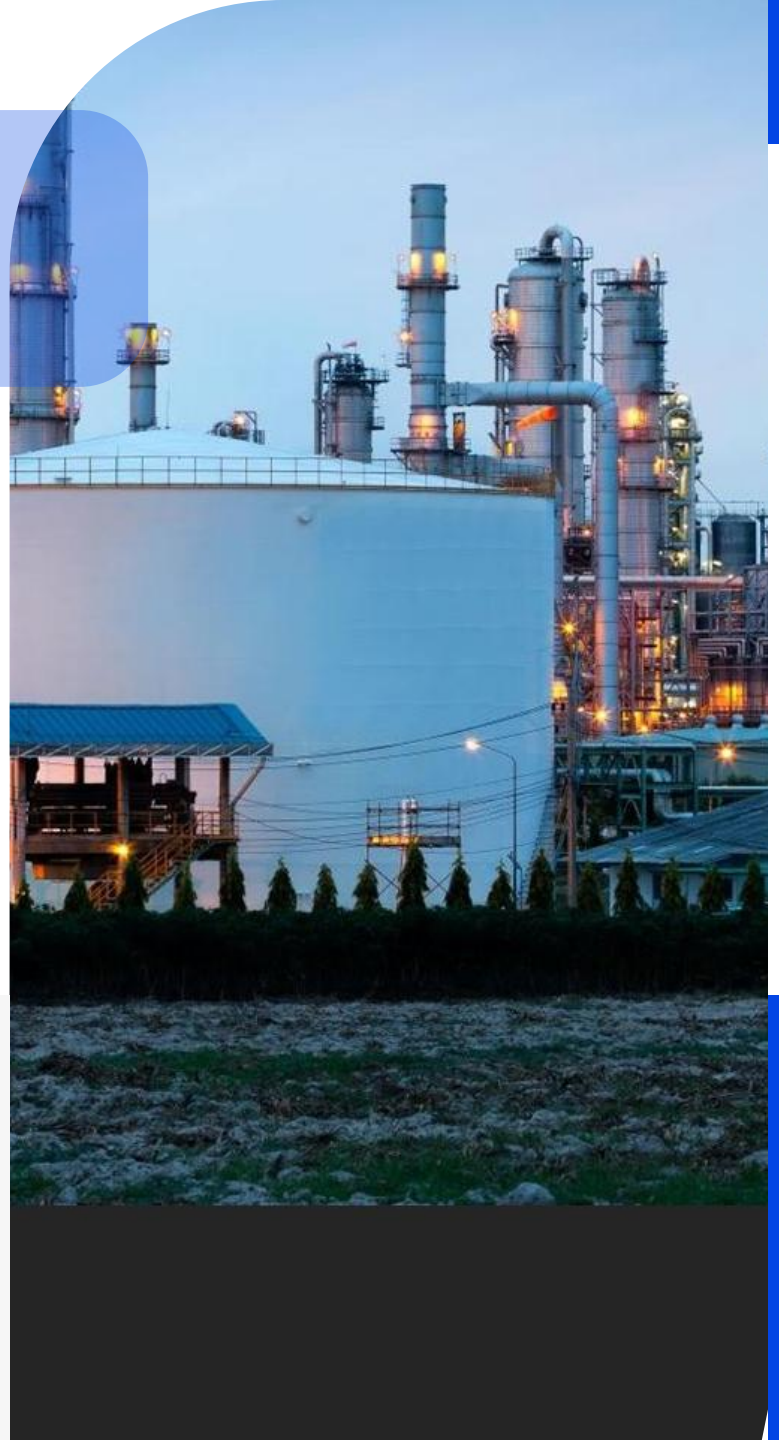
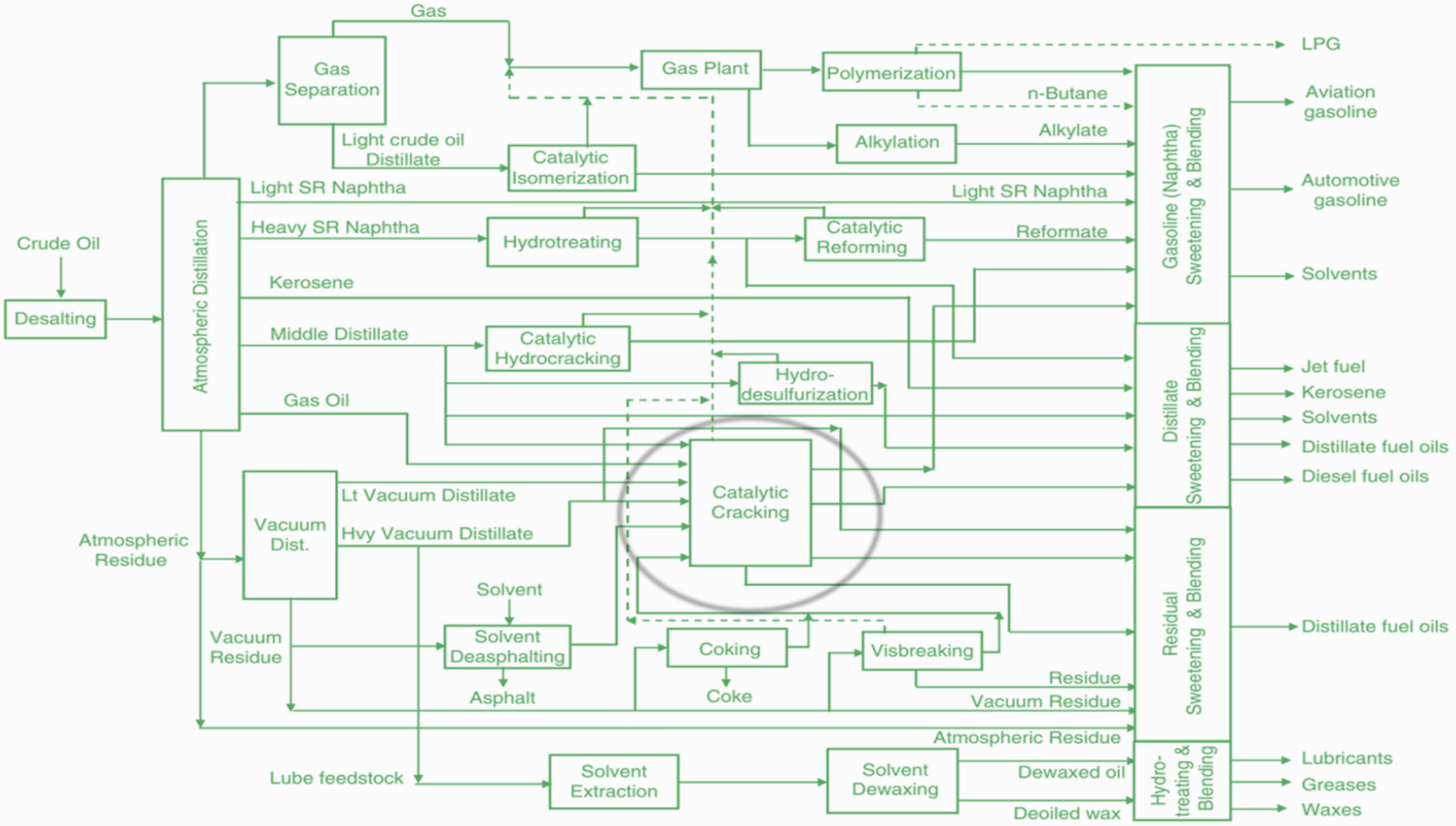
FLUID CATALYTIC CRACKING

Teknologi Minyak Bumi dan Gas Alam




Gas
Gas Separation
Gas Plant
Polymerization
LPG
n-Butane
Aviation gasoline
Alkylation
Alkylate
Light crude oil Distillate
Catalytic Isomerization
Light SR Naphtha
Light SR Naphtha
Automotive gasoline
Crude Oil
Heavy SR Naphtha
Hydrotreating
Catalytic Reforming
Reformate
Desalting
Atmospheric Distillation
Kerosene
Solvents
Middle Distillate
Catalytic Hydrocracking
Hydro-desulfurization
Jet fuel
Kerosene
Gas Oil
Solvents
Distillate fuel oils
Diesel fuel oils
Lt Vacuum Distillate
Vacuum Dist.
Catalytic Cracking
Hvy Vacuum Distillate
Atmospheric Residue
Solvent
Distillate fuel oils
Vacuum Residue
Solvent Deasphalting
Coking
Visbreaking
Residue
Asphalt
Coke
Vacuum Residue
Atmospheric Residue
Lube feedstock
Solvent Extraction
Solvent Dewaxing
Dewaxed oil
Lubricants
Greases
Deoiled wax
Waxes
Gasoline (Naphtha) Sweetening & Blending
Distillate Sweetening & Blending
Residual Sweetening & Blending
Hydro-treating & Blending

Fluid Catalytic Cracking Process - FCC

Pengertian FCC

FCC adalah proses katalitik yang memecah molekul hidrokarbon besar menjadi molekul kecil melalui kontak dengan katalis pada suhu tinggi (sekitar 500-550°C) dan tekanan rendah. Proses ini endotermik, sehingga memerlukan panas dari regenerasi katalis untuk menjaga keseimbangan termal, dan menghasilkan bensin beroktan tinggi serta olefin yang bernilai ekonomi lebih tinggi daripada cracking termal

Tahapan Proses

- Feedstock dipanaskan hingga 300-400°C lalu disuntikkan ke riser reaktor, di mana bereaksi dengan katalis zeolit pada 535°C selama 2-4 detik untuk membentuk produk crack seperti gasoline dan olefin.
- Uap hidrokarbon dipisahkan dari katalis spent melalui siklon, sementara katalis dikirim ke regenerator untuk membakar coke pada 650-750°C menggunakan udara, menghasilkan panas untuk siklus berikutnya

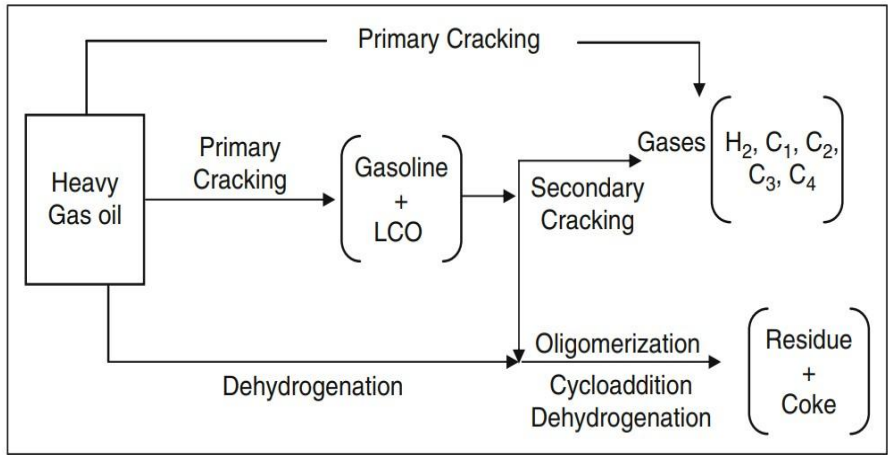


Figure 8.3 FCC reactions network

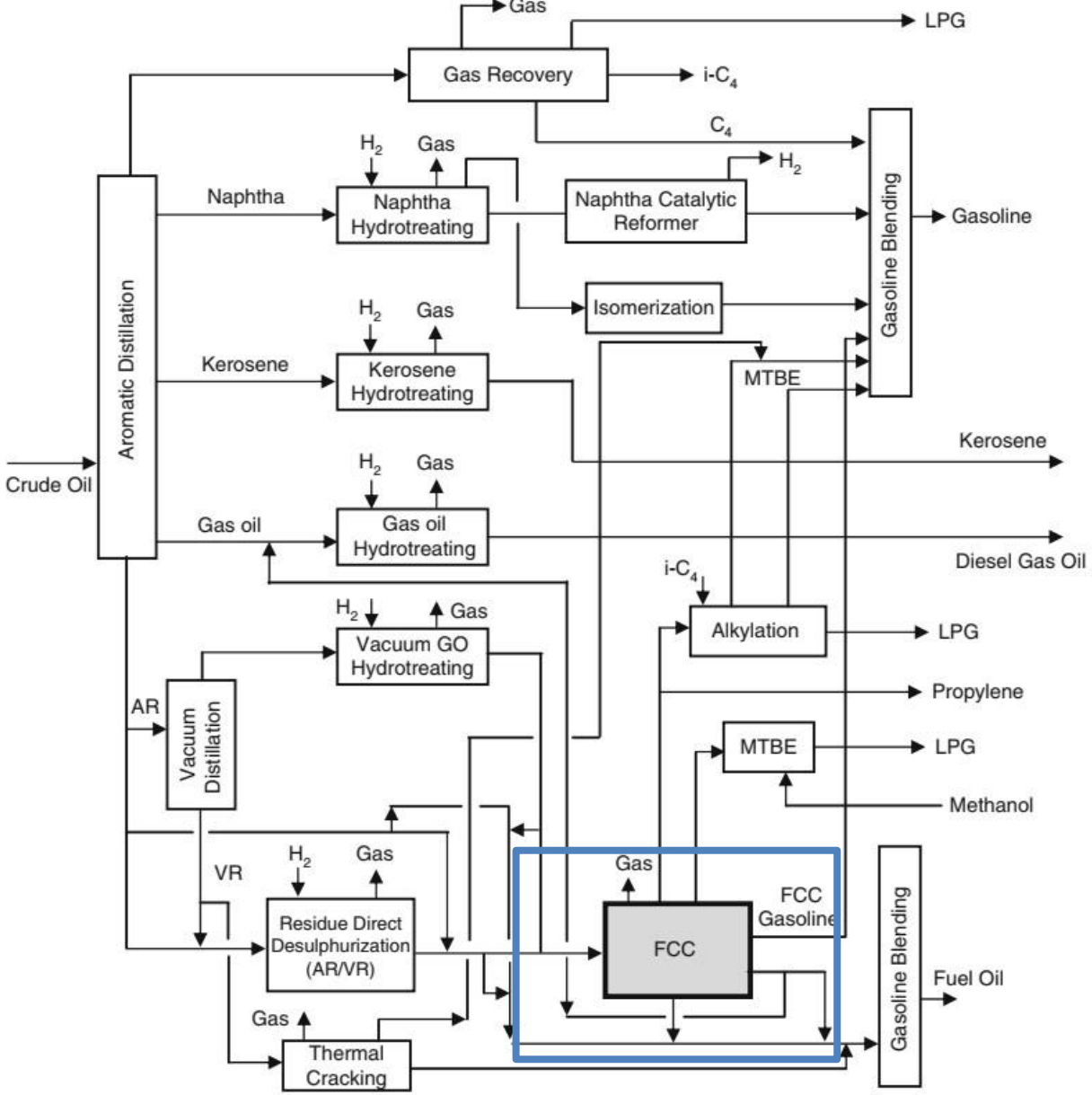
Product	Yield, wt% of feed	Disposition
Light Ends	16.5 ~ 22	LPG, Alkyl
Naphtha	44 ~ 56	Naphtha Hydrotreating
Light Cycle Oil	13 ~ 20	Distillate Hydrotreating
Medium Cycle Oil	10 ~ 26	Hydrocracking
Slurry Oil	4 ~ 12	Heavy fuel oil; carbon black processing
Coke	5 ~ 6	Flue gas to CO boiler

Komponen

- Unit FCC mencakup reaktor-riser untuk cracking, regenerator untuk aktivasi ulang katalis, sistem sirkulasi katalis (dengan slide valve), dan fractionator utama untuk memisahkan produk seperti FCC gasoline, light cycle oil, dan slurry oil.
- Katalis utama adalah zeolit Y dengan matriks alumina, yang sirkulasi mencapai 5 kg per kg feedstock untuk menjaga aktivitas

Produk dan Manfaat

- Produk utama: meliputi bensin (50-60% yield), propylene, butylene, dan coke (4-6%), dengan konversi hingga 80% untuk feed waxy gasoil.
- Manfaat: FCC meningkatkan efisiensi kilang dengan mengoreksi ketidakseimbangan antara permintaan bensin dan residu berat dari distilasi crude oil, serta mendukung produksi petrokimia



Proses FCC (Fluid Catalytic Cracking) melibatkan siklus kontinu antara cracking katalitik dan regenerasi katalis untuk mengonversi fraksi minyak berat menjadi produk ringan bernilai tinggi

Preparasi Feed

Feedstock seperti vacuum gas oil dipanaskan terlebih dahulu hingga 300-400°C di furnace untuk menguapkan sebagian besar hidrokarbon sebelum masuk ke riser reaktor.

Cracking di Riser

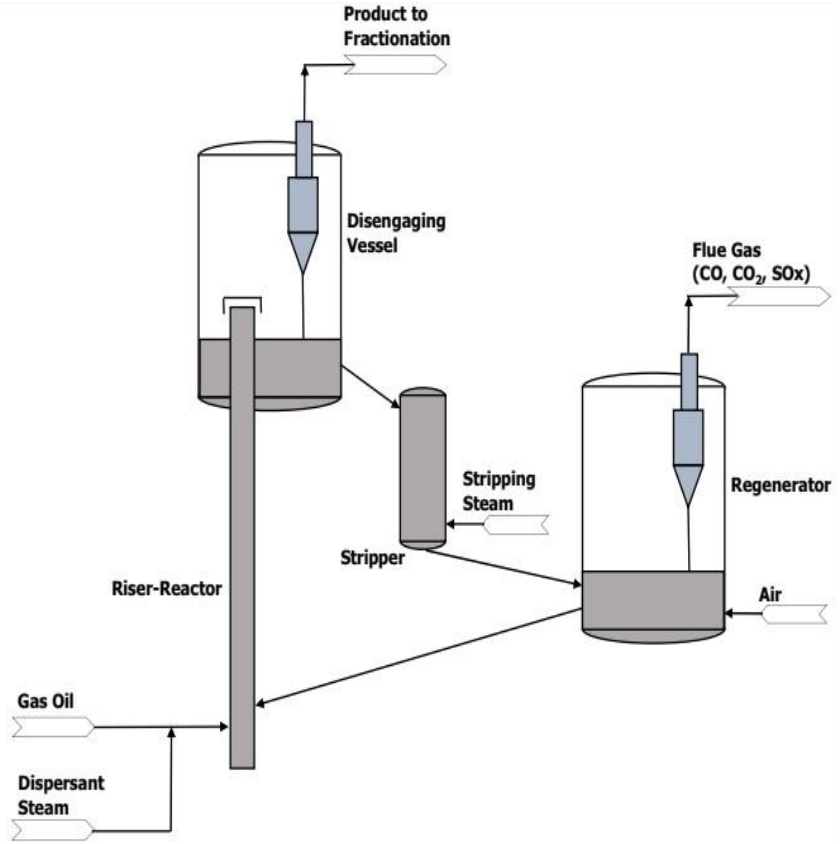
Di riser, feed bercampur dengan katalis panas (500-550°C) dari regenerator; reaksi cracking cepat (2-4 detik) memecah molekul besar menjadi gasoline, olefin, dan coke pada kondisi uap.

Pemisahan Produk

Campuran naik ke cyclone di atas reaktor untuk memisahkan uap hidrokarbon (produk) dari katalis spent yang mengandung coke; uap produk dikirim ke fractionator utama.

Stripping dan Regenerasi

Katalis spent turun ke stripper untuk menghilangkan hidrokarbon tersisa dengan steam, lalu ke regenerator di mana coke dibakar dengan udara pada 650-750°C untuk mengaktifkan ulang katalis dan menyediakan panas siklus berikutnya.



Riser dan regenerator merupakan dua komponen inti dalam unit FCC yang bekerja secara sinergis untuk cracking katalitik dan pemeliharaan katalis.

Fungsi Riser

Riser berfungsi sebagai tempat reaksi cracking cepat, di mana feedstock panas (300-400°C) dicampur dengan katalis regenerasi panas (500-550°C) untuk memecah molekul hidrokarbon berat menjadi produk ringan seperti bensin dan olefin dalam waktu 2-4 detik. Steam disuntikkan di bagian bawah untuk memfluidisasi katalis dan mencegah aliran balik, sementara suhu keluaran dikontrol melalui katup slide untuk mengoptimalkan konversi hingga 80%.

Fungsi Regenerator

Regenerator bertugas mengaktifkan ulang katalis spent dengan membakar coke (4-6% deposit) menggunakan udara pada suhu 650-750°C, menghasilkan panas endotermik yang dibutuhkan untuk siklus cracking berikutnya. Dalam desain dua tahap, tahap pertama membatasi suhu hingga 730°C untuk mencegah deaktivasi katalis, sementara tahap kedua memastikan kadar karbon <0.05% melalui pembakaran CO lengkap, dengan siklon memisahkan katalis dari gas buang.

Interaksi Riser-Regenerator

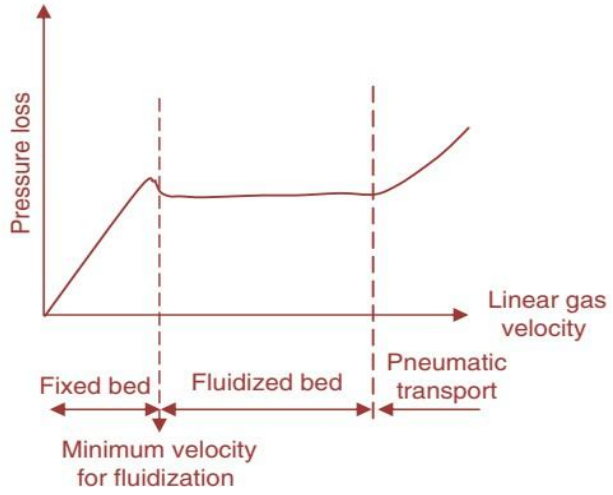
Katalis panas dari regenerator dialirkan ke riser melalui standpipe dengan aerasi untuk aliran stabil, menciptakan keseimbangan termal di mana panas regenerasi mendukung reaksi endotermik, memungkinkan sirkulasi hingga 5 kg katalis per kg feed.

Fluid Catalytic Cracking Process - FCC

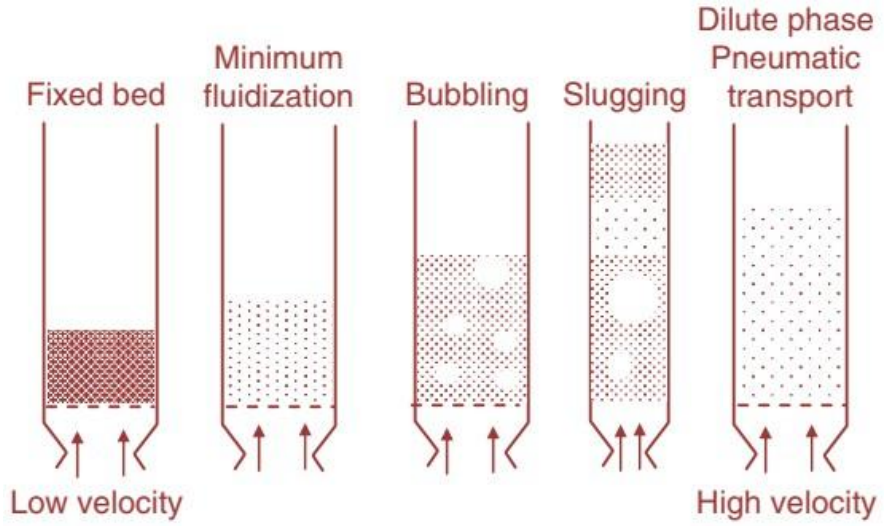
FCC Feedstocks

	Desulphurised vacuum gas oil	Atmospheric residue
Specific gravity (15/4 °C)	0.896	0.889
API	26.3	27.5
Gas oil fraction (GO), wt% (boiling point < 343 °C)	7	4
VGO fraction (VGO), wt% (boiling point 343–538 °C)	88.5	52.5
Vacuum residue fraction (VR), wt% (boiling point > 538 °C)	4.5	43.5
Conradson Carbon Residue (CCR), wt%	0.2	4.2
Sulphur, wt%	0.4	0.11
Nitrogen, wt%	0.064	0.19
Nickel (Ni), wppm	0.26	17
Vanadium (V), wppm	0.15	0.5

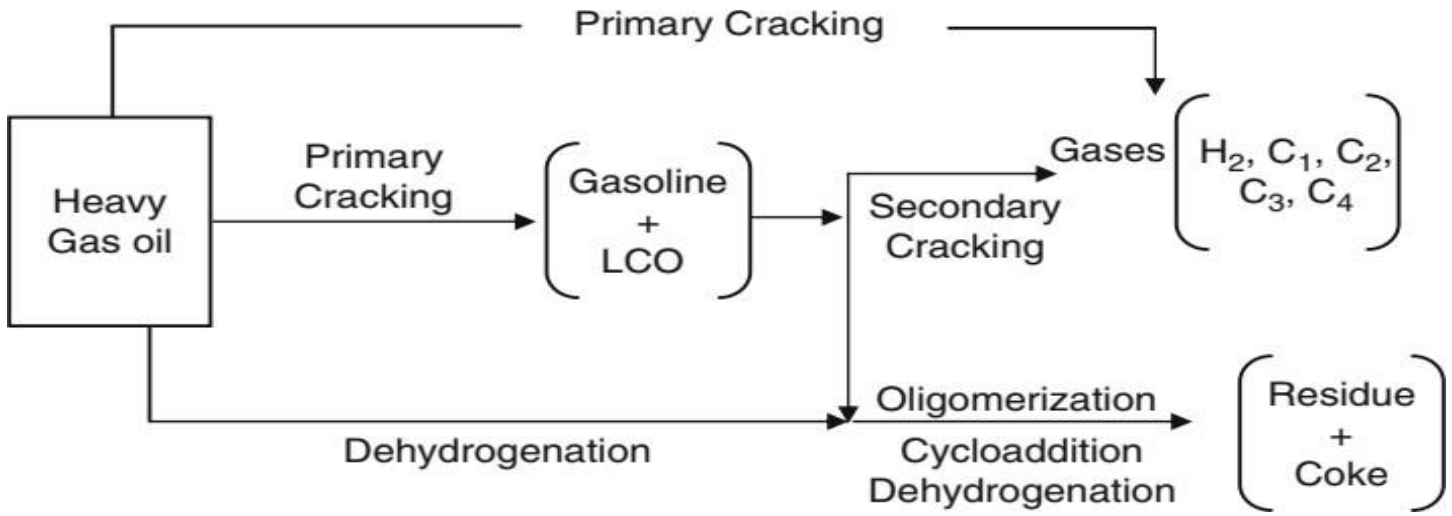
Products	Characteristics	Yield (wt%)
Dry gas + H_2S ($C_1 + C_2 + C_3 + H_2$) + H_2S	H_2S must be removed	3–5
LPG: C_3, $C_3^=$. C_4, $C_4^=$	Petrochemical feedstock	8–20
Gasoline	Main product, good octane number	35–60
Light cycle oil (LCO)	Rich in aromatics, high sulphur content, diluent for fuel	12–20
Heavy cycle oil (HCO) + slurry	Very rich in aromatics, slurry of solids, (mainly catalyst coke)	10–15
Coke	Consumed in regenerator	3–5



Modes of fluidization



Fluid Catalytic Cracking Reactions



The main reactions in the FCC reactor can be summarised as follow

- Paraffins
  Thermal catalytic cracking
  Paraffin cracking → Paraffins + Olefins
- Olefins
  The following reaction can occur with olefins:
  Olefin cracking → LPG olefins
  Olefin cyclisation → Naphthenes
  Olefin isomerisation → Branched olefins + Branched paraffins
  Olefin H-transfer → Paraffins
  Olefin cyclisation → Coke
- Naphthenes
  Naphthene cracking → Olefins
  Naphthene dehydrogenation → Aromatics
  Naphthene isomerisation → Restructured naphthenes
- Aromatics
  Aromatics (side chain) → Aromatics + Olefins
  Aromatic transalkylation → Alkylaromatics
  Aromatic dehydrogenation → Polyaromatics → Coke

Fluid Catalytic Cracking Reactions

		Log K_E equilibrium constant			Heat of reaction BTU/mole
		850 °F	950 °F	980 °F	950 °F
Cracking	$n\text{-}C_{10}H_{22} \rightarrow n\text{-}C_7H_{16} + C_3H_6$	2.04	2.46	–	32,050
	$1\text{-}C_8H_{16} \rightarrow 2C_4H_8$	1.68	2.1	2.23	33,663
Hydrogen transfer	$4C_6H_{12} \rightarrow 3C_6H_{14} + C_6H_6$	12.44	11.09	–	109,681
	$cyclo\text{-}C_6H_{12} + 3\ l\text{-}C_5H_{10} \rightarrow 3n\text{-}C_5H_{12} + C_6H_6$	11.22	10.35	–	73,249
Isomerisation	$l\text{-}C_4H_8 \rightarrow trans\text{-}2\text{-}C_4H_8$	0.32	0.25	0.09	−4,874
	$n\text{-}C_6H_{10} \rightarrow iso\text{-}C_6H_{10}$	−0.2	−0.23	−0.36	−3,420
	$o\text{-}C_6H_4(CH_3)_2 \rightarrow m\text{-}C_6H_4(CH_3)_2$	0.33	0.3	–	−1,310
	$cyclo\text{-}C_6H_{12} \rightarrow CH_3\text{-}cyclo\text{-}C_5H_9$	1	1.09	1.1	6,264
Transalkylation	$C_6H_6 + m\text{-}C_6H_4(CH_3)_2 \rightarrow 2C_6H_5CH_3$	0.65	0.65	0.65	−221
Cyclisation	$l\text{-}C_7H_{14} \rightarrow CH_3\text{-}cyclo\text{-}C_6H_{11}$	2.11	1.54	–	−37,980
Dealkylation	$iso\text{-}C_3H_7\text{-}C_6H_5 \rightarrow C_6H_6 + C_3H_6$	0.41	0.88	1.05	40,602
Dehydrogenation	$n\text{-}C_6H_{14} \rightarrow l\text{-}C_6H_{12} + H_2$	−2.21	−1.52	–	56,008
Polymerisation	$3C_2H_4 \rightarrow l\text{-}C_6H_{12}$	–	–	−1.2	–
Paraffin alkylation	$l\text{-}C_4H_8 + iso\text{-}C_4H_{10} \rightarrow iso\text{-}C_8H_{18}$	–	–	3.3	–

- Reaction can be both exothermic and endothermic reactions which impact the overall heat balance.
- The reaction is mainly endothermic, requiring heat supplied during catalyst regeneration by coke combustion.
- The cracking of larger molecules results in a high volume of products.
- Low operating pressure (1-5 bars) is necessary due to the large product volume.
- The high endothermic nature of cracking reactions requires high reactor temperatures (480-550°C or 869-1022°F).

Penjelasan FCC Reaksi

1. Reaksi bisa eksoterm maupun endoterm

- Di reaktor FCC, reaksi cracking hidrokarbon besar menjadi molekul yang lebih kecil bersifat **endoterm** (menyerap panas).
- Di regenerator, pembakaran coke di permukaan katalis bersifat **eksoterm** (melepaskan panas).
- Keduanya membentuk satu neraca panas: panas dari pembakaran coke di regenerator dibawa oleh katalis panas ke riser untuk "membiayai" reaksi cracking yang menyerap panas.

2. Reaksi endoterm – butuh suplai panas dari regenerasi

- Mayoritas reaksi kimia di riser adalah pemutusan ikatan C–C dan pembentukan produk ringan; ini membutuhkan energi sehingga suhu reaktor cenderung turun jika tidak ada suplai panas.
- Karena itu katalis keluar regenerator harus sangat panas: ketika bercampur dengan umpan dingin di riser, panas katalis ditransfer ke fase gas sehingga reaksi cracking tetap berlangsung pada suhu operasi yang diinginkan.

3. Cracking molekul besar → volume produk tinggi

- Satu molekul berat (misalnya C30) ketika di-crack bisa menjadi beberapa molekul yang lebih kecil (misalnya beberapa C3, C4, C5, dan seterusnya).
- Jumlah mol meningkat, sehingga volume gas/uap di riser dan di atas reaktor menjadi jauh lebih besar dibanding volume umpan cair yang masuk.

4. Tekanan operasi rendah (1–5 bar)

- Karena jumlah mol dan volume gas/uap sangat besar, tekanan dijaga relatif rendah (sekitar 1–5 bar) agar:
    - beban mekanik peralatan dan kolom fractionator tidak berlebihan,
    - aliran gas-padat di riser tetap "fluidized" dan tidak menyebabkan back-mixing berlebihan.
- Tekanan rendah juga membantu memindahkan kesetimbangan ke arah fase gas dan memudahkan pemisahan fraksi di fractionator setelah reaktor.

5. Sifat endotermik → suhu reaktor tinggi (480–550°C)

- Untuk memecah ikatan C–C dalam hidrokarbon berat diperlukan energi aktivasi yang tinggi; itu sebabnya riser dioperasikan pada suhu sekitar 480–550°C.
- Suhu tinggi ini:
    - memastikan laju reaksi cukup besar sehingga waktu tinggal bisa dibuat sangat singkat (orde detik) namun konversi tetap tinggi,
    - membantu menjaga katalis tetap aktif (tidak tertutup kondensat) dan semua fraksi berada dalam fase uap sehingga kontak gas–padat dengan katalis optimum.

Fluid Catalytic Cracking Catalyst

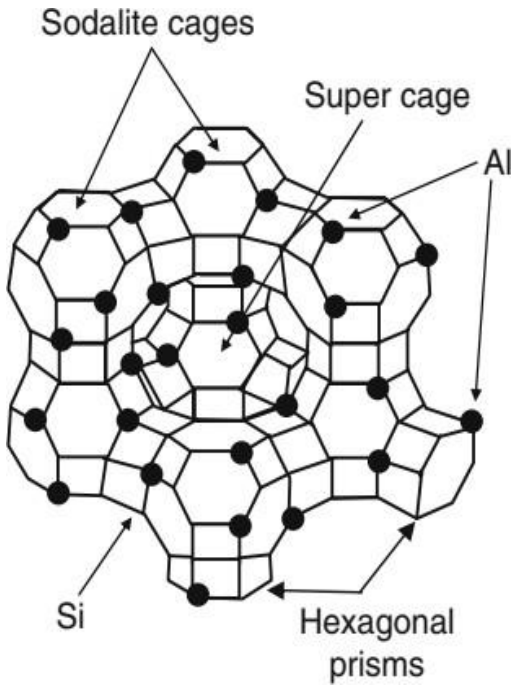
Katalis Fluid Catalytic Cracking (FCC catalyst) adalah serbuk mikrosfer yang menyediakan situs asam untuk memecah hidrokarbon berat menjadi bensin, LPG, dan olefin pada proses FCC.

Pengertian dan Tujuan

- FCC menggunakan katalis padat berbentuk serbuk halus (mikrosfer) yang dibuat mengalir seperti fluida oleh gas/uap untuk mempercepat reaksi pemutusan rantai hidrokarbon panjang menjadi molekul lebih pendek. Tujuannya menghasilkan bensin beroktan tinggi, olefin (propylene, butylene), dan LPG, sekaligus mengurangi fraksi berat yang kurang laku seperti gas oil dan residu.

Cara Kerja

- Umpan minyak berat dipanaskan lalu disemprotkan ke dalam *riser* dan langsung kontak dengan katalis panas; reaksi cracking berlangsung sangat cepat dalam fase uap pada suhu sekitar 480–550°C dan tekanan rendah (1–5 bar). Campuran uap produk dan katalis kemudian dipisahkan di *cyclone*; katalis yang tertutup coke dikirim ke *regenerator* untuk dibakar cokenya, sehingga katalis aktif dan panas lagi untuk siklus berikutnya, sedangkan uap produk masuk ke kolom *fractionator* untuk dipisahkan menjadi gas, LPG, bensin, LCO, dan slurry.

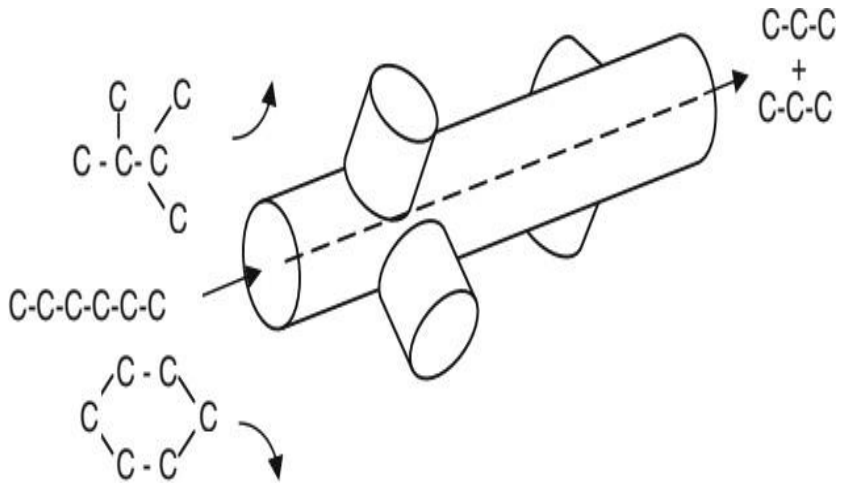


Fluid Catalytic Cracking Catalyst

Komposisi dan Struktur ; Tersusun dari **zeolit Y** sebagai komponen aktif (±15–30%), matriks silika-alumina, binder, dan filler untuk kekuatan mekanik dan stabilitas hidrotermal. Bentuknya mikrosfer berukuran ±60–90 µm yang berperilaku seperti fluida dalam aliran gas di riser dan regenerator sehingga kontak gas–padat sangat intens.

Fungsi Utama; Menyediakan situs asam Brønsted/Lewis yang menginisiasi mekanisme karbokation sehingga cracking berlangsung cepat pada 480–550°C dan tekanan rendah. Mengontrol selektivitas produk: formulasi katalis (jenis zeolit, porositas, nivel rare earth) diatur untuk menyeimbangkan yield bensin, propilena, LCO, serta meminimalkan coke dan gas ringan.

Deaktivasi dan Pengelolaan; Aktivitas menurun akibat endapan coke, kontaminasi logam (Ni, V), dan kerusakan struktur zeolit oleh suhu/steam tinggi, sehingga katalis harus terus diregenerasi dengan pembakaran coke di regenerator. Di kilang, katalis segar secara berkala ditambahkan dan katalis spent dibuang sehingga yang beroperasi adalah *equilibrium catalyst* (E-cat) dengan sifat yang stabil terhadap kondisi FCC aktual.



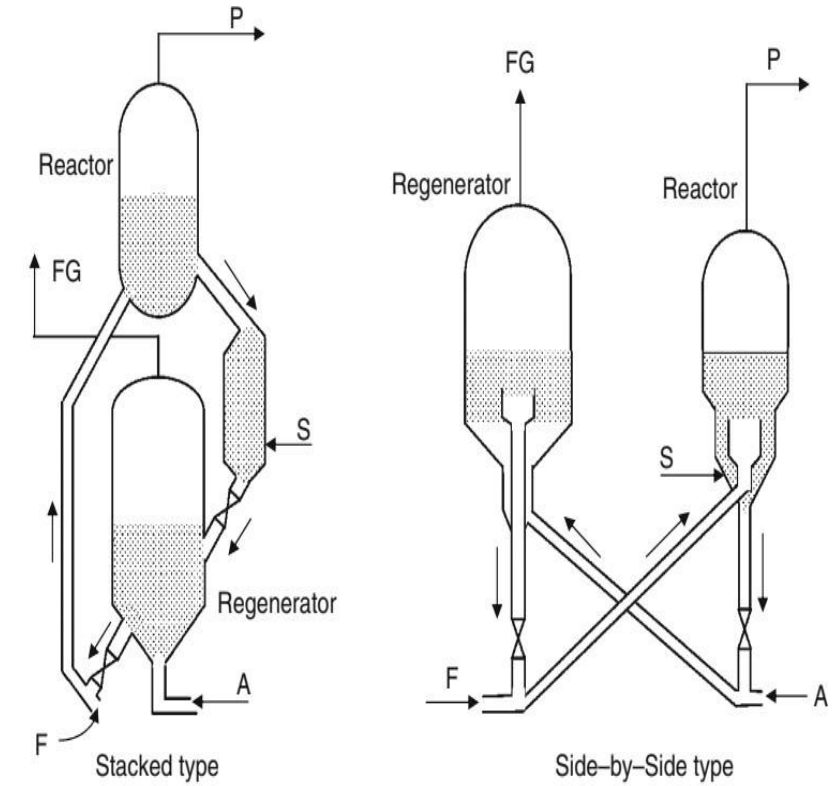
shape-selective cracking with ZSM-5 zeolite

Fluid Catalytic Cracking Configuration

Fluid Catalytic Cracking Configuration pada dasarnya menjelaskan **bagaimana unit-unit utama FCC diatur dan dihubungkan** untuk mengolah umpan berat menjadi produk ringan secara kontinu.

Unit utama dalam konfigurasi FCC

- **Reaktor–riser**: zona kontak cepat antara umpan (VGO/resid) dan katalis panas; di sini reaksi cracking endotermik berlangsung dalam hitungan detik pada suhu tinggi dan tekanan rendah.
- **Stripper**: bagian bawah reaktor yang dialiri steam untuk mengeluarkan hidrokarbon yang masih teradsorpsi dari permukaan katalis sebelum katalis masuk ke regenerator (memisahkan produk dari katalis)
- **Regenerator**: tempat pembakaran coke di permukaan katalis dengan udara sehingga katalis kembali aktif dan menjadi sumber panas untuk reaktor.
- **Main fractionator (fractionation column)**: kolom distilasi atmosferik yang menerima uap produk dari reaktor dan memisahkannya menjadi wet gas, LPG, gasoline, LCO, HCO, dan slurry.



F = Feed, P = Products, S = Steam, FG = Flue gas, A = Air

Konfigurasi umum aliran proses

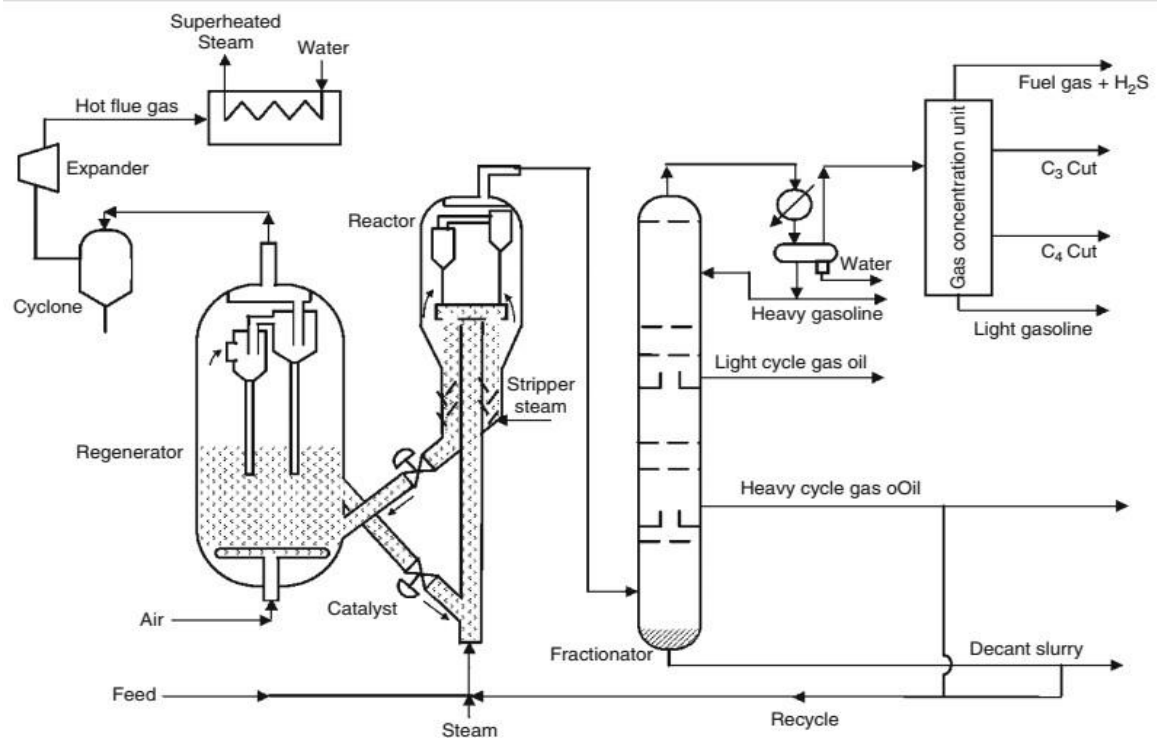
- Umpan dipanaskan di furnace lalu masuk ke **riser**, bercampur dengan katalis panas dari regenerator dan mengalami cracking.
- Campuran gas + katalis keluar riser menuju **vessel reaktor** dengan sistem siklon untuk memisahkan katalis; gas produk menuju **main fractionator**, sedangkan katalis turun ke **stripper** dan kemudian ke **regenerator**.
- Di regenerator, coke dibakar; katalis yang sudah panas kembali ke dasar riser (melalui standpipe dan slide valve), sehingga terbentuk **sirkulasi katalis tertutup** antara reaktor dan regenerator.
- Dari main fractionator, setiap fraksi (gas, LPG, gasoline, LCO, HCO, slurry) punya jalur lanjutannya sendiri (gas concentration unit, hydrotreating, recycle ke FCC, atau ke storage).

Variasi konfigurasi modern

- **Side-by-side vs stacked**: reaktor dan regenerator bisa disusun berdampingan (side-by-side) atau vertikal (stacked) untuk menghemat ruang dan mengoptimalkan aliran katalis.
- **Single-riser vs dual-riser**: beberapa konfigurasi memakai dua riser untuk mengolah dua jenis umpan atau untuk memaksimalkan produk tertentu (misal max-propylene).
- **RFCC / resid FCC**: konfigurasi yang diperkuat (material, sistem air distribution, regenerator dua tahap) agar mampu mengolah umpan residu yang lebih berat dan tinggi logam

Secara praktis, konfigurasi FCC menentukan fleksibilitas kilang: seberapa jauh unit mampu menerima variasi umpan, menaikkan konversi, mengatur selektivitas (gasoline vs propylene), dan menekan konsumsi energi maupun emisi

Fluid Catalytic Cracking Configuration – Side To Side



Variable	Value
Reactor Feed Rate, MBPSD	40
Feed Temperature, °F	446
Catalyst/Oil Ratio	5.4
Catalyst Circulation Rate, tons/min	21.7
Catalyst Makeup Rate, tons/day	2.5
Riser Outlet Temperature, °F	991
Dispersion Steam, wt% feed	0.9
Stripping Steam, tons/ton catalyst	0.0213
Reactor Pressure, psig	30
Regenerator Pressure, psig	33
Regenerator Temperature, °F	1341
Flue Gas Temperature, °F	1355

Mode of Fluidization

Location in FCC	Mode of fluidisation
Regenerator	Turbulent fluidisation: to attain uniform burning temperature in bed.
Line for catalyst transport from regenerator to riser	Bubbling fluidisation
Riser	Pneumatic transport: Catalyst and products are carried out from riser. Plug flow has a few seconds of residence time.
Stripper	Bubbling fluidisation: Steam is injected in the stripper to vaporise and recover heavy oil and reduce coke formation.
Lift line from regenerator to reactor	Pneumatic transport

Mode Fluidization

FCC	Mode Fluidisasi
Regenerator	Turbulent fluidisation: untuk mencapai suhu pembakaran yang seragam di dalam bed.
Line for catalyst transport from regenerator to riser	Bubbling fluidization
Riser	Pneumatic transport: Katalis dan produk dibawa keluar dari riser dengan aliran plug flow dengan waktu tinggal beberapa detik.
Stripper	Bubbling fluidisation: Uap disuntikkan untuk menguapkan dan memulihkan minyak berat serta mengurangi pembentukan coke.
Lift line from regenerator to reactor	Pneumatic transport

FCC - Yield Correlation

FCC yield mengacu pada persentase atau volume produk yang dihasilkan dari unit Fluid Catalytic Cracking (FCC), seperti gasoline (50-60% vol), LCO (15-20% vol), coke (4-6 wt%), dan gas ringan (LPG/dry gas 15-25 wt%) pada konversi tipikal 75-85%

Pengertian dan Perhitungan

Yield dihitung sebagai fraksi massa/volume produk spesifik dari umpan (feed), misalnya gasoline

yield = (volume FCC gasoline / volume feed) × 100%, diukur pada konversi tetap untuk membandingkan katalis atau umpan.

Konversi = 100% - cycle stock (LCO + HCO), di mana cycle stock adalah fraksi tak tereaksi yang bisa didaur ulang

$$\text{CONV}\% = \left(\frac{\text{volume of oil feed} - \text{volume of cycle stock}}{\text{volume of oil feed}}\right) \times 100$$

Products	Correlation
Coke wt%	$0.05356 \times \text{CONV} - 0.18598 \times \text{API} + 5.966975$
LCO LV%	$0.0047 \times \text{CONV}^2 - 0.8564 \times \text{CONV} + 53.576$
Gases wt%	$0.0552 \times \text{CONV} + 0.597$
Gasoline LV%	$0.7754 \times \text{CONV} - 0.7778$
iC_4 LV%	$0.0007 \times \text{CONV}^2 + 0.0047 \times \text{CONV} + 1.40524$
nC_4 LV%	$0.0002 \times \text{CONV}^2 + 0.019 \times \text{CONV} + 0.0476$
$C_4^=$ LV%	$0.0993 \times \text{CONV} - 0.1556$
C_3 LV%	$0.0436 \times \text{CONV} - 0.8714$
$C_3^=$ LV%	$0.0003 \times \text{CONV}^2 + 0.0633 \times \text{CONV} + 0.0143$
HCO	$100 - \text{CONV} - (\text{LCO LV\%})$
Wt% S in Gases	$3.9678 \times (\text{wt\% S in feed}) + 0.2238$
Wt% S in LCO	$1.04994 \times (\text{wt\% S in feed}) + 0.00013$
Wt% S in HCO	$1.88525 \times (\text{wt\% S in feed}) + 0.0135$
S in Coke[a]	wt% S in feed – wt% S in gases – wt% S LCO – wt% S HCO
Gasoline API	$-0.19028 \times \text{CONV} + 0.02772 \times (\text{Gasoline LV\%}) + 64.08$
LCO API	$-0.34661 \times \text{CONV} + 1.725715 \times (\text{Feed API})$

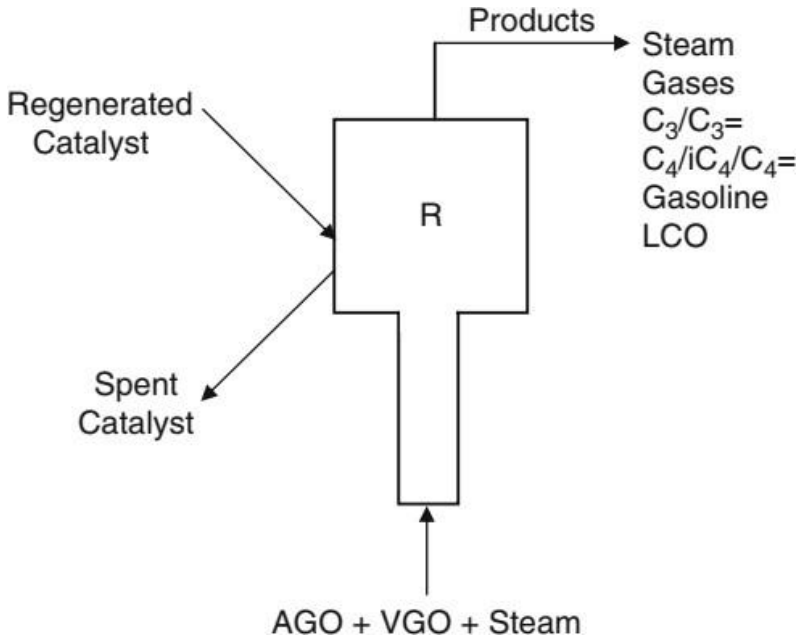
Faktor Penentu Yield

- Umpan: VGO dengan TBP 370-550°C dan rendah logam (<10 ppm Ni+V) maksimalkan gasoline >55 vol%; resid berat tingkatkan coke >6 wt%.
- Katalis: Zeolit Y hasilkan gasoline 62 vol% vs amorf 55 vol% pada 80% konversi, dengan oktane lebih tinggi.
- Kondisi operasi: Suhu riser 480-550°C, C/O ratio 3-9, dan waktu kontak 1-6 detik optimalkan yield; regenerator 650-750°C kurangi coke pada katalis

Produk	Yield (wt% atau vol%)	Keterangan
Gasoline (C5-390°F)	50-62	Utama, RON 89-94
LCO (cycle oil)	15-27	Diesel blendstock
Coke	4-6	Dibakar di regenerator
Dry gas + LPG	15-25	Propylene source

Example 1

Suatu campuran bahan baku sebesar 20.000 BPD AGO (650–850 °F) dengan API 24 dan kandungan belerang 0,2% berat, dicampur dengan campuran bahan baku lain sebesar 15.000 BPD VGO (850–1050 °F) yang memiliki API 15 dan kandungan belerang 0,35% berat. Campuran ini digunakan sebagai bahan baku untuk unit FCC. Gunakan korelasi FCC untuk menentukan keseimbangan material di sekitar unit reaktor. Asumsikan konversi sebesar 75% LV.Gambar di bawah menunjukkan aliran masuk dan keluar reaktor.Translated with DeepL.com (free version)



Solution:

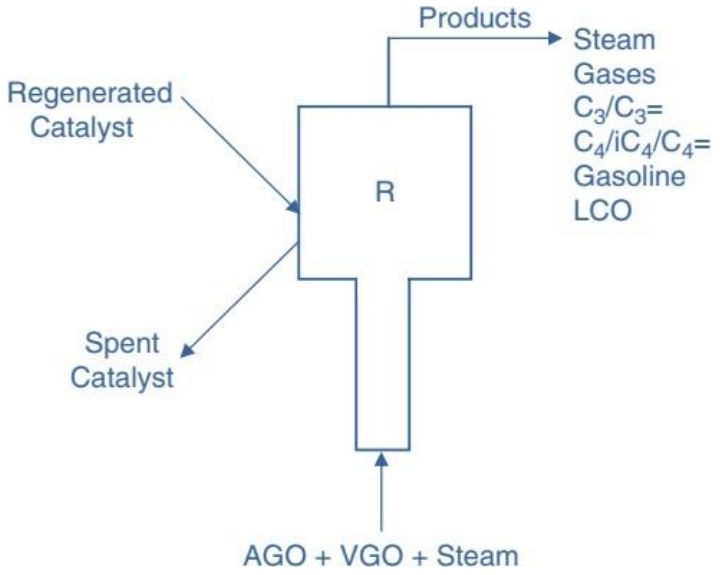
AGO = 20000 (bbl/day) × 318.6 (lb/bbl) × (1 day/24 h) = 265,000 lb/h
VGO = 15000 (bbl/day) × 338 (lb/bbl) × (1 day/24 h) = 211250 lb/h
S in AGO = 265000 × 0.2/100 = 530 lb/h
S in VGO = 211250 × 0.35/100 = 739 lb/h
S in feed = 1269/476250 × 100 = 0.266%
Conversion = ((Vol. of feed – Vol. of cycle stock)/Vol. of feed) × 100 = 75%
Cycle stock = unconverted portion below gasoline = (LCG + HCGO) = 25

API of mixture:
Total feed = 476,250 lb/h
SG for AGO = 0.9099 and SG for VGO = 0.9659

$$\text{Then SG for mixed feed} = \frac{20000}{20000+15000}(0.9099) + \frac{15000}{20000+15000}(0.9659)$$
$$= 0.9339$$

This gives feed API = 20.02

Solution



Feed properties

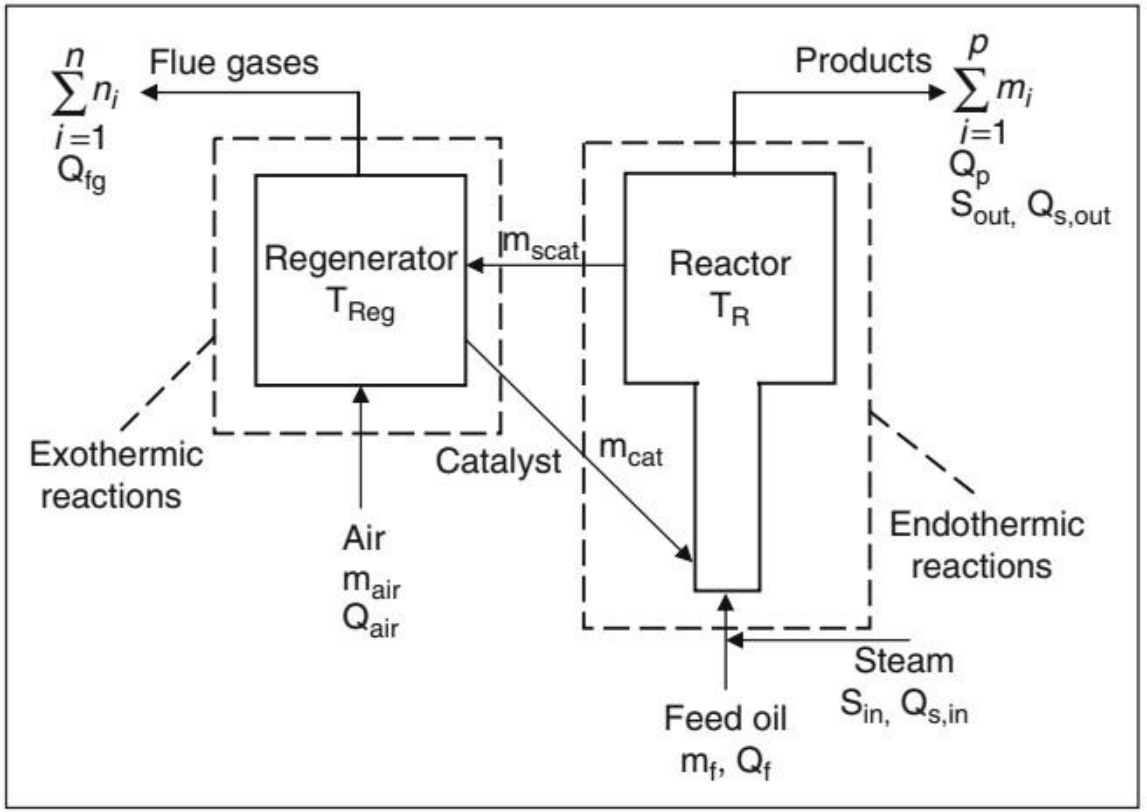
Stream	BPD	API	lb/h	wt% S	lb S/h
AGO	20,000	24	265,000	0.2	530
VGO	15,000	15	211,250	0.35	739
		20.02	476,250		1269

Yields and properties of products

			lb/h
Coke wt%	$0.05356 \times (75) - 0.18598 \times (20.02) + 5.966975$	6.3	30,004
LCO LV%	$0.0047 \times (75)^2 - 0.8564 \times (75) + 53.576$	15.8	81,337
Gases wt%	$0.0552 \times (75) - 0.597$	4.7	22,574
Gasoline LV%	$0.7754 \times (75) - 0.7778$	57.4	226,816
iC_4 LV%	$0.0007 \times (75)^2 + 0.0047 \times (75) + 1.40524$	5.7	16,375
nC_4 LV%	$0.0002 \times (75)^2 + 0.019 \times (75) + 0.0476$	2.6	7735
$C_4^=$ LV%	$0.0993 \times (75) - 0.1556$	7.3	22,356
C_3 LV%	$0.0436 \times (75) - 0.8714$	2.4	6230
$C_3^=$ LV%	$0.0003 \times (75)^2 + 0.0633 \times (75) + 0.0143$	6.4	16,987
HGO wt%	$100 - 75 - 15.8$	9.7	46,027
S in H_2S wt%	$3.9678 \times (0.266) + 0.2238$	1.28	289
S in LCO wt%	$1.04994 \times (0.266) + 0.00013$	0.278	226
S in HCO wt%	$1.88525 \times (0.266) + 0.0135$	0.515	237
S in Coke wt%	$(1269 - 289 - 226 - 237)/29,813$	1.734	517
Gasoline API	$-0.19028 \times (75) + 0.02772 \times (59.1) + 64.08$	51.4	
LCO API	$-0.34661 \times (75) + 1.725715 \times (20.02)$	8.5	

Mass Balance of FCC (Reactor)

Reactor Material Balance



Reactor input:

- Oil feed (VGO) to the riser: F (BPD) or m_f (lb/h)
- Injection steam: S_{in} (lb/h)
- Regenerated catalyst: m_{cat} (lb/h)

Reactor output:

- Masses of products m_i, as calculated from FCC yield correlations. These correlations require some feed properties such as: API, sulphur content and degree of severity expressed as conversion.
- Spent catalyst circulation rate m_{scat} (lb/h)
- Steam present in cracked products, S_{out} (lb/h)

Thus, a material balance around the reactor is

$$m_f + S_{in} + m_{cat} = \sum_{i=1}^{p} m_i + S_{out} + m_{scat}$$

$$m_{coke} = m_{scat} - m_{cat}$$

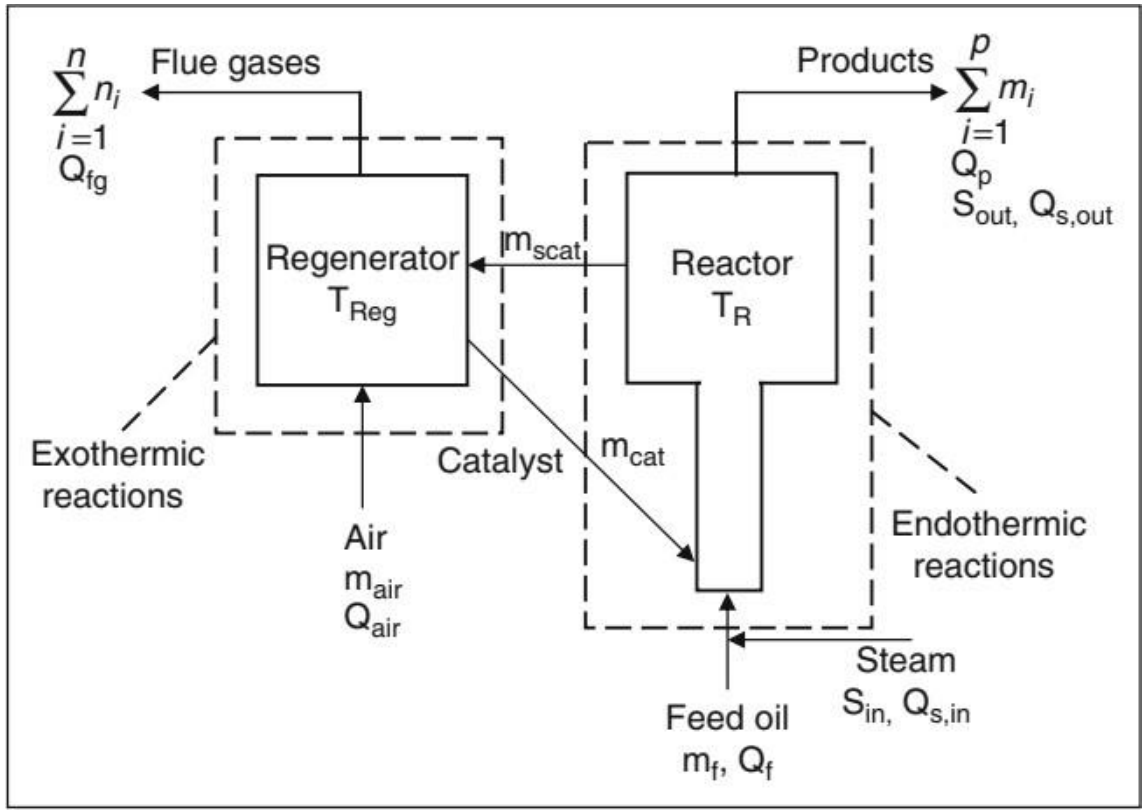
can be rewritten as follows:

$$m_f = \sum_{i=1}^{F} m_i + m_{coke}$$

where p is the total number of vapour products and assuming Sin does not condense and is present in the exiting vapour products at the same rate (Sin = Sout). mi is the mass of each product that can be calculated using the FCC correlations. The produced coke is present in spent catalyst.

Mass Balance of FCC (Regenerator)

Regenerator Material Balance



Regenerator input:

- Spent catalyst circulation rate m_{scat} (lb/h)
- Air for coke burning m_{air} (lb/h)

Regenerator output:

- Flue gases n_i (lb/h)
- Regenerated catalyst m_{cat} (lb/h)

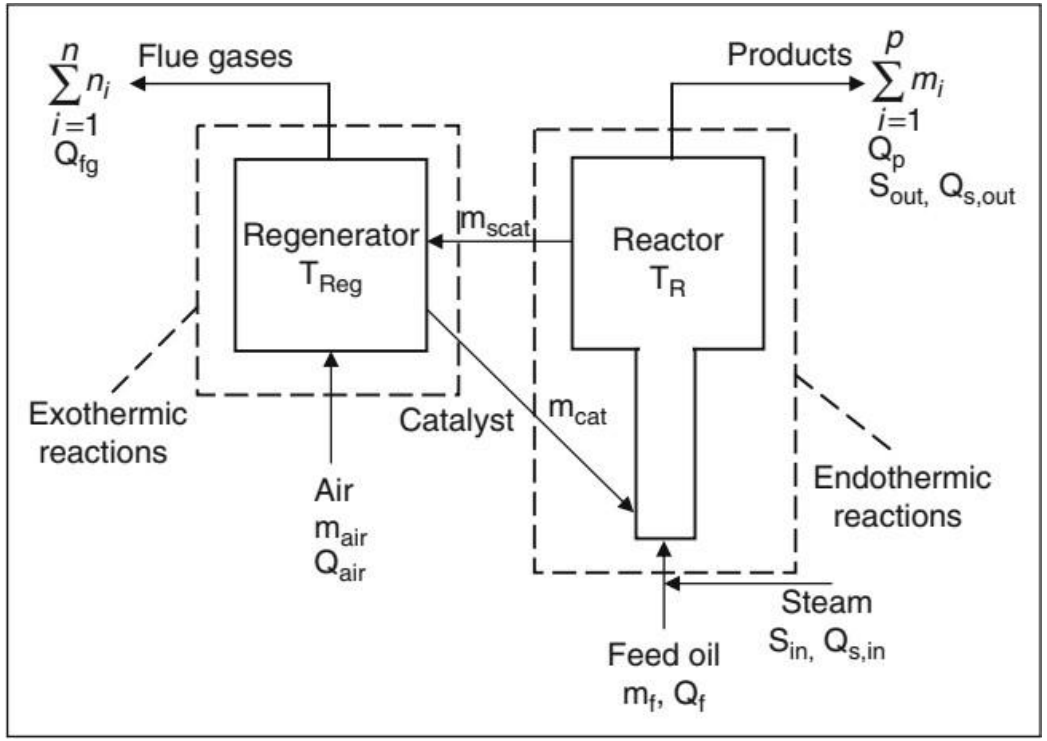
Thus, the material balance around the regenerator produces:

$$m_{air} + m_{scat} = \sum_{i=1}^{N} n_i + m_{cat}$$

where n_i is the mass of each gas produced from the coke burning which may contain
CO_2, CO, H_2O, SO_2, N_2 and O_2 (from excess air).

Heat Balance of FCC (Reactor)

Reactor Heat Balance



Heat input:

- Heat of feed oil Q_F (Btu/h) at inlet feed temperature (T_f)
- Heat of steam injected Q_S (Btu/h) at T_s
- Heat of regenerated catalyst Q_{cat} (Btu/h) at regenerator outlet temperature (T_{Reg})

Heat output:

- Heat in vapour products, Q_p (Btu/h) at reactor outlet temperature (T_R)
- Heat of spent catalyst Q_{scat} (Btu/h) at T_R
- Heat of exit steam $Q_{s,out}$ (Btu/h) at T_R

Then the energy balance can be expressed as

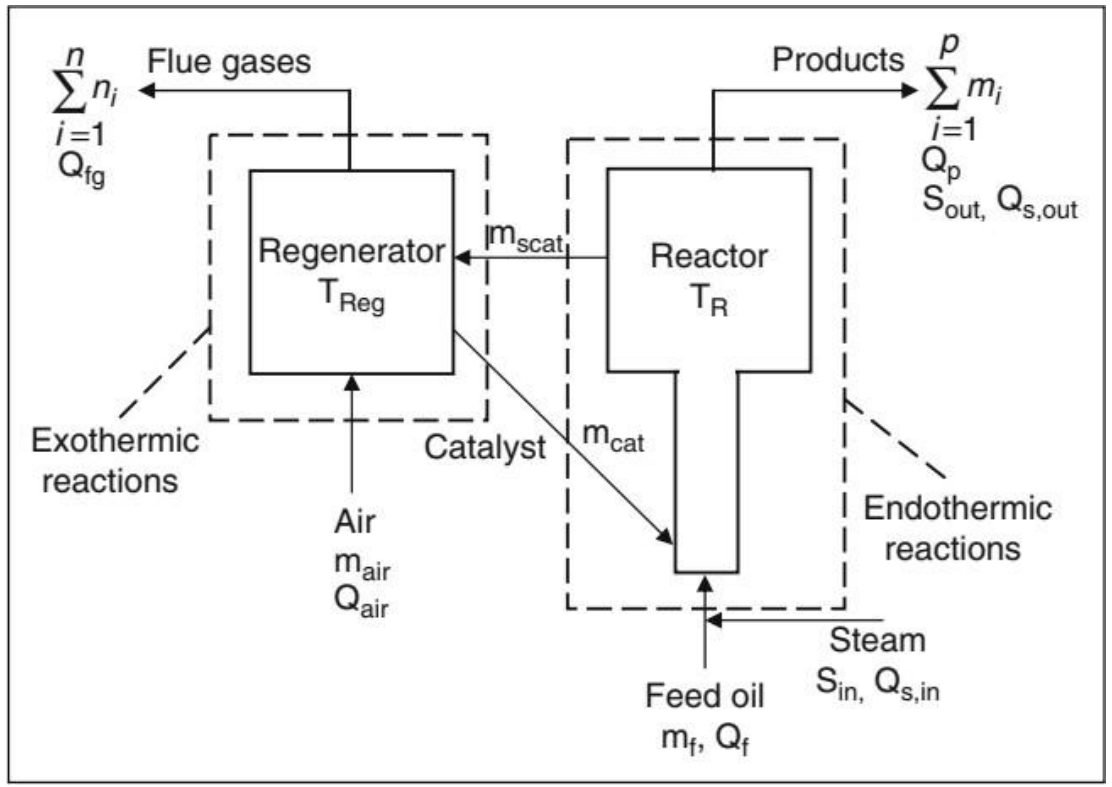
$$m_f C_{p,f}(T_f - T_o) + m_f(-\Delta H_R) + m_{cat} C_{P,cat}(T_{Reg} - T_o) + S_{in} C_{ps}(T_s - T_o)$$
$$= (T_R - T_o)\sum m_i C_{P,i} + m_{scat} C_{P,scat}(T_R - T_o) + S_{out} C_{ps}(T_R - T_o)$$

Since, $m_{coke} = m_{scat} - m_{cat}$ and $S_{in} = S_{out}$,

$$m_f C_{p,f}(T_f - T_o) + m_f(-\Delta H_R) + m_{cat} C_{P,cat}(T_{Reg} - T_R) + S_{in} C_{ps}(T_s - T_R)$$
$$= (T_R - T_o)\sum m_i C_{P,i} + m_{coke} C_{P,coke}(T_R - T_o)$$

Heat Balance of FCC (Regenerator)

Regenerator Heat Balance



Heat input:

- Heat of spent catalyst Q_{scat} (Btu/h) at T_R
- Heat of input air for coke burning Q_{air} (Btu/h) at T_{air}
- Heat of coke combustion q_{coke} (Btu/h)

Heat output:

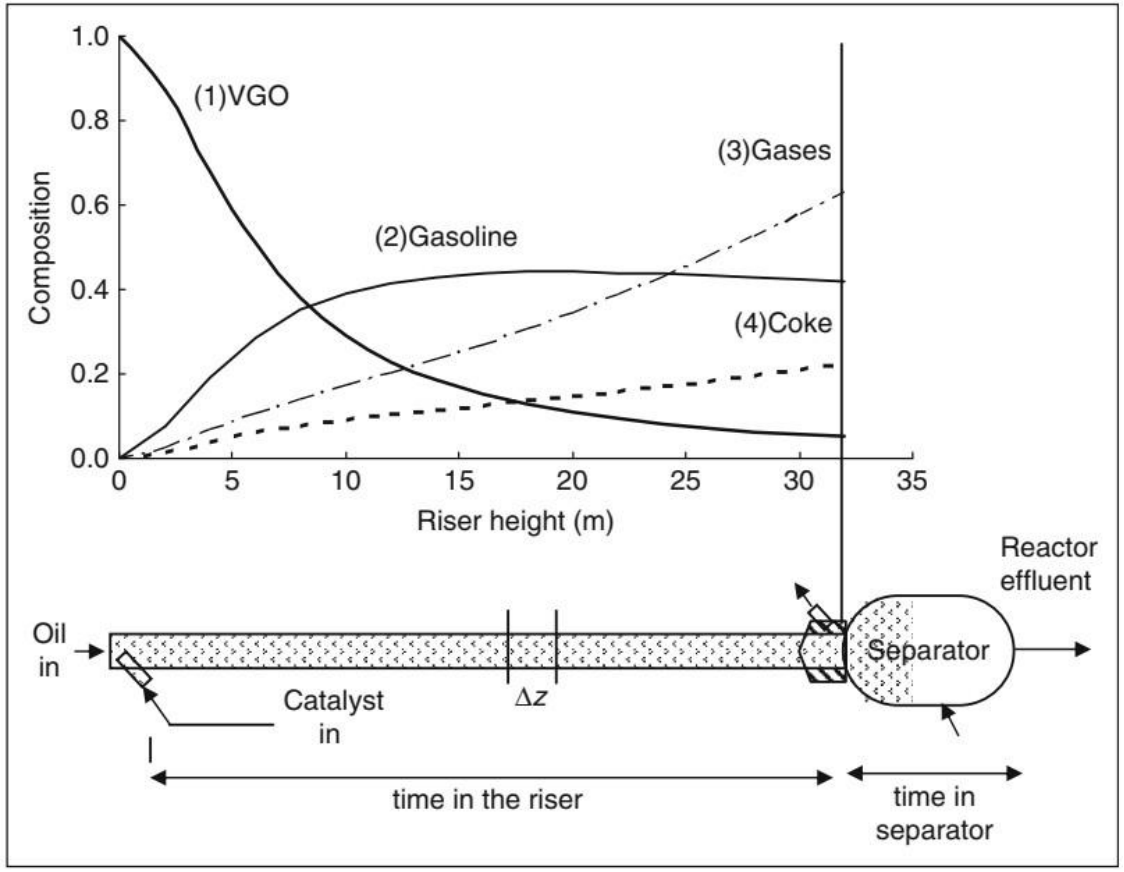
- Heat of flue gas Q_{fg} (Btu/h) at T_{Reg}
- Heat of regenerated catalyst Q_{cat} (Btu/h) at T_{Reg}

Thus the heat balance around the regenerator can expressed as

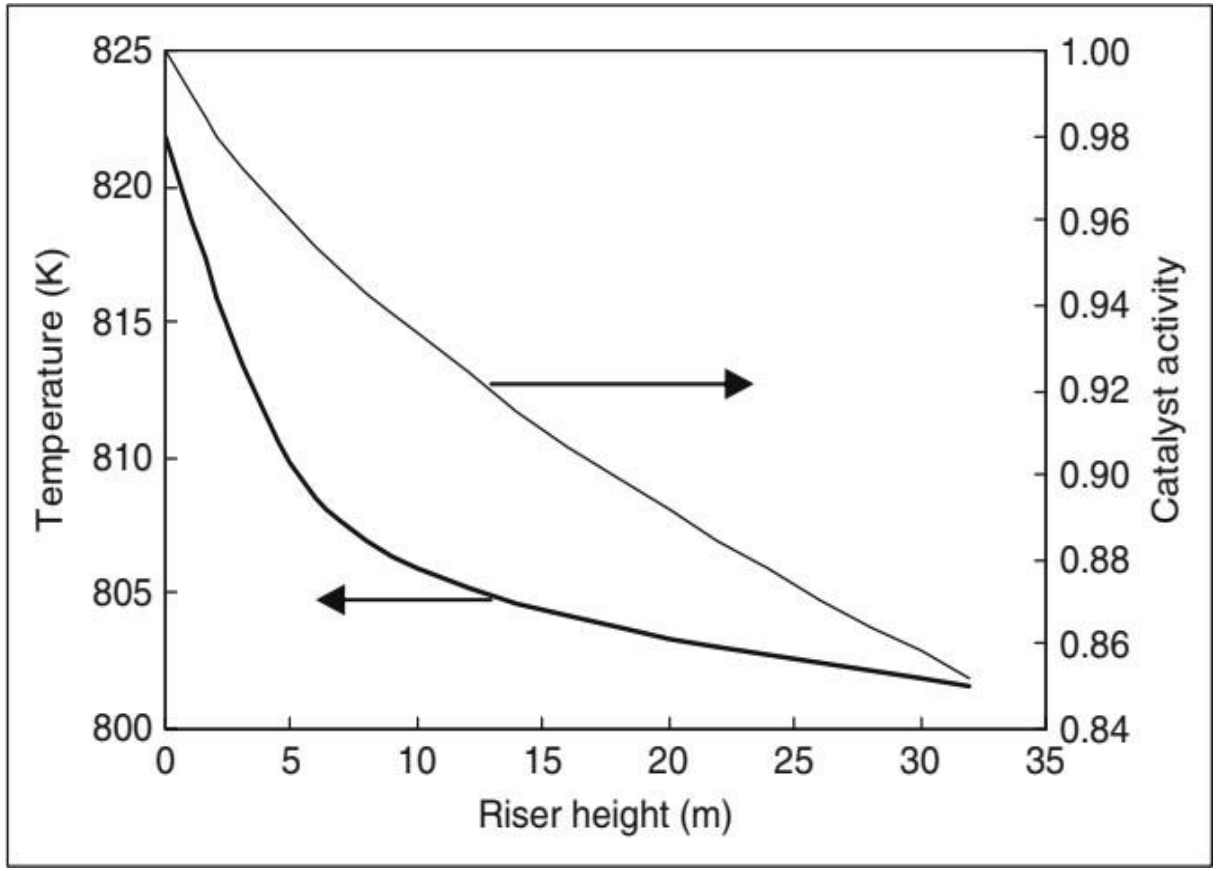
$$m_{air}C_{p,air}(T_{air} - T_o) + m_{coke}C_{P,coke}(T_R - T_o) + q_{coke} = (T_{Reg} - T_o)\sum n_i C_{P,gi} + m_{cat}C_{P,cat}(T_{Reg} - T_R)$$

Concentration and Temperature Profiles in the Riser

FCC riser composition profiles as a function of riser height >> Product concentration along the riser



The temperature and activity of catalyst profiles in the riser



PRODUCT BLENDING

Table 9.1 Typical properties for gasoline blending components (Gary and Handwerk, 2001)

Component	RVP (psi)	MON	RON	API
iC_4	71.0	92.0	93.0	
nC_4	52.0	92.0	93.0	
iC_5	19.4	90.8	93.2	
nC_5	14.7	72.4	71.5	
iC_6	6.4	78.4	79.2	
LSR gasoline	11.1	61.6	66.4	78.6
HSR gasoline	1.0	58.7	62.3	48.2
Light hydrocracker gasoline	12.9	82.4	82.8	79.0
Heavy hydrocracker gasoline	1.1	67.3	67.6	49.0
Coker gasoline	3.6	60.2	67.2	57.2
FCC Light gasoline	1.4	77.1	92.1	49.5
FCC gasoline	13.9	80.9	83.2	51.5
Reformate 94 RON	2.8	84.4	94.0	45.8
Reformate 98 RON	2.2	86.5	98.0	43.1
Alkylate $C_3^=$	5.7	87.3	90.8	
Alkylate $C_4^=$	4.6	95.9	97.3	70.3
Alkylate $C_5^=$	1.0	88.8	89.7	

Motor octane number (MON)

PRODUCT BLENDING

Additive properties include specific gravity, boiling point and sulphur content.
However, properties like viscosity, flash temperature, pour point, aniline point, RVP and cloud point are not additive.

- Reid Vapour Pressure Blending
- Flash Point Blending
- Pour Point Blending
- Cloud Point Blending
- Aniline Point Blending
- Smoke Point Blending
- Viscosity Blending
- Gasoline Octane Number Blending

$$BI_{RVPi} = RVP_i^{1.25} \longrightarrow BI_{RVP,Blend} = \sum_{i=1}^{n} x_{vi} BI_{RVPi}$$

$$BI_{PPi} = 3,262,000 \times (PP_i/1000)^{12.5} \longrightarrow BI_{PP,Blend} = \sum_{i=1}^{n} x_{vi} BI_{PPi}$$

$$SP_{Blend} = -255.26 + 2.04\ AP_{Blend} - 240.8 \ln(SG_{Blend}) + 7727(SG_{Blend}/AP_{Blend}) \quad (9.14)$$

For $76 \leq ON \leq 103$

$$BI_{ONi} = -299.5 + 1272(ON/100) - 1552.9(ON/100)^2 + 651(ON/100)^3 \quad (9.20b)$$

$$BI_{ON,Blend} = \sum_{i=1}^{n} x_{vi} BI_{ONi}$$

- Specific Gravity blending

$$SG_{Blend} = \sum_{i=1}^{n} x_{vi} SG_i$$

Alkylation

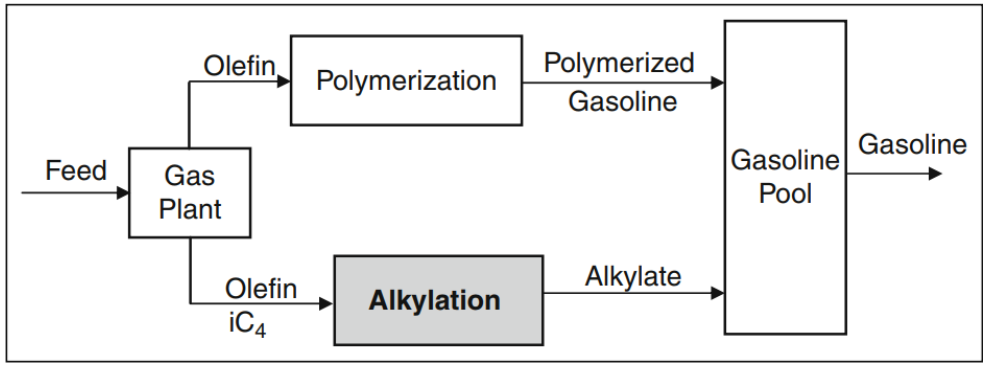


Figure 10.1 Role of alkylation and polymerization units in the refinery

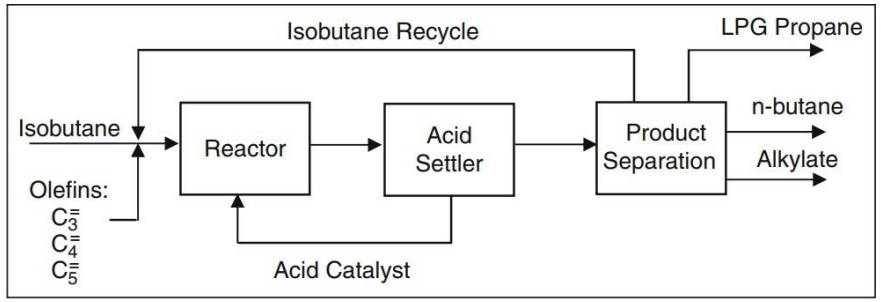


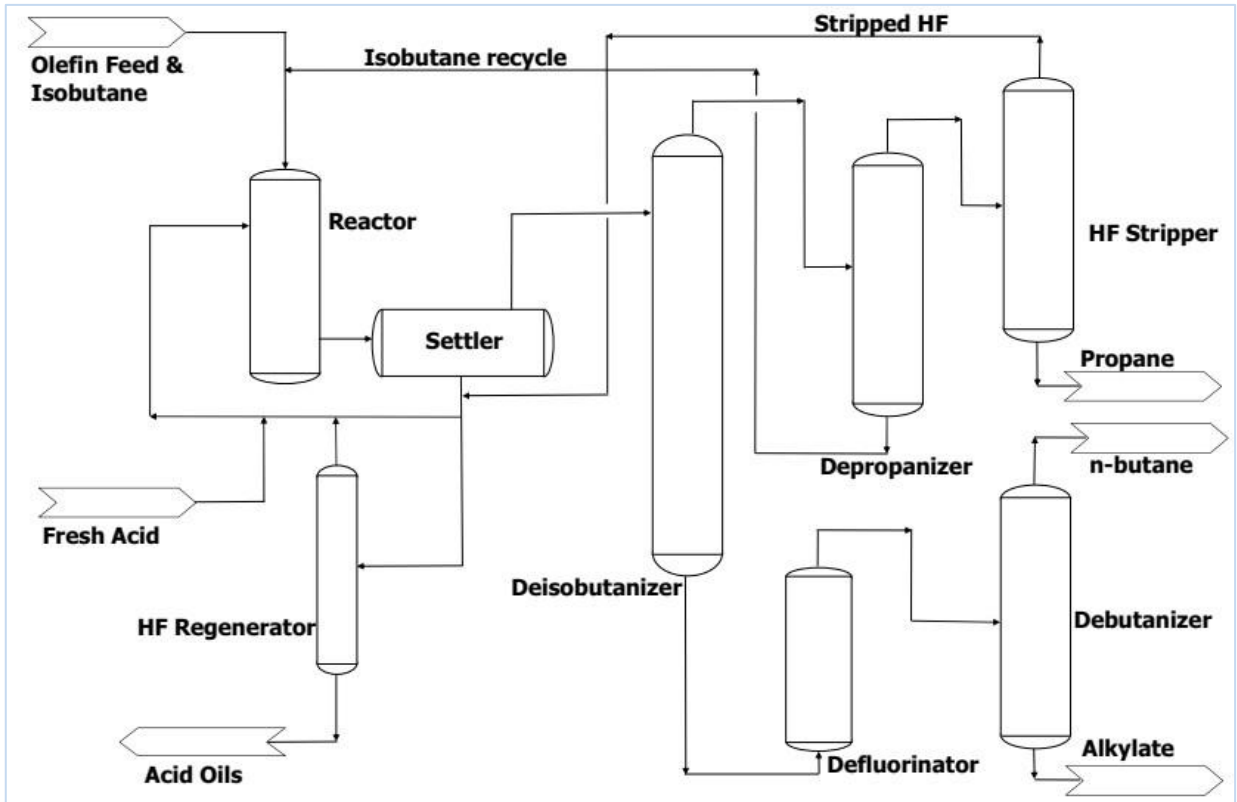
Figure 10.2 Block diagram of alkylation process

Process Objective:

To combine light olefins (propylene and butylene) with isobutane to form a high octane gasoline (alkylate).

Process Technique:

Alkylation occurs in the presence of a highly acidic catalyst (hydroflouric acid or sulfuric acid).



Alkylation Reaction

Alkane hydrocarbons such as C_3, C_4 and C_5, can be produced from the reaction of iC_4 with the corresponding olefin. For example C_3 is produced from the following reaction:

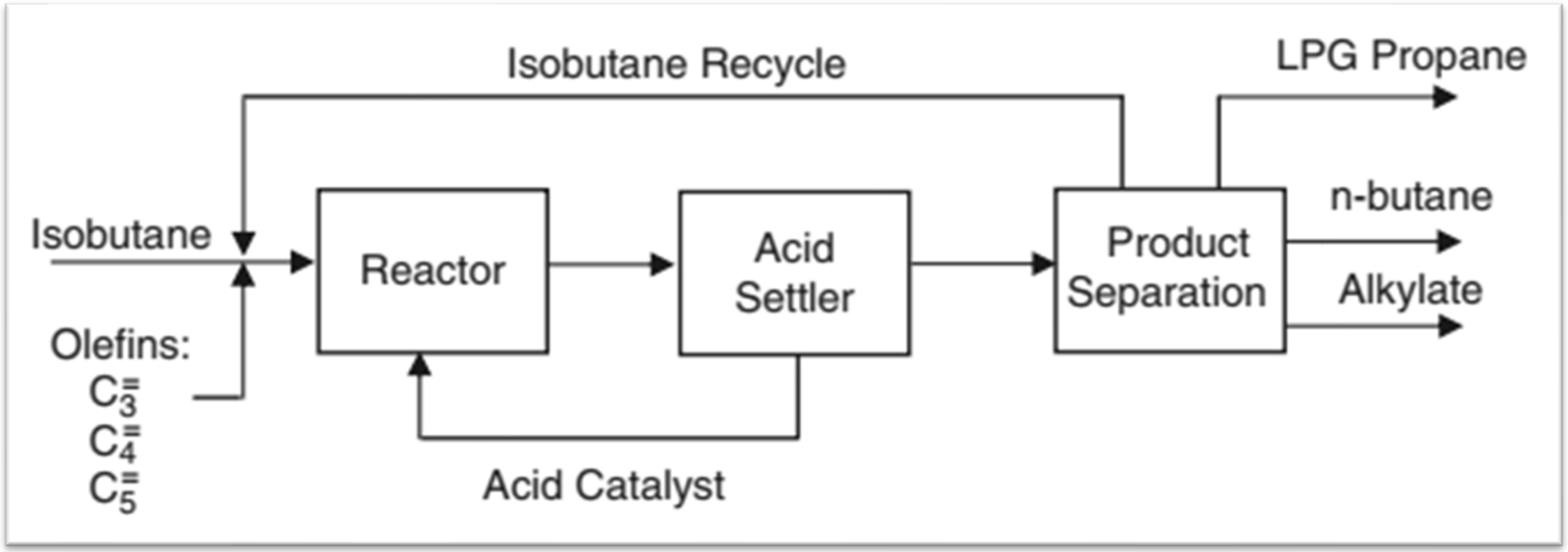
$$C_3^{=} + iC_4 \rightarrow C_3 + iC_4^{=}$$

$$iC_4^{=} + iC_4 \rightarrow \ iC_8 \text{ alkylate}$$

$$C_3^{=} + 2iC_4 \rightarrow C_3 + C_8 \text{ alkylate}$$

Alkylation Processes

- In the **absence of catalysts**, alkylation between isobutane and olefin must be run under severe conditions such as T = 500 ^{o}C and P = 200–400 bars
- In the **presence of an acid catalyst**, the reaction temperature will be lower than 50 ^{o}C and the pressure will be lower than 30 bars
- Reaction:



1. Sulphuric Acid Alkylation Process

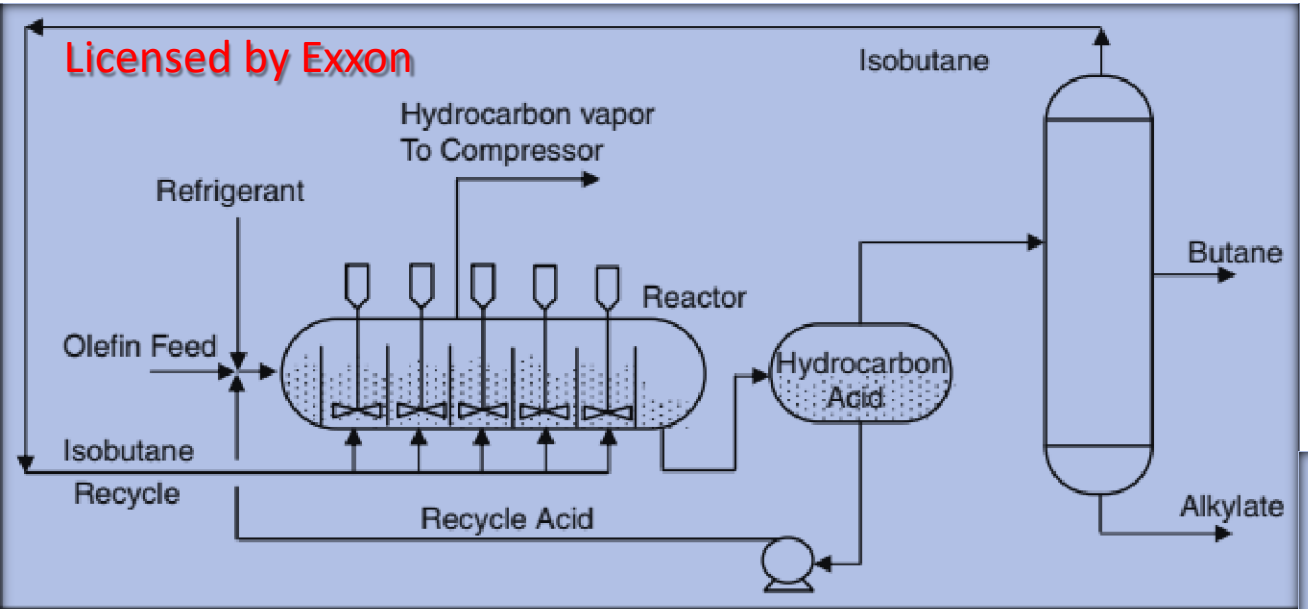
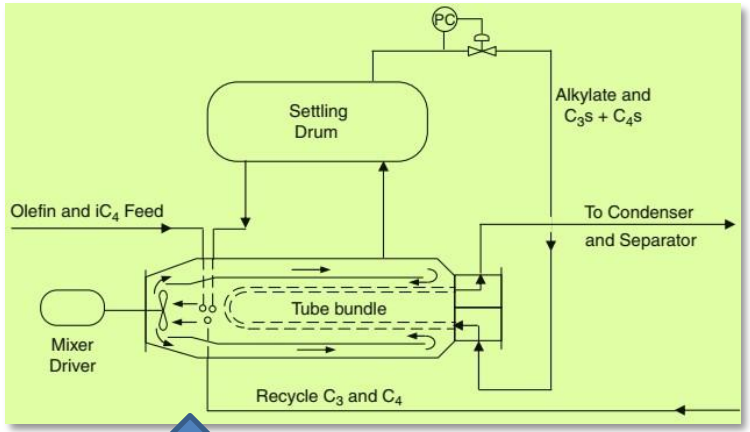


Figure 10.3 Auto-refrigerated sulphuric acid alkylation process

In the auto-refrigeration process, the evaporation of iC4 and C_4 induces cooling of the emulsion in the reactor

In the effluent refrigeration process, a refrigeration unit provides cooling to the reactor



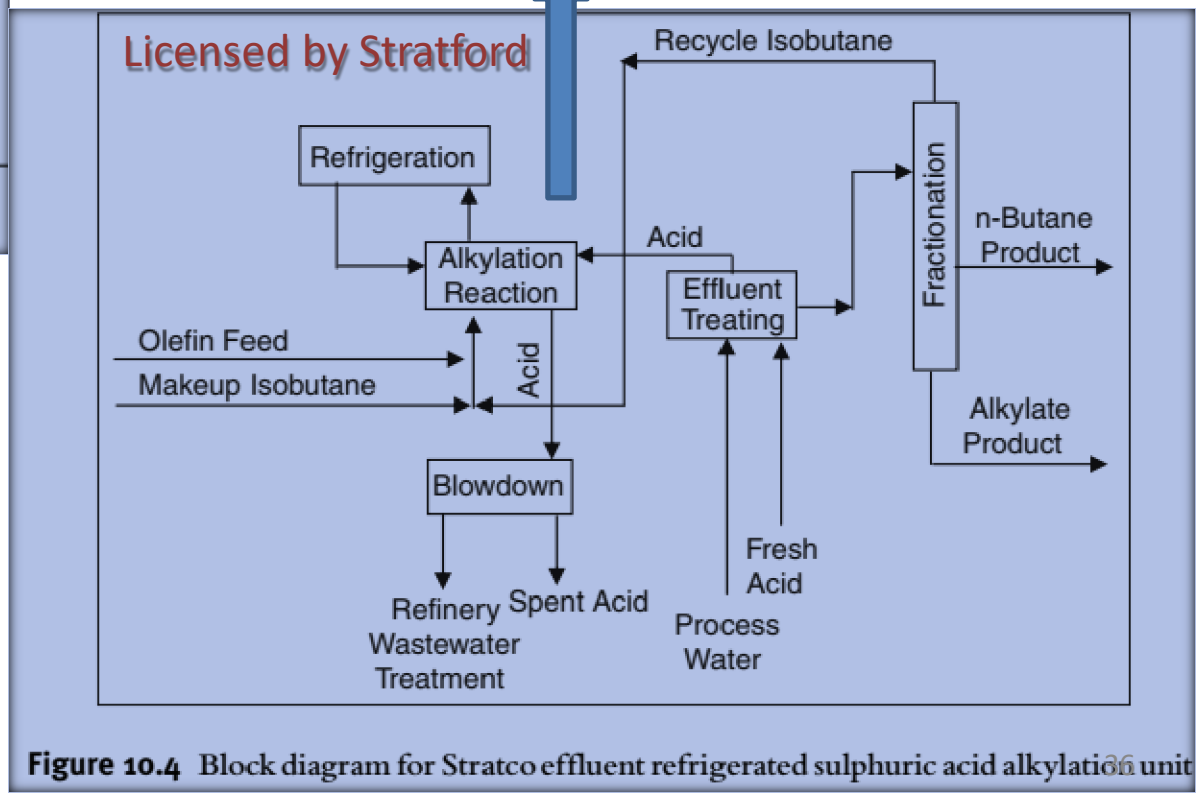
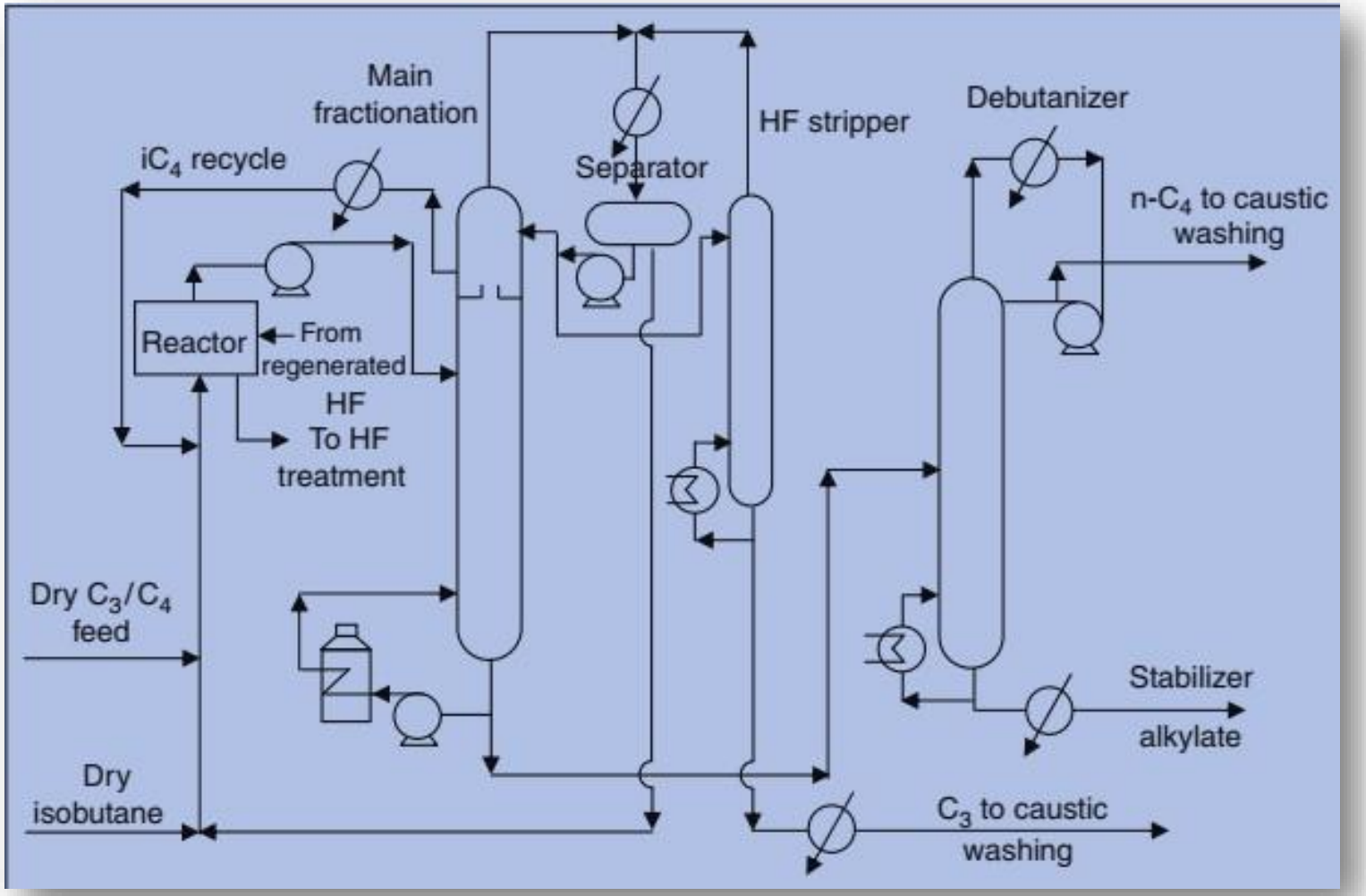


Figure 10.4 Block diagram for Stratco effluent refrigerated sulphuric acid alkylation unit

2. Hydrofluoric Acid Alkylation



- Reaction:

- The emulsion is obtained by injecting the hydrocarbon feed into the continuous HF phase through nozzles at the bottom of a tubular reactor
- Reaction temperature is about 30 C, The residence time in the reactor is 20–40 s.

H2SO4 alkylation processes are favoured over the HF processes because of the recent concern about the mitigation of HF vapour.

3. Solid Catalyst Alkylation

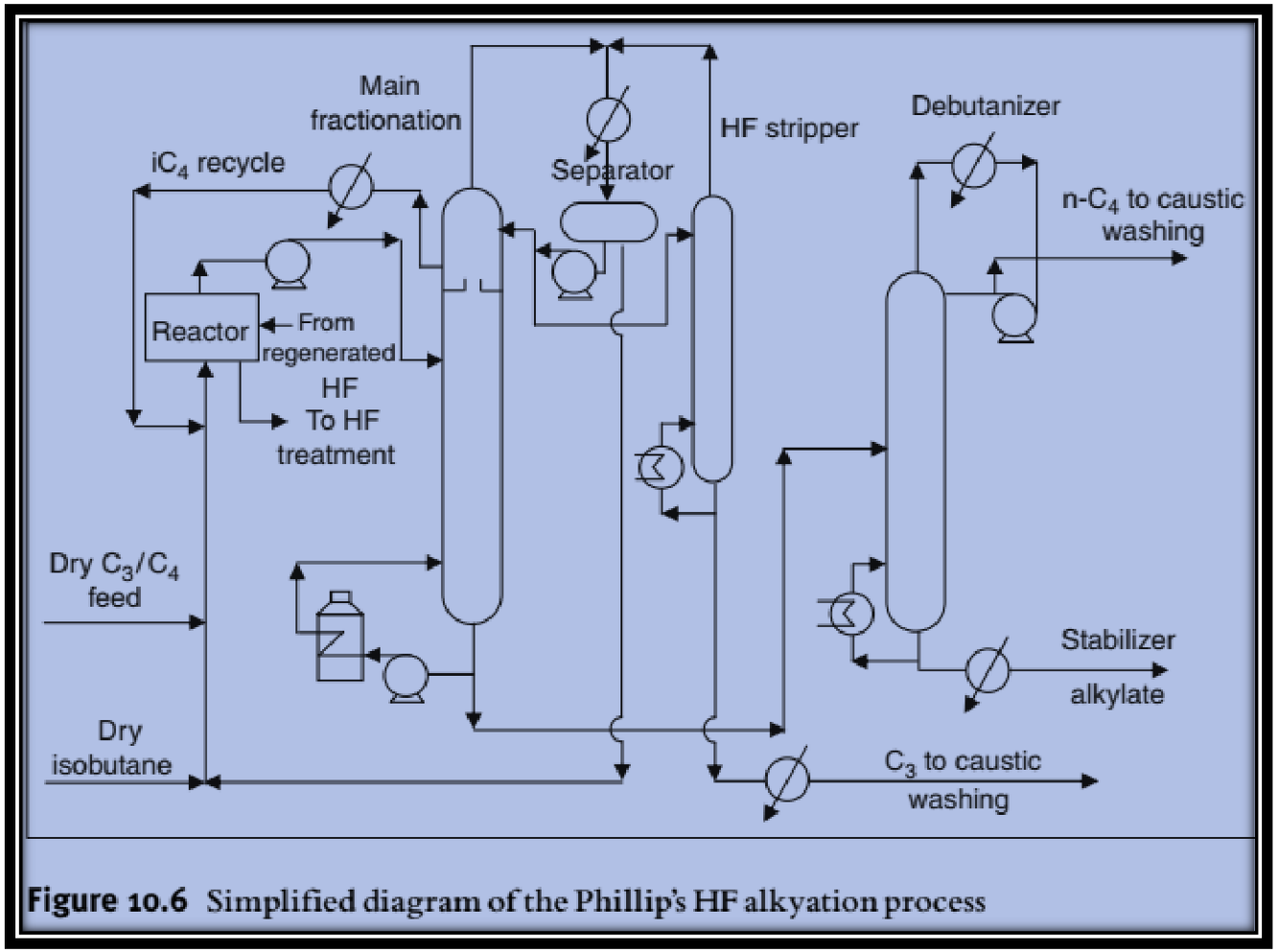


Figure 10.6 Simplified diagram of the Phillip's HF alkyation process

Table 10.2 Solid acid alkylation processes

Process	Reaction temperature (°C)	*i*C$_4$/olefin	Catalyst
UOP alkylene	10–40	6–15	HAL-100
Lurgi Eurofuel	50–100	6–12	Faujasite-derived
Haldor Topsoes FBA	0–20		CF_3SO_3H/SiO_2
ABB Lummus AlkyClean	50–90	8–15	Zeolite-derived (SAC)

4. AlkyClean Process

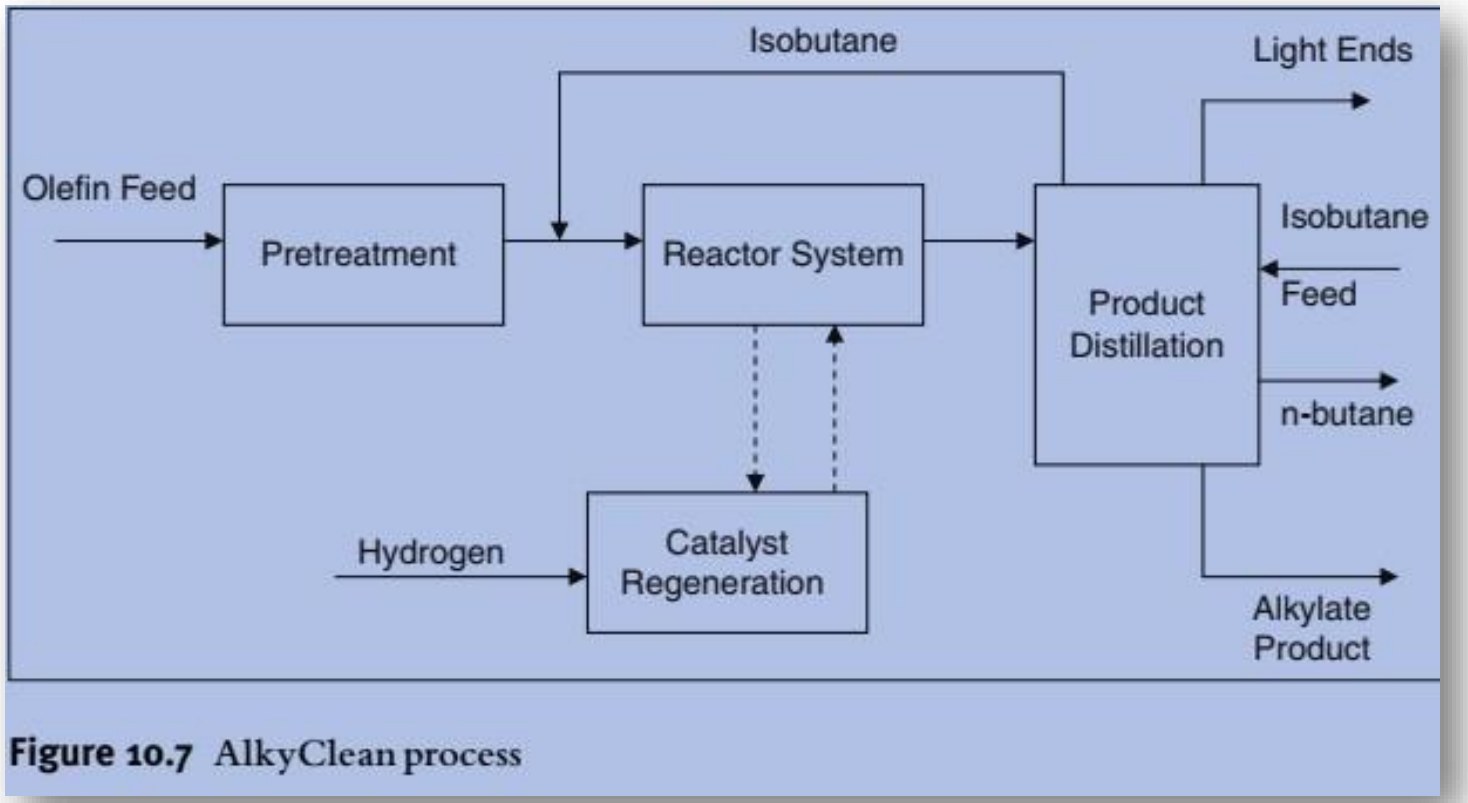


Figure 10.7 AlkyClean process

Employs a zeolite catalyst coupled with a novel reactor processing to yield a high quality alkylate product.

- Olefin feed is preheated and combined with isobutane recycle before entering the reactor.
- The reactor operates in liquid phase conditions within the temperature range of 50–90°C.
- Multiple reactors are used to facilitate the catalyst regeneration cycle.
- During regeneration, olefin is stopped, and hydrogen is added to reduce dissolved hydrogen concentration while maintaining liquid phase alkylation conditions.

Kinetics and Thermodynamics of Alkylation

Consider the simple liquid phase reaction of isobutene (A) and isobutane (B) giving isooctane (A1)

$$A + B \leftrightharpoons A_1$$

$$K_{xeq} = \frac{x_{A1}}{(x_A)(x_B)} = \frac{\gamma(1+\delta-\gamma)}{(1-\gamma)(\delta-\gamma)} \qquad K_p = K_{xeq}K_p^o \qquad K_p^o = \frac{P_{A1}^o}{P_A^o P_B^o}$$

Table 10.3 Equilibrium constant K_p for alkylation reactions at 1 bar in ideal gas phase (Zhorov, 1987)

Reaction	K_p (MPa^{-1})					Equations
	300 K	400 K	500 K	600 K	800 K	
Ethylene + isobutane ↔ 2,3-dimethylpentane	7.7×10^9	5.4×10^5	170.0	39	0.4	(10.8)
Propene + isobutane ↔ 2,3-dimethylpentane	1.3×10^8	2.6×10^5	168.0	6.0	0.1	(10.9)
n-Butene + isobutane ↔ 2,2,4-trimethylpentane	21.7×10^6	2.82×10^3	14.0	0.40	5.2×10^{-3}	(10.10)
1-Pentene + isobutane ↔ 2,2,5-trimethylhexane	55.5×10^6	2.9×10^4	85.0	2.0	1.7×10^{-2}	(10.11)
Isobutene + isobutane ↔ 2,2,4-trimethylpentane	0.11×10^6	76.0	1.0	0.06	1.7×10^{-3}	(10.12)
cis-2-Butene + isobutane ↔ 2,2,4-trimethylpentane	2.4×10^6	662.0	4.0	0.2	4.5×10^{-3}	(10.13)
trans-2-Butene + isobutane ↔ 2,2,4-trimethylpentane	0.77×10^6	303.0	3.0	0.1	3.0×10^{-3}	(10.14)
2-Methyl-2-butene + isobutane ↔ 2,2,5-trimethylhexane	0.23×10^6	105.0	1.0	0.06	1.9×10^{-3}	(10.15)

Effect of Operating Conditions

Process conditions that influence the **quality of alkylate product** and acid consumption rate:

- Olefin Type
- Isobutane Concentration

Table 10.4 Effect of type of olefin on alkylate octane number

	RON		MON	
Types of Olefin	HF	H_2SO_4	HF	H_2SO_4
Propylene	91–93	91–92	89–91	90–92
Butene-1	90–91	97–98	88–89	93–94
Butene-2	96–97	97–98	92–93	93–94
Isobutene	94–95	90–91	91–92	88–89
Amylene	90–92	91–92	88–89	89–91

- iC4/ olefin C4 ratio is kept in industrial operation between 5:1 and 15:1 as the external isobutane to olefin (I/O) ratio.
- Inside a reactor with high circulation, this ratio becomes 100–1000:1.

- Acid Strength

$$(SV)_o = \frac{\text{Olefin volumetric rate (bbl/h)}}{\text{Acid volume in contactor (bbl)}}$$

- At lower strength, polymerization occurs and a ‘‘runaway’’ condition prevails.
- To provide a sufficient margin of safety, acid strength is kept around 90 wt%.

- Degree of Agitation
- Space Velocity
- Reaction Temperature → low temperature

SV increases, RON tends to decrease while acid consumption tends to increase.
Residence time H2SO4 is usually from 5 to 40 min, and for HF, it is 5–25 min

$$\frac{R_{iC_8}}{R_{\text{heavy alkylate}}} = \frac{(\text{Const})[iC_4]_h N^{0.75}(1 - H_a)}{(SV)_o}$$

Material Balance of Alkylation

Table 10.5 Volume and mass factors for alkylation conversions

	$C_3^=$		$C_4^=$		$C_5^=$	
lb iC_4 consumed/lb olefin consumed	1.7132		1.1256		1.2025	
bbl iC_4 consumed/bbl olefin consumed	1.6		1.2		1.4	
Total volume of feed/total volume product	1.234		1.2		1.158	
Product composition %	vol%	wt%	vol%	wt%	vol%	wt%
C_3	14.15	10.71	–	–	–	–
nC_4	–	–	6.93	5.83	–	–
nC_5	3.40	3.14	3.71	3.33	21.80	19.74
Alkylate	75.66	78.34	82.36	83.06	70.23	71.81
Heavy alkylate	5.98	6.70	6.48	7.07	6.95	7.98
Tar	0.811	1.11	0.52	0.71	1.02	1.36

Performance Factor of Alkylation Process

See sub chapter 10.5 + Example E10.2

Material Balance Calculations Using Yield Factors

See sub chapter 10.6 + Example E10.3

Example 1

Example E10.2

Find alkylate yield and MON for an alkylate unit having a $C_4^=$ feed of 2000 BPD and an (I/O) ratio = 10. The acid make-up rate is 54,000 lb/day and the acid dilution ratio = 1.5. Assume volume shrinkage = 22% and an olefin residence time of 40 min. Find the reactor volume (ft^3).

Solution

$x_4 = 1.5 =$ dilution ratio lb acid/lb alkylate

$$V_4 = V_1(1.12 + 0.13167(\mathrm{I/O})_\mathrm{F} - 0.0067(\mathrm{I/O})_\mathrm{F}^2)$$
$$= 2000(1.12 + 0.13167(10) - 0.0067(100)) = 3533 \text{ BPD}$$

Make-up $i\mathrm{C}_4$ is:

$$V_5 = 1.22\ V_4 - V_1$$
$$V_5 = 1.22(3533) - 2000 = 2310 \text{ BPD}$$
$$\mathrm{I/O} = (V_2 + V_5)/V_1 = (V_2 + 2310)/2000 = 10$$
$$V_2 = 17{,}690 \text{ BPD}$$

$$\text{Acid strength} = x_2 = \frac{0.98\,m}{V_4 x_4 + m} \times 100 = \frac{0.98(54,000)}{3533(1.5) + 54,000} \times 100 = 89.24$$

$$\mathrm{MON} = 86.35 + 1.098(\mathrm{I/O})_\mathrm{F} - 0.038(\mathrm{I/O})_\mathrm{F}^2 + 0.325(x_2 - 89)$$
$$= 86.35 + 1.098(10) - 0.038(100) + 0.325(89.24 - 89)$$
$$\mathrm{MON} = 93.6$$

The performance factor F is defined as:

$$F = -133 + 3(93.6) = 147.8$$

Residence time = 40 min. Therefore,

$$(\mathrm{SV})_\mathrm{o} = \frac{60}{40} = 1.5 \text{ h}^{-1}$$

The reactor volume (V_R) can be calculated from the space velocity as:

$$(\mathrm{SV})_\mathrm{o} = 1.5 \text{ h}^{-1} = \frac{2000 \text{ bbl/day}}{V_\mathrm{R}} = \frac{2000 \text{ bbl/day} \times 1 \text{ day}/24 \text{ h}}{V_\mathrm{R}} = \frac{2000}{24\ V_\mathrm{R}}$$

$$V_\mathrm{R} = \frac{2000 \text{ bbl}}{1.5(24)} \times \frac{5.6 \text{ ft}^3}{1 \text{ bbl}} = 311 \text{ ft}^3 (\text{note } 1 \text{ bbl} = 5.6 \text{ ft}^3)$$

Example 2

Example E10.3

A feed stream composed of 3600 BPD isobutane and 4000 BPD butene is introduced into a sulphuric acid alkylation unit. Assuming that all isobutane is consumed in the reaction, calculate the effluent rates. The liquid densities (lb/h/BPD) of components involved in this example are given in Table E10.3.

Solution

Solution:

Using the empirical factor for $C_4^=$ listed in Table 10.5 on volume basis,

Amount of $C_4^=$ consumed = 3600/1.2 = 3000 BPD (all iC_4 consumed)

Remaining $C_4^=$ = 4000–3000 = 1000 BPD

Volume of products = volume of feed/1.2 = (3600 + 3000)/1.2 = 5500BPD (volume basis)

If we use mass factors

iC_4 consumed = 3600 (BPD) × 8.22 (lb/h BPD) = 29,592 lb/h

$C_4^=$ consumed = 29592/1.1256 = 26,290 lb/h

$C_4^=$ remaining = 4000 (BPD) × 8.78 (lb/h BPD) – 26,290 = 8750 lb/h

Table E10.3 Summary of component material balance

Feed	BPD	Lb/h	Density Lb/h/BPD
iC_4	3600	29,592	8.22
$C_4^=$	4000	35,040	8.76
Total	7600	64,632	
Products			
nC_4	381.2	3258.0	8.51
nC_5	204.0	1860.8	9.12
Alkylate	4529.8	46,415.6	10.25
Heavy alkylate	356.4	3950.9	11.09
Tar	28.6	396.7	13.87
Remaining $C_4^=$	1000	8750	
Total	6500	64,632	

Total feed consumed = 29,592 + 26,290 = 55,882 lb/h (mass basis)

Total feed consumed = total weight of product

Using composition data of the products in Table 10.5 the effluent flow rates are calculated as shown in Table E10.3.

The way to get started is to quit complaining and begin doing.

Walt Disney

See you on the next lecture