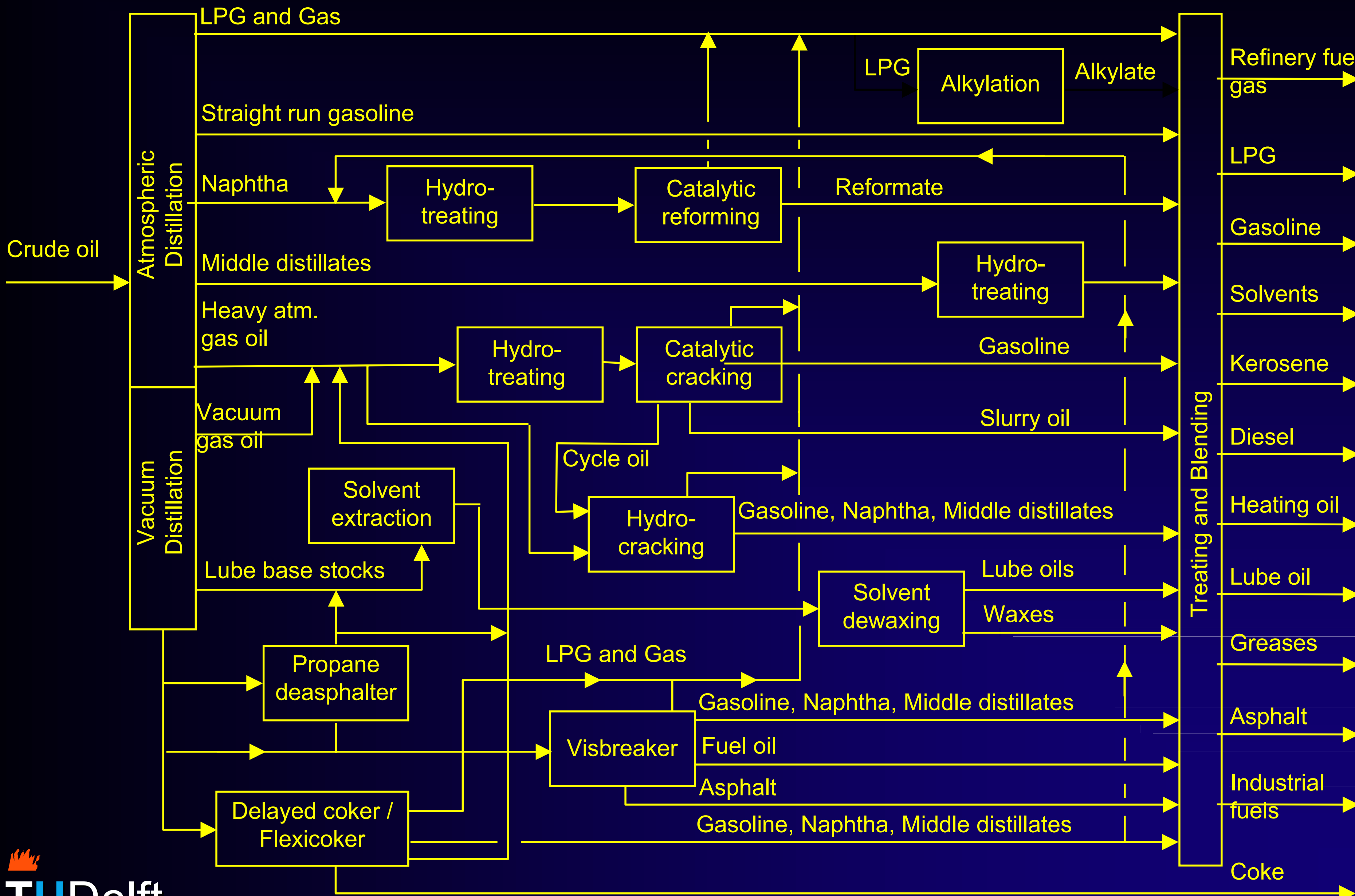
Modern oil refinery



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Distillation Fractions

Distillate fraction	Boiling point (°C)	C-atoms/ molecule
Gases	<30	1-4
Gasoline	30-210	5-12
Naphta	100-200	8-12
Kerosine (jet fuel)	150-250	11-13
Diesel, Fuel oil	160-400	13-17
Atmospheric Gasoil	220-345	
Heavy Fuel Oil	315-540	20-45
Atmospheric Residue	>540	>30
Vacuum Residue	>615	>60

Middle Destillates

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Processes in an Oil Refinery

Physical processes	Chemical processes	
	Thermal	Catalytic
Distillation	Visbreaking	Hydrotreating
Solvent extraction	Delayed coking	Catalytic reforming
Propane deasphalting	Flexicoking	Catalytic cracking
Solvent dewaxing		Hydrocracking
Blending		Catalytic dewaxing
		Alkylation
		Polymerization
		Isomerization

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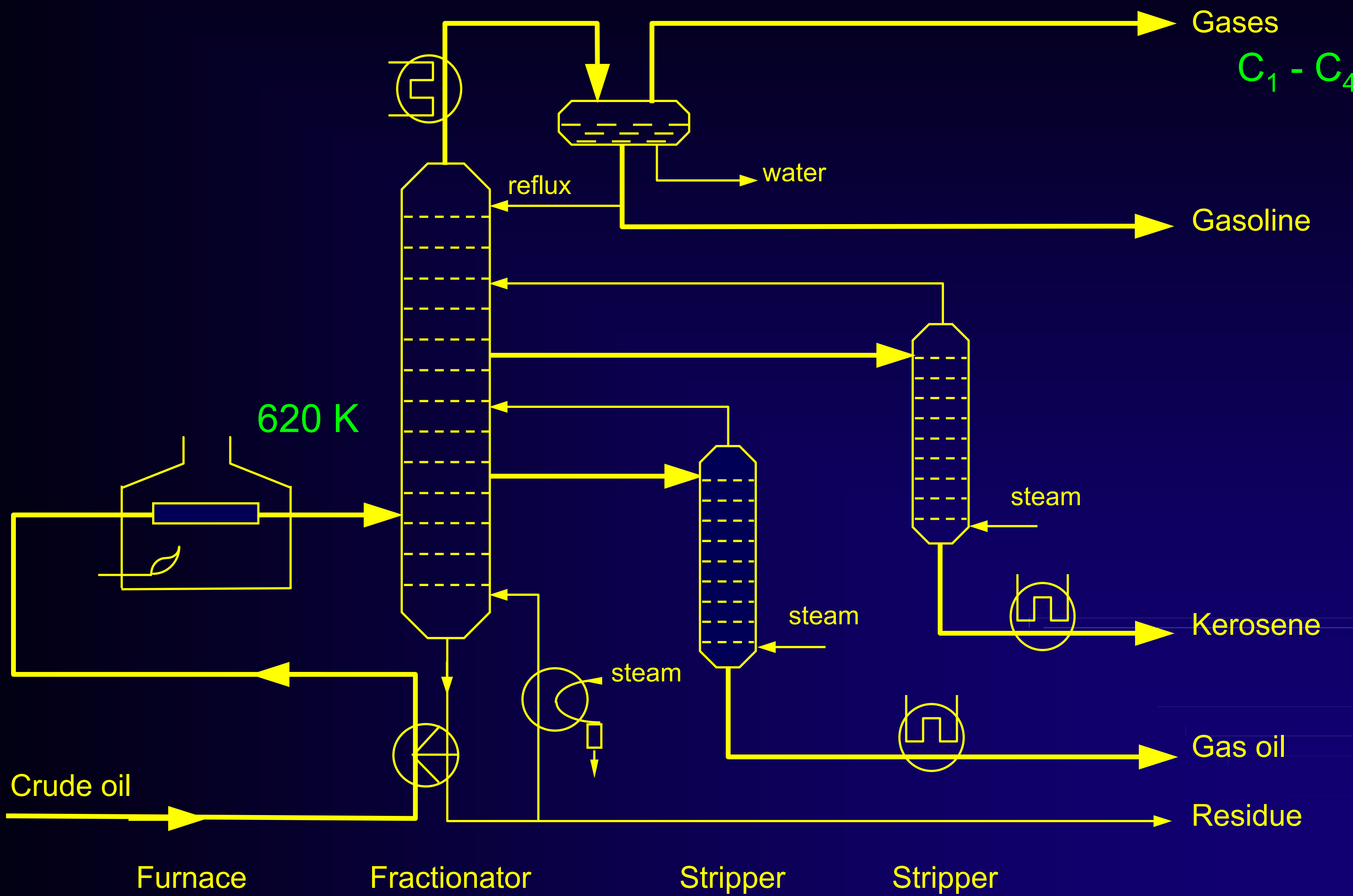
Simple Crude Distillation



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Market Demands

- Clean products (no S, N, O, metals, etc.)
- More gasoline (high octane number)
- More diesel (high cetane number)
- Specific products (Aromatics, alkenes, etc.)
- Less residue

How to meet these demands?

- More sophisticated distillation
- Physical separation steps
- Chemical conversion steps

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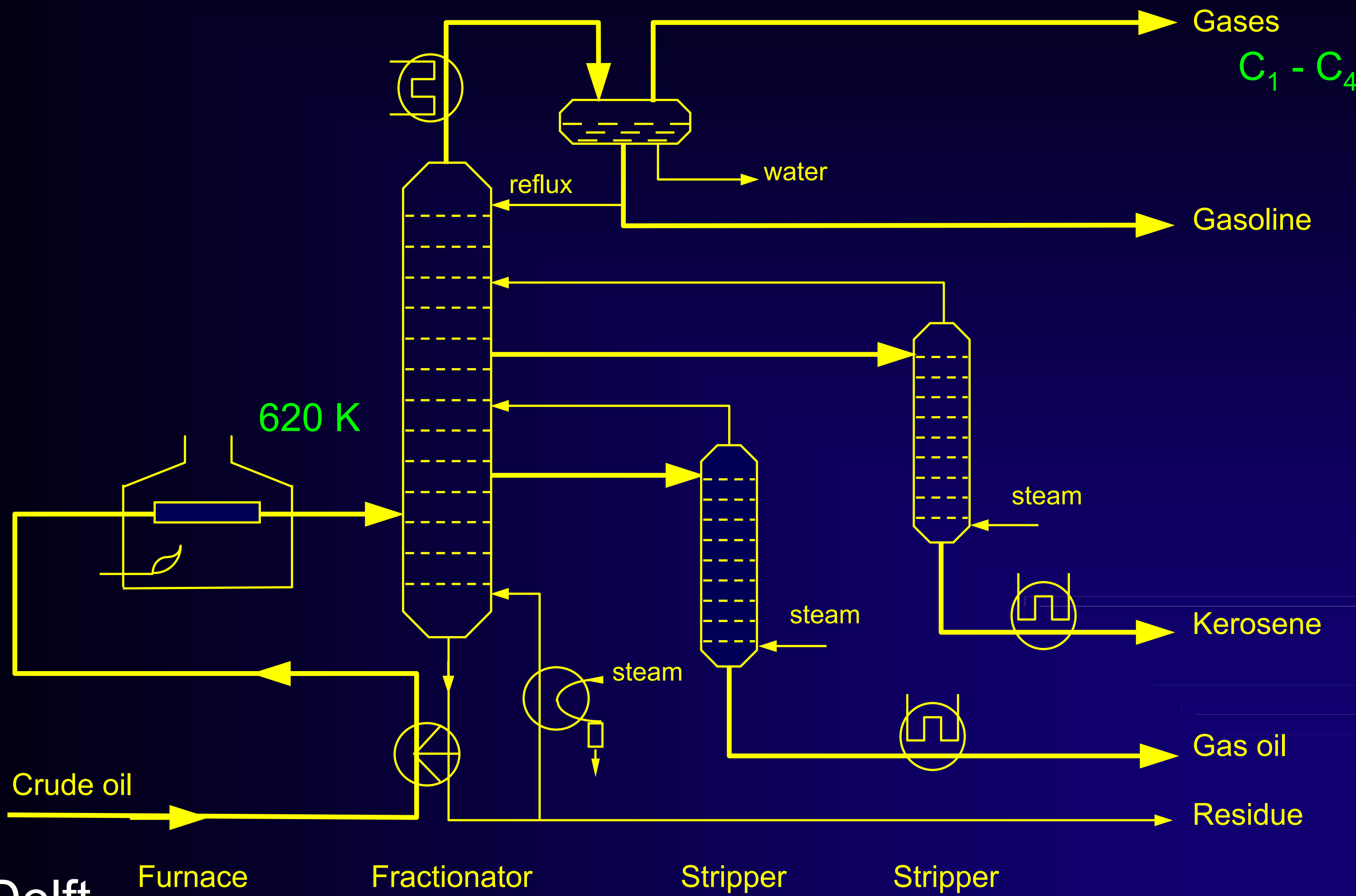
More sophisticated ???

Higher $T_{distillation}$??



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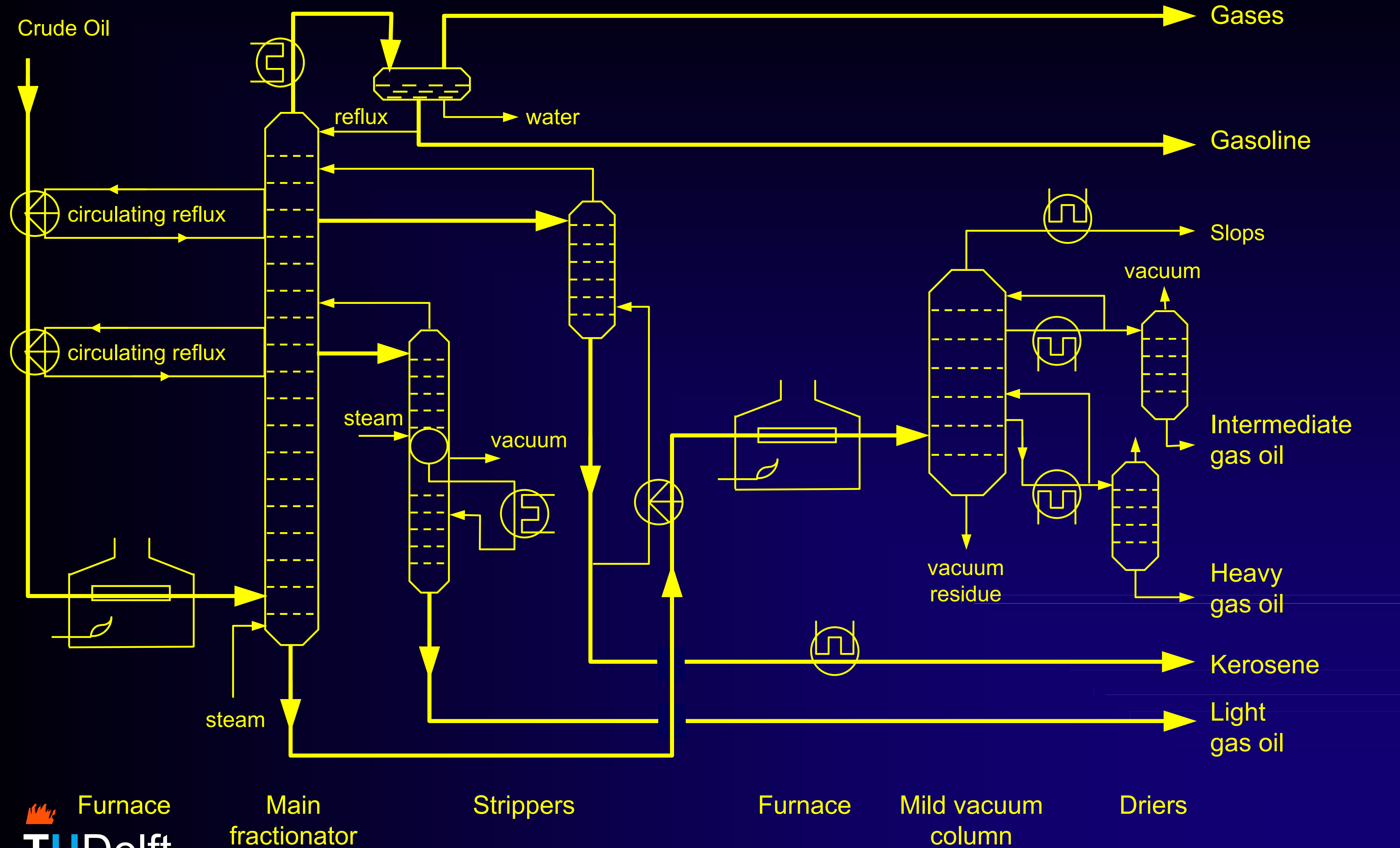
Modern Crude Distillation Unit



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Propane Deasphalting Extraction

Reason

Coke-forming tendencies of asphaltenic materials

How?

Reduction by extraction with suitable solvent

- propane
- butane, pentane

Why propane?

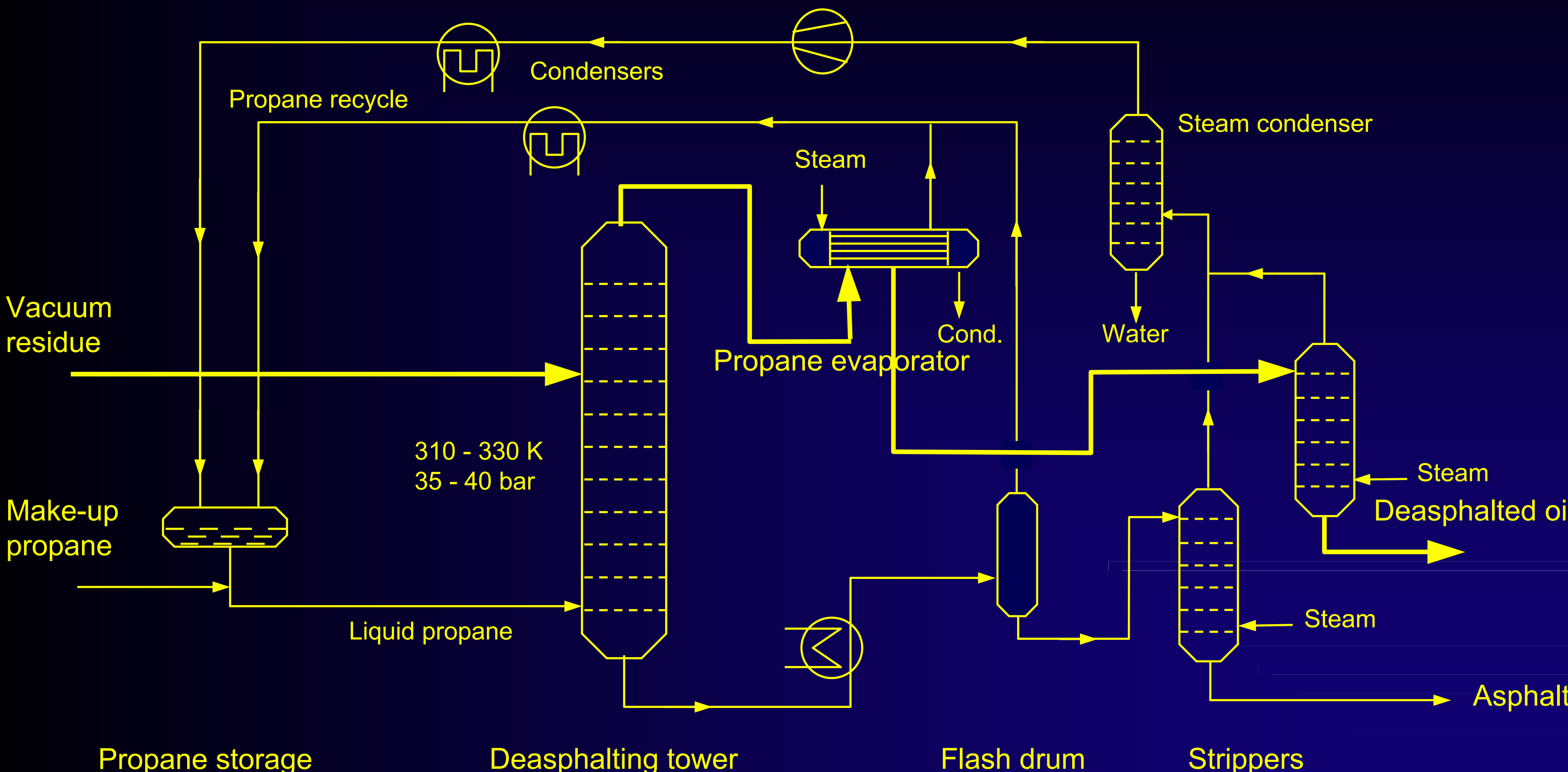
- Easy separation
- Available
- ...

Conditions?

- Modest temperature
- High pressure

Flow scheme?

Propane Deasphalting



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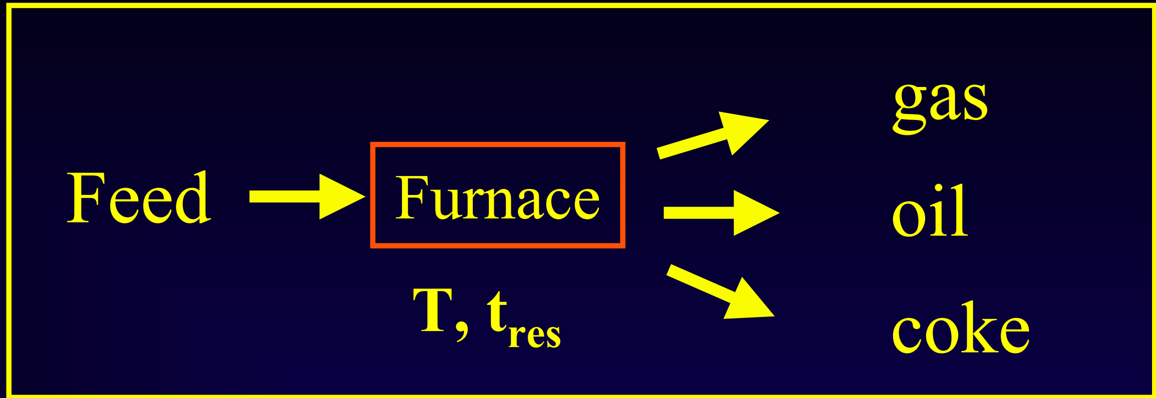
Thermal Processes



Visbreaking
- mild conditions

Delayed Coking
- long residence time (24 h)

Flexicoking
- combination thermal cracking and coke gasification/combustion

Steam Cracking
- production lower olefins

Thermal Processes

- **VISBREAKING**
  - **Mild thermal cracking**
  - **Reduction of viscosity**
- **DELAYED COKING**
  - **Long residence times (24 h)**
  - **Heavy feed → coke + oil + gas**
- **FLEXICOKING**
  - **Combination of thermal cracking and**
  - **coke gasification / combustion**

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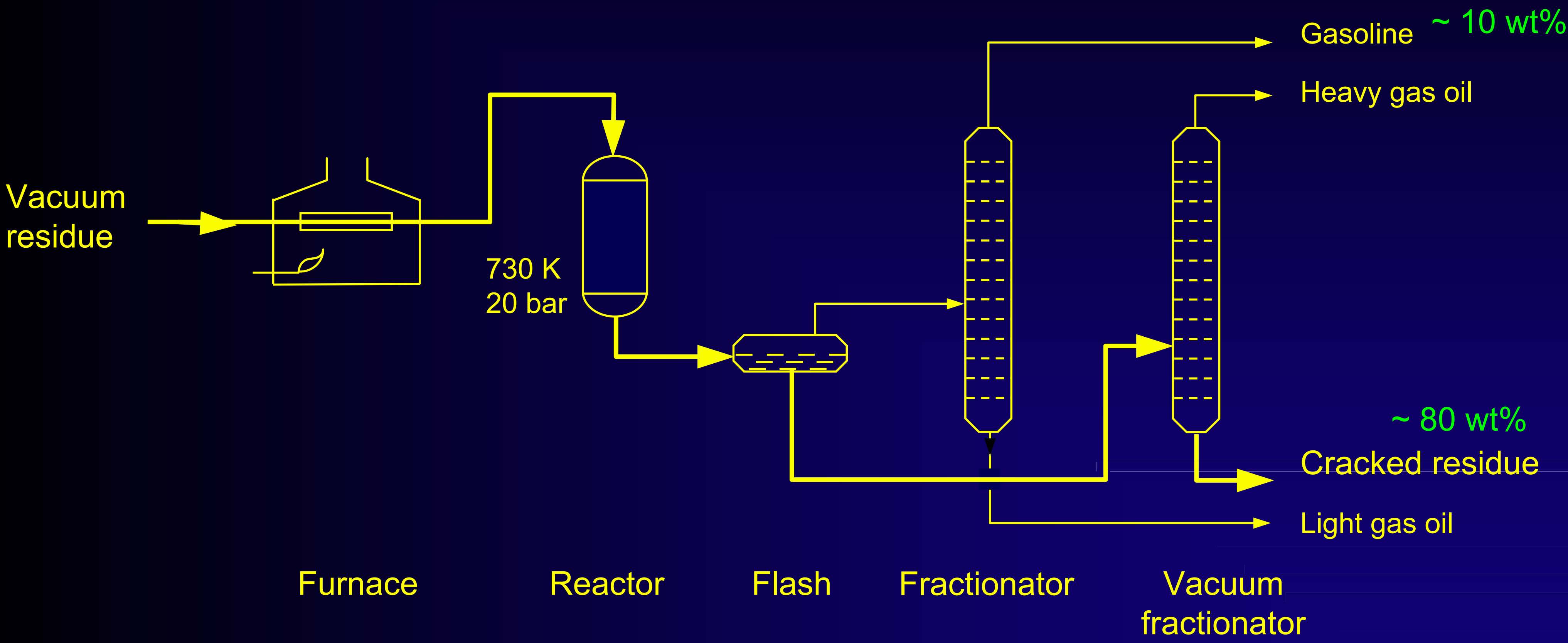
Visbreaking



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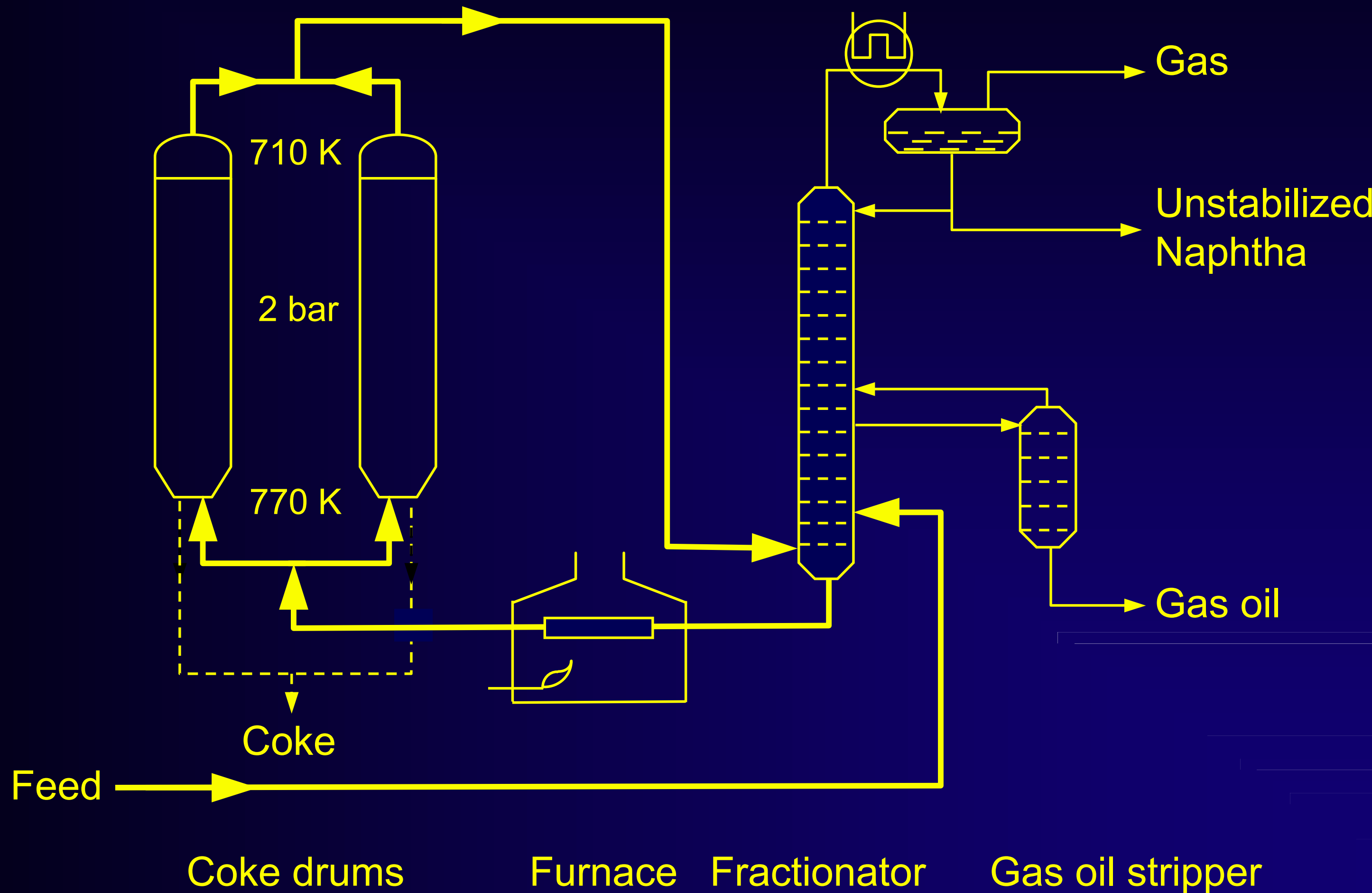
Delayed Coking



Octane Numbers, Boiling Points

• n-pentane	62	309 K
• 2-methyl butane	90	301
• cyclopentane	85	322
• n-hexane	26	342
• 2,2-dimethylbutane	93	323
• benzene	>100	353
• cyclohexane	77	354
• n-octane	0	399
• 2,2,3-trimethylpentane	100	372
• methyl-tertiary-butyl-ether	118	328

• straight run gasoline	68	67 (MON)
• FCC light gasoline	93	82
• alkylate	95	92
• reformate (CCR)	99	88

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Cetane Numbers

• n-alkanes	100-110
• n-hexadecane (cetane)	100
• iso-alkanes	30-70
• alkenes	40-60
• cycloalkanes	40-70
• alkylbenzenes	20-60
• naphtalenes	0-20
• α-methyl naphtalene	0
• straight run gas oil	40-50
• FCC cycle oil	0-25
• thermal gas oil	30-50
• hydrocracking gas oil	55-60

Hydrotreating and Hydrocracking

HYDROTREATING

- Conversion with hydrogen
- Reactions: hydrogenation & hydrogenolysis
- Removal of hetero-atoms (S, N, O)
- Some hydrogenation of double bonds & aromatic rings
- Molecular size not drastically altered
- Also termed hydropurification

HYDROCRACKING

- Similar to hydrotreating
- But, drastic reduction in molecular size

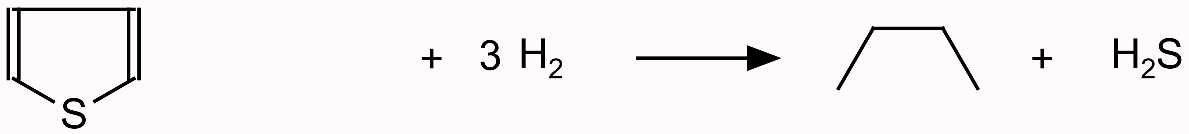
Why Hydrotreating ?

- Protection of the environment
  - reduction acid rain
- Protection of downstream catalysts
  - in further processing
  - S-compounds in Diesel fuel give difficulties in catalytic cleaning of exhaust gases
- Improvement of gasoline properties
  - odour, colour, stability, corrosion

Hydrotreating Reactions

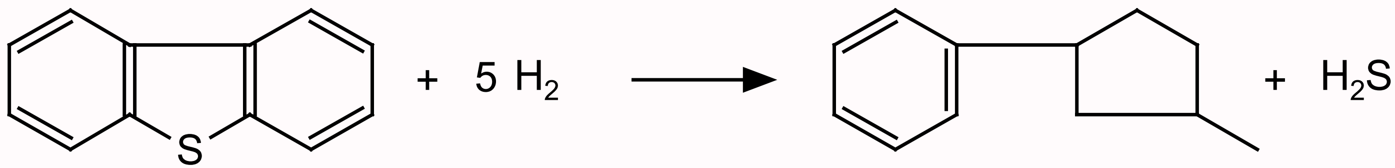
1) Mercaptans $RSH + H_2 \longrightarrow RH + H_2S$ **HDS**

2) Thiophenes



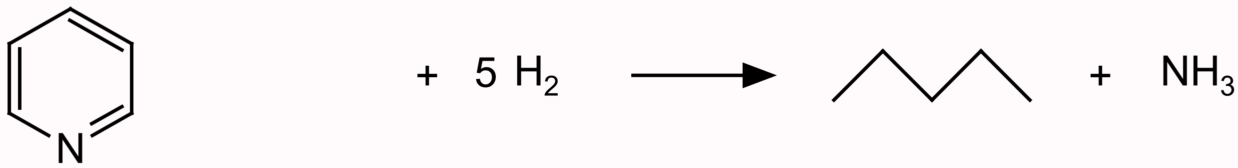
HDS

3) Benzothiophenes



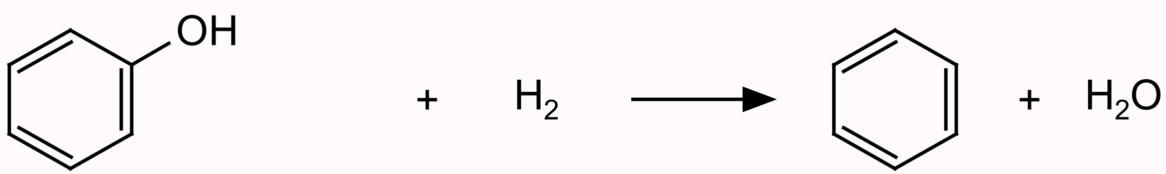
HDS

4) Pyridines



HDN

5) Phenols



HDO

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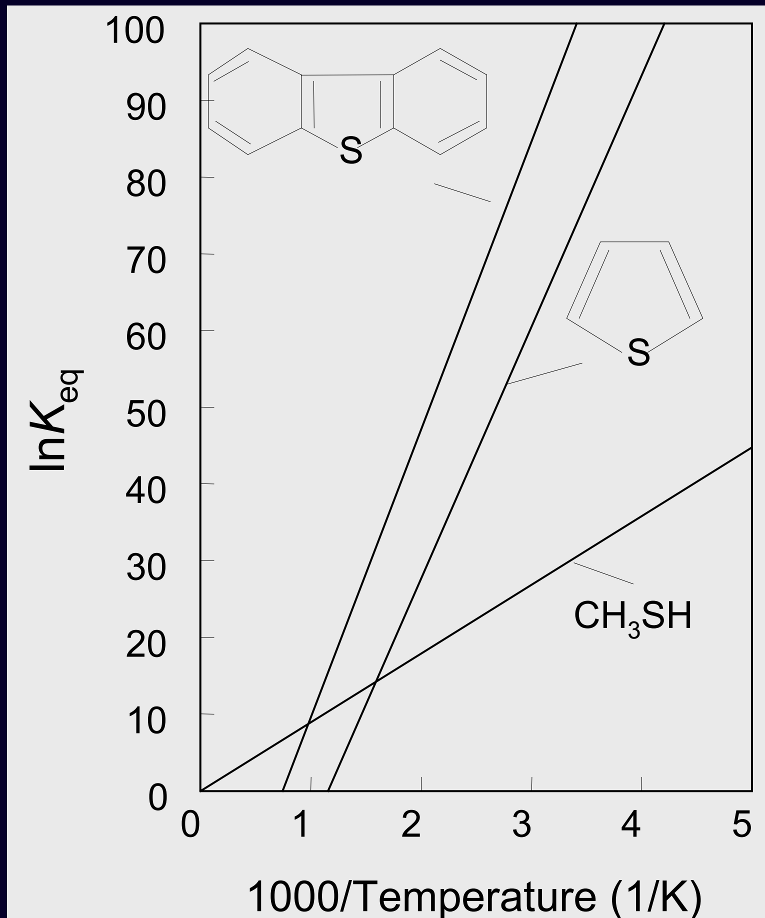
Equilibrium data



Optimal conditions??

Industrial conditions

600-650 K

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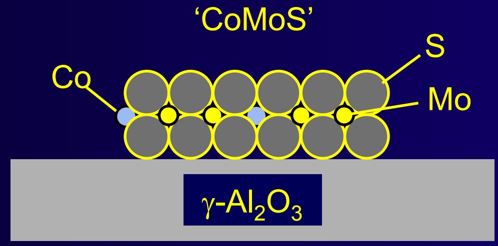
Typical process conditions

	Naphtha	Gas Oil
■ Temperature (K):	590 - 650	600 - 670
■ Pressure (bar):	15 - 40	40 - 100
■ H_2/oil (Nm^3/kg):	0.1 - 0.3	0.15 - 0.3
■ WHSV (kg feed/(m^3 catalyst)/h)	2000 - 5000	500 - 3000

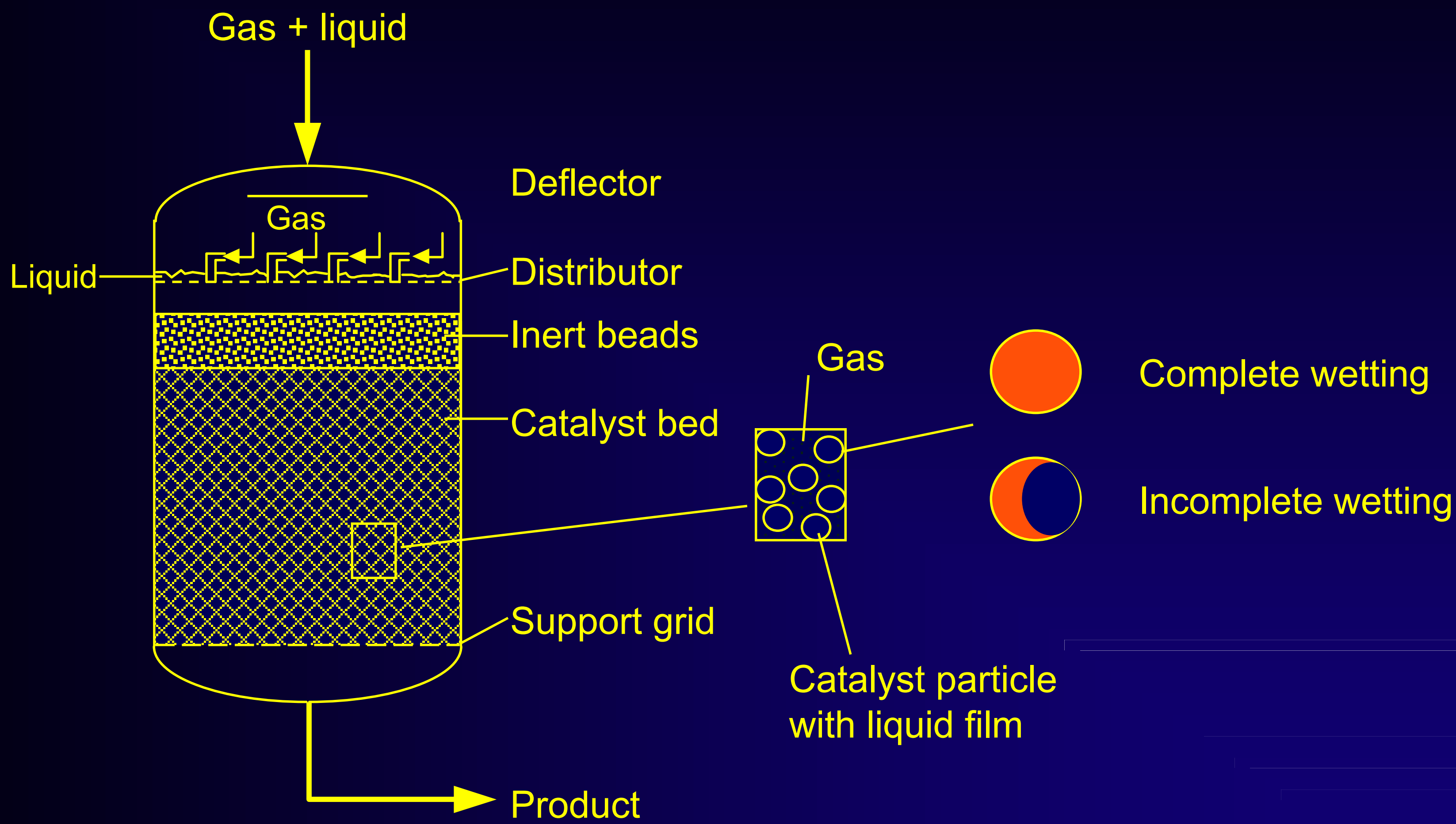
- Catalyst: mixed metal sulfides (CoS and MoS_2 or NiS and WS_2 on Al_2O_3)



Process design ???

Residence time in reactor?
Phases in reactor (Gas, Liquid,..?)

Trickle-bed Reactor



What could go wrong in operation?

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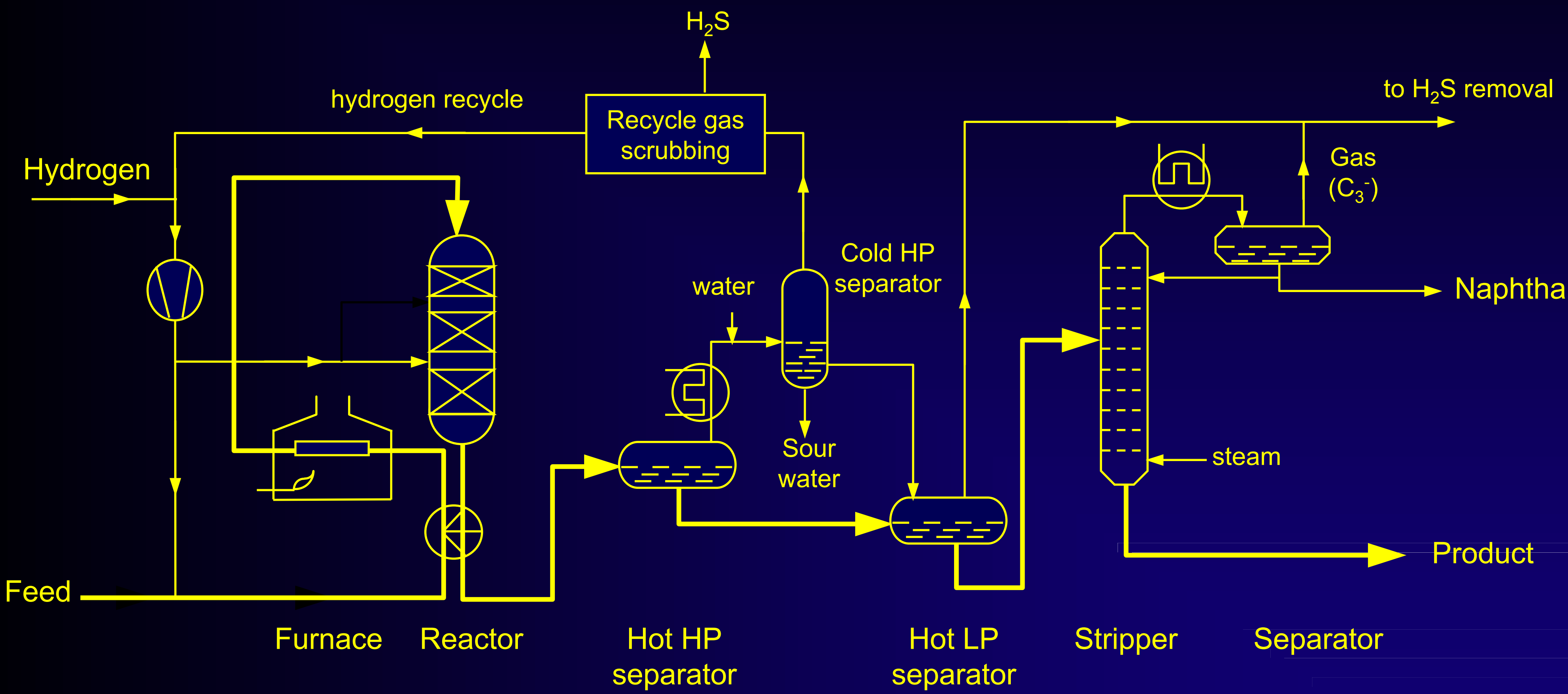
Hydrotreating Process (trickle bed)



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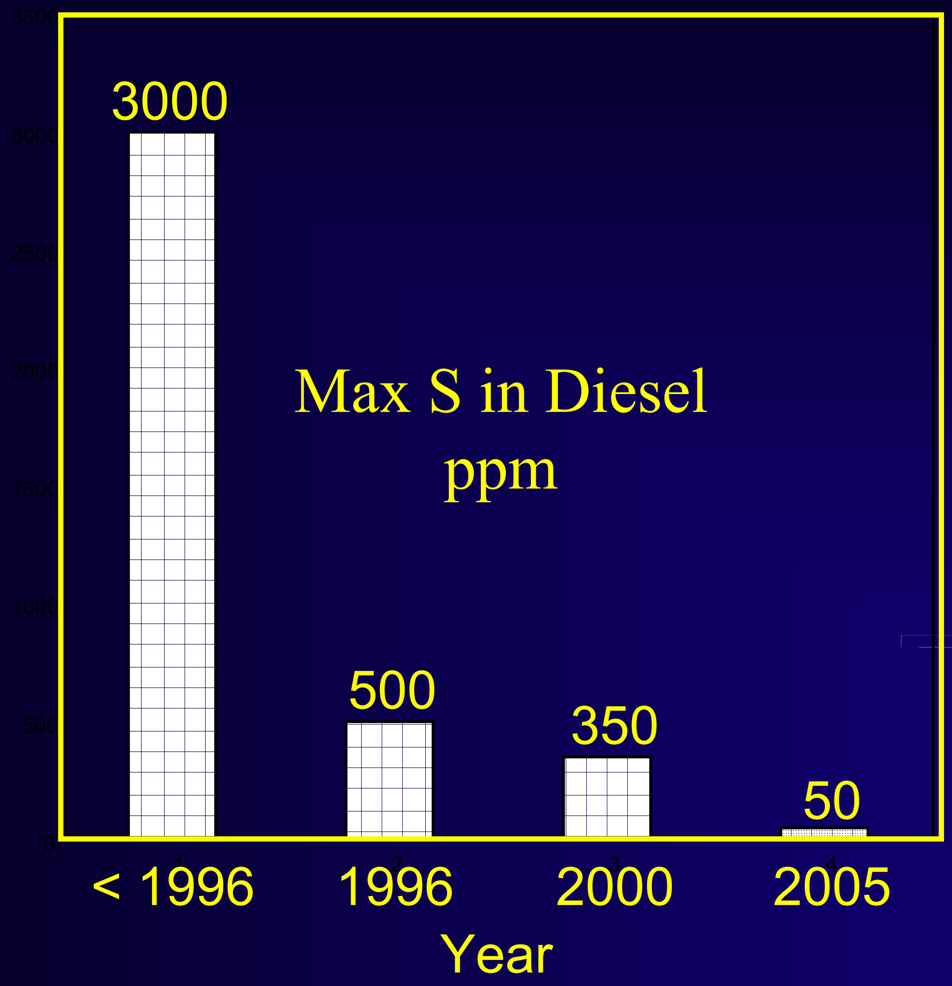
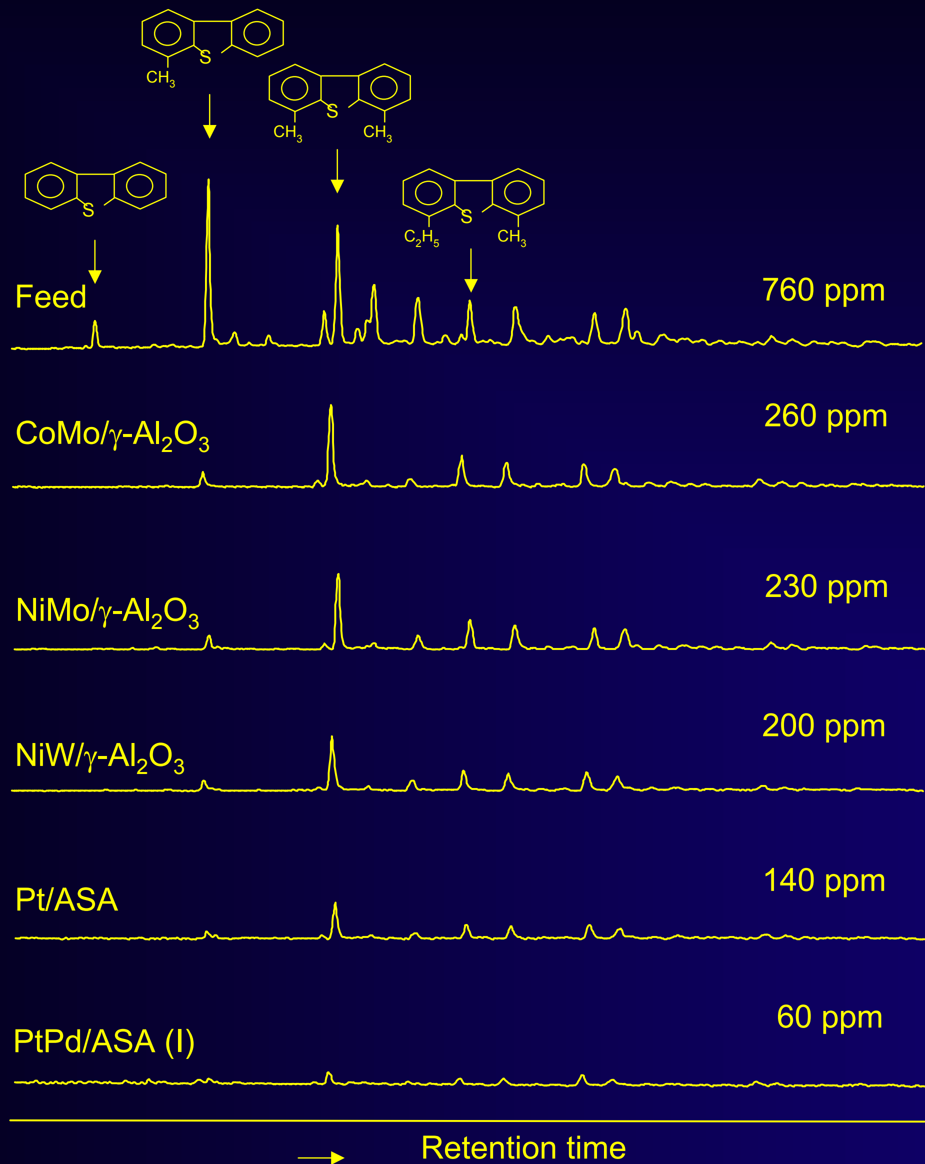
Development of maximum Sulfur Content in automotive Diesel in Europe



Activity of Various Catalysts for HDS of Pretreated Gas Oil



What catalyst do you select for

Naphta
Heavy gasoil ***???***

Deep desulphiding ***???***

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Catalytic Reforming

- Important for gasoline production
  - Increases octane number
- Important for base chemicals production
  - aromatics
  - H_2

Octane Numbers, Boiling Points

n-pentane	62	309 K
2-methyl butane	90	301
cyclopentane	85	322
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straight run gasoline	68	67 (MON)
FCC light gasoline	93	82
alkylate	95	92
reformate (CCR)	99	88

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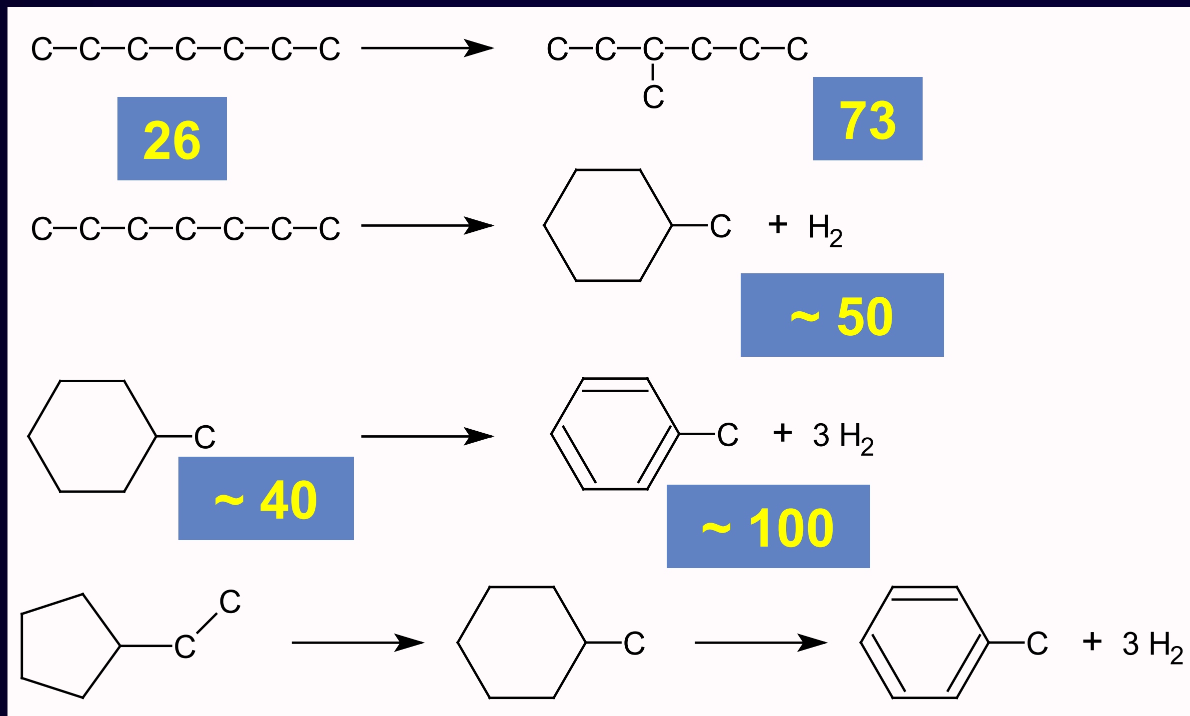
What reactions would you carry out??

Reactions for Increase of Octane Number

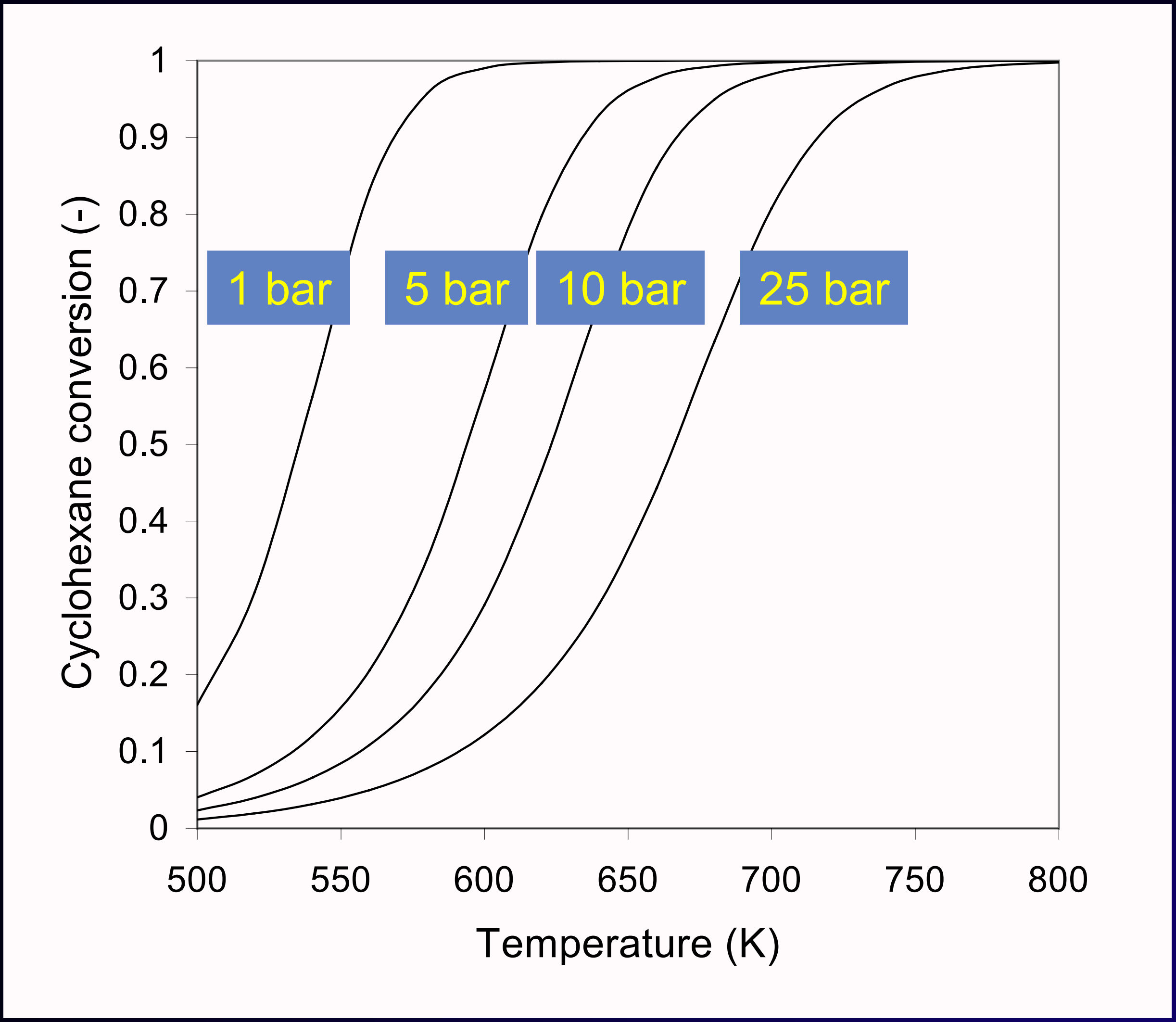
ΔH^0_{208} (kJ/mol)

Isomerization		- 4
Cyclization		+ 33
Aromatization		+ 205
Combination		+ 177



Octane number

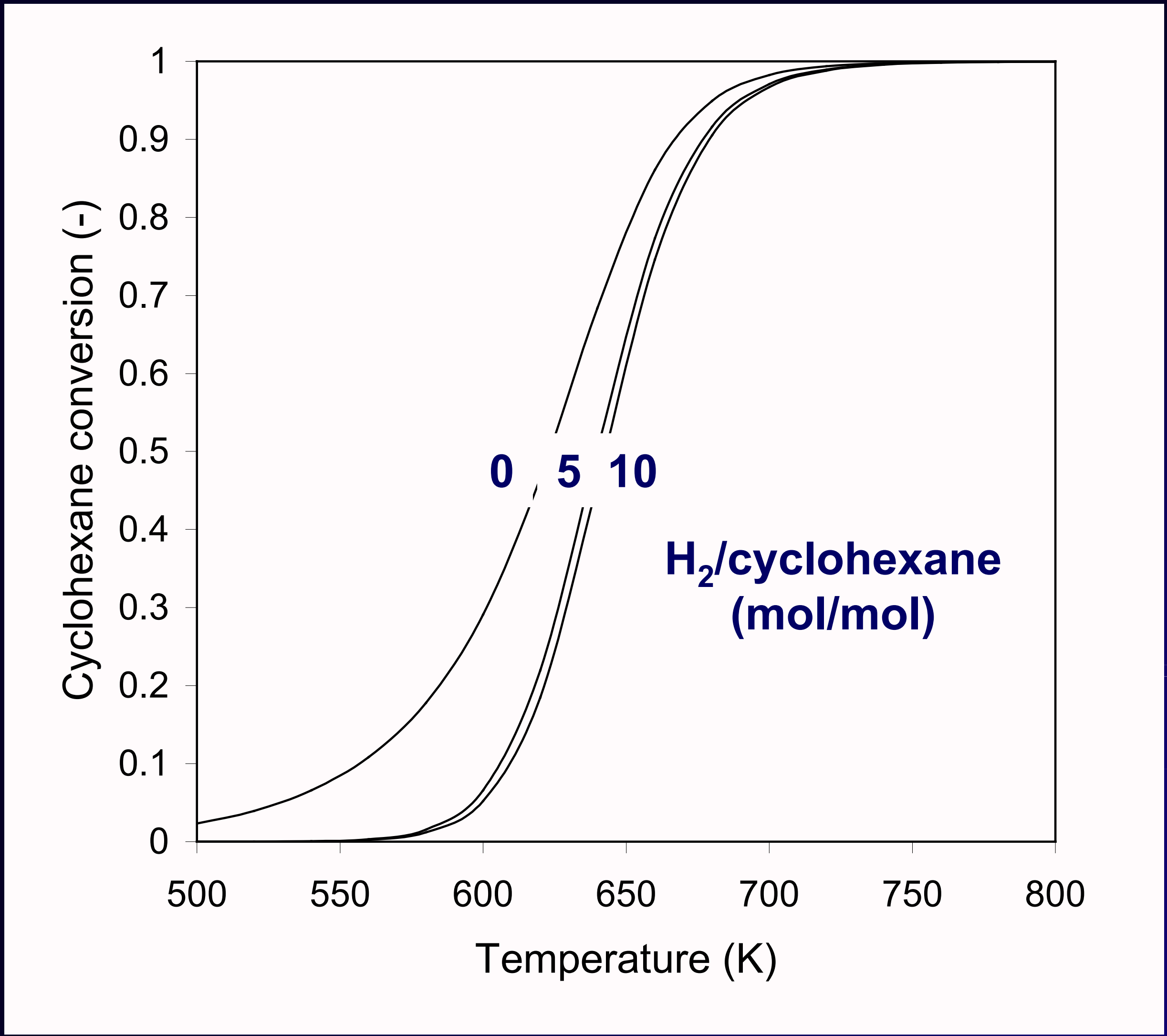
Aromatization of Cyclohexane
Effect of T and p



Favourable

- low pressure
- high temperature

Aromatization of Cyclohexane
Effect of *T* and H_2/CH feed ratio



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Conceptual process design?

Thermodynamics

- high T
- low p
- $\Delta H >> 0$

Catalyst stability highest for

- low T
- excess H_2
- low S impurity

Catalyst regeneration possible

- removal coke by combustion
- restoring acidity by Cl_2 treatment

Time scale stability dependent on conditions

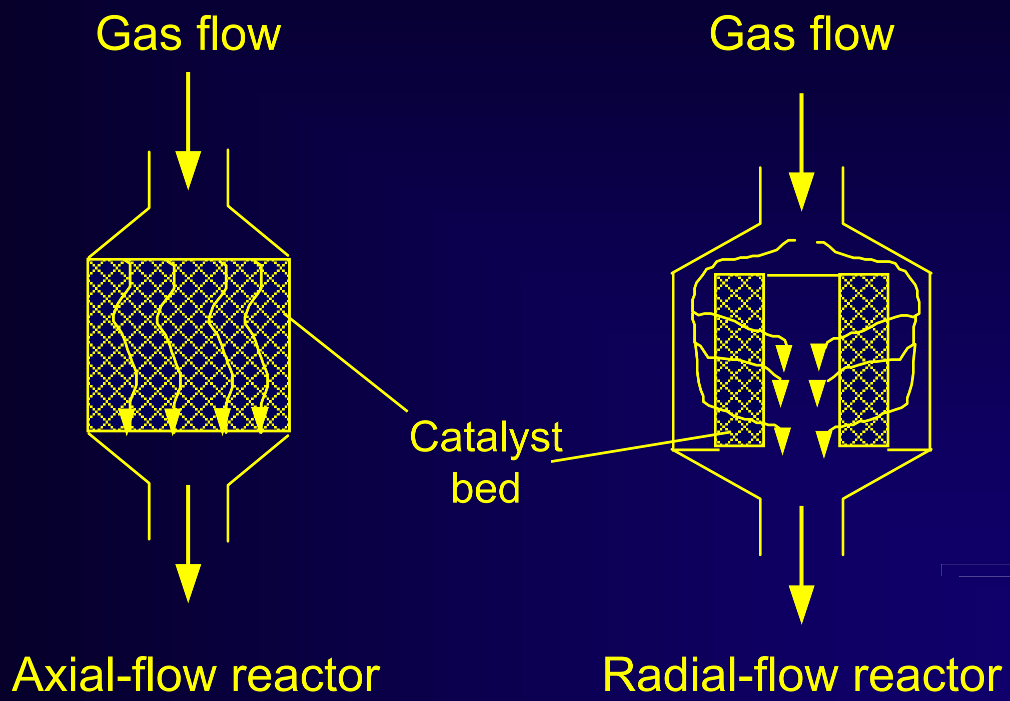
- months
- days

How to handle deactivation??

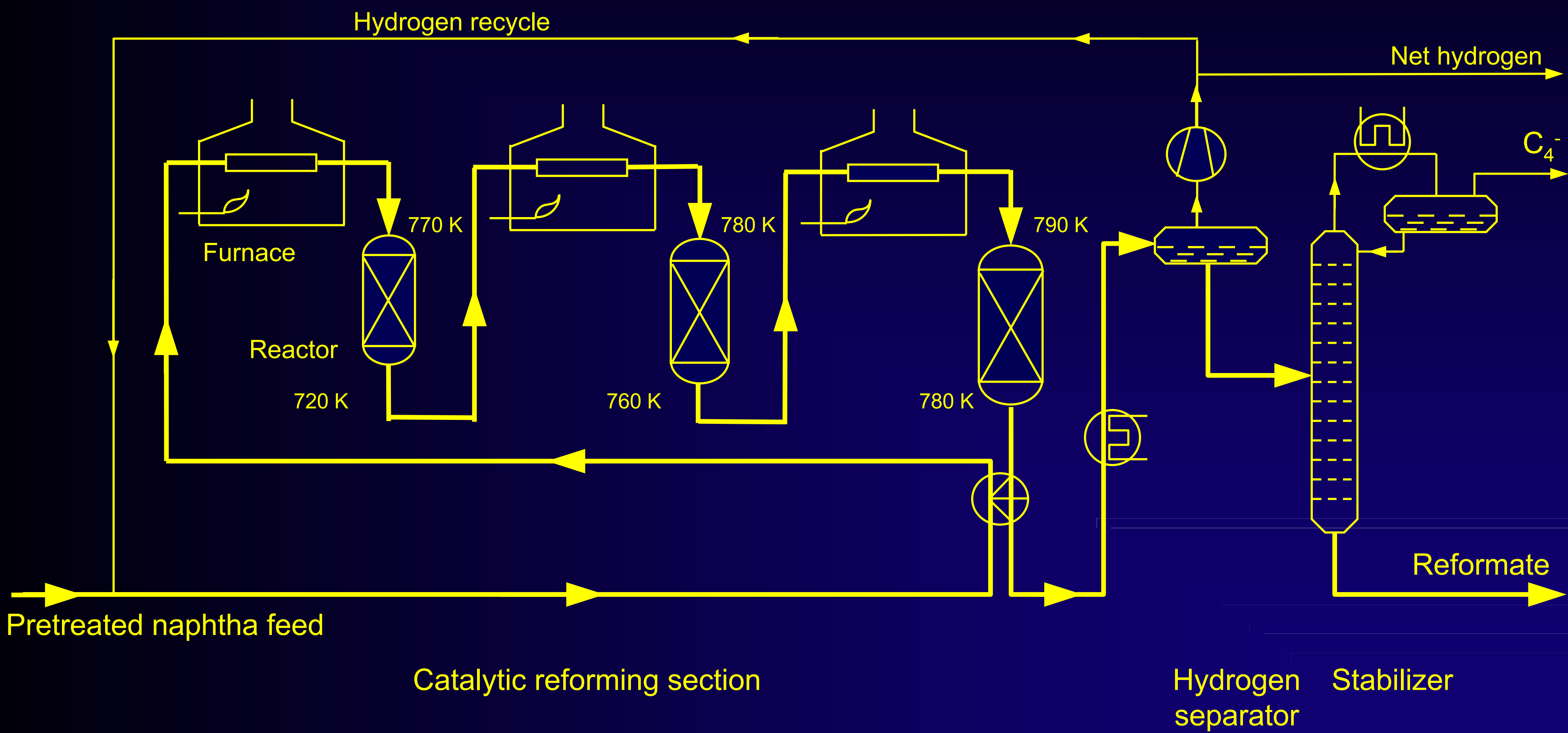
Reactor ???

Fixed Bed and Moving Bed are used

Reactors for Catalytic Reforming



Semi-Regenerative Catalytic Reforming (SRR)



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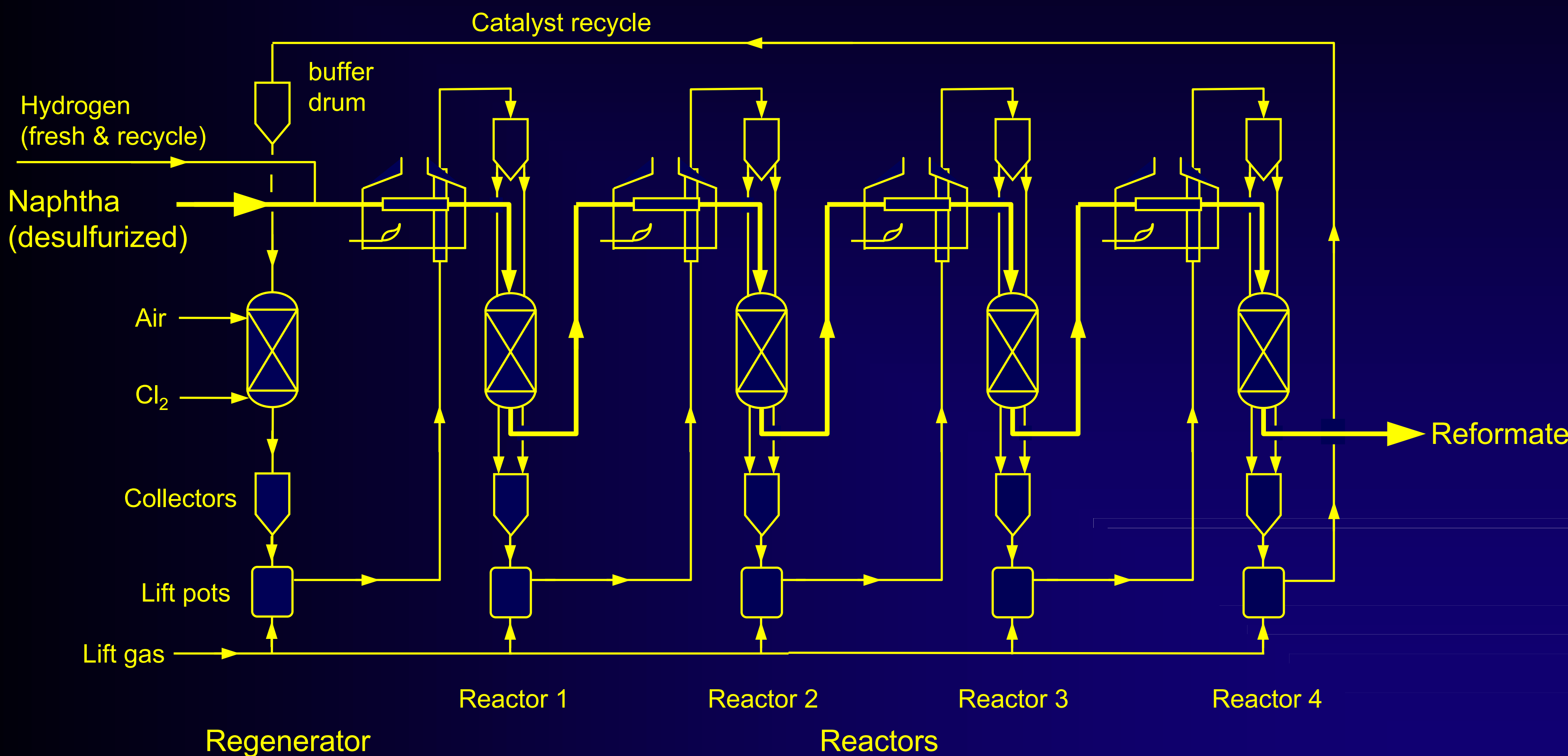
Continuously-Regenerative Catalytic Reforming (CRR)



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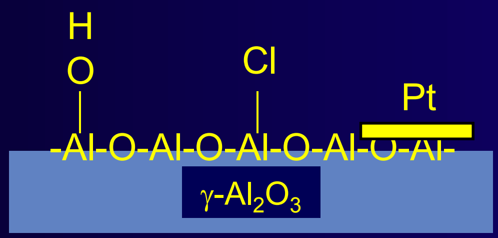
Operating conditions in catalytic reforming

	semi	fully	continuous
H_2/HC (mol/mol)	10	4-8	4-8
Pressure (bar)	15-35	7-15	3-4
Temperature (K)	740-780	740-780	770-800
Catalyst life	0.5-1.5 y	days-weeks	days-weeks



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Catalytic Reforming Typical Feedstock and Product Composition (vol%)

Component	Feed	Product
Alkanes	45 – 55	30 – 50
Alkenes	0 – 2	0
Naphthenes	30 – 40	5 – 10
Aromatics	5 – 10	45 – 60