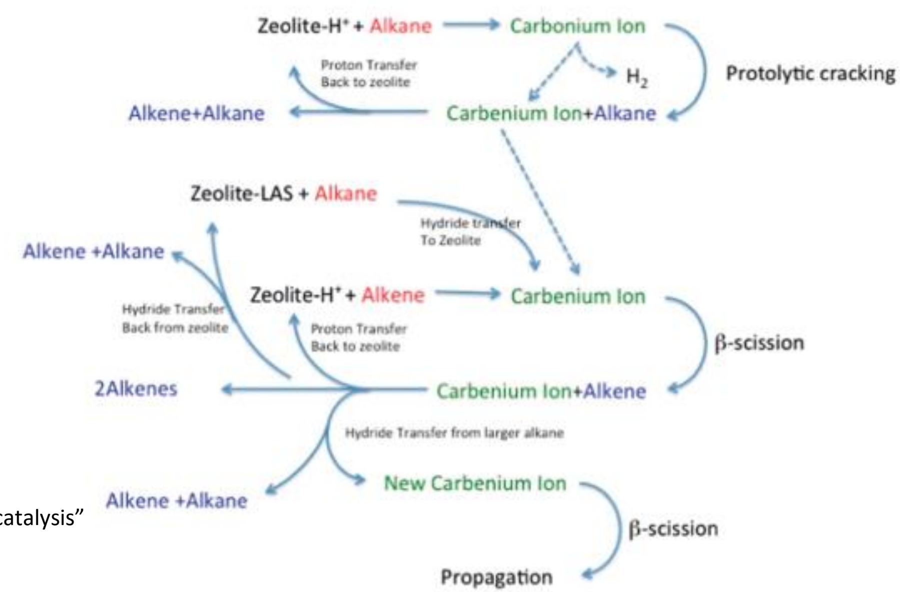
$$CH3CH2CH2CH2CH2CH2CH2CH3 \rightarrow CH3CH2CH2CH2CH3 + CH{=}CHCH3$$

- 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







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E.T.C. Vogt & B.M. Weckhuysen, *Chem Soc Rev*, 2015, 44, 7342-7370

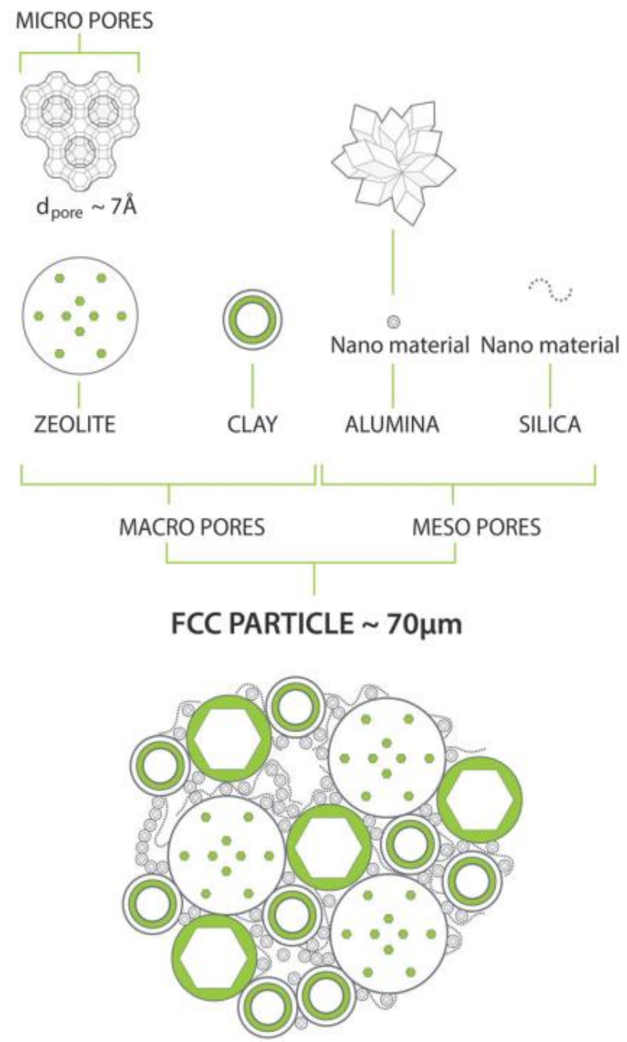
Catalysts & Chemistry

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



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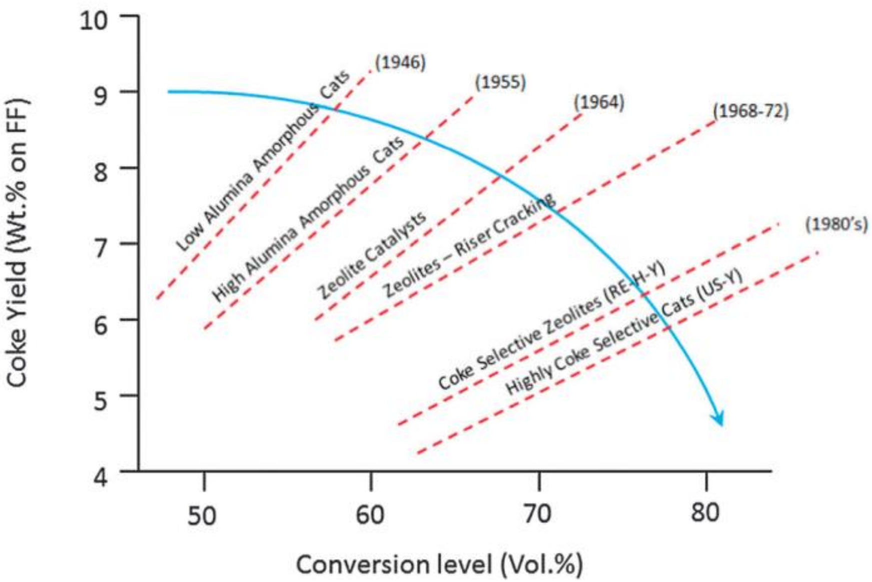
Catalysts & Chemistry

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



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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

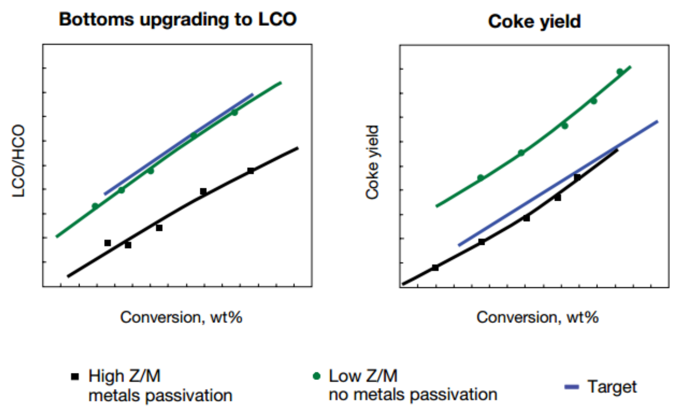


Figure 5: Defining the project objective for the development of Stamina

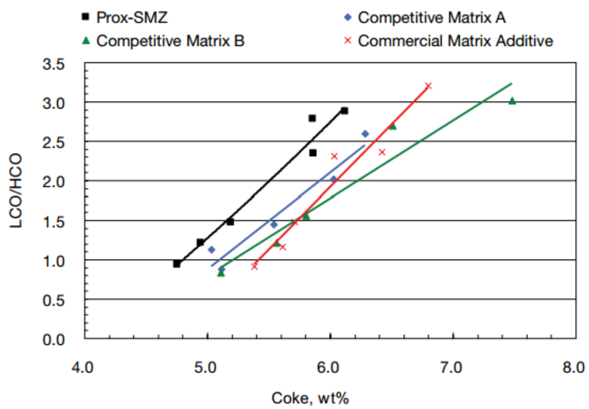


Figure 3: Bottoms upgrading of commercial FCC catalyst matrix materials in comparison to the novel Prox-SMZ matrix.

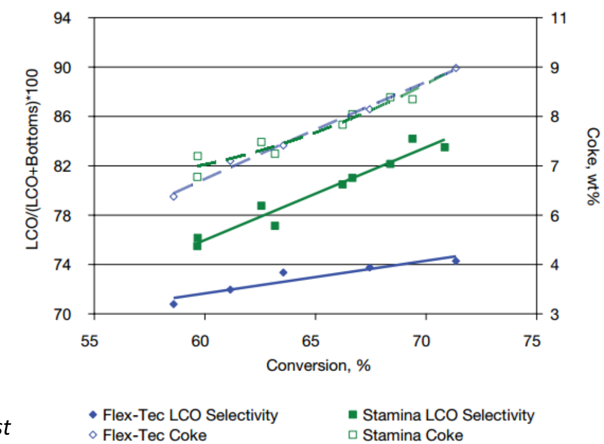


Figure 6: Comparison of the coke yield and the LCO selectivity of Flex-Tec and Stamina

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

Operating Conditions & Design Features

Designed to provide balance of reactor & regenerator capabilities

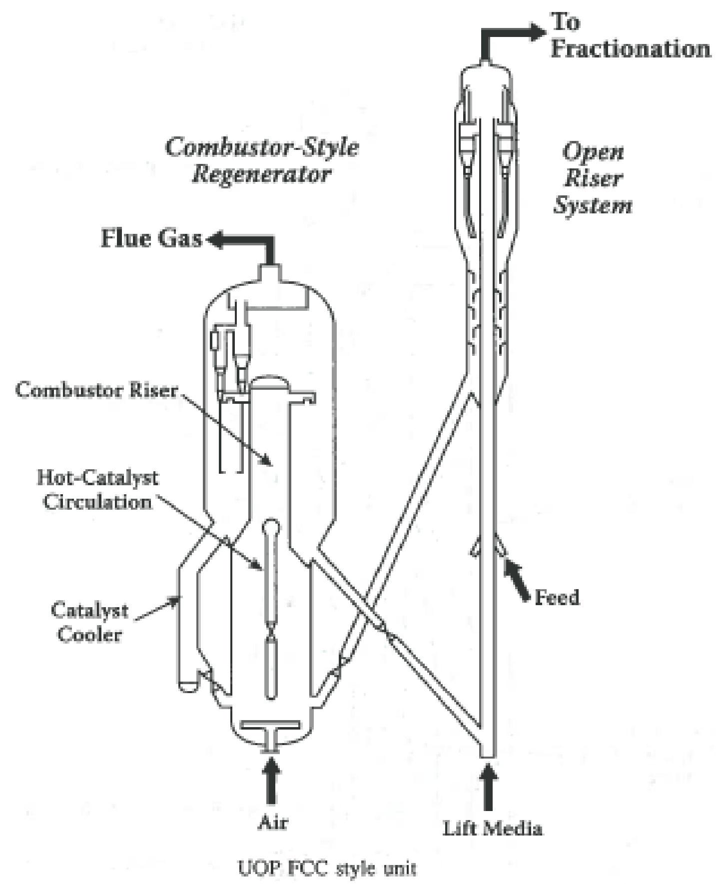
Usually operate to one or more mechanical limits

- 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

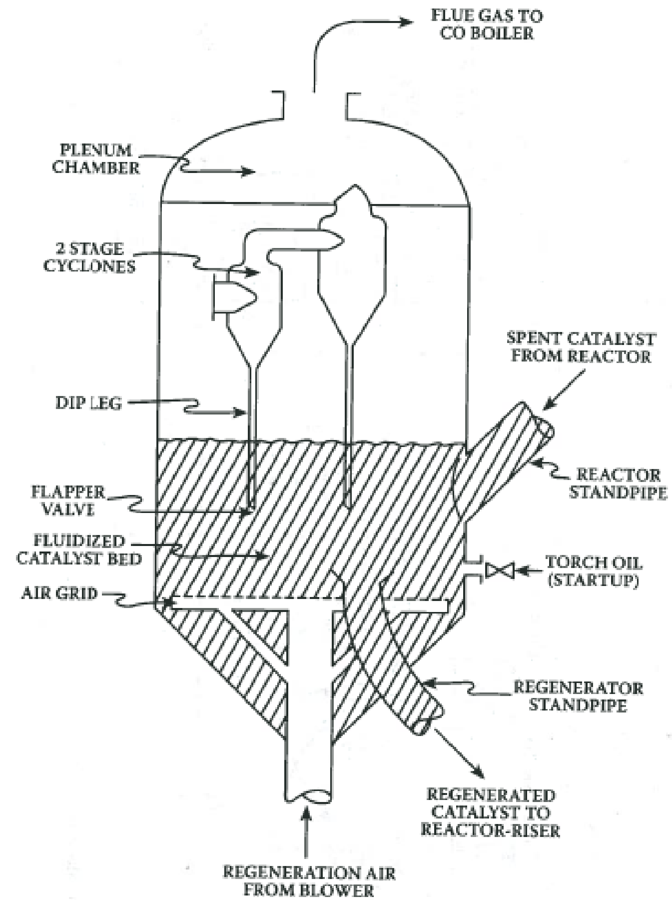
FCC Riser/Regenerator Combination

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 CO_2
  - 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.

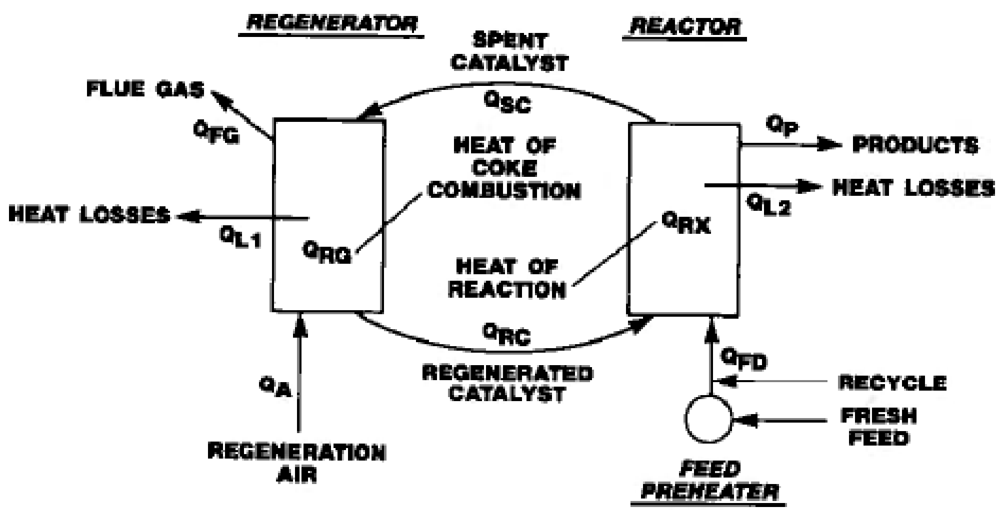


Petroleum Refining Technology & Economics – 5th Ed.
by James Gary, Glenn Handwerk, & Mark Kaiser, CRC Press, 2007

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.



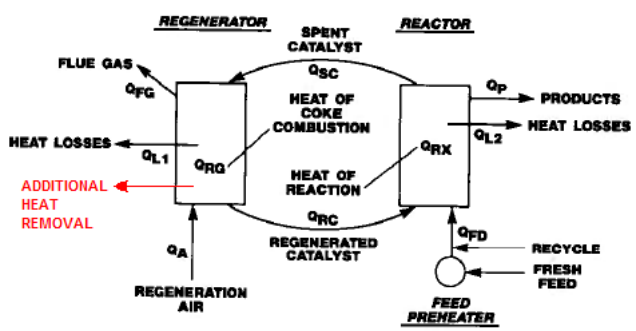
Resid Catalytic Cracking

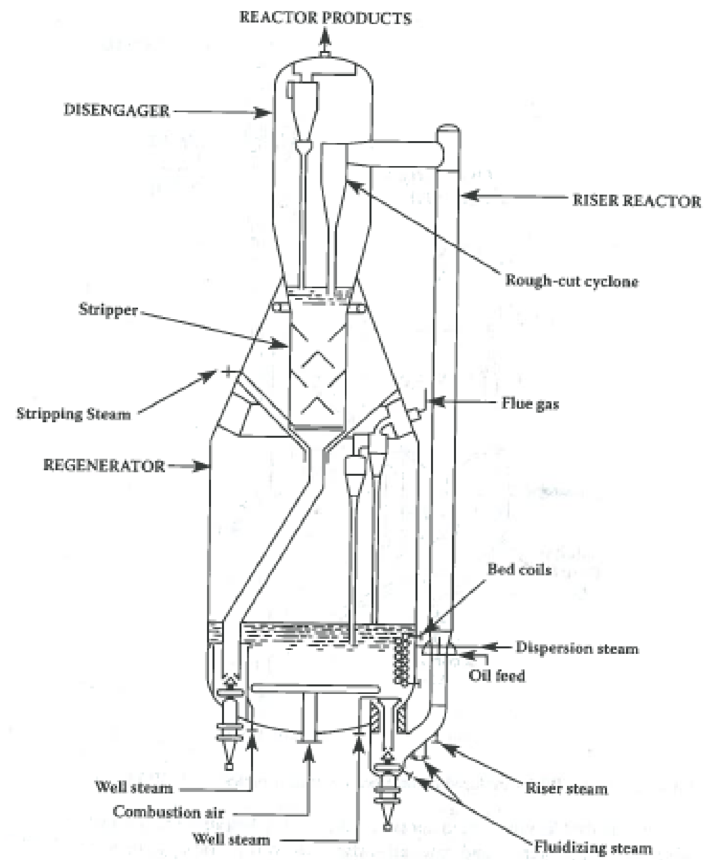
Economics favoring direct cracking of heavier crudes & resids

- 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





M. W. Kellogg resid fluid catalytic cracking (RFCC) unit.

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

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Summary

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 1, 2019

FCC vs. Hydrocracker Installed Cost

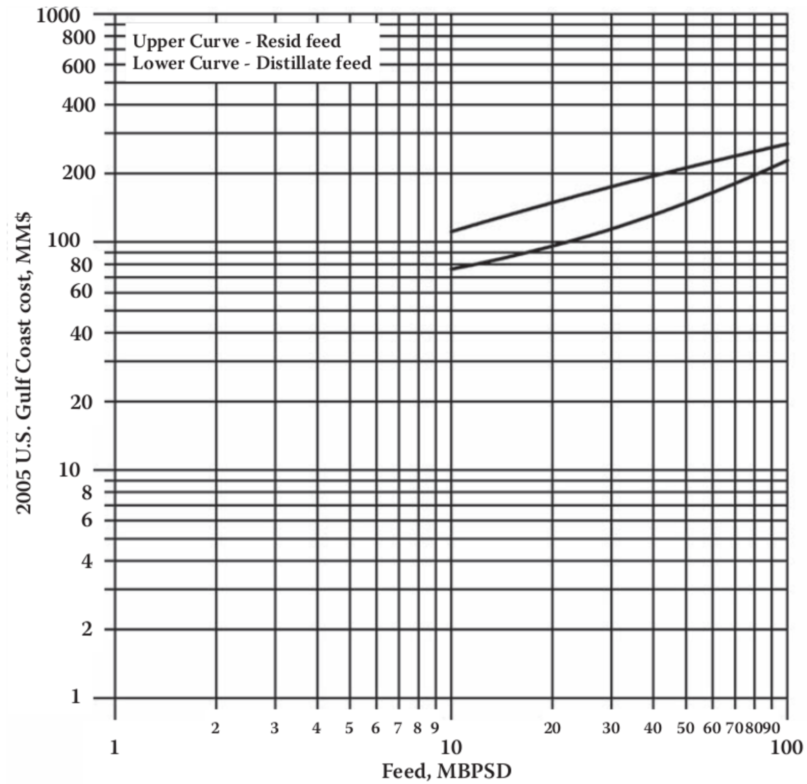


FIGURE 6.28 Fluid catalytic cracking units investment cost: 2005 U.S. Gulf Coast (see Table 6.5).

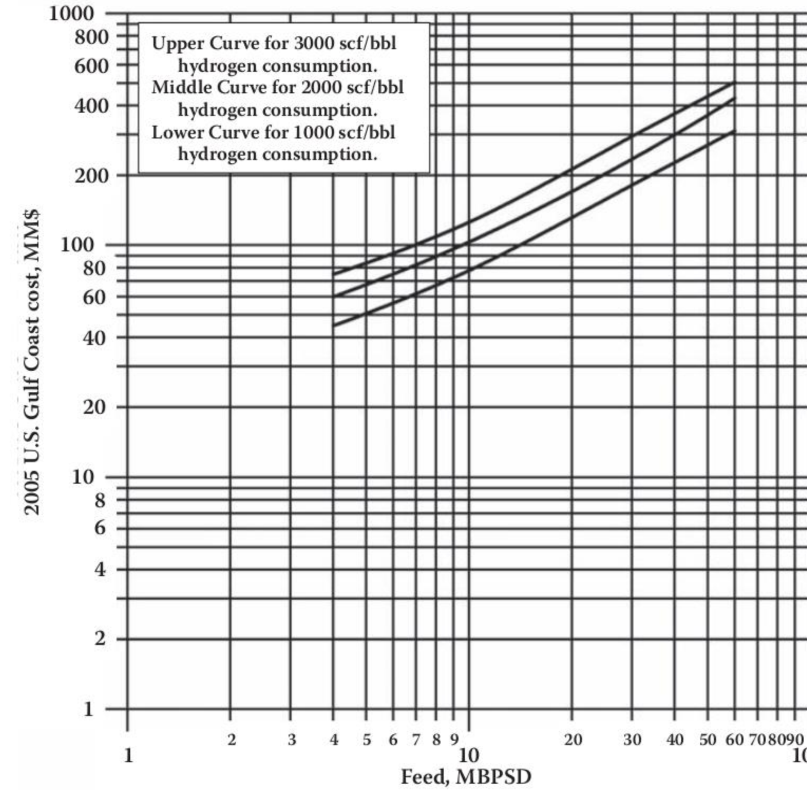


FIGURE 7.7 Catalytic hydrocracking unit investment cost: 2005 U.S. Gulf Coast (see Table 7.4).

FCCs tend to be less expensive than Hydrocrackers

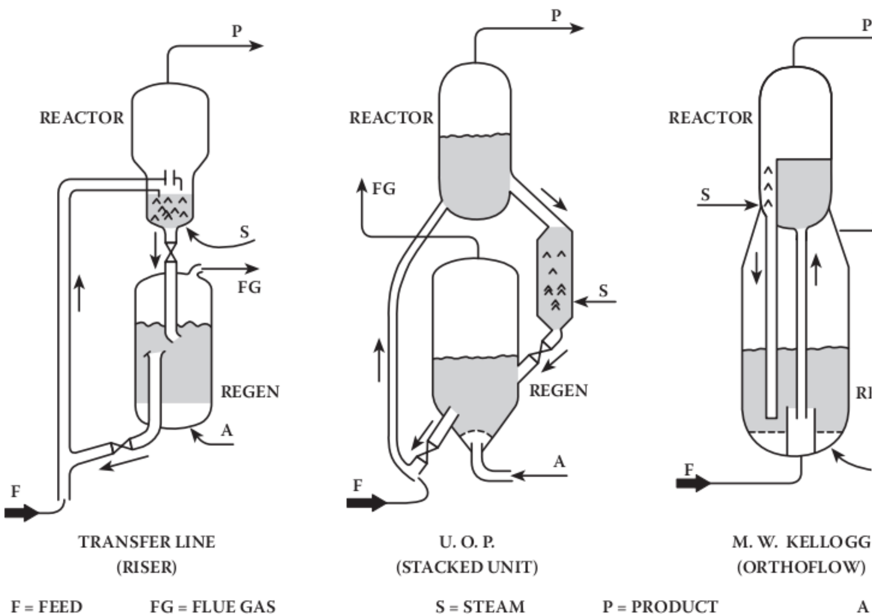
- 50,000 bpd distillate FCC – $150 million installed cost
- 50,000 bpd @ 2000 scf/bbl – $350 million installed cost

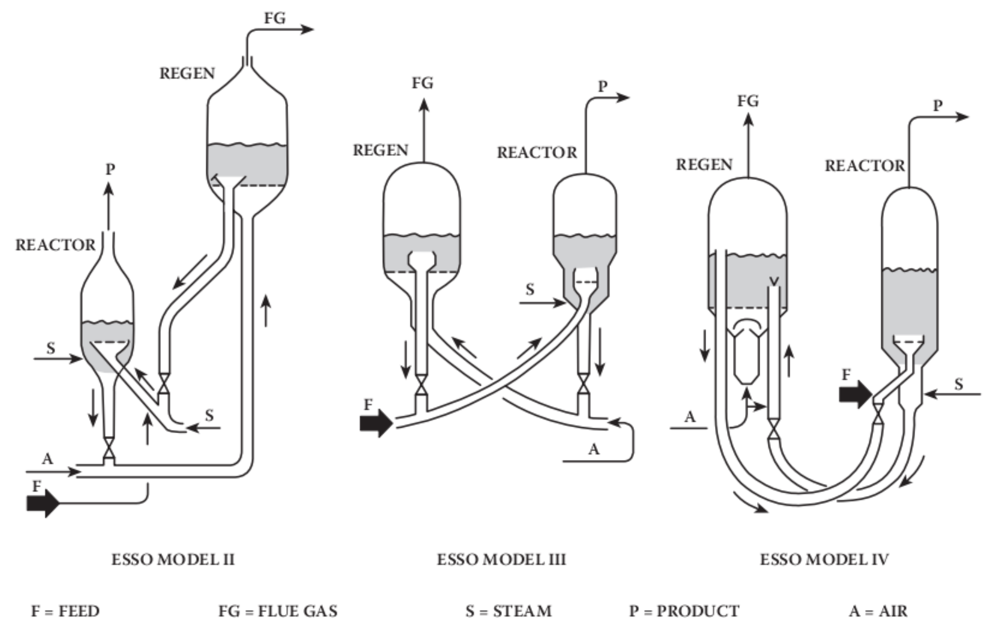
Petroleum Refining Technology & Economics, 5th ed.
Gary, Handwerk, & Kaiser
CRC Press, 2007

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





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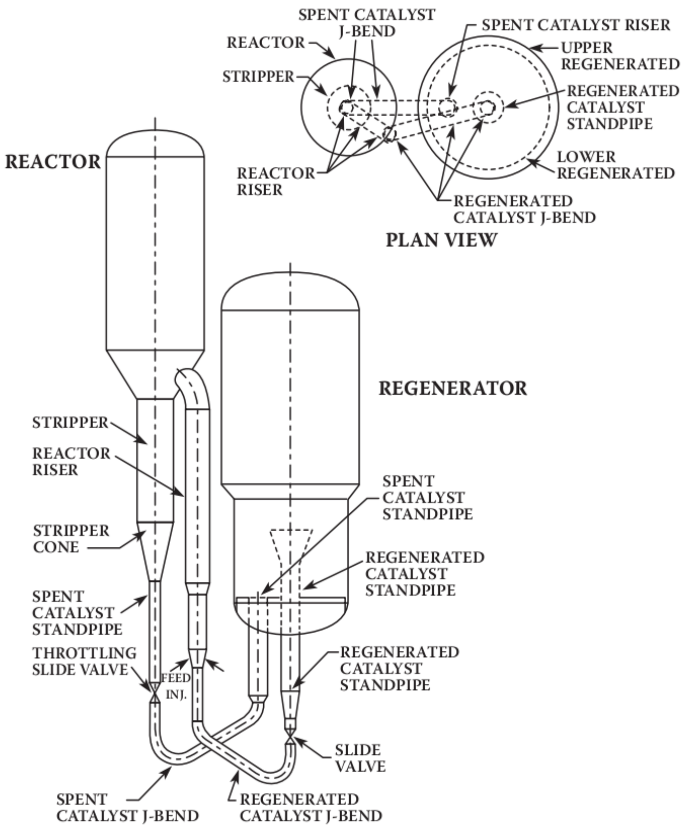
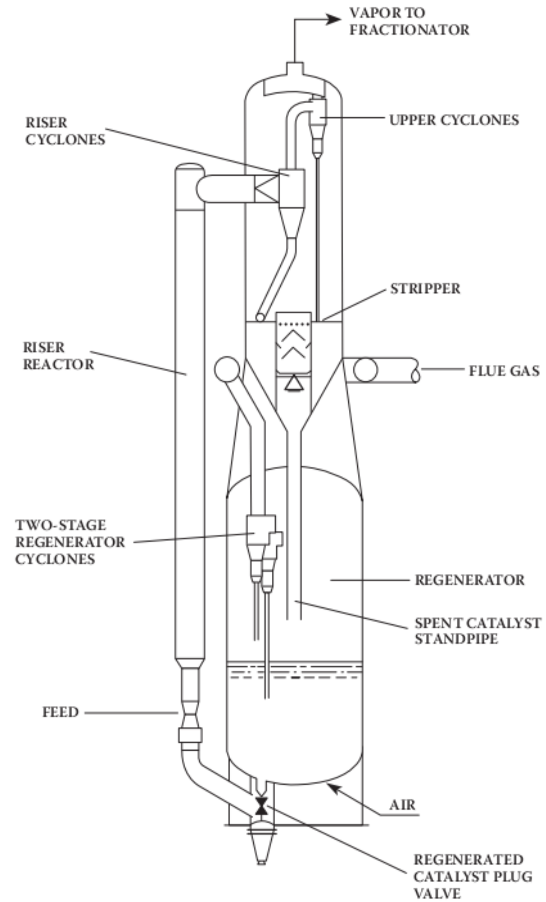
Other FCC Configurations



Exxon Flexicracking IIR FCC Unit



M.W. Kellogg Design

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

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/

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 SOx 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
- SOx-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

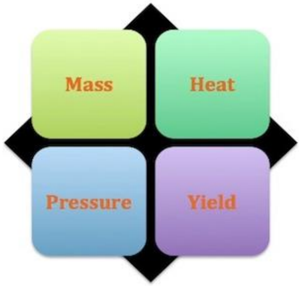
- Drives reliability & long-term safe operation
- Understand pressure profiles including: air blower, regenerator, reactor, & wet gas compressor
- Help troubleshoot mechanical issues –air grids & cyclones

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