Petroleum Refining Engineering-II
(CHE425PG 2 credit hours)
2016

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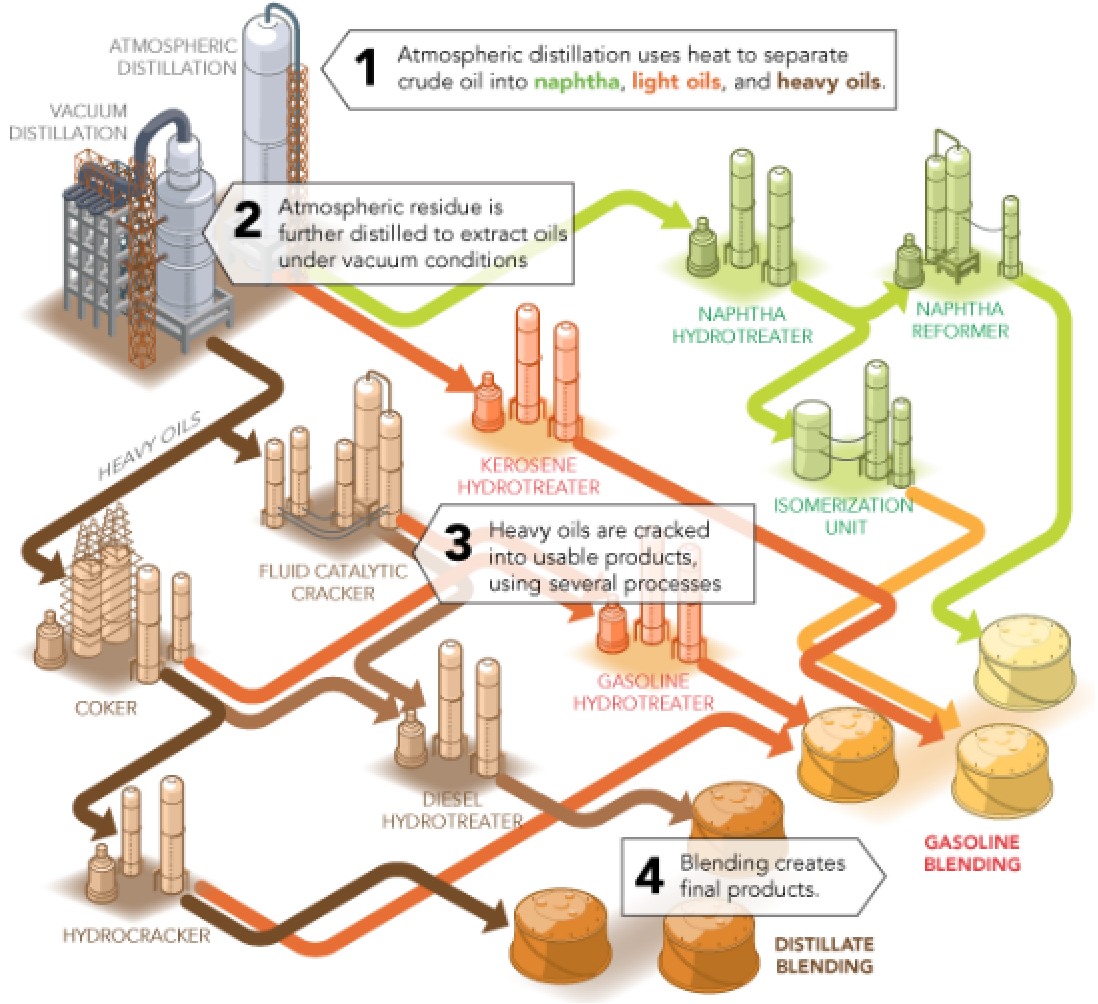
Crude oil refining



1 Atmospheric distillation uses heat to separate crude oil into **naphtha**, **light oils**, and **heavy oils**.

2 Atmospheric residue is further distilled to extract oils under vacuum conditions

3 Heavy oils are cracked into usable products, using several processes

4 Blending creates final products.

Iamge taken from: http://heatexchanger-design.com/2011/10/06/heat-exchangers-6/ Dated: 17-Jan-2012

Course outline

1. Simplified overall crude oil refinery picture
2. Major refinery products and tests: Brief description
3. Separation process: Atmospheric and vacuum distillations, lube oil extraction, dewaxing, deasphalting, and clay treatment.
4. Catalysts used in refinery operations
5. Conversion processes: Brief description of alkylation, polymerization, isomerization of light paraffins, hydrotreating, catalytic reforming, catalytic cracking, hydrocracking, visbreaking of resids, and coking.
5. Material and energy balances for refinery processes: Simulation of refinery processes
6. Design guidelines for the selected refinery equipment

Evaluation

Mid term exam: 35 Marks
Final term exam: 40 Marks
Assignment: 25 Marks

The assignment may include attendance marks, theoretical or experimental problems, quizzes, etc.

Communication with the instructor will be through email only. **Please see your emails regularly.**

Instructor email: mrusman.icet@pu.edu.pk

Text books

- **Gary**, J.H.; Handwerk, G.E. **2001**. Petroleum refining: Technology and economics. 4th ed. Marcel Dekker, Inc.
- **Fahim**, M.A.; Al-Sahhaf, T.A.; Elkilani, A. **2010**. Fundamentals of petroleum refining. Elsevier.

Suggested books

[1] Gary, J.H.; Handwerk, G.E. 2001. Petroleum refining: Technology and economics. 4th ed. Marcel Dekker, Inc.

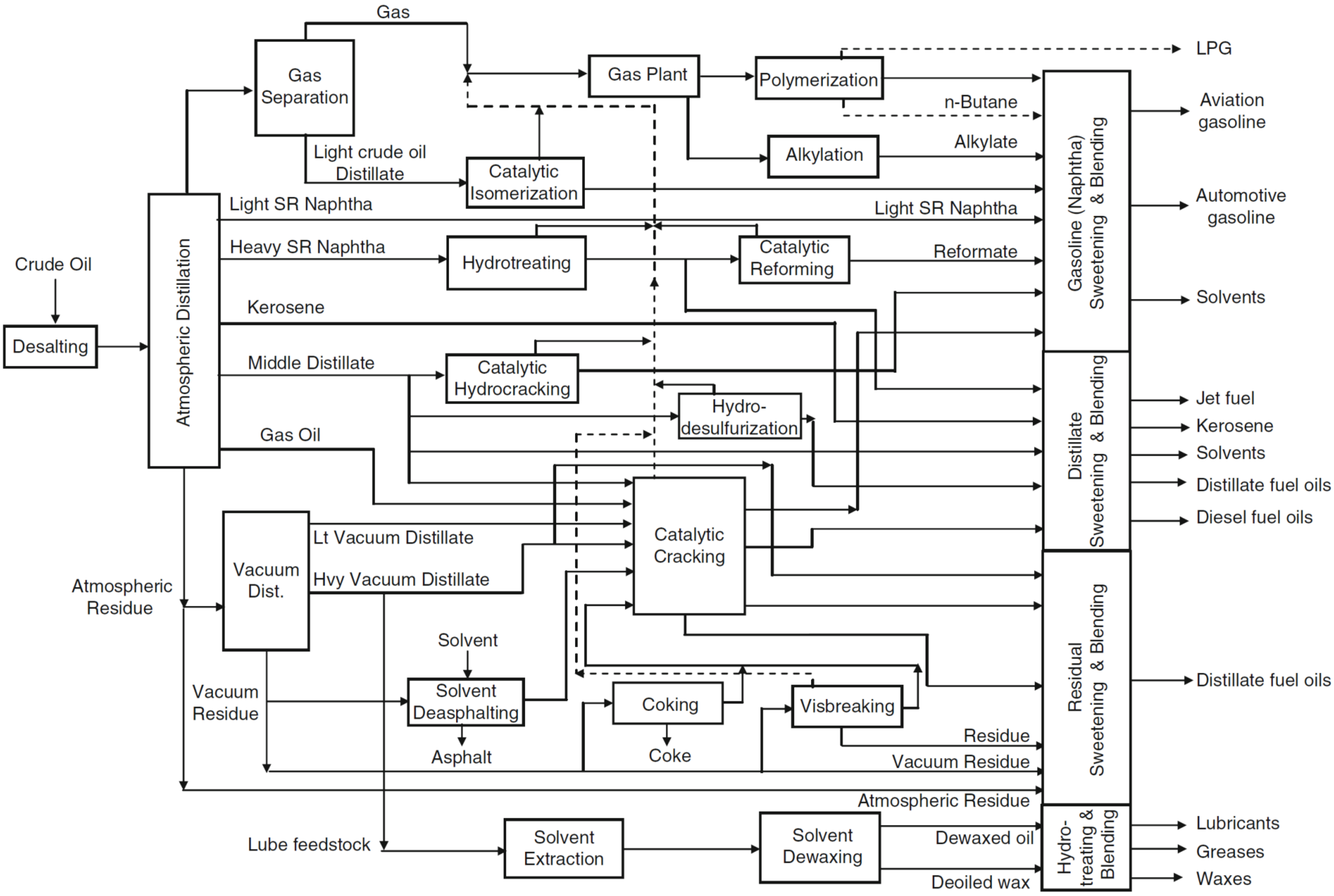
[2] Fahim, M.A., AlSahhaf, T.A. and Elkilani, A. 2010. Fundamentals of petroleum refining. Elsevier.

[3] Parkash, S. 2003. Refining processes handbook. Gulf professional publishing, Elsevier. Singapore.

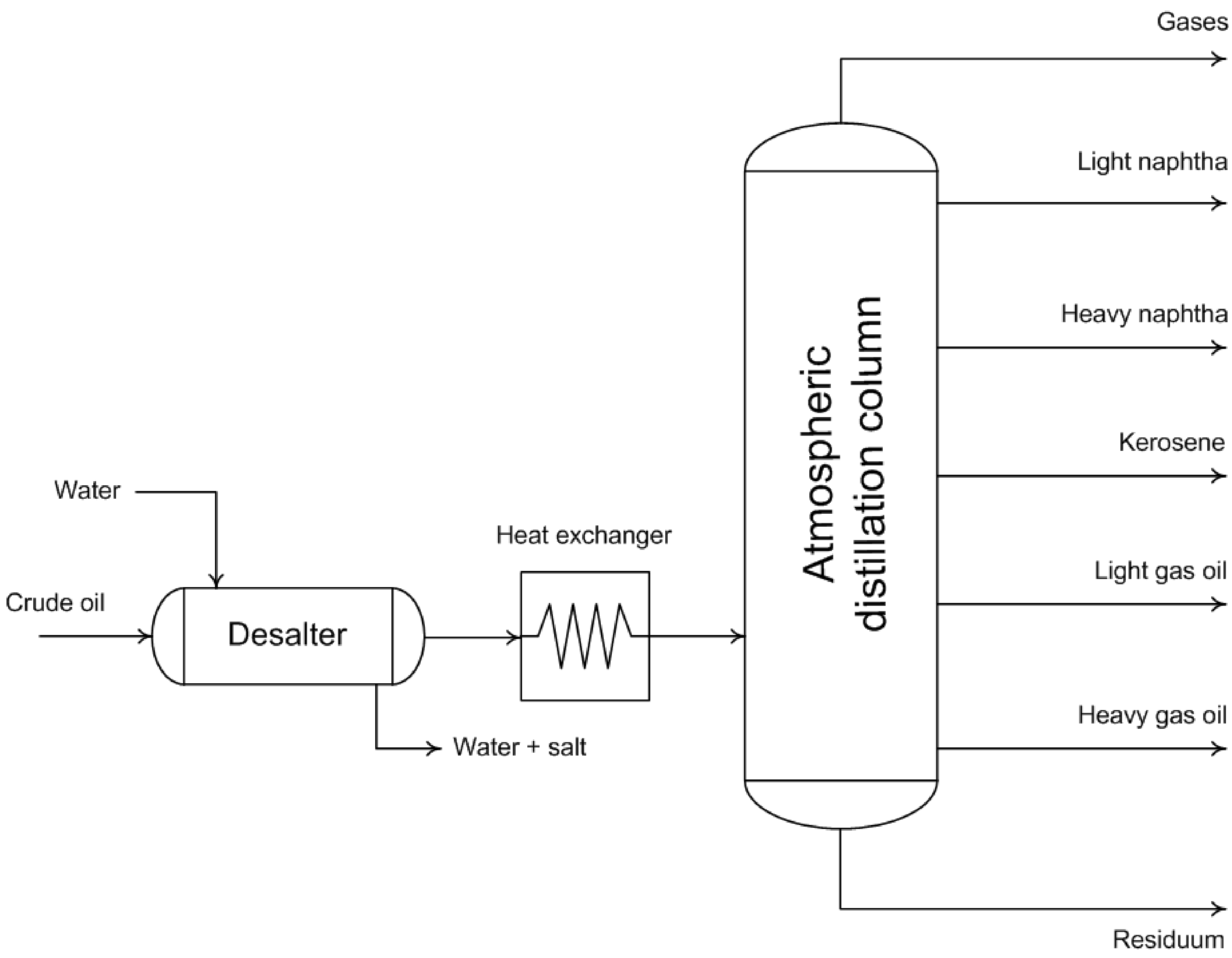
[4] Wauquier, J.-P. (ed.). 1998. Petroleum refining: Separation processes. Vol. 2. Technip.

[5] Meyers, R.A. 2004. Handbook of petroleum refining processes. 3rd ed. McGraw-Hill.

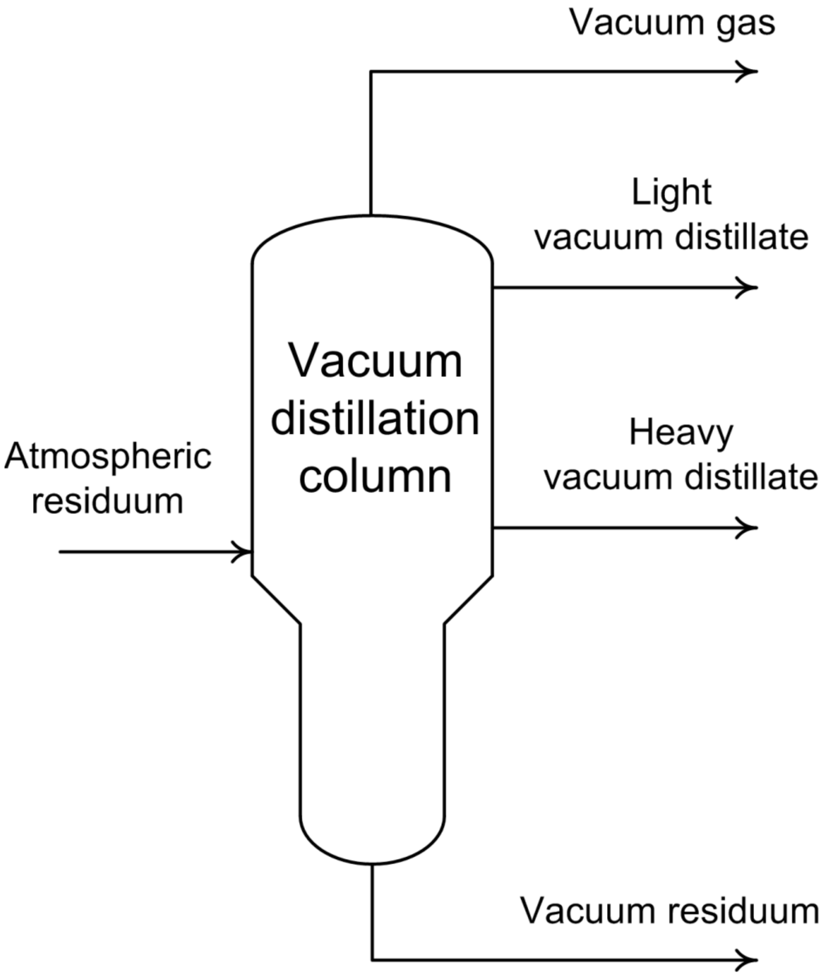
Overall refinery flow [2]



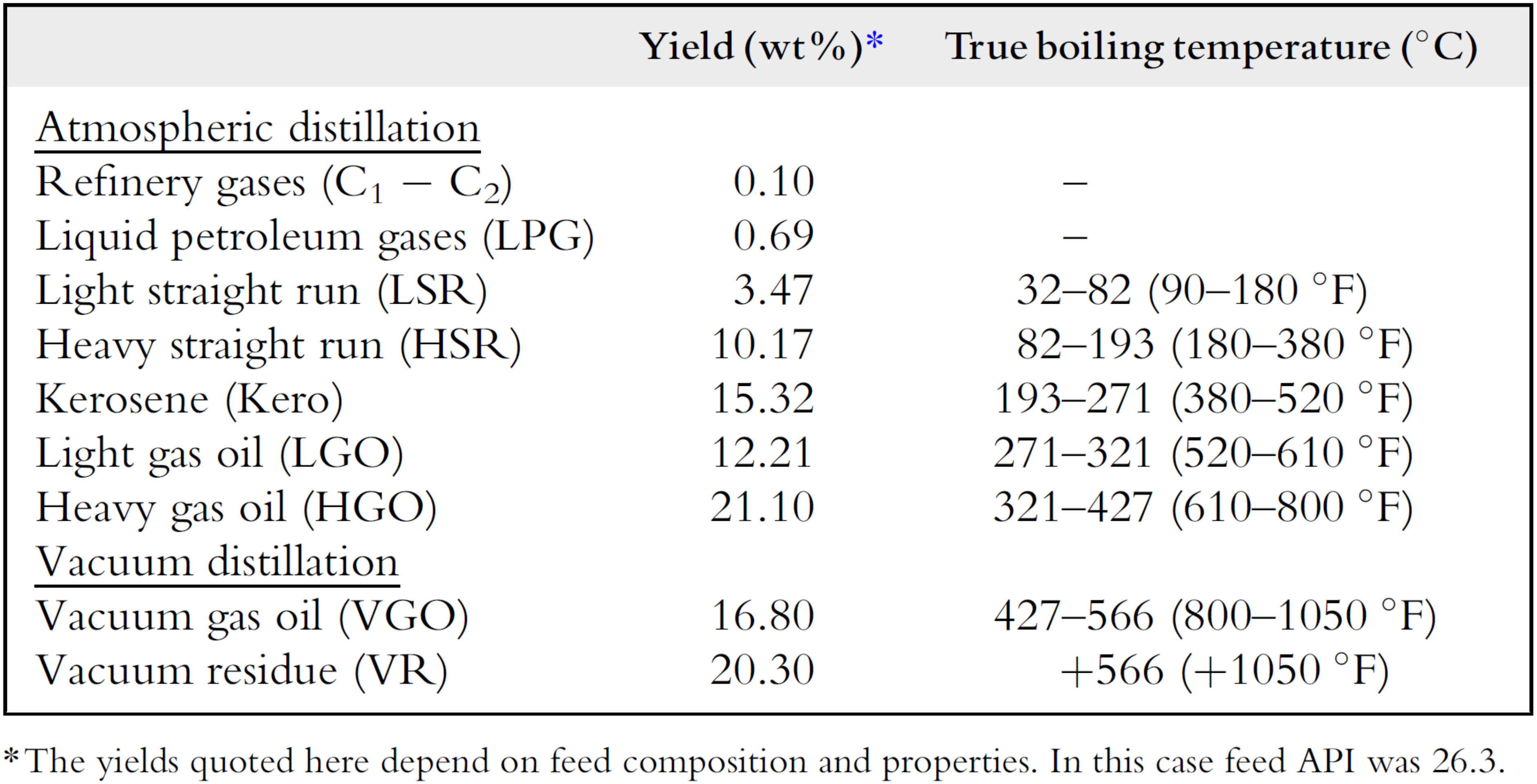
Crude oil distillation: Atmospheric



Crude oil distillation: Vacuum



Approximate ranges of crude distillation products [2]



	Yield (wt%)*	True boiling temperature (°C)
Atmospheric distillation		
Refinery gases ($C_1 - C_2$)	0.10	–
Liquid petroleum gases (LPG)	0.69	–
Light straight run (LSR)	3.47	32–82 (90–180 °F)
Heavy straight run (HSR)	10.17	82–193 (180–380 °F)
Kerosene (Kero)	15.32	193–271 (380–520 °F)
Light gas oil (LGO)	12.21	271–321 (520–610 °F)
Heavy gas oil (HGO)	21.10	321–427 (610–800 °F)
Vacuum distillation		
Vacuum gas oil (VGO)	16.80	427–566 (800–1050 °F)
Vacuum residue (VR)	20.30	+566 (+1050 °F)

*The yields quoted here depend on feed composition and properties. In this case feed API was 26.3.

Refinery processes

Separation processes:

Crude distillation (atmospheric distillation and vacuum distillation), solvent extraction, solvent deasphalting, solvent dewaxing, and clay treatment.

Conversion processes:

Catalytic reforming, hydrotreating, hydrocracking, catalytic cracking, alkylation, isomerization, delayed coking, flexicoking, and visbreaking.

Separation processes

Atmospheric distillation: Desalted crude oil is flashed in the atmospheric distillation unit and the crude oil is fractionated into various fractions. Light gases, light and heavy naphthas, kerosene, light and heavy gas oils, and atmospheric residuum may be the principal fractions.

Vacuum distillation: The atmospheric residue is vacuum fractionated and vacuum gas oil and vacuum residuum may be the products.

Solvent deasphalting: A solvent usually liquid propane is employed to remove asphaltenes from heavy crude fractions such as vacuum resid.

Solvent dewaxing: Paraffins of high molecular weight (wax) are removed from the lube oil stock to adjust the pour point.

Separation processes

Solvent extraction: Lube oil stock is treated with a solvent and aromatics are removed.

Clay treatment: Lube oil stocks are subjected to clay treatment to remove impurities to better stabilize and to improve the color.

Conversion processes

Alkylation: As an example, it is the addition of isobutane to butenes to produce high grade gasoline range product (alkylate).

Hydrotreating: It is carried out to remove impurities such as sulfur, nitrogen, halides etc.

Isomerization: For example, n-butane is isomerized to isobutane to feed the alkylation plant. n-hexane is isomerized to branched alkanes to produce a high octane rating product.

Catalytic reforming: It is used to process low grade (octane number) fraction such as straight run gasoline and naphthas to produce high grade gasoline range products. Dehydrogenation, isomerization, and hydrocracking may occur during the course of catalytic reforming.

Conversion processes

Catalytic cracking: The catalytic cracking of heavy oil fractions to produce mainly of gasoline range products.

Hydrocracking: The cracking of heavy oil fractions to produce low boiling products in the presence of hydrogen and catalyst.

Coking: It is severe thermal cracking that results in light gases,, coker naphtha, and solid coke.

Visbreaking: It stands for viscosity breaking. Liquid phase mild thermal cracking of heavy feedstocks.

Conversion and separation processes

- The crude oil is heated in a furnace and flash-charged to an atmospheric distillation tower (ADU). Here, it is separated into light wet gases, unstabilized light naphtha, heavy naphtha, kerosene, light and heavy atmospheric gas oils, and atmospheric reduced crude.
- The atmospheric reduced crude enters the vacuum reduced distillation column (VDU) and separated into vacuum gas oil streams and vacuum reduced crude.
- The vacuum reduced crude is sent to a coker where it is thermally cracked to produce wet gas, gasoline and gas oil range products and solid coke.
- The gas oil ranged products from the ADU and VDU and gas oil from the coking process are subjected to catalytic and hydrocracking. The purpose is usually to produce products of gasoline and diesel range.

Conversion and separation processes

- "The light naphtha streams from the crude tower, coker and cracking units are sent to an isomerization unit to convert straight-chain paraffins to isomers that have higher octane numbers" [1].
- "The heavy naphtha streams from the crude tower, coker and cracking units are fed to the catalytic reformer to improve their octane numbers" [1].
- "The wet gases streams from the crude units, coker, and cracking units are separated in the vapor recovery section (gas plant) into fuel gas, liquefied petroleum gas (LPG), unsaturated hydrocarbons (propylene, butylenes, and pentenes), normal butane, and isobutane. The fuel gas is burned as a fuel in refinery furnaces and normal butane is blended into gasoline or LPG. The unsaturated hydrocarbons and isobutane are sent to the alkylation unit for processing" [1].

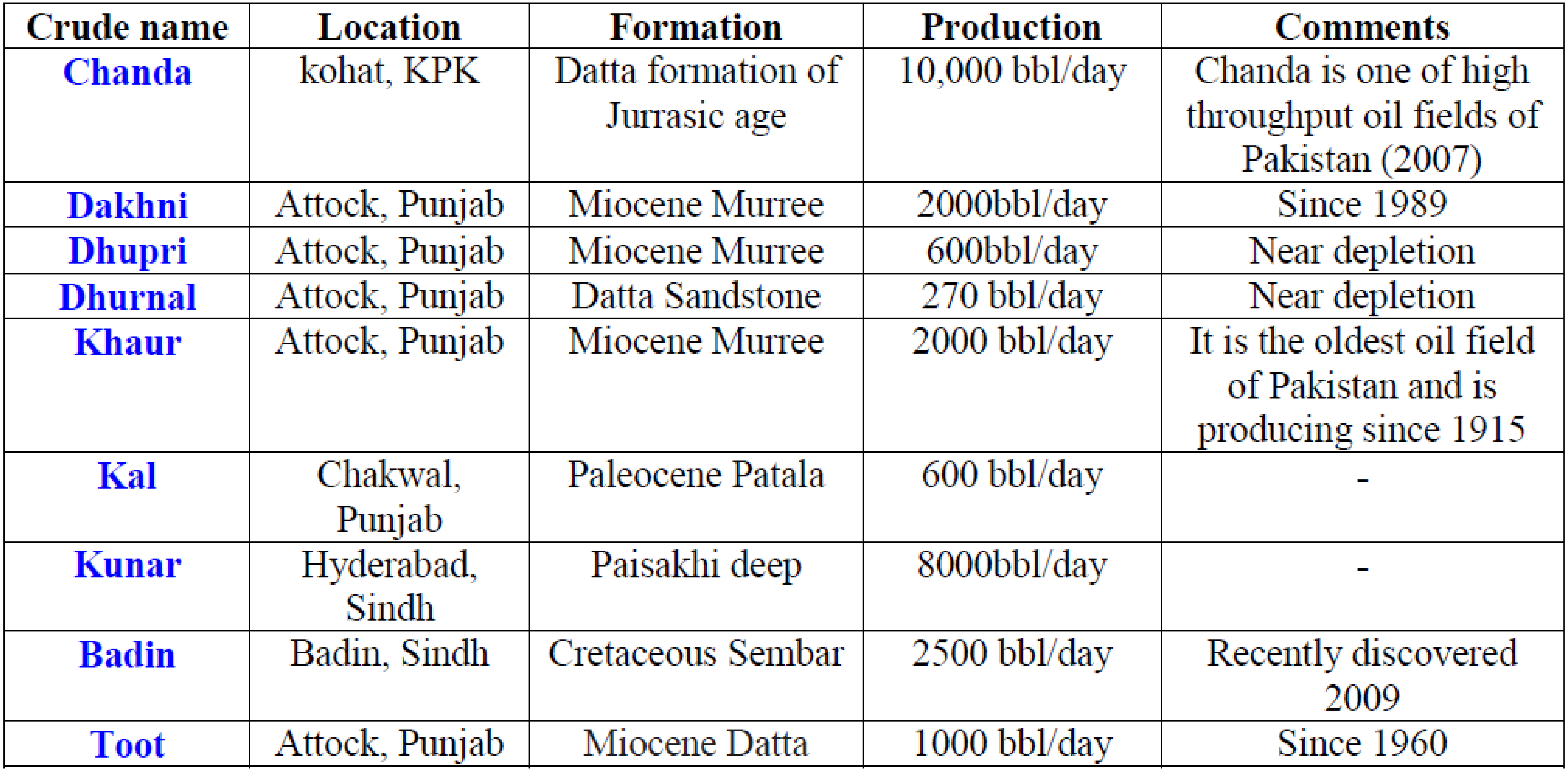
Conversion and separation processes

- "In some refineries, the heavy vacuum gas oil and reduced crude from paraffinic or naphthenic base crude oils are processed into lubricating oils" [1].
- "The vacuum gas oils and deasphalted stocks are first solvent-extracted to remove aromatic compounds and then dewaxed to improve the pour point. They are then treated with special clays or high-severity hydrotreating to improve their color and stability before being blended into lubricating oils" [1].

Optimum refinery operation

“Each refinery has its own unique processing scheme which is determined by the process equipment available, crude oil characteristics, operating costs, and product demand. The optimum flow pattern for any refinery is dictated by economic considerations and no two refineries are identical in their operation.” [1]

Some crude oils of Pakistan (From thesis of my student Ahmad)



Crude name	Location	Formation	Production	Comments
Chanda	kohat, KPK	Datta formation of Jurrasic age	10,000 bbl/day	Chanda is one of high throughput oil fields of Pakistan (2007)
Dakhni	Attock, Punjab	Miocene Murree	2000bbl/day	Since 1989
Dhupri	Attock, Punjab	Miocene Murree	600bbl/day	Near depletion
Dhurnal	Attock, Punjab	Datta Sandstone	270 bbl/day	Near depletion
Khaur	Attock, Punjab	Miocene Murree	2000 bbl/day	It is the oldest oil field of Pakistan and is producing since 1915
Kal	Chakwal, Punjab	Paleocene Patala	600 bbl/day	-
Kunar	Hyderabad, Sindh	Paisakhi deep	8000bbl/day	-
Badin	Badin, Sindh	Cretaceous Sembar	2500 bbl/day	Recently discovered 2009
Toot	Attock, Punjab	Miocene Datta	1000 bbl/day	Since 1960

Refining facility in Pakistan

Byco	35,000 bbl/day
ARL	40,000 bbl/day
PRL	50,000 bbl/day
NRL	65,000 bbl/day
PARCO	100,000 bbl/day

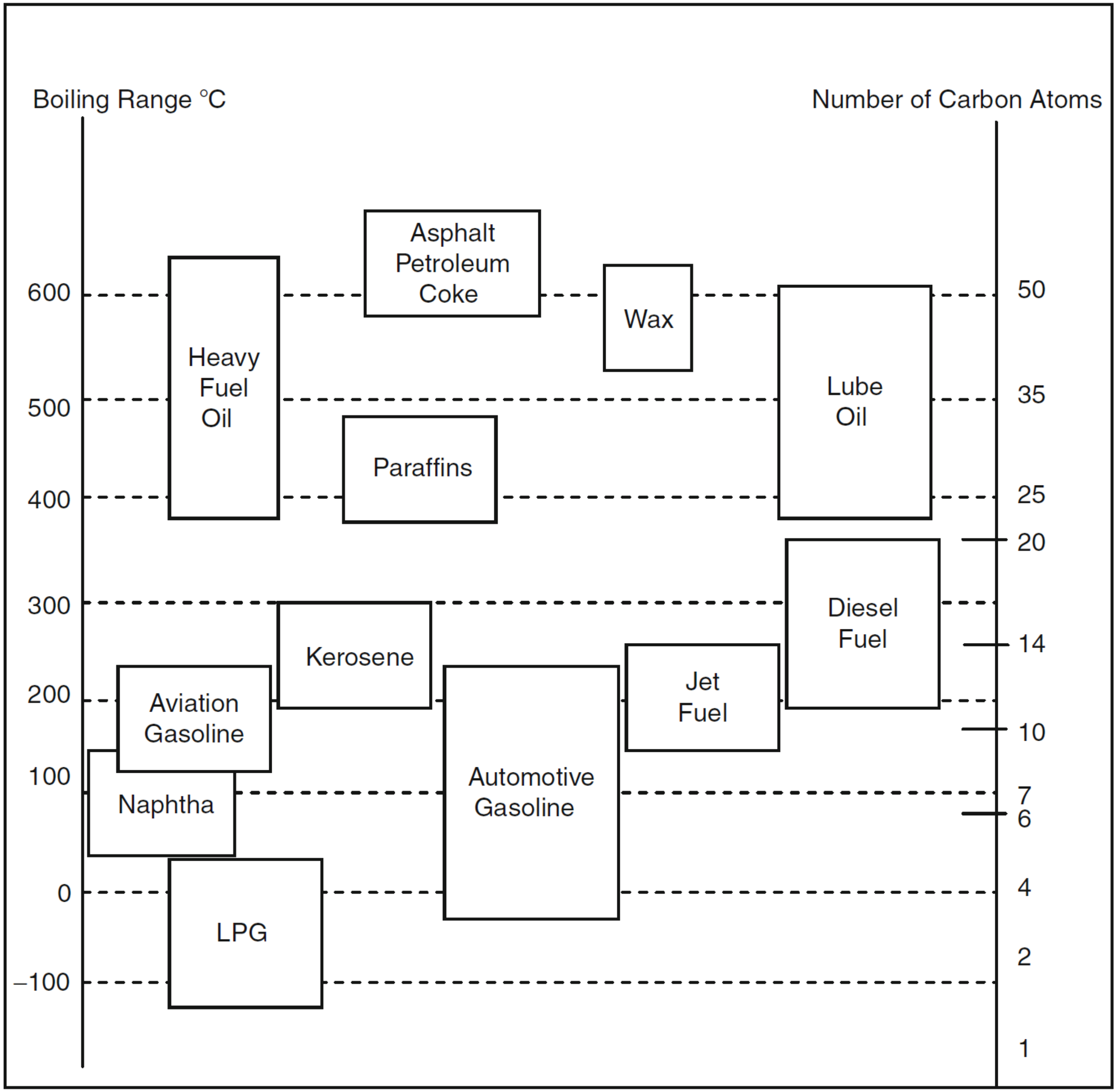
Byco has added nearly 120,000 bbl/day capacity in its new installation.

In the past, further new installations were expected including KCR, Indus, and Trans Asia.

General refinery products

- Refinery fuel gas
- Liquefied petroleum gas
- Solvent naphtha
- Gasoline
- Kerosene
- Jet fuel or gas turbine fuel
- Diesel fuel
- Fuel oil
- Residual fuel oil
- Lubricating oil or lube oil
- Wax
- Asphalt
- Petroleum coke

Refinery products: Brief description[2]



Tests on petroleum fraction

Pour point: A lower pour point means paraffinic content is low. It is a measure of ease or difficulty of a fraction to be pumped in cold conditions.

Viscosity: It is usually measured in centi Stokes or Saybolt seconds at 37.8 and 99 ºC. These two points are used to find viscosity index of the fraction.

Aniline point: It is an indication of the amount of the aromatic content in a given fraction.

Flash point: It is important for gasoline and naphtha.

Octane number: Motor octane number (MON) is the test carried out at high speed (900 rpm). Research octane number (RON) is measured at low speed (600 rpm). PON (posted octane number is the arithmetic average of RON and MON).

Tests on petroleum fraction

Reid vapor pressure: Vapor pressure determined in a volume of air four times the liquid volume at 37.8 °C (100 °F). It indicates vapor lock characteristics and explosion hazards.

Carbon residue: It indicates the soot forming characteristics of a fuel.

Smoke point: It is a measure of the burning qualities of kerosene and jet fuels. It is measured in terms of the maximum height in mm of a smokeless flame of fuel.

Refractive index: It is the ratio of the velocity of light in vacuum to the velocity of light in the oil. It is a used to characterize a petroleum fraction.

Cetane number: It measures the ability for autoingnition in diesel (compression ignition) engines. It is the percentage of pure cetane (n-hexadecane) in a blend of cetane and alpha methyl naphthalene which corresponds to the ignition characterstics of a given diesel sample.

Tests on petroleum fraction

Freezing point: It is the temperature at which the hydrocarbon liquid solidifies at atmospheric pressure. It is one of the important property specifications for kerosene and jet fuels due to the low temperatures encountered at high altitudes in jet planes.

Sediments: These are solid materials that are not soluble in the hydrocarbon or water and can be comprised of sand, drilling mud, rock or minerals, particles from erosion of metal pipes, tanks, and other process equipments.

Separation processes

Generally, separation processes may be classified as either mechanical-physical separation processes or mass transfer operations.

- Mechanical-physical separation processes

  (do not require a mass transfer gradient for the separation)
- Mass transfer operations

  (based on diffusion and require a mass transfer gradient for the separation)

Separation processes

Examples of mechanical-physical separation processes are:

- Size reduction
- Size enlargement (not crystallization)
- Size separation (screening, etc.)
- Filtration
- Some and not all membrane separation processes
- Sedimentation (Thickening and clarification)
- Elutriation
- Floatation
- Centrifugation

Separation processes

Examples of mass transfer operations are:

- Distillation
- Drying
- Liquid-liquid extraction
- Leaching or lixiviation
- Gas absorption
- Membrane separation

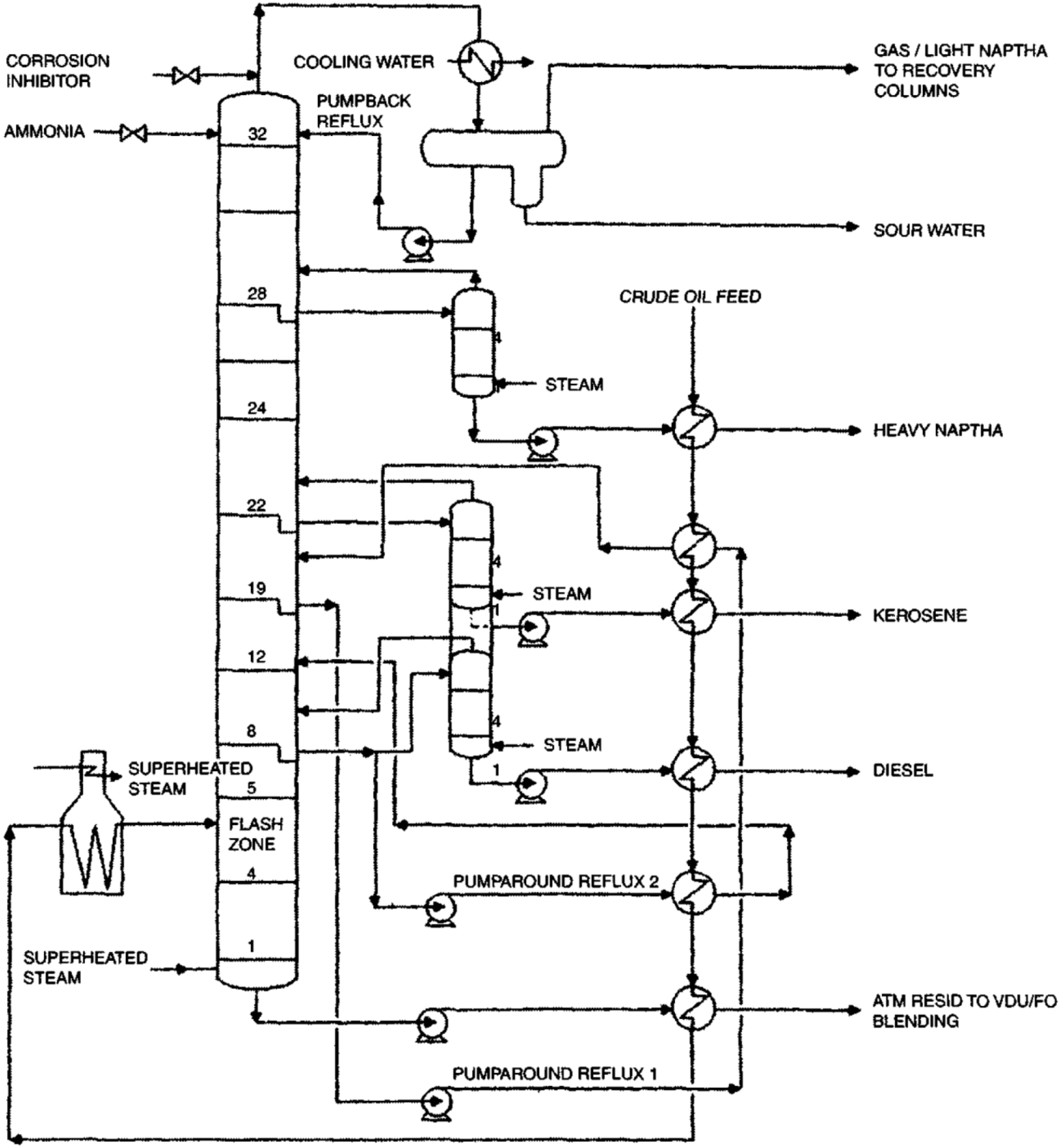
  (Not all membrane separation processes)
- Humidification
- Adsorption

Atmospheric distillation unit (ADU)

What is distillation?

Why do we need distillation of a crude oil?

Atmospheric distillation unit (ADU)[3]



Atmospheric distillation unit (ADU)

The column operates generally at a pressure greater than atmospheric pressure. This may be done for pressure drop considerations, to flow the vapors from one location to the desired location, and/or cooling water to be used for the overhead condenser. A higher pressure increases the bubble point.

What is the criteria for setting pressure in the overhead condenser (column)?

Atmospheric distillation unit (ADU)

- Nearly 50–60% of the crude oil is vaporized in the flash zone of the tower [3].
- A preflash tower is sometimes added before the atmospheric column, if the crude oil contains appreciable amounts of lighter products.

How is this advantageous?

- The bottom temperature is bounded in the range of 700-750 °F [3]. This is done avoid cracking.
- The superheated steam required to boil off the crude bottoms is usually at about 600 °F [3].
- The steam consumption is usually 5–10 lb/bbl of stripped product [3].

Vacuum distillation unit (VDU)

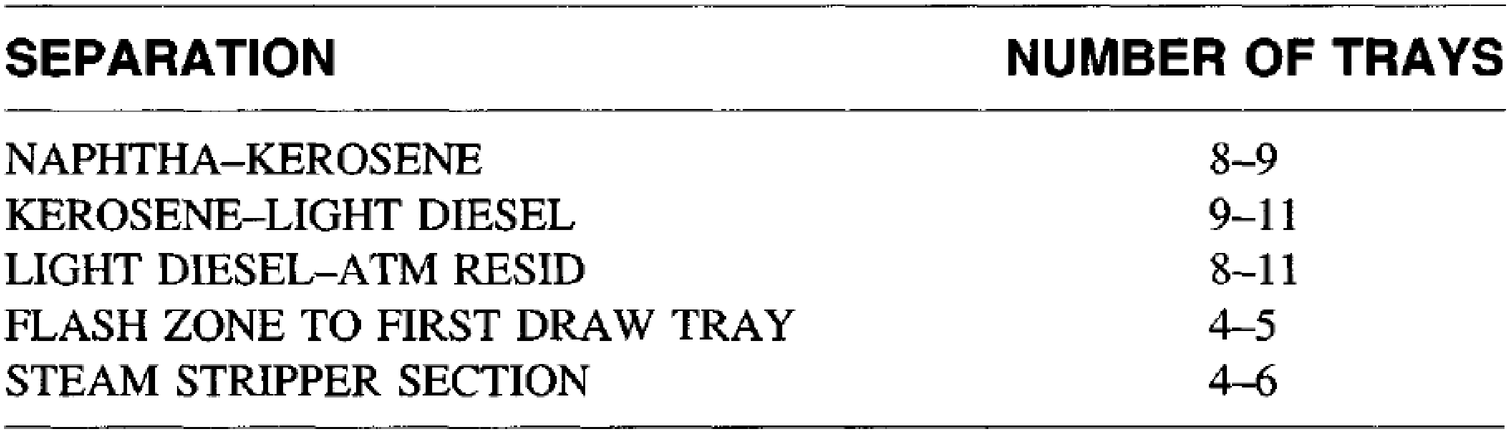
Overflash: 5 to 10% of the bottoms that acts as an internal reflux to better fractionate the few trays above the flashzone.

Pumparound reflux is used to remove heat from the column. A stream at a higher temperature in a column is taken out of the column, exchanges heat with the crude oil feed and heats it, and then returns back to the column at some higher position in the column (lower temperature).

Atmospheric distillation unit (ADU)

Most atmospheric towers contain 25–35 trays between the flash zone and the top tower.

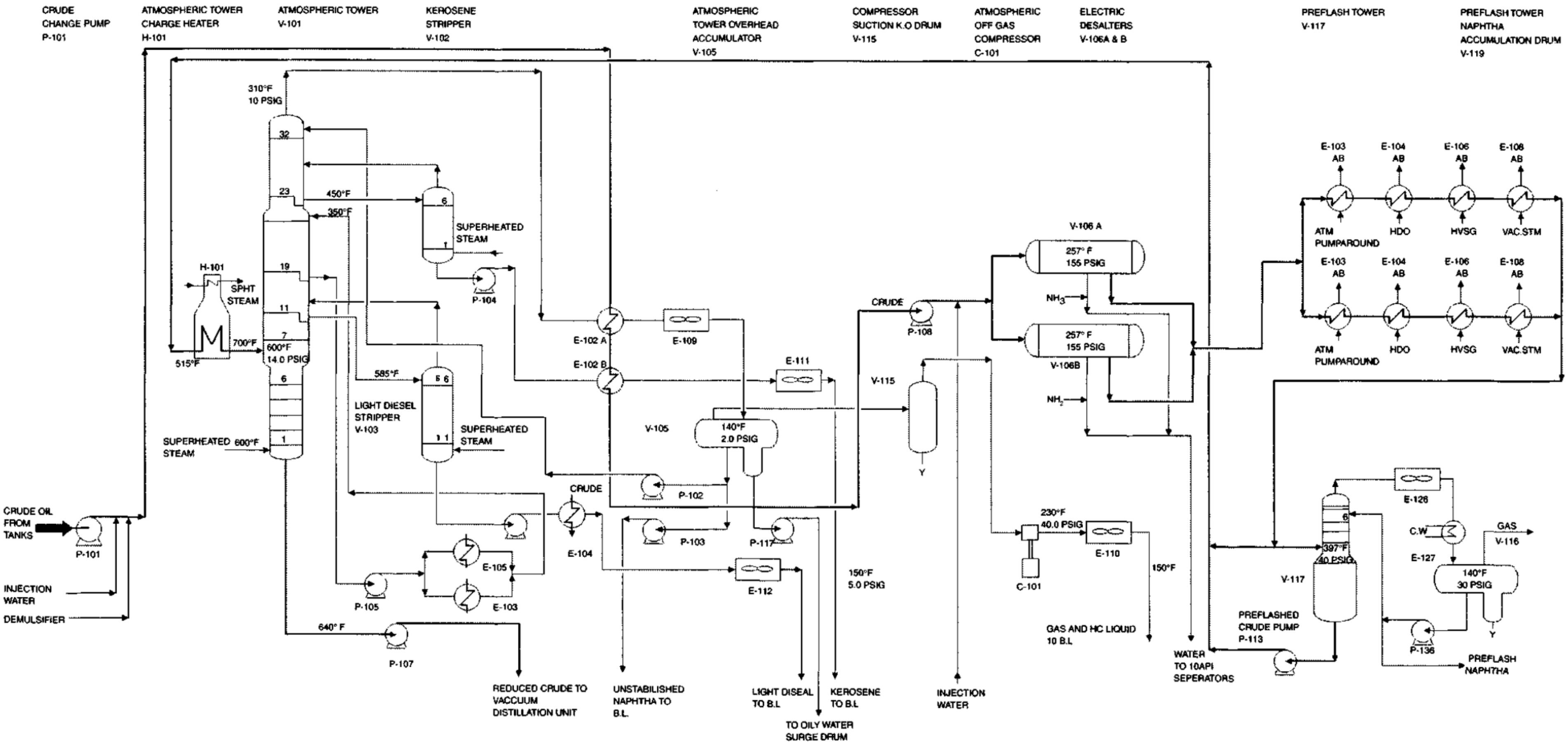
The allowable pressure drop for trays is approximately 0.1–0.2 psi per tray. Generally a pressure drop of 5 psi is allowed between the flash zone and the top tower.



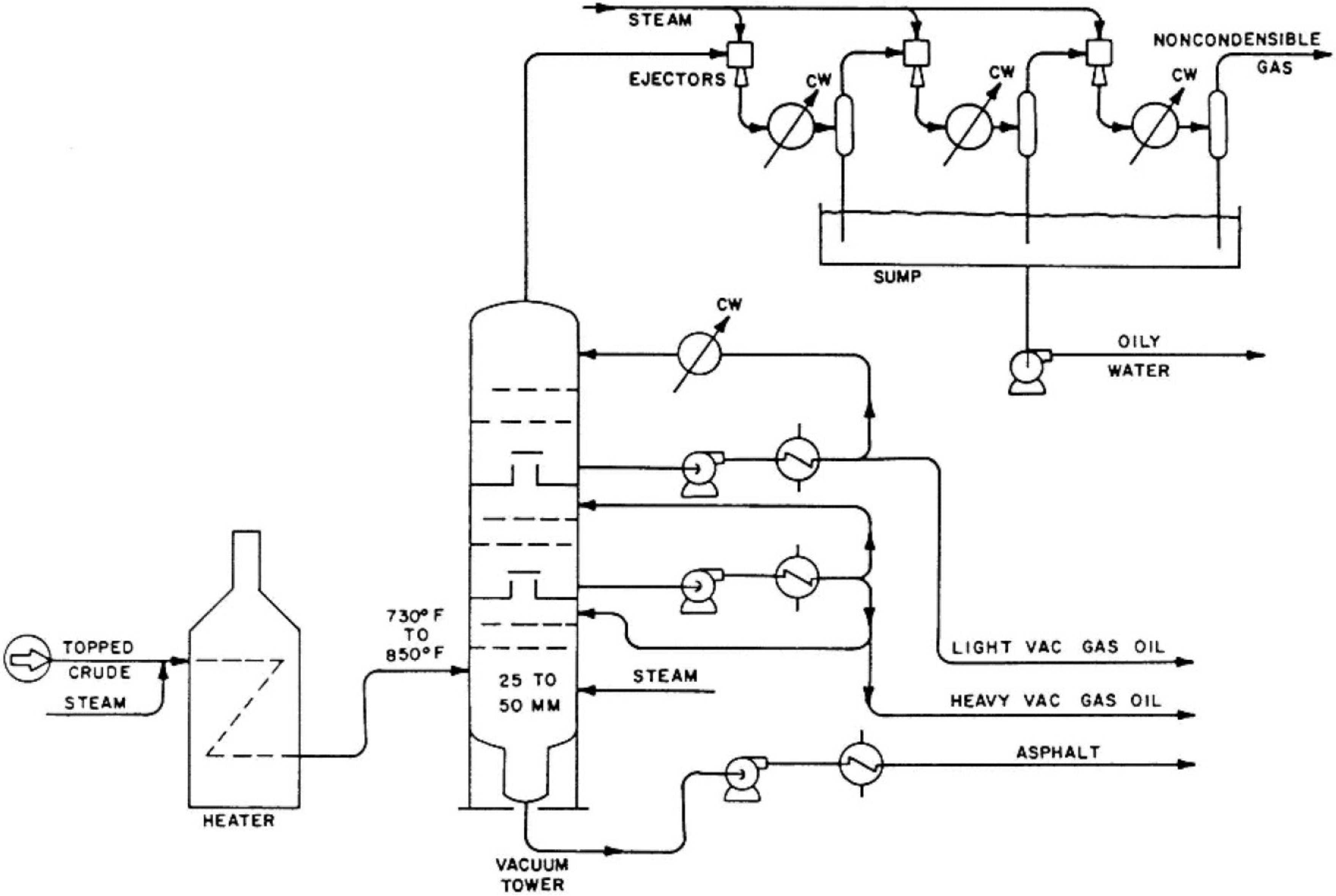
SEPARATION	NUMBER OF TRAYS
NAPHTHA–KEROSENE	8–9
KEROSENE–LIGHT DIESEL	9–11
LIGHT DIESEL–ATM RESID	8–11
FLASH ZONE TO FIRST DRAW TRAY	4–5
STEAM STRIPPER SECTION	4–6

Ref.: 3

Atmospheric distillation unit (ADU)[3]



Vacuum distillation unit (VDU)[1]



Vacuum distillation unit (VDU)

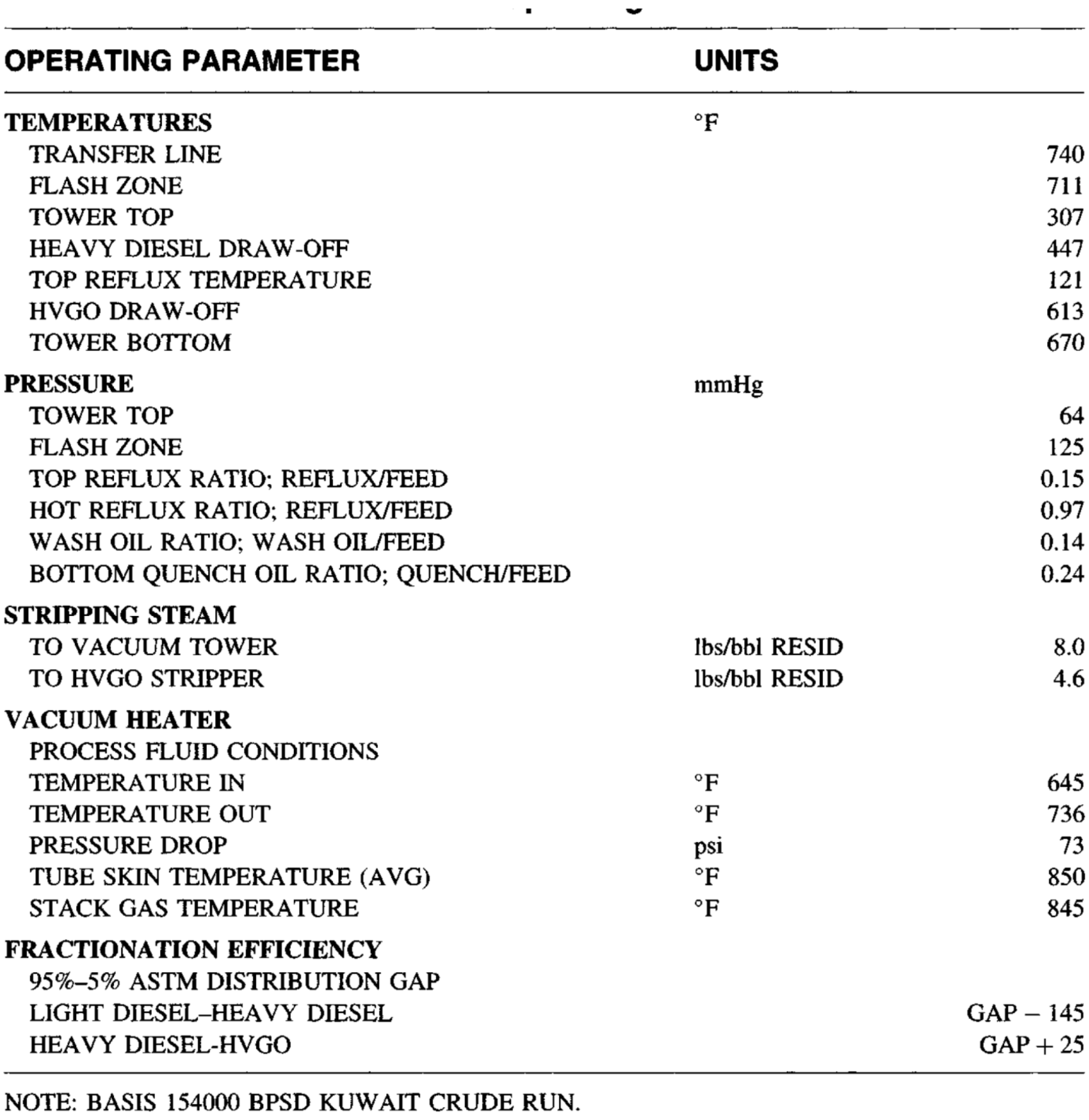
The temperature required at the furnace outlet for atmospheric distillation unit (ADU) will be excessive if the heavier fractions will be distilled in the ADU. This will be resulted in thermal cracking and loss of the product and fouling of the equipment. This necessitates the use of vacuum distillation column where the distillation occurs under sub-atmospheric conditions.

Decreasing pressure of a component decreases the boiling point and vice versa.

Vacuum distillation unit (VDU)

- Furnace outlet temperatures are usually in range of 730–850 °F (388–454 °C) [1].
- The pressure in the flash zone is around 25–40 mm Hg [1].
- The effective pressure for hydrocarbon vaporization is reduced by using stripping steam in the furnace as well as at the tower bottom. The steam added to the furnace increases the velocity of the fluid and decreasing the coke formation.
- The steam consumption is usually 10–50 lb/bbl of feed [1].
- The lower pressure in the tower increases the diameter of column. A higher pressure increases the boiling temperatures and difficulty of separation. Vacuum distillation columns have large diameters and the diameter may easily reach 40 ft [1].

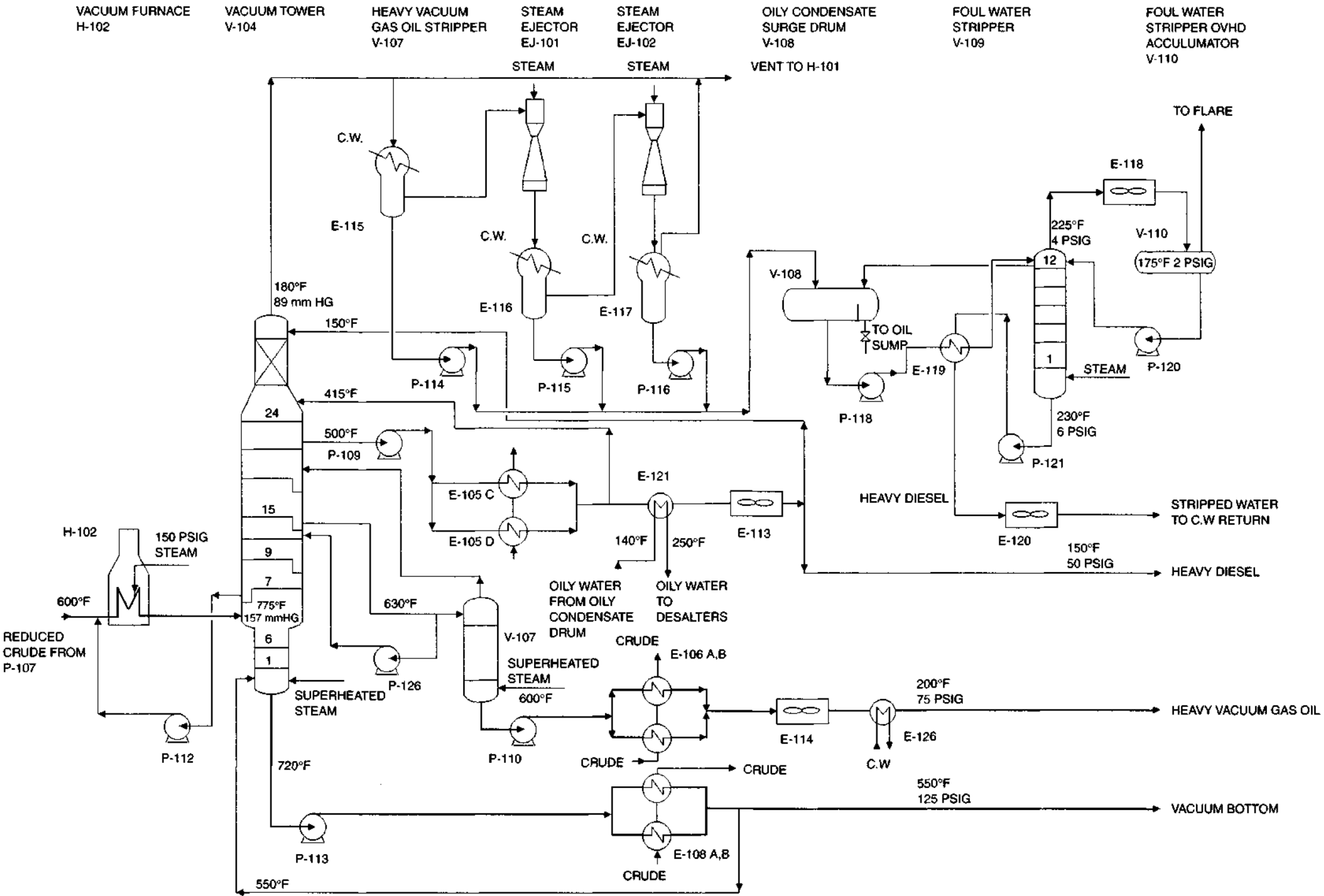
Vacuum distillation unit (VDU)[3]



OPERATING PARAMETER	UNITS	
TEMPERATURES	°F	
TRANSFER LINE		740
FLASH ZONE		711
TOWER TOP		307
HEAVY DIESEL DRAW-OFF		447
TOP REFLUX TEMPERATURE		121
HVGO DRAW-OFF		613
TOWER BOTTOM		670
PRESSURE	mmHg	
TOWER TOP		64
FLASH ZONE		125
TOP REFLUX RATIO; REFLUX/FEED		0.15
HOT REFLUX RATIO; REFLUX/FEED		0.97
WASH OIL RATIO; WASH OIL/FEED		0.14
BOTTOM QUENCH OIL RATIO; QUENCH/FEED		0.24
STRIPPING STEAM		
TO VACUUM TOWER	lbs/bbl RESID	8.0
TO HVGO STRIPPER	lbs/bbl RESID	4.6
VACUUM HEATER		
PROCESS FLUID CONDITIONS		
TEMPERATURE IN	°F	645
TEMPERATURE OUT	°F	736
PRESSURE DROP	psi	73
TUBE SKIN TEMPERATURE (AVG)	°F	850
STACK GAS TEMPERATURE	°F	845
FRACTIONATION EFFICIENCY		
95%–5% ASTM DISTRIBUTION GAP		
LIGHT DIESEL–HEAVY DIESEL		GAP – 145
HEAVY DIESEL-HVGO		GAP + 25

NOTE: BASIS 154000 BPSD KUWAIT CRUDE RUN.

Vacuum distillation unit (VDU)[3]



Vacuum distillation unit (VDU)

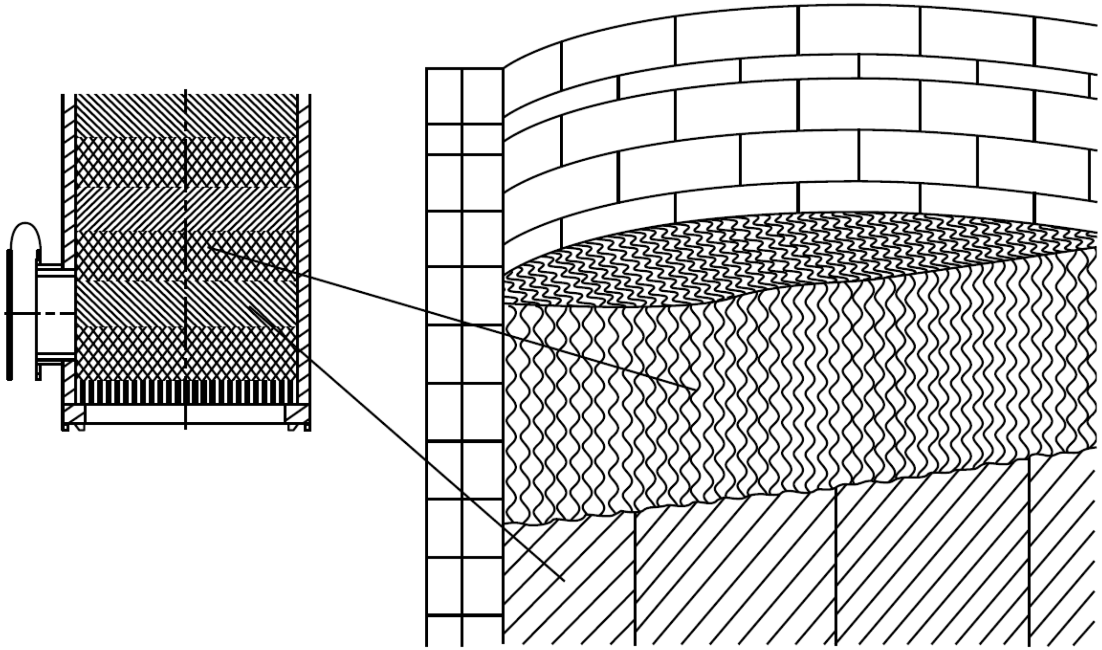
- The gases produced at the top of the column are sent to the fired heater and burned to release heat.
- The gases separated from the sour water in foul water stripper are sent to the flare system. Part of the water recovered in the stripper is sent to the desalters.
- Vacuum gas oil produced may be sent to hydrocracking, catalytic cracking, or lube oil processing.

What for vacuum residue?

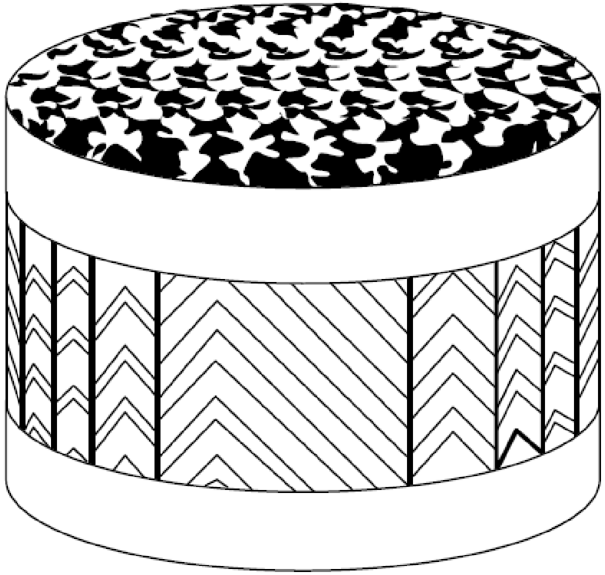
Vacuum distillation unit (VDU)

- “It is essential to design the fractionator tower, overhead lines, and condenser to minimize the pressure drop between the vacuum-inducing device and the flashzone. A few millimeters decrease in pressure drop will save many dollars” [1]. Structured packings may be employed in the column as having high HETP and offer low pressure drop.
- “The desired operating pressure in column is maintained using steam ejectors and barometric condensers or vacuum pimps and surface condensers. For a flash zone pressure of 25 mmHg, three ejector stages are usually required” [1].
- “The vacuum produced is limited to the vapor pressure of the water used in the condensers”[1].

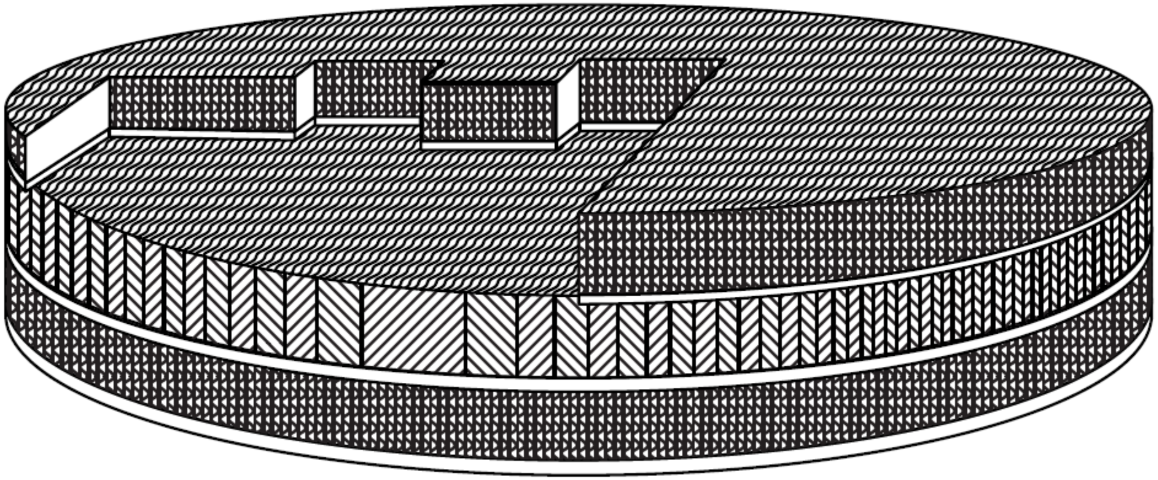
Vacuum distillation unit (VDU): Examples of structured packings [7]



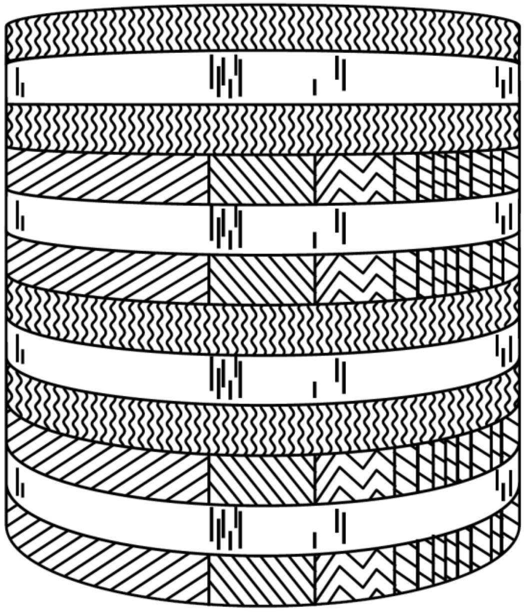
Flexiceramic Flexeramic®



Mellapak™

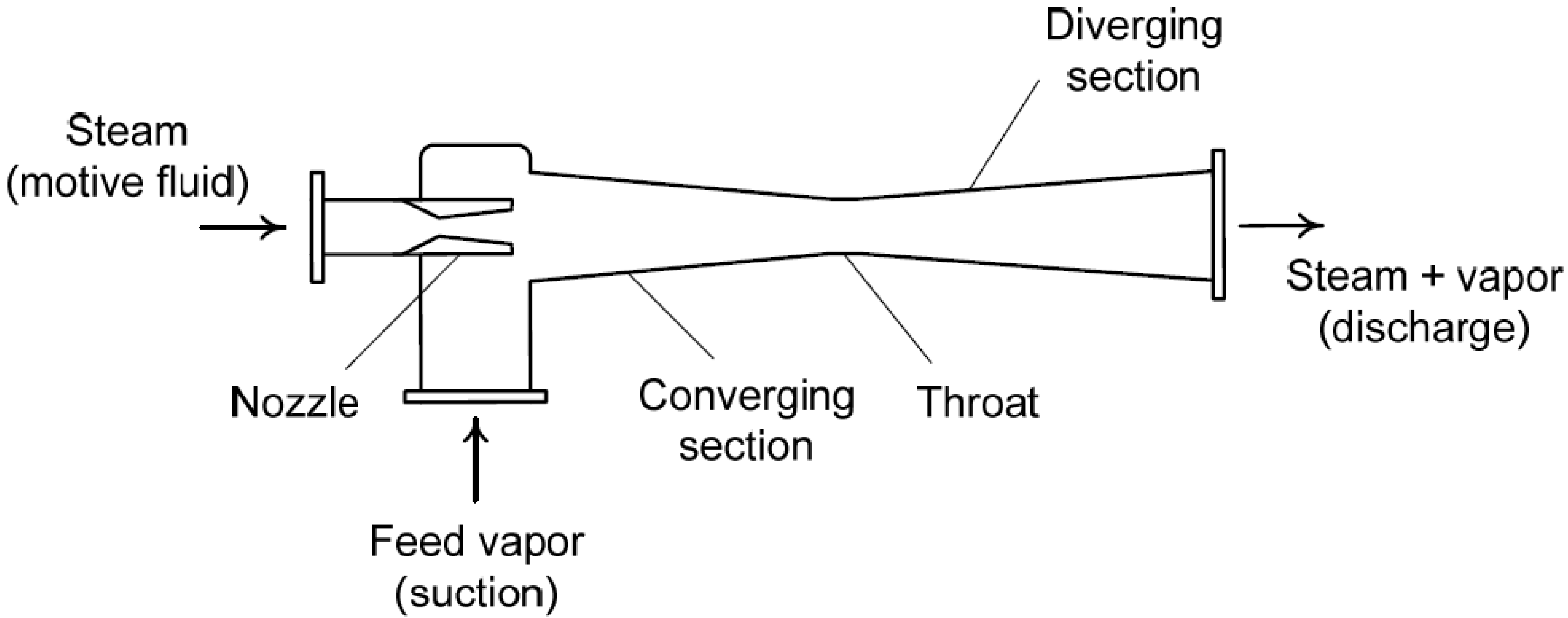


Montz™

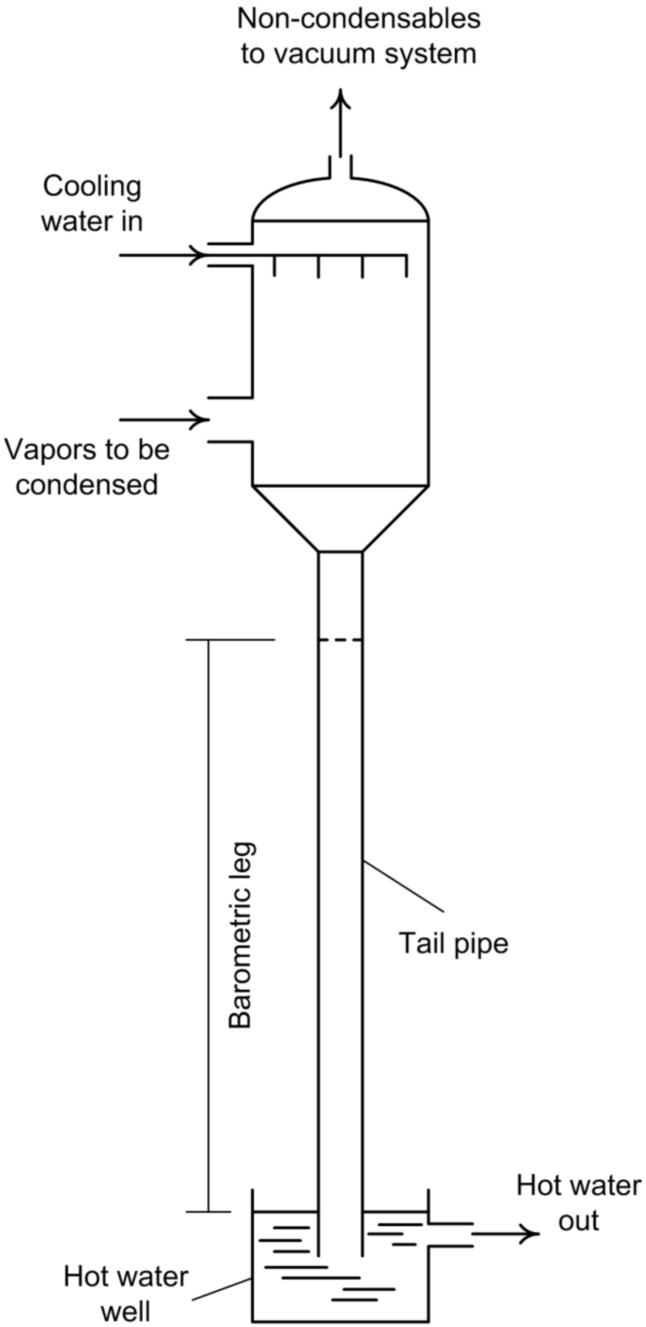


Flexipac®

Vacuum distillation unit (VDU): Steam ejector [8]



Vacuum distillation unit (VDU): Barometric condenser [8]



Separation processes (Lube oil processing)

What is a lubricating (lube) oil?

What is its function?

Separation processes (Lube oil processing)

What should be the important properties of lube oils?

1. Viscosity
2. Viscosity change with temperature (viscosity index)
3. Pour point
4. Oxidation resistance
5. Flash point
6. Boiling temperature
7. Acidity (neutralization number)
8. Thermal stability
8. Color

See Chapter 14 of Ref. 1.

Separation processes (Lube oil processing)

Viscosity: Higher the viscosity, the thicker the film of the oil. However, too high a viscosity may cause undesirable friction and heat. Higher the boiling range of the fraction, usually greater the viscosity.

What boiling range should be selected for a lube oil that requires a high viscosity?

Viscosity index: Higher the viscosity index, the smaller the change in viscosity with temperature. It may a negative or even greater than 100. Additives such as polyisobutylenes and polymethacrylic acid esters are added to improve the viscosity index characteristics.

Separation processes (Lube oil processing)

Pour point: For motor oils, a low pour point is very important to obtain ease of starting and proper start up lubrication on cold days.

Oxidation resistance: At high temperatures such as in an internal combustion engine can cause rapid oxidation. Oxidation causes the coke formation and the formation of asphaltic type materials. These products can injure the metal surfaces and can block the flow lines. Additives such as phenolic compounds and zinc dithiophosphates are added to inhibit the oxidation reactions.

Separation processes (Lube oil processing)

Flash point: It may indicate the type of hydrocarbons are present in the lube oil and determines the volatility of the oil and the possible emissions it may cause.

Boiling point: It tells the type of the hydrocarbons present and gives an idea of the viscosity of the oil.

Acidity: Organic acids formed by the oxidation of oil or that formed as byproducts in the combustion of oil may cause corrosion and therefore needed to be reduced. Lube oil blending stocks from paraffinic crude oils have excellent thermal and oxidation stability and exhibit lower acidity than do the oils from the naphthenic crude oils. Acidity characteristics are determined by neutralization number.

Can you define acid number, base number, and neutralization number?

Separation processes (Lube oil processing)

Thermal stability: It ensures that the lubricating oil is stable under the conditions of operation and not cracked or reactive.

Color: Reasonably unacceptable color may a sign of the presence of olefins, metal complexes, and heteroatoms such as nitrogen.

Separation processes (Lube oil processing)

Undesirable characteristics of raw lube oils [1]:

1. High cloud and pour points
2. Large viscosity change with temperature, i.e., low viscosity index
3. Poor oxidation resistance
4. Poor color
6. High organic acidity
7. High coke forming and sludge forming ability

Definitions of lube oils

Neutral oil:

Straight run distillation fraction suitable for lube oil products.

Bright stock:

Deasphlated vacuum residue suitable for lube oil.

Finished lube oil:

The blended lube oil product of final desired properties.

Paraffinic lube oils: "These are all grades of lube oils, from both neutral and bright stocks, that have a finished viscosity index greater than 75" [6]

Naphthenic lube oils: Lube oils with a finished viscosity index of less than 75 [6].

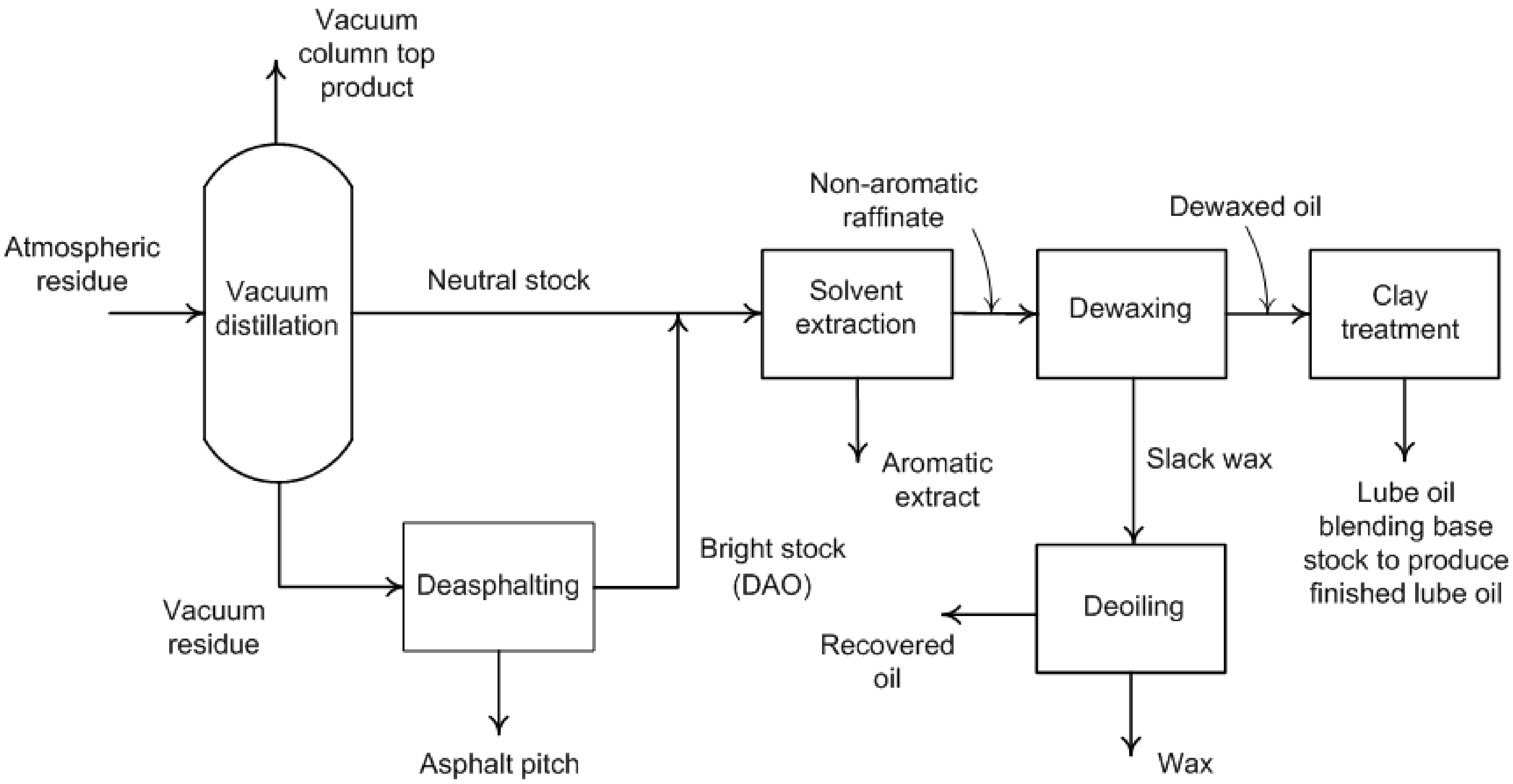
Separation processes (Lube oil processing)

The processes used to change the above mentioned undesirable properties of the raw lube oils are as follows:

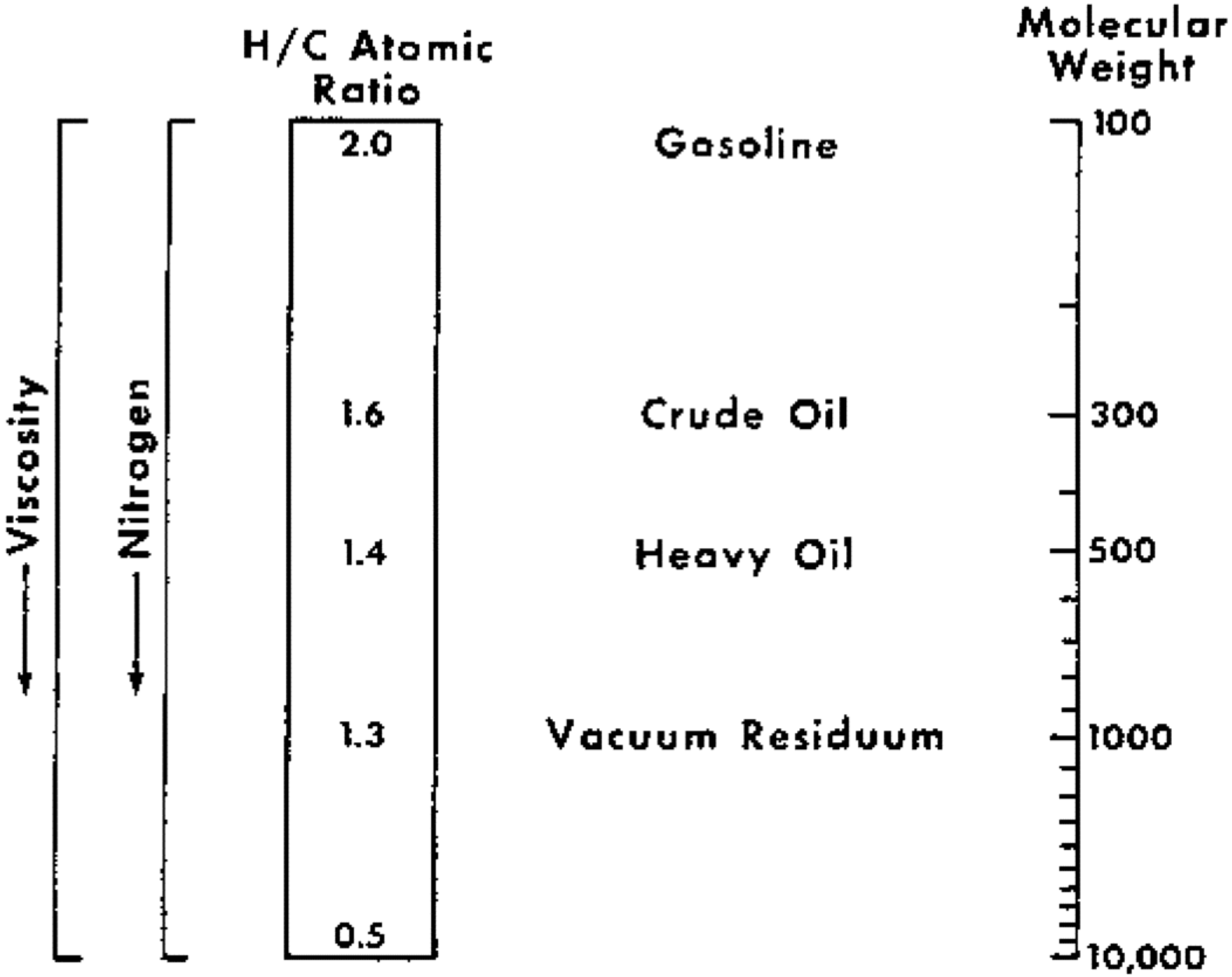
1. Solvent deasphalting
2. Solvent extraction or Hydrocracking
3. Solvent dewaxing or selective hydrocracking (hydrodewaxing)
4. Clay treatment or Hydrotreating

The modern trend is to use hydroprocesses, however, we will go through separation processes here and similar hydroprocesses will be discussed in rather detail in the final term.

Separation processes (Lube oil processing)



Atomic H/C ratios of various species [9]



Solvent deasphalting

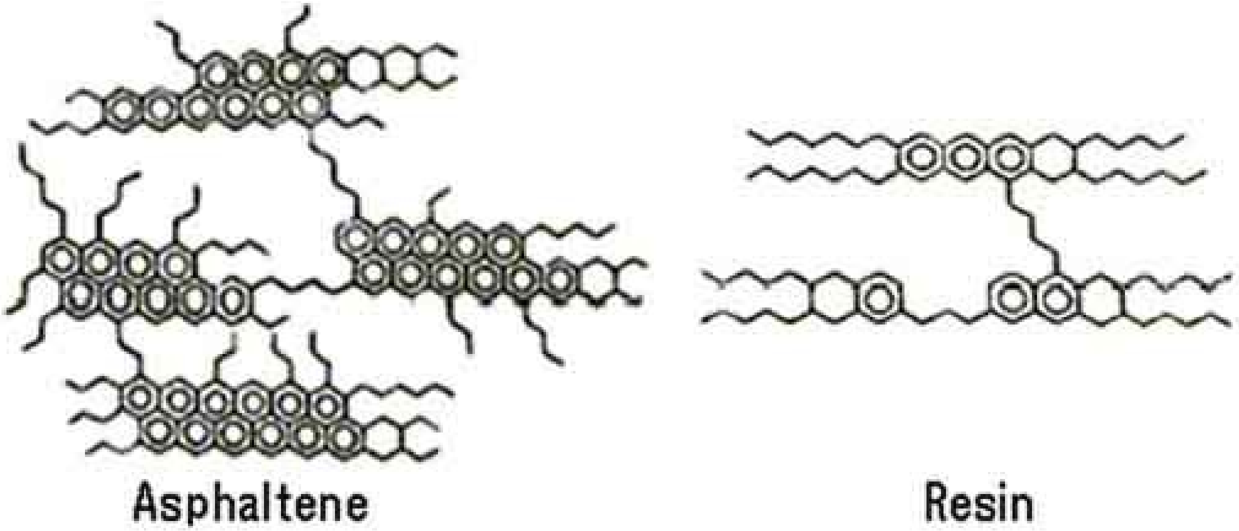
The purpose of deasphalting is to remove asphaltenes and resins and that it is required to reduce metallic contents and coke and sludge formation tendencies. For maximizing fuel (in fuel refinery) or when the vacuum fraction is not suitable for lube oil production, the deasphalting is carried out to prepare feed for the subsequent conversion processes. So, it is not always carried out for preparing lube oil stock. Owing to the high carbon residues and metal contents (sulfur contents may well be) of the asphaltene and resin fraction, removal of asphaltenes and resins reduces these contents in the feed for catalytic conversion units. Catalysts involved in the conversion processes may be damaged and greatly deactivated in the presence of metals and high carbon residue. Severe fouling of the process equipment may also be a reason.

Solvent deasphalting

Removal of sulfur, metal, and nitrogen from a vacuum residue is usually less expansive by deasphalting than by hydrotreating. The desulfurized, demetallized, etc., residue may be used as a blending stock for the feed for hydrocracking and catalytic cracking.

The light lube oil fractions, if any, can avoid deasphalting and directly treated in solvent extraction.

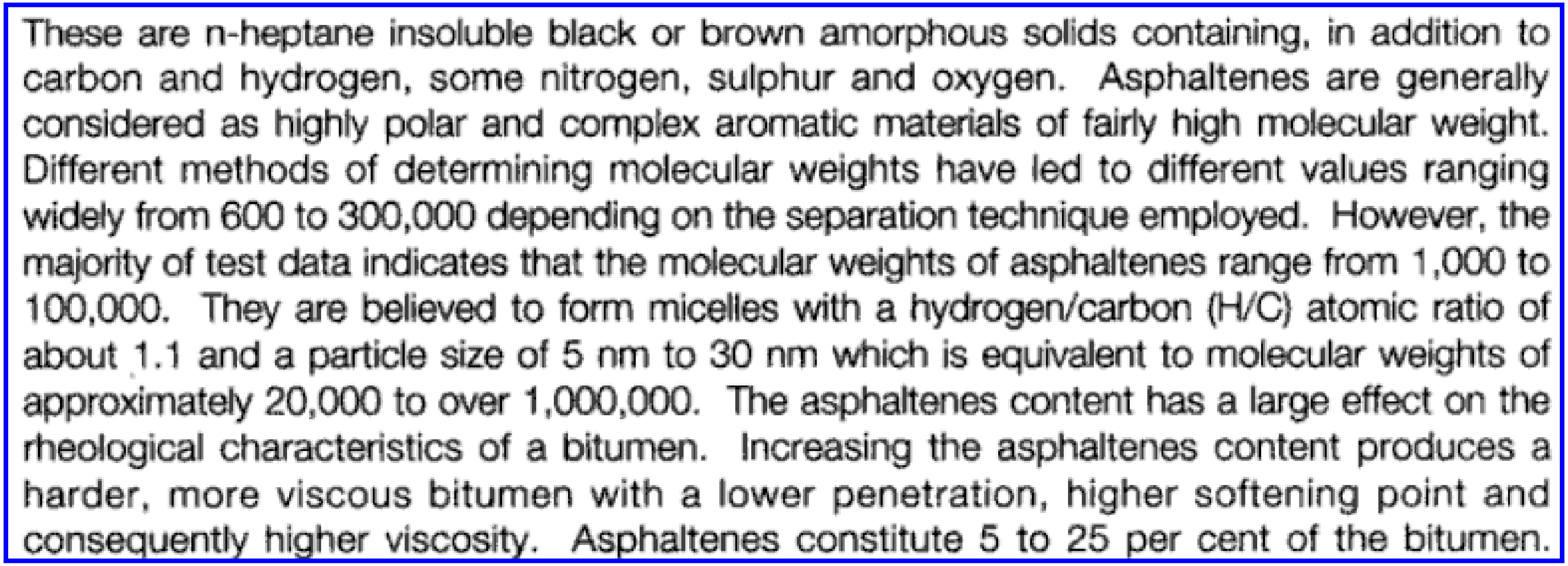
Solvent deasphalting



Structures of asphaltene and resin from Khafji crude oil

From: http://www.pcs.gr.jp/doc/EMousse/text.htm

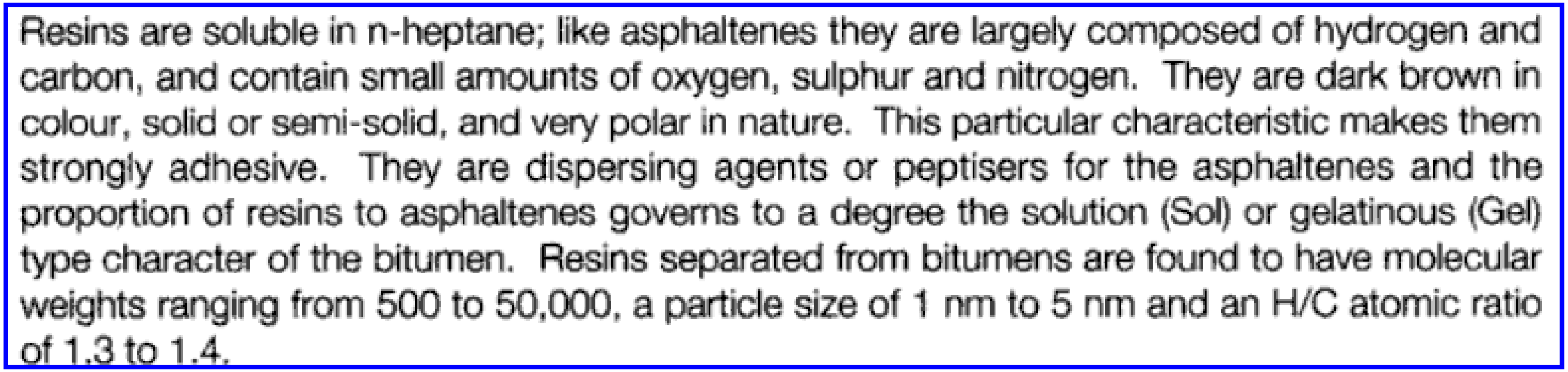
Asphaltenes (Solvent deasphalting)



These are n-heptane insoluble black or brown amorphous solids containing, in addition to carbon and hydrogen, some nitrogen, sulphur and oxygen. Asphaltenes are generally considered as highly polar and complex aromatic materials of fairly high molecular weight. Different methods of determining molecular weights have led to different values ranging widely from 600 to 300,000 depending on the separation technique employed. However, the majority of test data indicates that the molecular weights of asphaltenes range from 1,000 to 100,000. They are believed to form micelles with a hydrogen/carbon (H/C) atomic ratio of about 1.1 and a particle size of 5 nm to 30 nm which is equivalent to molecular weights of approximately 20,000 to over 1,000,000. The asphaltenes content has a large effect on the rheological characteristics of a bitumen. Increasing the asphaltenes content produces a harder, more viscous bitumen with a lower penetration, higher softening point and consequently higher viscosity. Asphaltenes constitute 5 to 25 per cent of the bitumen.

From: The shell bitumen industrial handbook, p. 53.

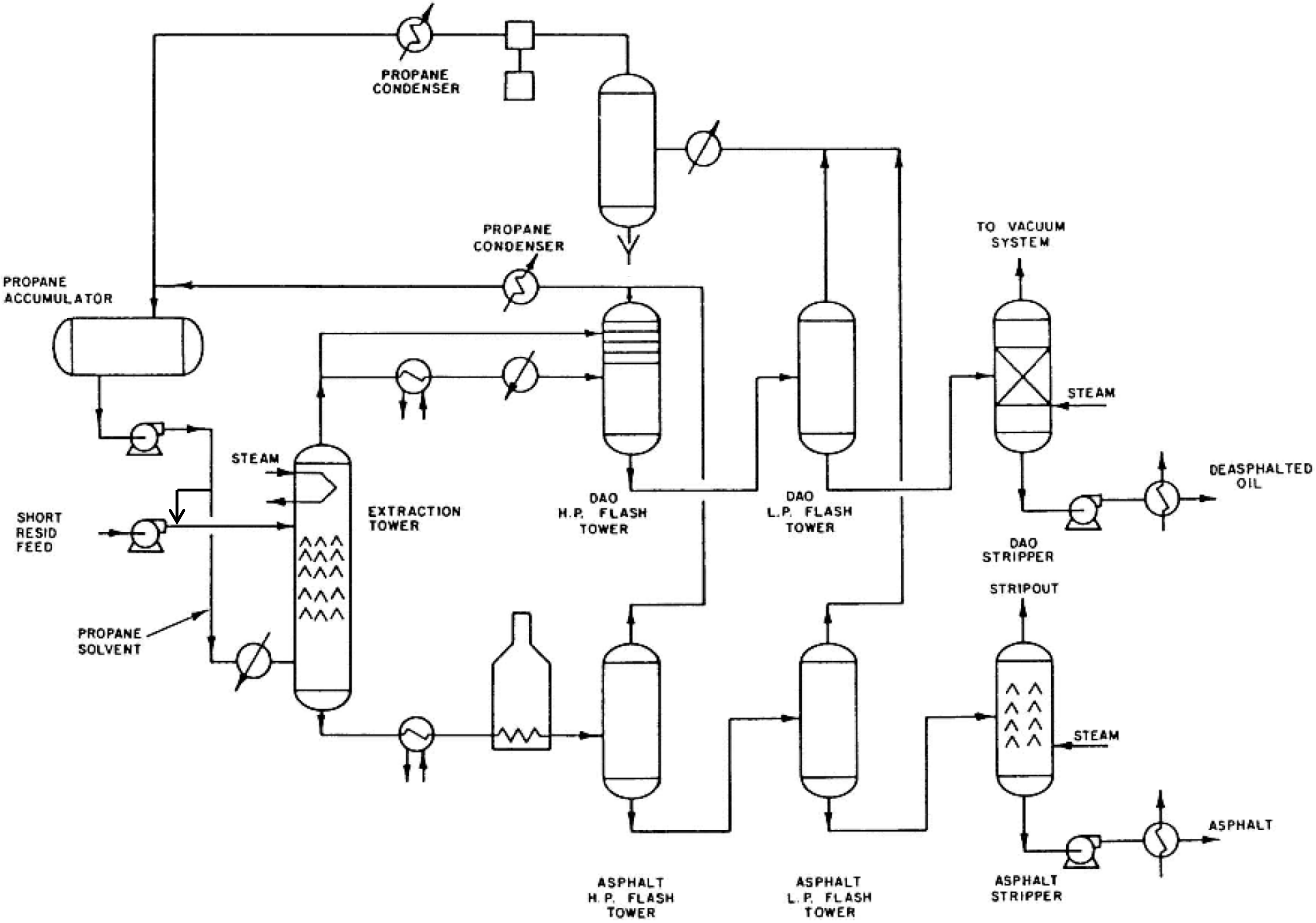
Resins
(Solvent deasphalting)



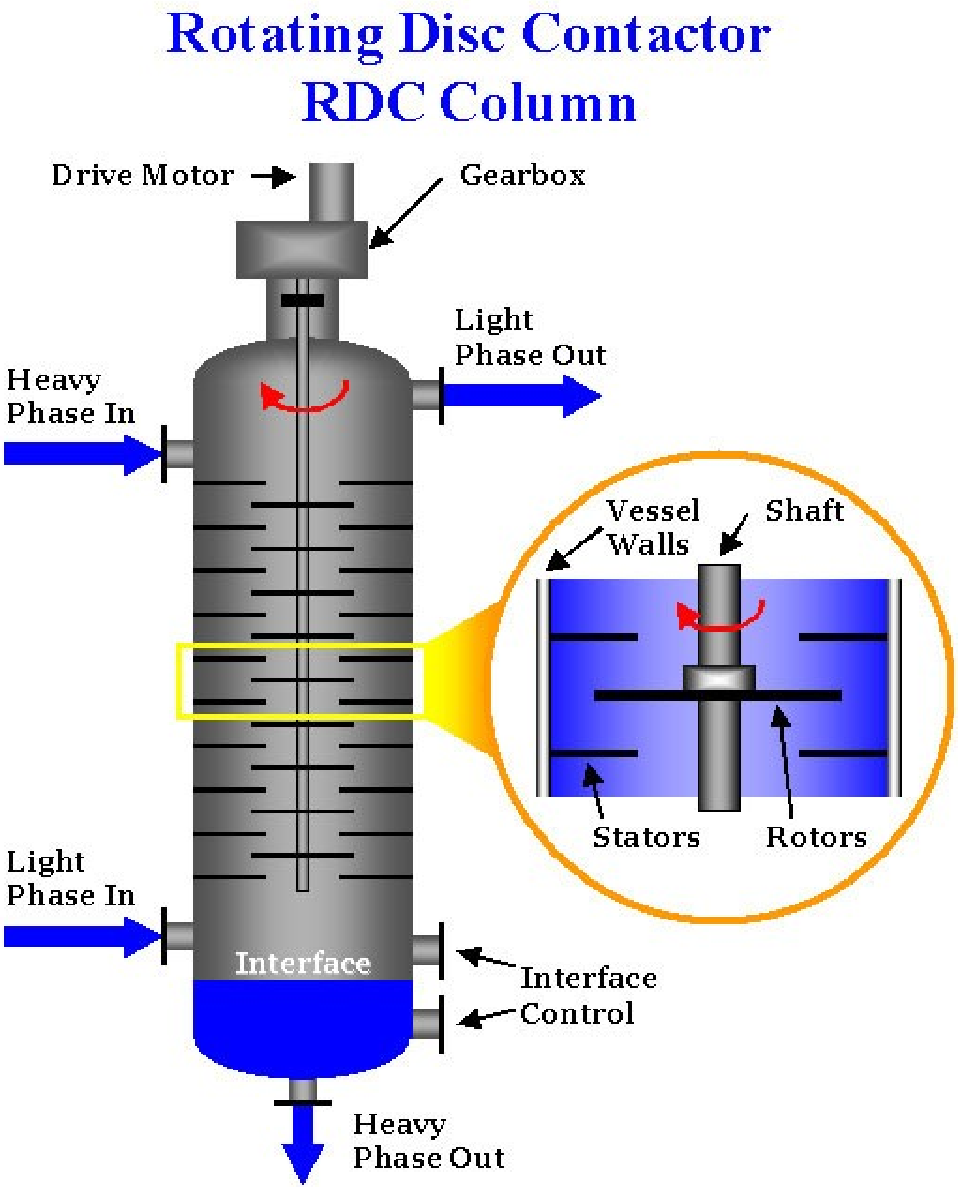
Resins are soluble in n-heptane; like asphaltenes they are largely composed of hydrogen and carbon, and contain small amounts of oxygen, sulphur and nitrogen. They are dark brown in colour, solid or semi-solid, and very polar in nature. This particular characteristic makes them strongly adhesive. They are dispersing agents or peptisers for the asphaltenes and the proportion of resins to asphaltenes governs to a degree the solution (Sol) or gelatinous (Gel) type character of the bitumen. Resins separated from bitumens are found to have molecular weights ranging from 500 to 50,000, a particle size of 1 nm to 5 nm and an H/C atomic ratio of 1.3 to 1.4.

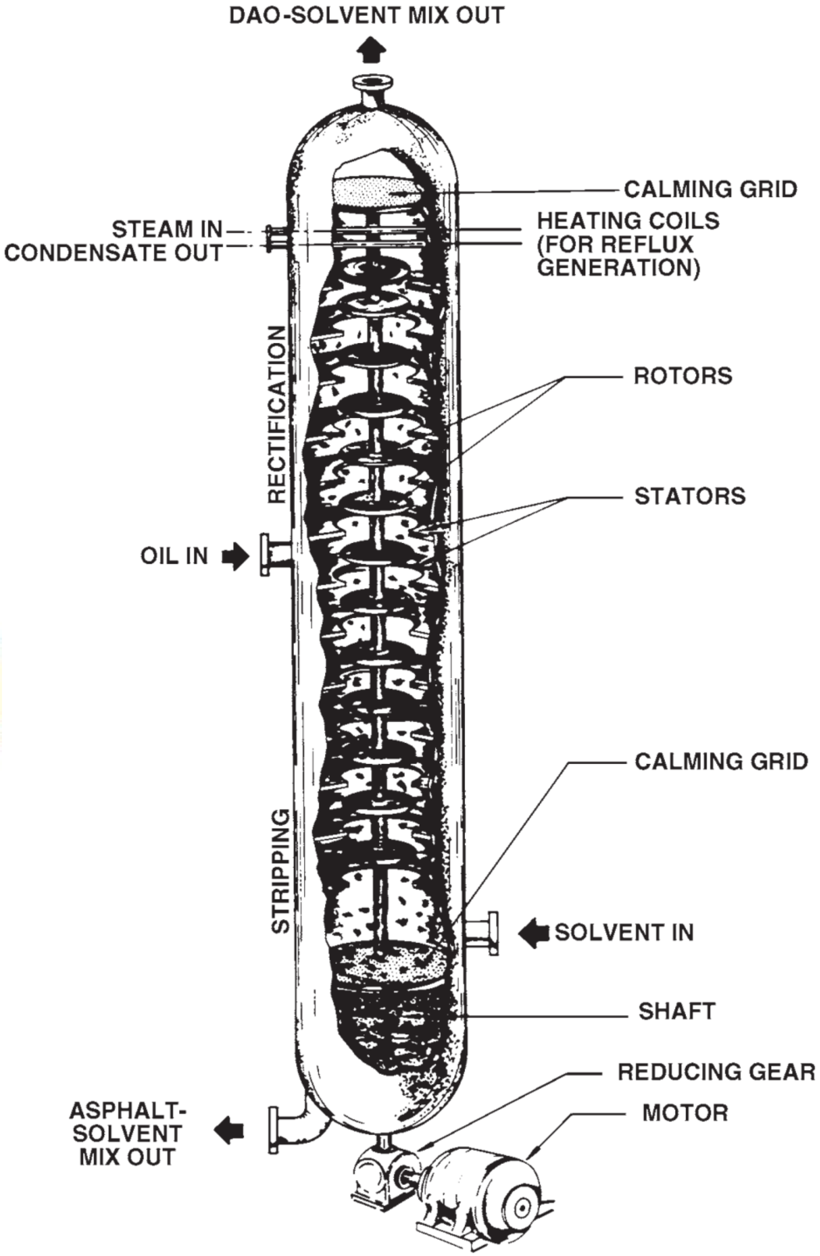
From: The shell bitumen industrial handbook, p. 53.

Propane deasphalting [1]



Rotating disc contactor (RDC) [5]





From: http://www.liquid-extraction.com/rdc-column.htm

Rotating disc contactor (RDC)

What would be the name of extractor if the moving rotor is made to stop in an RDC?

Propane deasphalting [1]

- Feed is mixed with a small amount of solvent to increase the fluidity of the feed.
- The feedstock is usually treated with 4 to 8 volumes of liquid propane.
- The extractor is usually a baffle column or rotating disc contactor.

Name the other types of column extractors.

- The extract phase contains from 15 to 20% by weight of oil with the remainder solvent. The raffinate phase contains from 30 to 50% propane by volume.
- The heavier the feedstock, the higher the ratio of propane to oil required.

Propane deasphalting

- “The propane deasphalting tower is operated at a pressure sufficiently high to maintain the solvent in the liquid phase. This is usually about 500 psig (3448 kPa).” [1].
- The critical temperature of propane is 96.8 °C so the upper limit may have to be set below this temperature (gases cannot be liquefied above critical temperature). The temperature is usually limited to 82 °C [9].
- Solvent to oil ratio is a function of feedstock properties and the required product specifications. An increase in the solvent to oil ratio increases the product quality.

Selection of solvent for liquid-liquid extraction: Class input

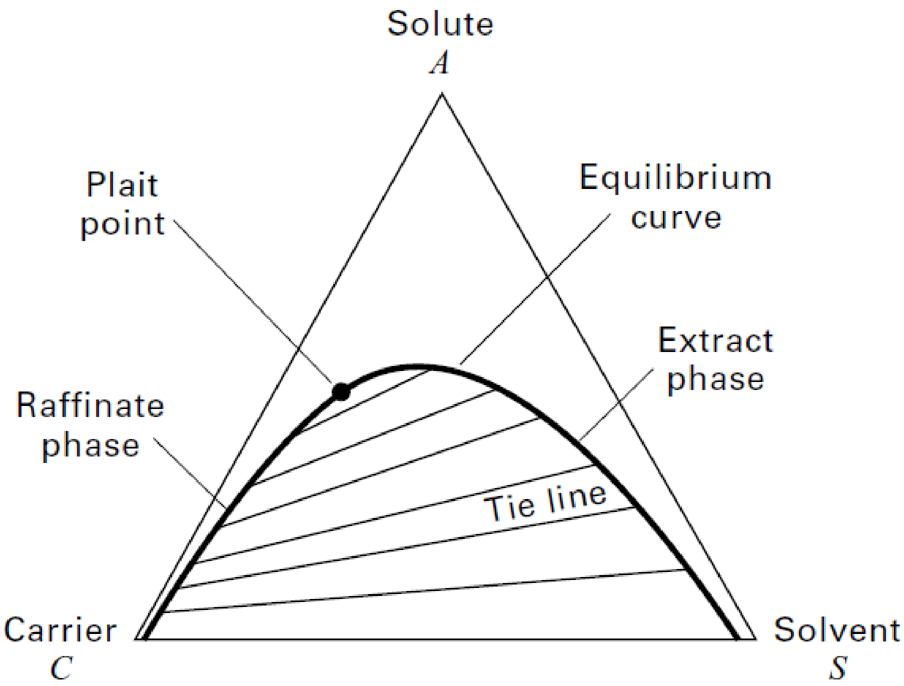
1. Start…

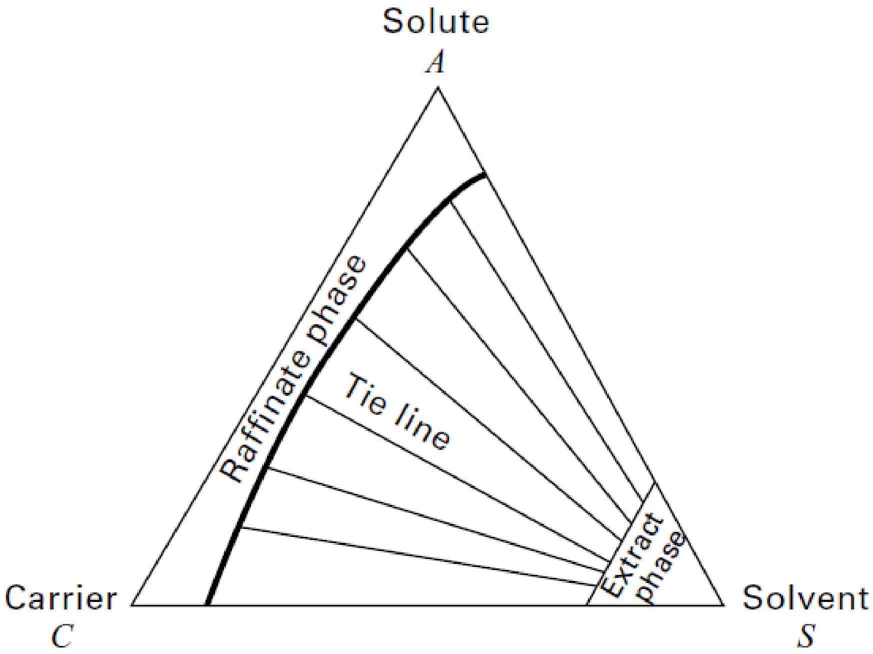
Selection of solvent for liquid-liquid extraction

1. High solubility of the solute in the solvent but low solubility or preferably immiscibility with feed solvent
2. Should not be reactive with the feed
3. Phases should have high density difference.
4. Solute and solvent should be economically separable.
5. High distribution coefficients
6. Should be stable and non-volatile under the conditions of operation
7. Should have low cost
8. Easy and regular availability (no inventory problems)
9. Non-corrosive, non-toxic, and environmental friendly.

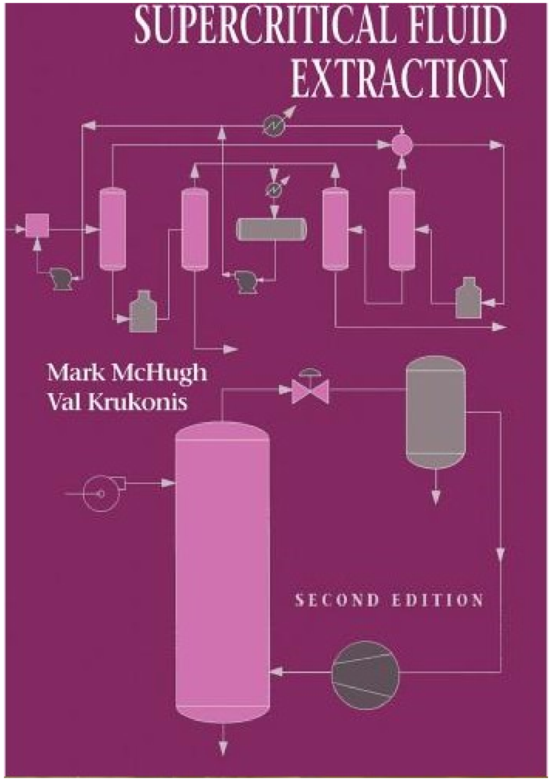
Selection of solvent for liquid-liquid extraction

Do you have an idea of ternary phase diagrams used in liquid-liquid extraction?





Propane deasphalting



SUPERCRITICAL FLUID EXTRACTION

Mark McHugh
Val Krukonis

SECOND EDITION

Butterworth-Heinemann. 1994.

https://books.google.com.pk/books?id=VTIvBQAAQBAJ&pg=PA149&dq=propane+deasphalting+ternary+diagram&hl=en&sa=X&ved=0CBoQ6AEwAGoVChMIxYzExdGKxwIVSF0sCh0ZFgbL#v=onepage&q&f=true

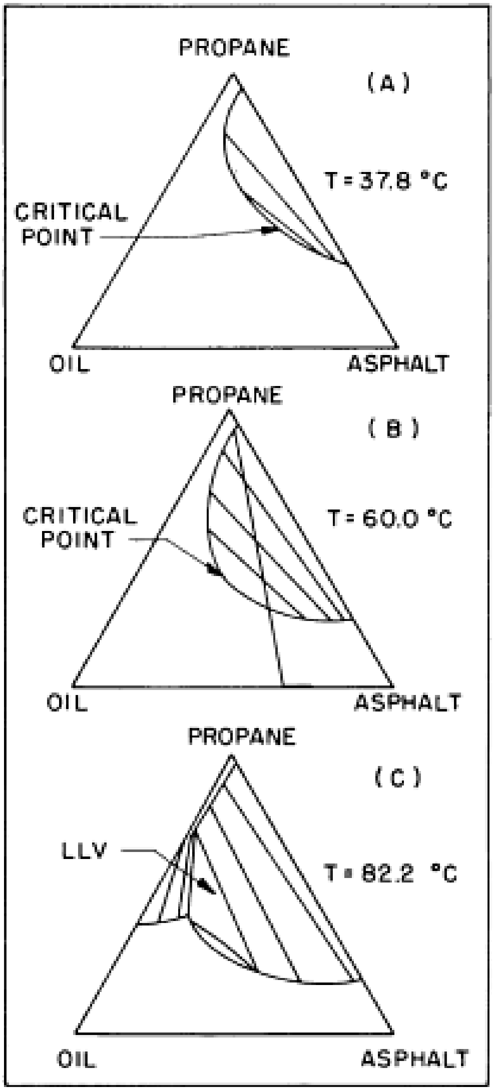


Figure 7.3 Ternary phase behavior of the asphalt–oil–propane mixture at three different temperatures (Wilson, Keith, and Haylett, 1936).

Propane deasphalting

How does the solvent to feed ratio affect the design and performance of a liquid-liquid extractor?

What are dispersed phase, continuous phase, flooding, dispersed phase holdup, mass transfer efficiency (overall mass transfer coefficient or overall height of transfer unit), interfacial tension, drop diameter, and drop distribution in relation to a continuous liquid-liquid extractor?

Propane deasphalting

“Propane, usually, is used as the solvent in deasphalting but it may also be used with ethane or butane in order to obtain the desired solvent properties. Propane has unusual solvent properties in that from 100 to 140 °F (40 to 60 °C) paraffins are very soluble in propane, but the solubility decreases with an increase temperature until at the critical temperature of propane [206 °F (96.8 °C)] all hydrocarbons become insoluble. In the range of 100 to 206 °F (40 to 96.8 °C) the high molecular weight asphaltenes and resins are largely insoluble in propane” [1]

Propane deasphalting

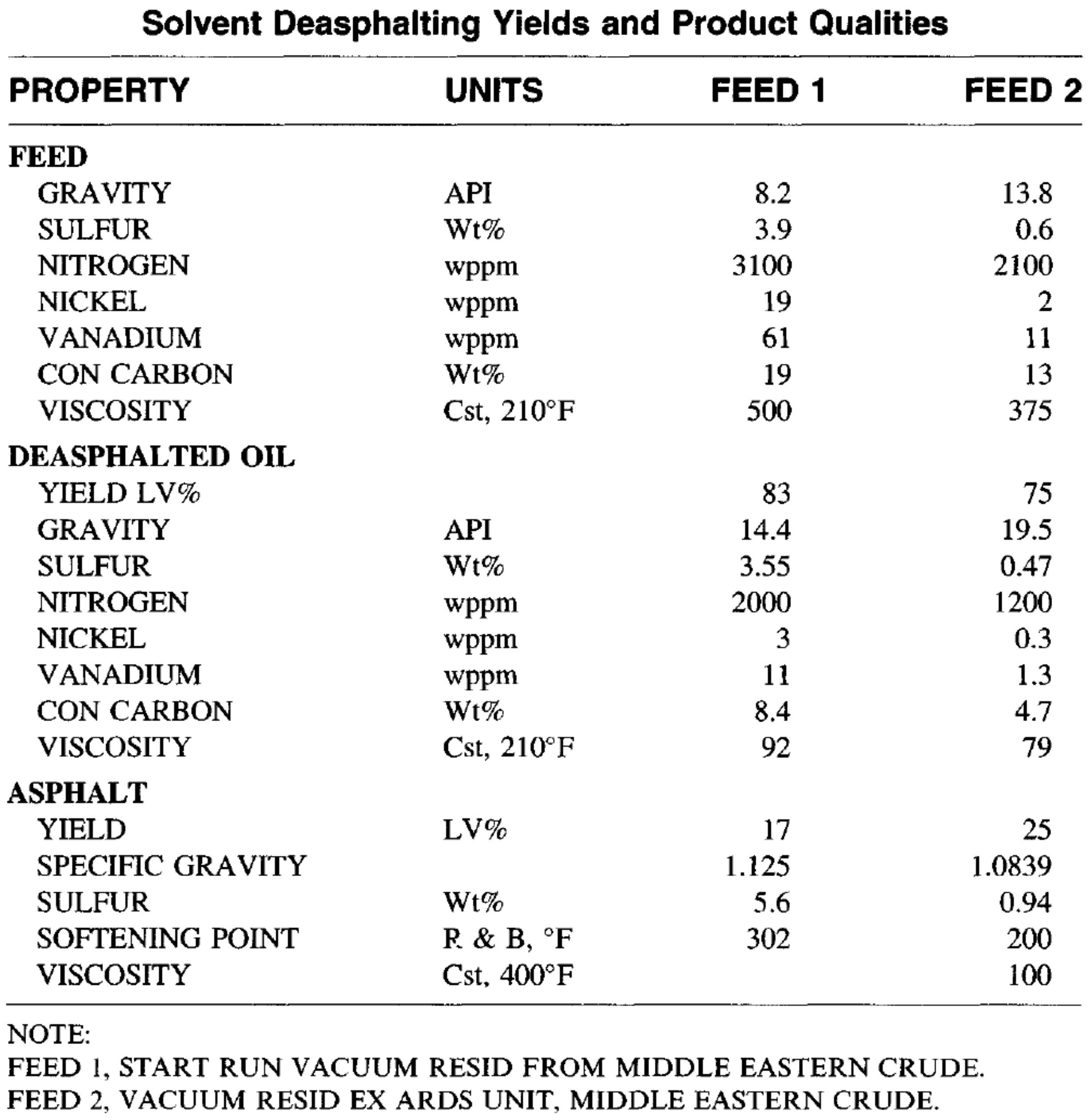
As the metal, sulfur, and nitrogen are generally concentrated in the larger molecules, the metal, sulfur, and nitrogen content of deasphalted oil is considerably reduced as shown in the next slide [3].

Asphalt may be burned to produce energy, but due to fluidity problems and stack gas issues (high cost for gas cleaning) it is commonly used for road paving, water proofing, and insulation. Asphalt may be air treated (asphalt blowing) to improve its properties.

Residue oxidation or asphalt blowing is carried out to increase softening point by removing aromatics and polar aromatics.

http://en.academic.ru/dic.nsf/enwiki/206538

Propane deasphalting [3]



Solvent Deasphalting Yields and Product Qualities

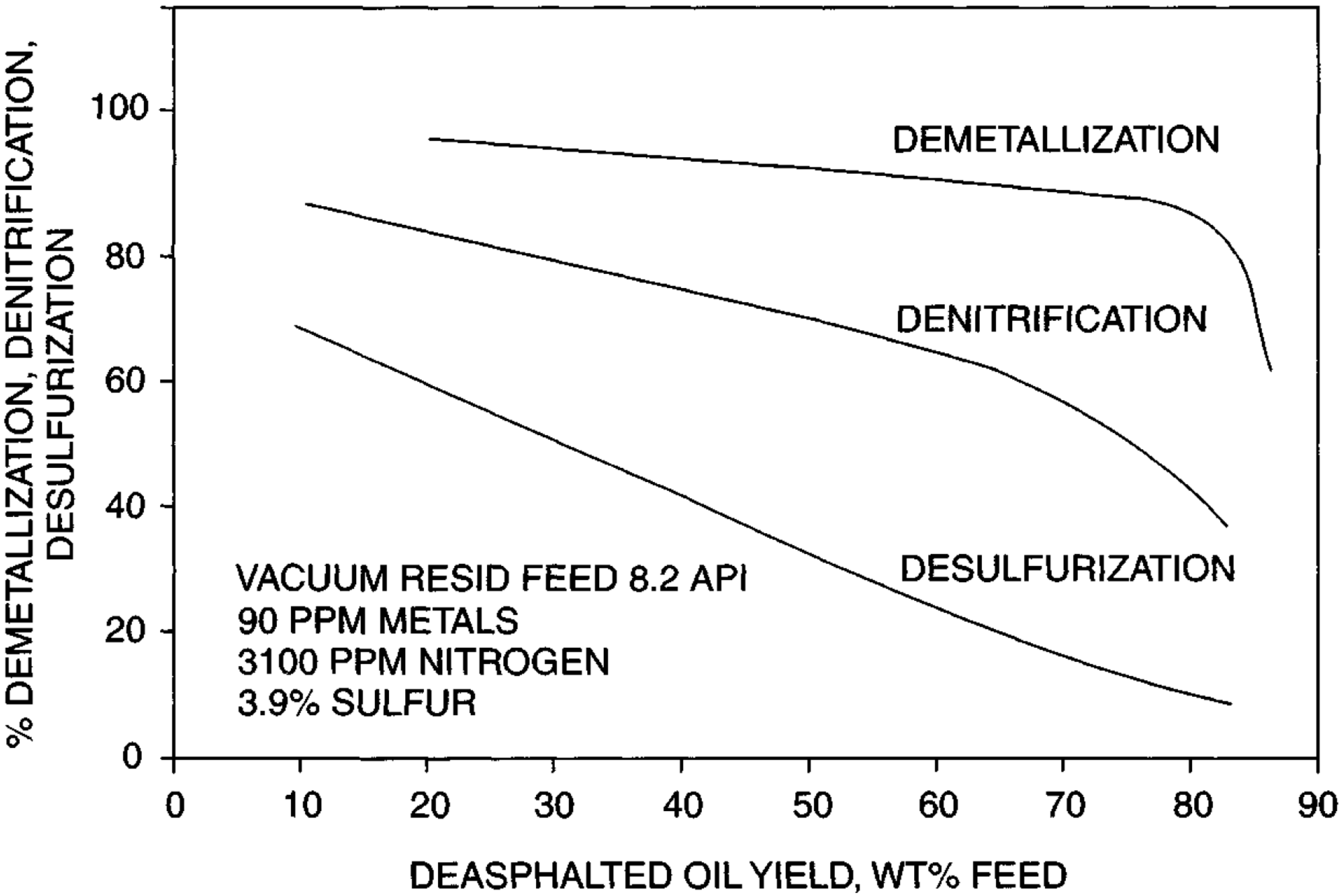
PROPERTY	UNITS	FEED 1	FEED 2
FEED			
GRAVITY	API	8.2	13.8
SULFUR	Wt%	3.9	0.6
NITROGEN	wppm	3100	2100
NICKEL	wppm	19	2
VANADIUM	wppm	61	11
CON CARBON	Wt%	19	13
VISCOSITY	Cst, 210°F	500	375
DEASPHALTED OIL			
YIELD LV%		83	75
GRAVITY	API	14.4	19.5
SULFUR	Wt%	3.55	0.47
NITROGEN	wppm	2000	1200
NICKEL	wppm	3	0.3
VANADIUM	wppm	11	1.3
CON CARBON	Wt%	8.4	4.7
VISCOSITY	Cst, 210°F	92	79
ASPHALT			
YIELD	LV%	17	25
SPECIFIC GRAVITY		1.125	1.0839
SULFUR	Wt%	5.6	0.94
SOFTENING POINT	R & B, °F	302	200
VISCOSITY	Cst, 400°F		100

NOTE:
FEED 1, START RUN VACUUM RESID FROM MIDDLE EASTERN CRUDE.
FEED 2, VACUUM RESID EX ARDS UNIT, MIDDLE EASTERN CRUDE.

Propane deasphalting [9]

Crude source	Arab	West Texas	California	Canadian	Kuwait	Kuwait
Feedstock						
Crude, vol%	23.0	29.2	20.0	16.0	22.2	32.3
Gravity, °API	6.8	12.0	6.3	9.6	5.6	8.1
Conradson carbon, wt%	15.0	12.1	22.2	18.9	24.0	19.7
SUS at 210°F	75,000	526	9600	1740	14,200	3270
Metals, wppm						
Ni	73.6	16.0	139	46.6	29.9	29.7
V	365.0	27.6	136	30.9	110.0	89
Cu + Fe	15.5	14.8	94	40.7	13.7	7.5
Deasphalted oil						
Vol% feed	49.8	66.0	52.8	67.8	45.6	54.8
Gravity, °API	18.1	19.6	18.3	17.8	16.2	17.1
Conradson carbon, wt%	5.9	2.2	5.3	5.4	4.5	5.4
SUS at 210°F	615	113	251	250	490	656
Metals, wppm						
Ni	3.5	1.0	8.1	3.9	0.9	0.6
V	12.4	1.3	2.3	1.4	0.7	4.0
Cu + Fe	0.2	0.8	3.5	0.2	0.8	0.8
Asphalt						
Vol% feed	50.2	34.0	47.2	32.2	54.4	45.2
Gravity, °API	–1.3	–0.9	–5.1	–5.1	–1.3	–2.0

Propane deasphalting [3]

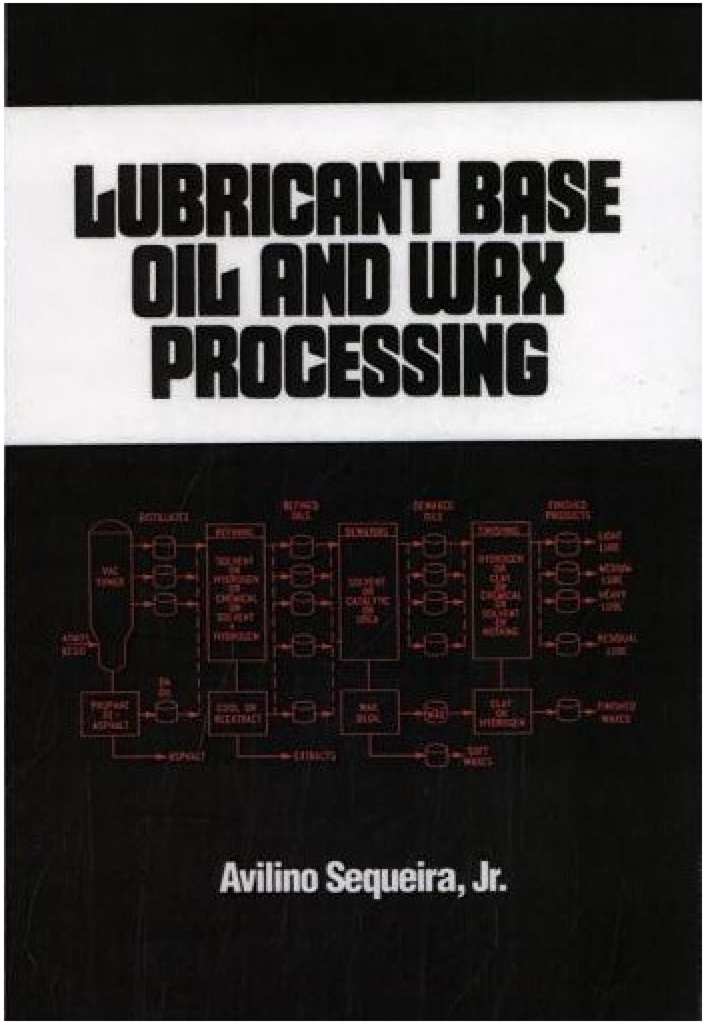


Propane deasphalting [10]

Generally deasphalting:

1. decreases asphaltene and resin content
2. decreases metal amounts
3. decreases carbon residue
4. increases pour point?
5. increases API gravity (decreases specific gravity)
6. improves color
7. decreases aromatic content
8. decreases nitrogen and sulfur content
9. decreases viscosity

Propane deasphalting [10]



LUBRICANT BASE OIL AND WAX PROCESSING

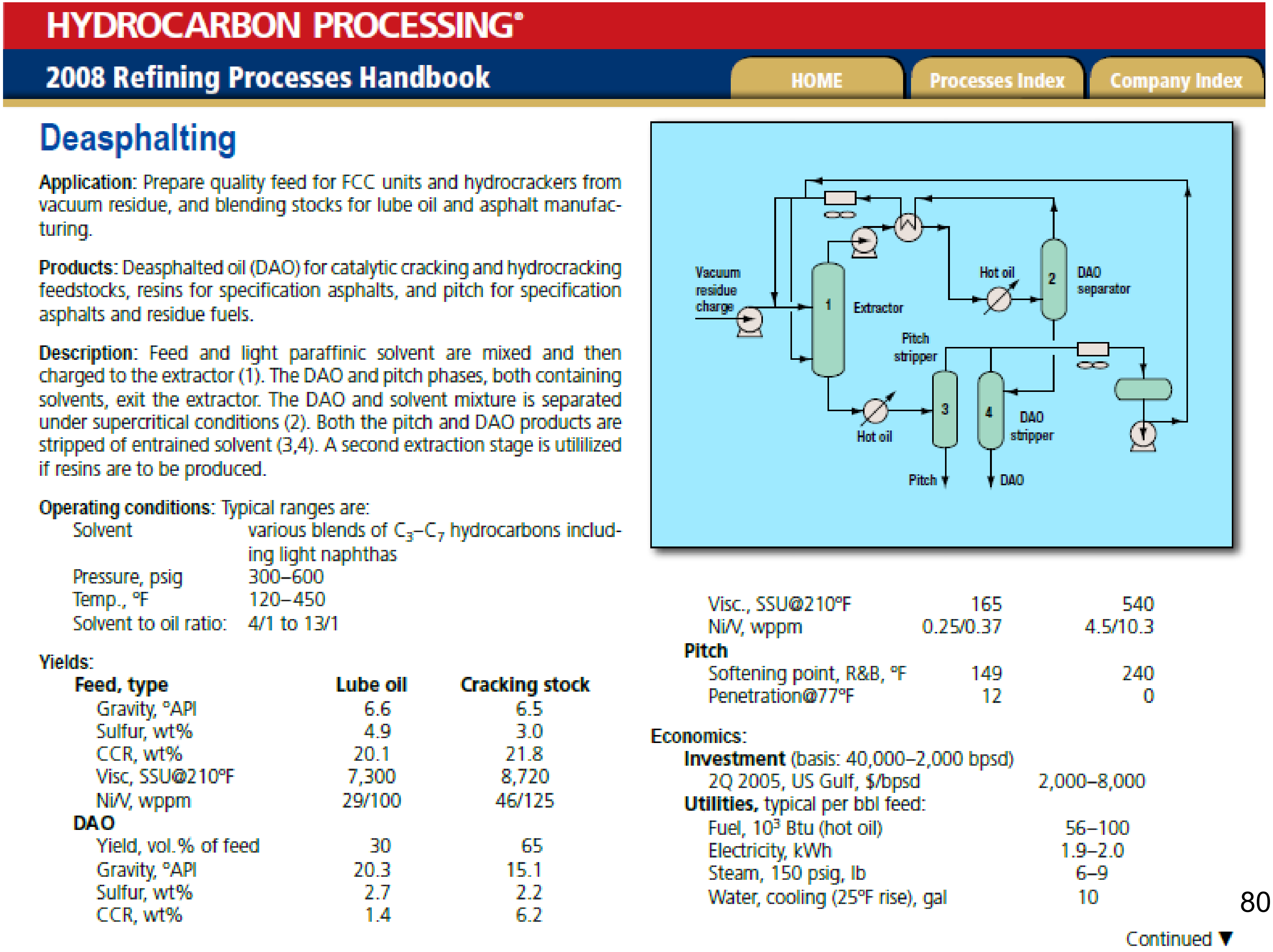
Avilino Sequeira, Jr.

Macrcel-Dekker.
1994.

For more details and design consideration.
pp. 53-80 (Chapter 4)

Available at:
https://books.google.com.pk/books?id=TAzJvJ1HmFQC&printsec=frontcover#v=onepage&q&f=false (accessed on 02-Aug-2015)

Propane deasphalting [11]



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2008 Refining Processes Handbook

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Deasphalting

Application: Prepare quality feed for FCC units and hydrocrackers from vacuum residue, and blending stocks for lube oil and asphalt manufacturing.

Products: Deasphalted oil (DAO) for catalytic cracking and hydrocracking feedstocks, resins for specification asphalts, and pitch for specification asphalts and residue fuels.

Description: Feed and light paraffinic solvent are mixed and then charged to the extractor (1). The DAO and pitch phases, both containing solvents, exit the extractor. The DAO and solvent mixture is separated under supercritical conditions (2). Both the pitch and DAO products are stripped of entrained solvent (3,4). A second extraction stage is utililized if resins are to be produced.

Operating conditions: Typical ranges are:

Solvent	various blends of C_3–C_7 hydrocarbons including light naphthas
Pressure, psig	300–600
Temp., °F	120–450
Solvent to oil ratio:	4/1 to 13/1

Yields:

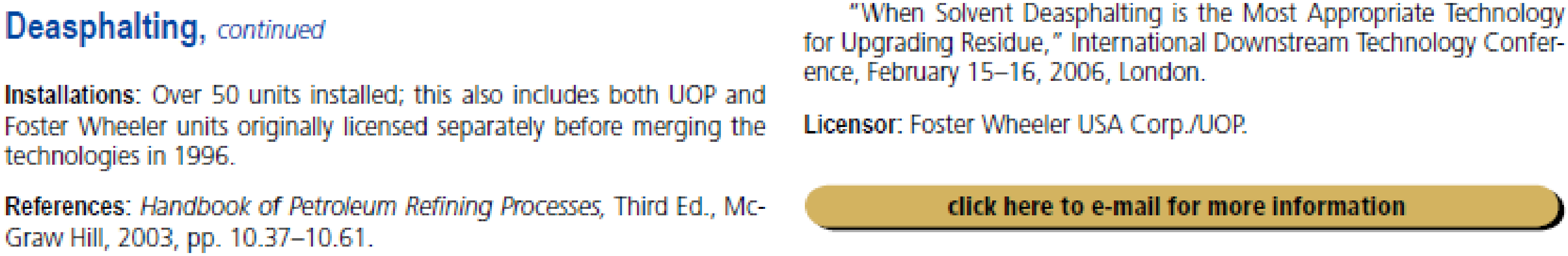
Feed, type	**Lube oil**	**Cracking stock**
Gravity, °API	6.6	6.5
Sulfur, wt%	4.9	3.0
CCR, wt%	20.1	21.8
Visc, SSU@210°F	7,300	8,720
Ni/V, wppm	29/100	46/125
DAO		
Yield, vol.% of feed	30	65
Gravity, °API	20.3	15.1
Sulfur, wt%	2.7	2.2
CCR, wt%	1.4	6.2
Visc., SSU@210°F	165	540
Ni/V, wppm	0.25/0.37	4.5/10.3
Pitch		
Softening point, R&B, °F	149	240
Penetration@77°F	12	0

Economics:

Investment (basis: 40,000–2,000 bpsd)	
2Q 2005, US Gulf, \$/bpsd	2,000–8,000
Utilities, typical per bbl feed:	
Fuel, 10^3 Btu (hot oil)	56–100
Electricity, kWh	1.9–2.0
Steam, 150 psig, lb	6–9
Water, cooling (25°F rise), gal	10

Continued ▼

Propane deasphalting [11]



Deasphalting, *continued*

Installations: Over 50 units installed; this also includes both UOP and Foster Wheeler units originally licensed separately before merging the technologies in 1996.

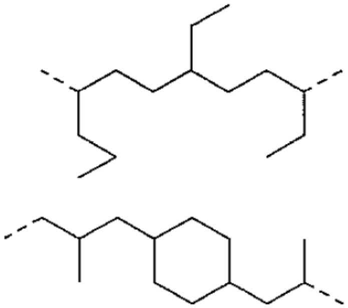
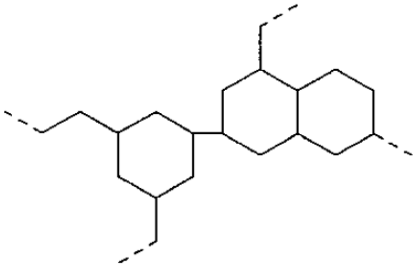
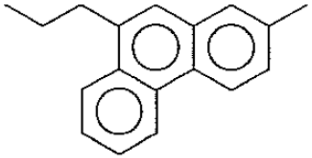
References: *Handbook of Petroleum Refining Processes,* Third Ed., McGraw Hill, 2003, pp. 10.37–10.61.

"When Solvent Deasphalting is the Most Appropriate Technology for Upgrading Residue," International Downstream Technology Conference, February 15–16, 2006, London.

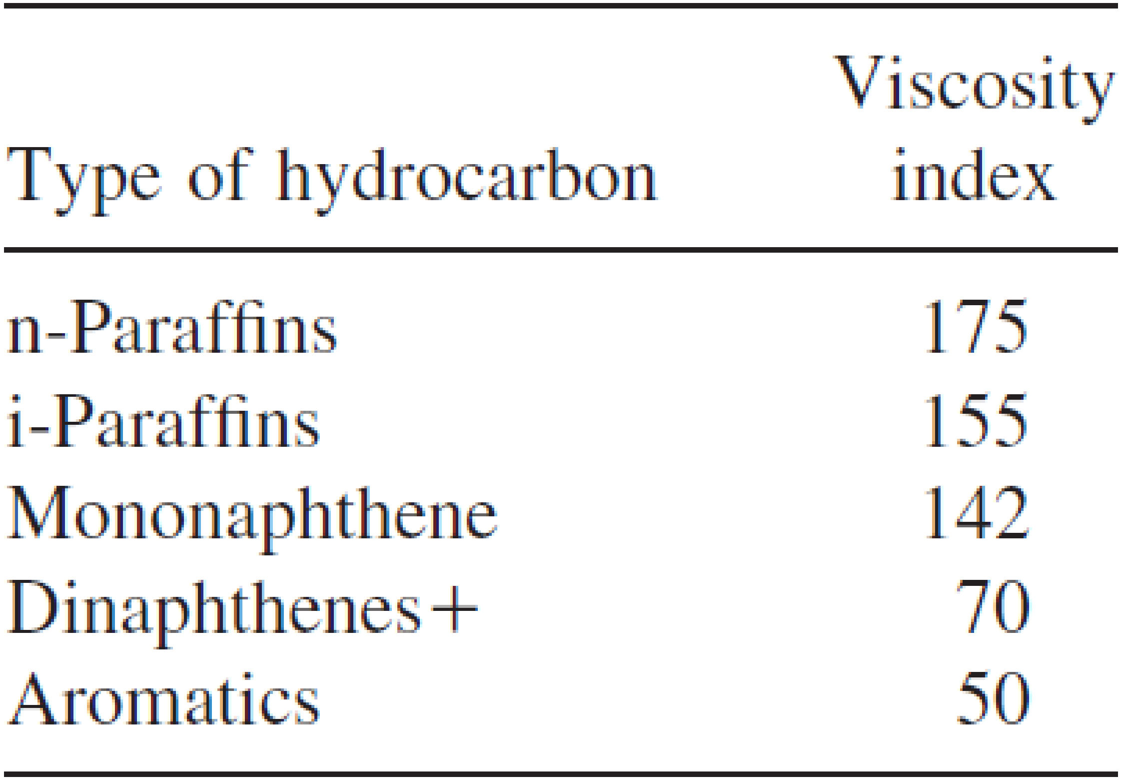
Licensor: Foster Wheeler USA Corp./UOP.

http://sts.aiche.org/webfm_send/410
[accessed on: 17-Aug-2015]

Characteristics of various families in lube oil stock [4]

Families	Typical structure	Main properties	
		Favorable	Unfavorable
Straight chain paraffins		High viscosity index	High pour point
Branched paraffins and paraffins with few rings		Good to high viscosity Good resistance to oxidation	
Naphthenics		Good resistance to oxidation Low pour point	Low viscosity index
Aromatics		Generally low-pour point-	Low viscosity index Very poor resistance to oxidation

Characteristics of various families in lube oil stock [1]



Type of hydrocarbon	Viscosity index
n-Paraffins	175
i-Paraffins	155
Mononaphthene	142
Dinaphthenes+	70
Aromatics	50

Solvent extraction: Purposes (lube oil extraction) [1]

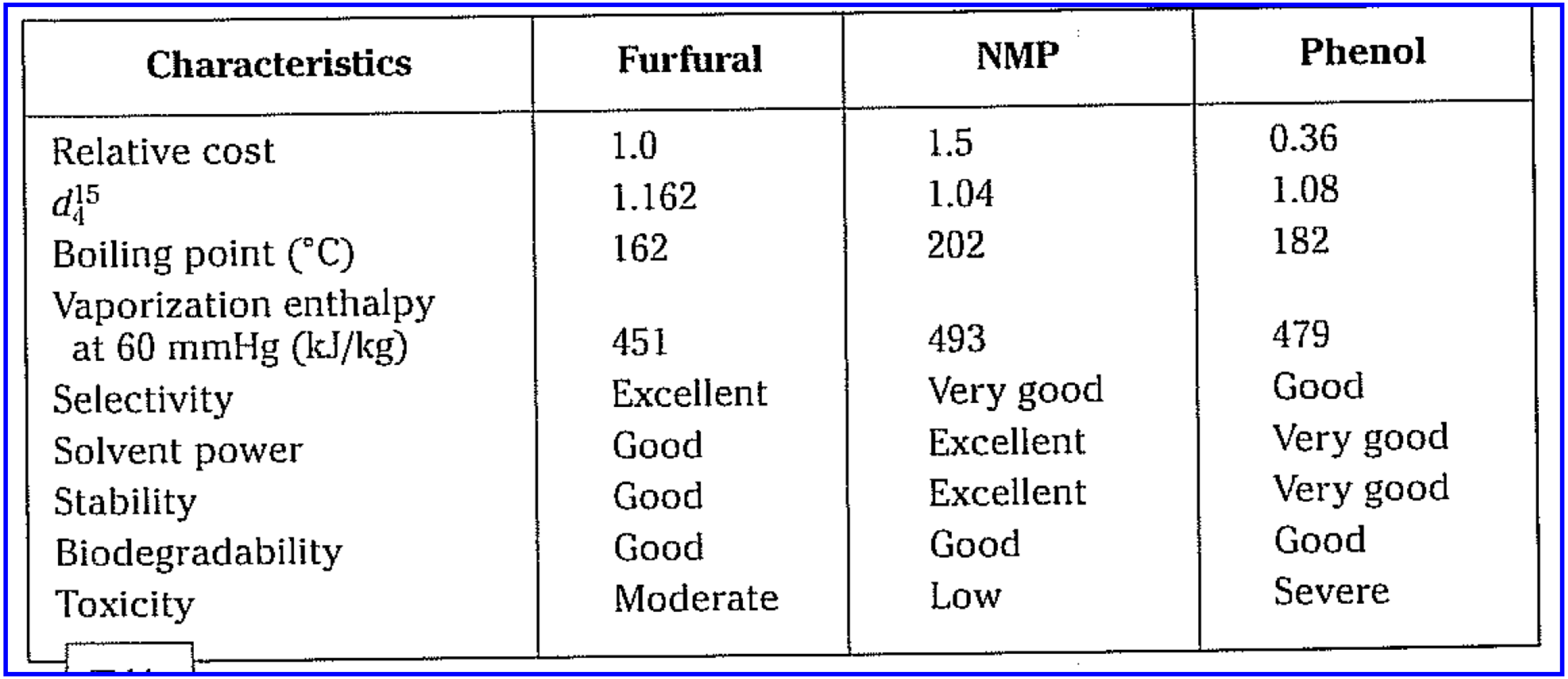
The purpose of solvent extraction is to remove the aromatics from the lube oil fraction and in doing so to improve the:

1. Viscosity index (VI)
2. Oxidation resistance
3. Color
4. Coke forming tendency, and
5. Sludge forming tendency.

Solvents commonly applied

1. Furfural
2. Phenol
3. N-methyl-2-pyrrolidone (NMP)

Comparison between the three solvents [4]



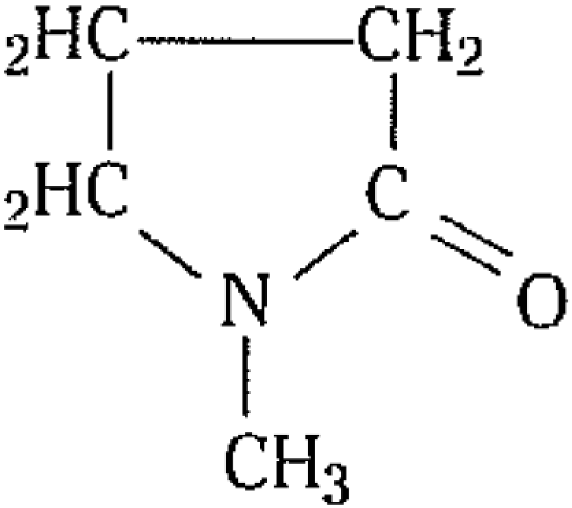
Characteristics	Furfural	NMP	Phenol
Relative cost	1.0	1.5	0.36
d_4^{15}	1.162	1.04	1.08
Boiling point (°C)	162	202	182
Vaporization enthalpy at 60 mmHg (kJ/kg)	451	493	479
Selectivity	Excellent	Very good	Good
Solvent power	Good	Excellent	Very good
Stability	Good	Excellent	Very good
Biodegradability	Good	Good	Good
Toxicity	Moderate	Low	Severe

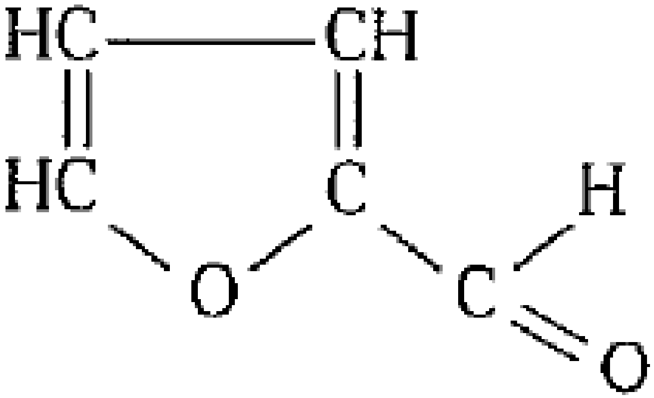
Phenol extraction [1]

Phenol being toxic is not studied further here.

Comparison between the NMP and furfural

NMP





Furfural

NMP advantages over furfural [4]

- Better stability
- Better oxidation resistance
- Less carryover in the raffinate and the extract
- Higher solvent power towards aromatics
- Lower process temperature
- Less toxicity

NMP advantages over furfural [4]

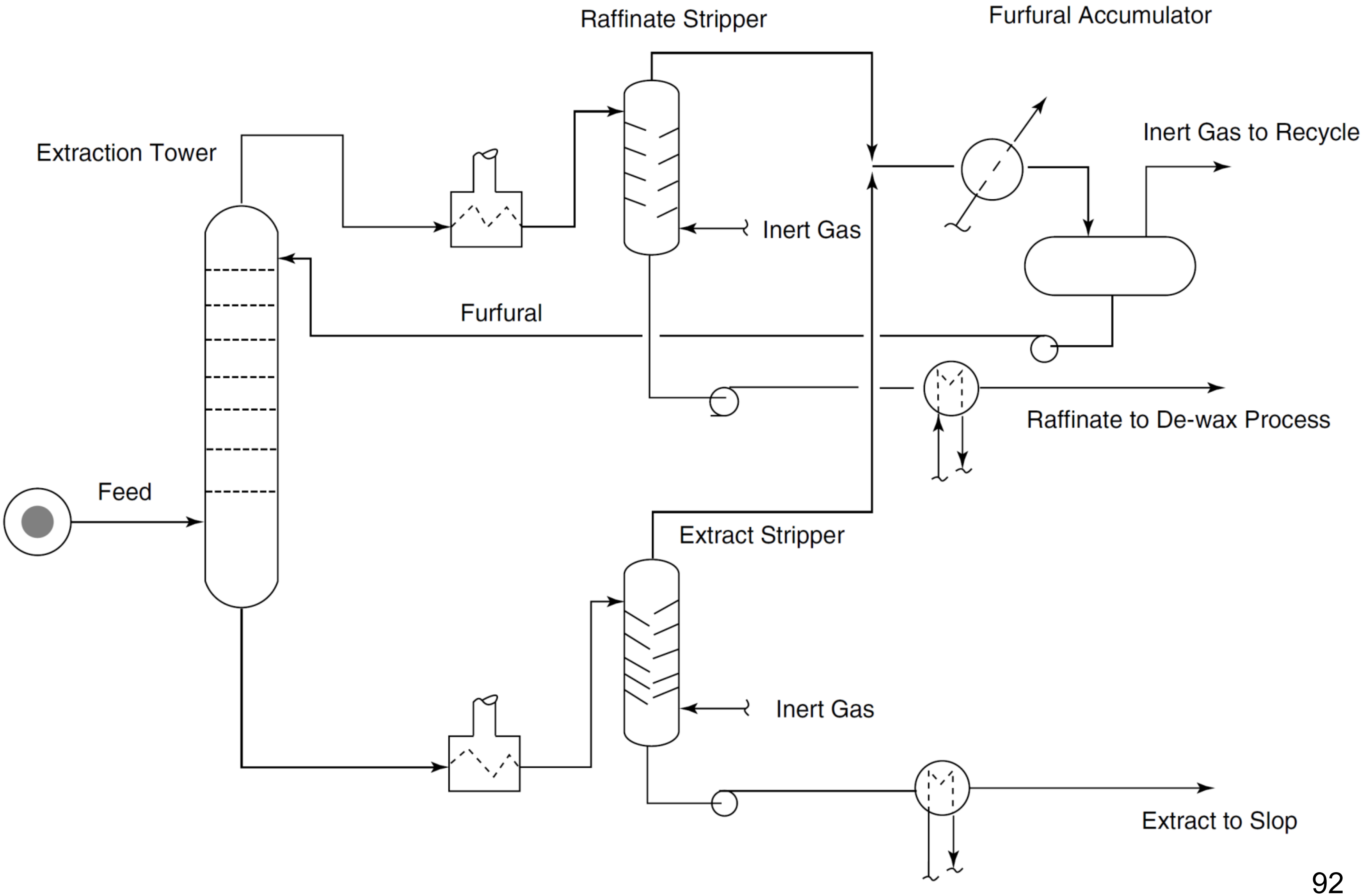
- Since NMP is much more stable than furfural, the pretreatment (deaeration) section is unnecessary and the feed can directly be let into the extraction tower.
- Solvent ratios in an NMP unit are significantly lower than for furfural, i.e., it has higher solvent power. A smaller plant size is therefore required.
- Solvent injection temperatures are lower by 10 to 20 °C for the same final viscosity index (VI) and an identical raffinate yield.
- Furfural is sensitive to oxidation and to the presence of water, which significantly lower extraction performance.

NMP disadvantages over furfural [4]

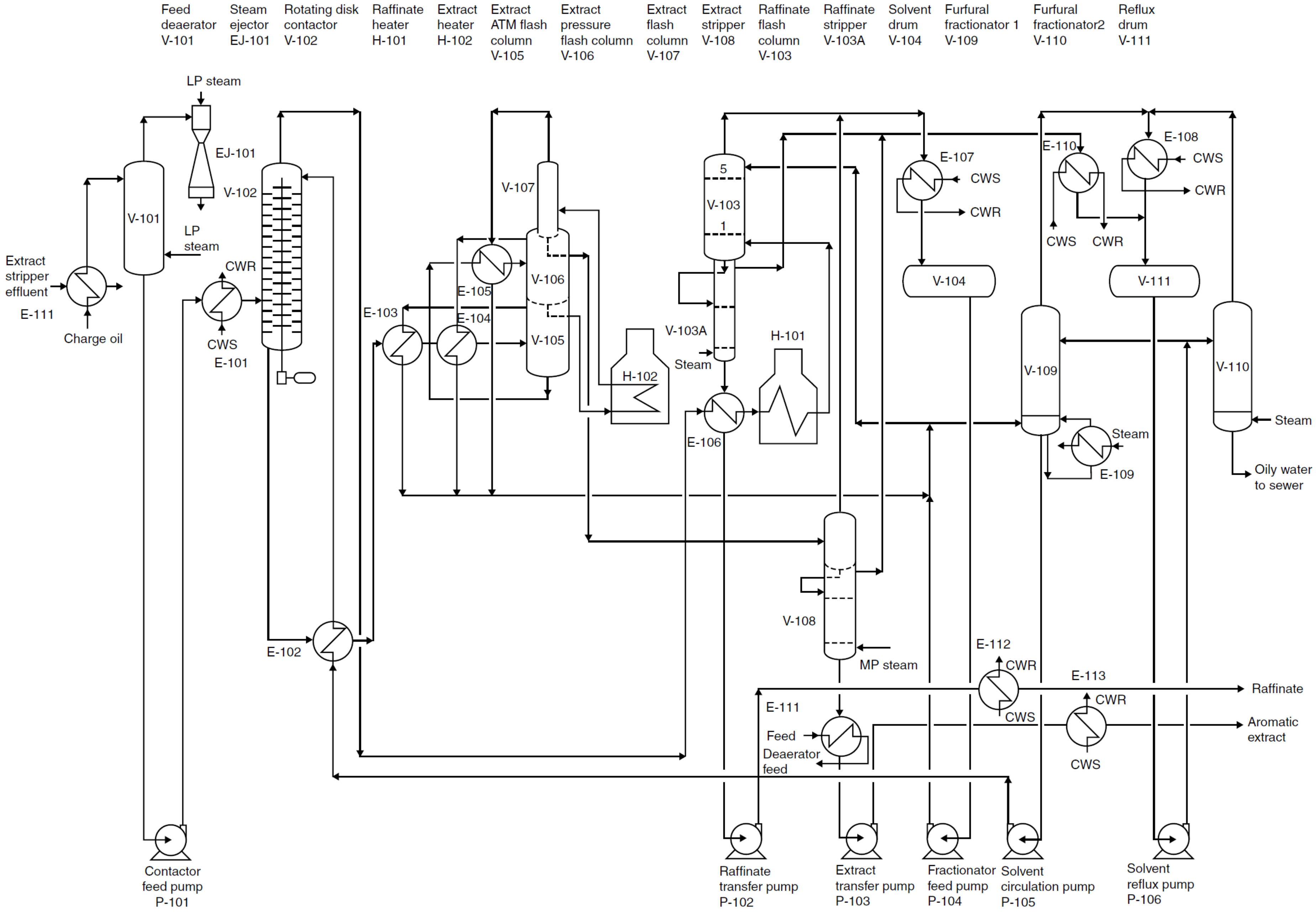
- Lower specific gravity
- Less selectivity
- Higher boiling points

NMP's higher boiling point and heat of vaporization requires higher temperatures and energy consumption is also greater than for furfural recovery.

Simplified furfural extraction process [6]



Rather detailed furfural extraction process [12]



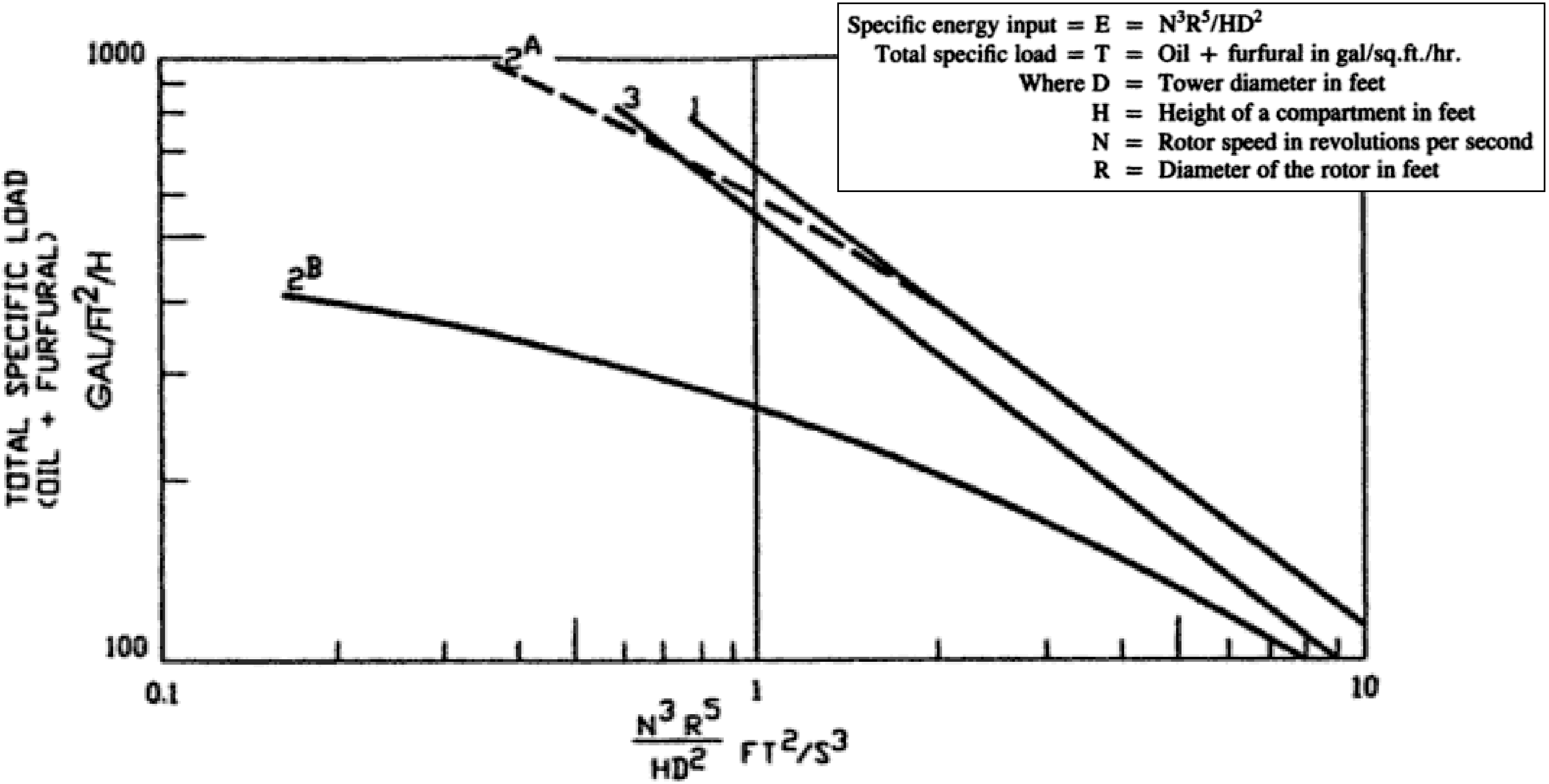
Furfural extraction

- The furfural is fed at the top while the oil flows countercurrently from the bottom.
- The extractor is commonly a packed column with Raschig rings or an RDC [1]. The main advantage of using RDC is that by varying the speed of rotor a wide range of throughputs can be handled [10].
- The oil behaves as a continuous phase while furfural acts as a dispersed phase.
- Furfural to oil ratio ranges between 2:1 for light stocks and 4.5:1 for heavy stocks [1].

Factors for furfural extraction process

- Extraction temperature depends upon the feed characteristics and adjust the viscosity of the oil-furfural mixture and miscibility of the furfural with oil.
- A part of the extract phase may be recycled and may affect the efficiency of the extraction.
- The extraction column operates between 50 and 200 psig [6] and at a top temperature of 105 to 150 °C [1]. The temperature gradient betweeen top and bottom of the extractor is between 30 to 50 °C [1].

Capacity curves for RDC [10]



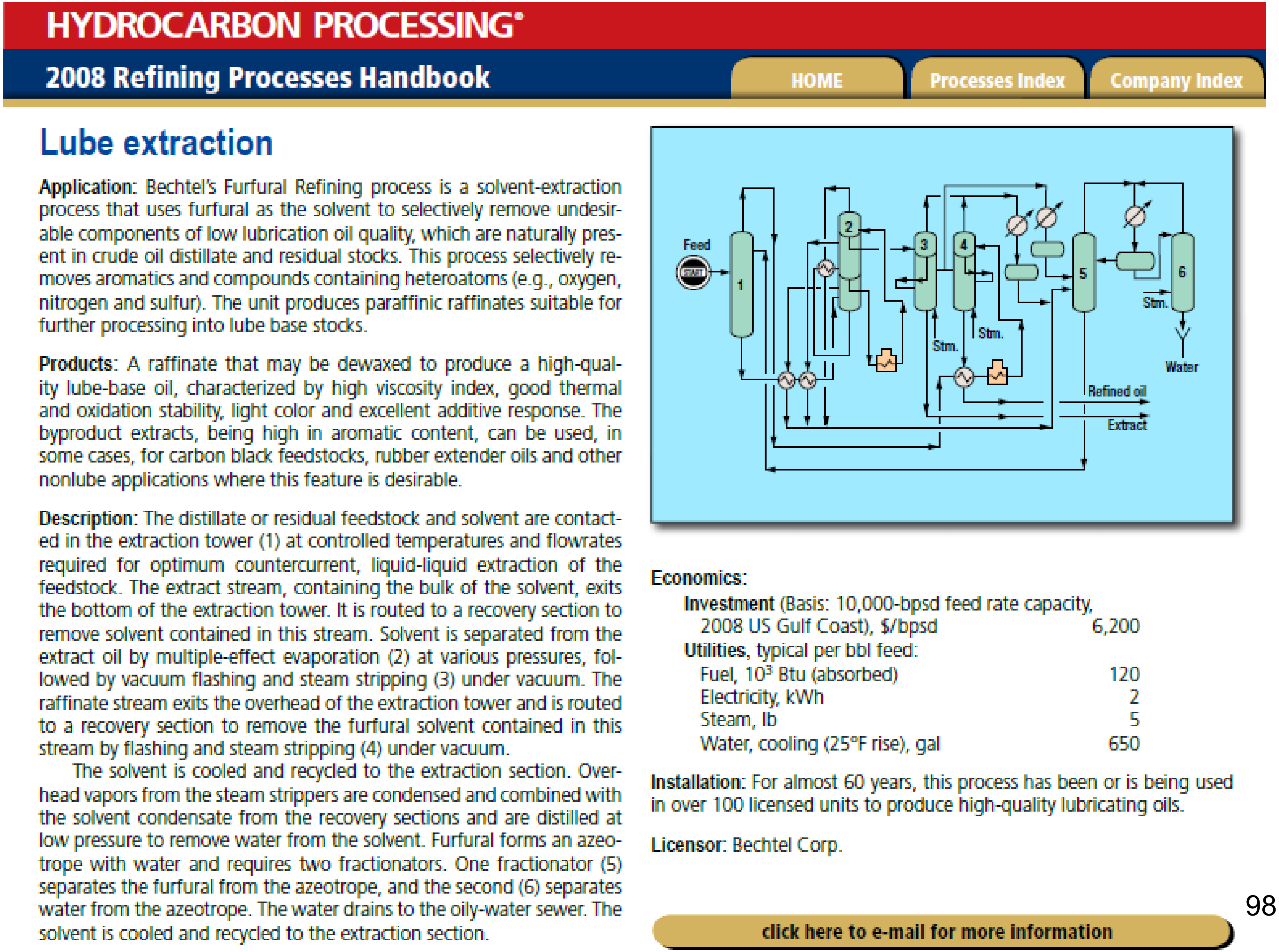
Specific energy input = E = N^3R^5/HD^2
Total specific load = T = Oil + furfural in gal/sq.ft./hr.
Where D = Tower diameter in feet
H = Height of a compartment in feet
N = Rotor speed in revolutions per second
R = Diameter of the rotor in feet

Figure 5.24 Flooding curves for various feedstocks with furfural. 1, Light and medium distillates—solvent ratio 2. O; 2, Heavy distillates—solvent ratio 3.0 (A = no emulsification, B = strong emulsification); 3, Deasphalted oils - solvent ratio 3.4.) (Reprinted from *Petroleum Refiner*, September, 1955, Gulf Publishing Co.)

Furfural extraction [6]

Untreated oil	Feed A	Feed B
Viscosity index	70	89
Gravity °API	25	28
Viscosity, SSU @ 210°F	55	44
Treated oil		
Yield vol %	69	55
Viscosity index (de-waxed)	102	113

Furfural extraction [11]



HYDROCARBON PROCESSING®

2008 Refining Processes Handbook

HOME Processes Index Company Index

Lube extraction

Application: Bechtel's Furfural Refining process is a solvent-extraction process that uses furfural as the solvent to selectively remove undesirable components of low lubrication oil quality, which are naturally present in crude oil distillate and residual stocks. This process selectively removes aromatics and compounds containing heteroatoms (e.g., oxygen, nitrogen and sulfur). The unit produces paraffinic raffinates suitable for further processing into lube base stocks.

Products: A raffinate that may be dewaxed to produce a high-quality lube-base oil, characterized by high viscosity index, good thermal and oxidation stability, light color and excellent additive response. The byproduct extracts, being high in aromatic content, can be used, in some cases, for carbon black feedstocks, rubber extender oils and other nonlube applications where this feature is desirable.

Description: The distillate or residual feedstock and solvent are contacted in the extraction tower (1) at controlled temperatures and flowrates required for optimum countercurrent, liquid-liquid extraction of the feedstock. The extract stream, containing the bulk of the solvent, exits the bottom of the extraction tower. It is routed to a recovery section to remove solvent contained in this stream. Solvent is separated from the extract oil by multiple-effect evaporation (2) at various pressures, followed by vacuum flashing and steam stripping (3) under vacuum. The raffinate stream exits the overhead of the extraction tower and is routed to a recovery section to remove the furfural solvent contained in this stream by flashing and steam stripping (4) under vacuum.

The solvent is cooled and recycled to the extraction section. Overhead vapors from the steam strippers are condensed and combined with the solvent condensate from the recovery sections and are distilled at low pressure to remove water from the solvent. Furfural forms an azeotrope with water and requires two fractionators. One fractionator (5) separates the furfural from the azeotrope, and the second (6) separates water from the azeotrope. The water drains to the oily-water sewer. The solvent is cooled and recycled to the extraction section.

Economics:

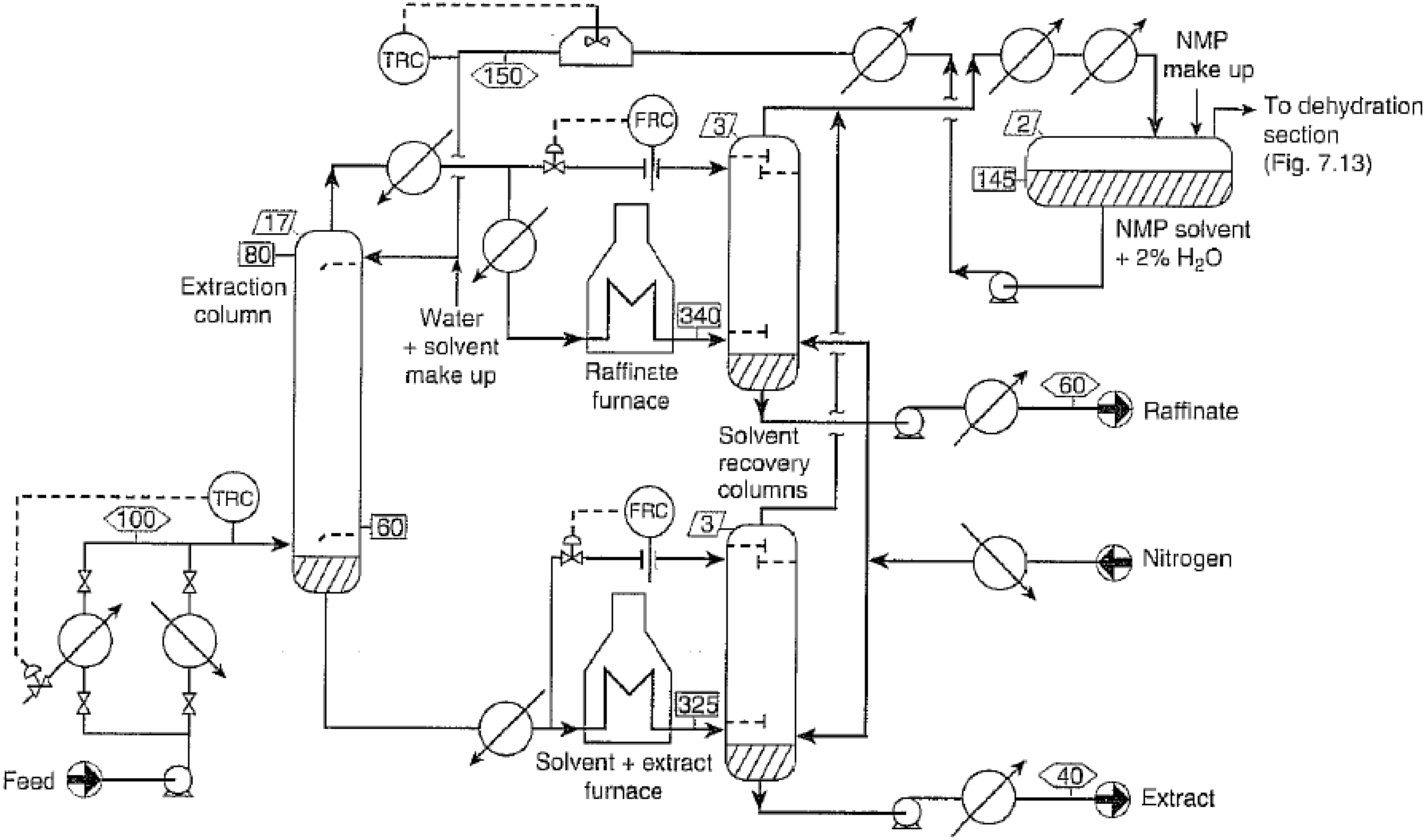
Investment (Basis: 10,000-bpsd feed rate capacity, 2008 US Gulf Coast), $/bpsd	6,200
Utilities, typical per bbl feed:	
Fuel, 10^3 Btu (absorbed)	120
Electricity, kWh	2
Steam, lb	5
Water, cooling (25°F rise), gal	650

Installation: For almost 60 years, this process has been or is being used in over 100 licensed units to produce high-quality lubricating oils.

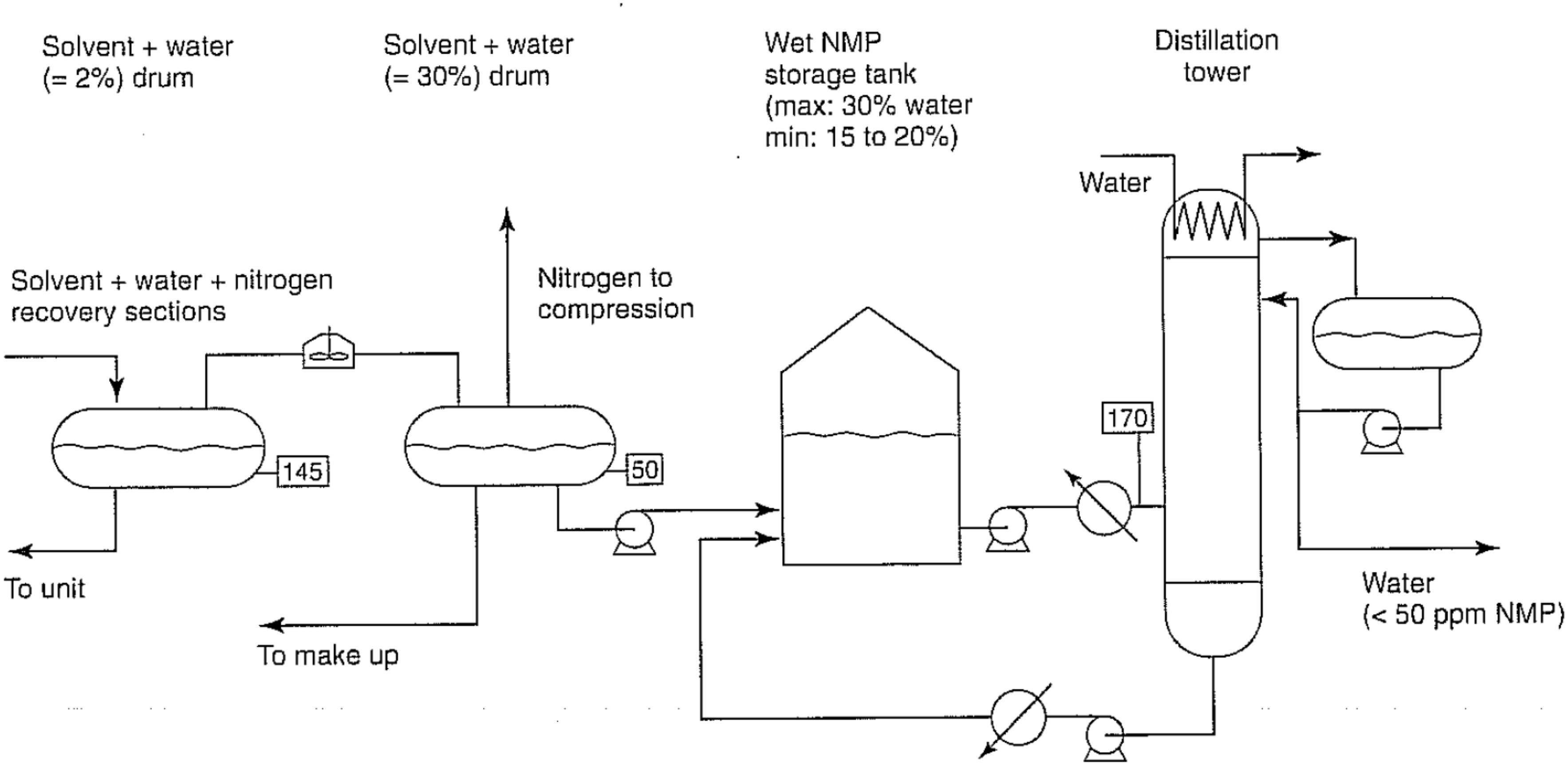
Licensor: Bechtel Corp.

click here to e-mail for more information

NMP extraction [4] (Not for the exam.)



NMP extraction [4] (Not for the exam.)



NMP extraction: Water addition [4]

NMP solvent power is very high towards aromatics, and also considerable towards paraffins, which consequently lowers the raffinate yield. To attenuate the solvent power of NMP, a small amount of water (0.8 to 3.0 wt%) is added and the solvent that circulates in the unit is a mixture of NMP and water. The amount of water required in the solvent depends on the target level of the extraction.

NMP extraction: Drying section [4]

After cooling to approximately 50°C, NMP containing some 30 wt% water is temporarily stored in a tank. When the tank has become full enough, the dehydration section is started up.

Modification of the existing plant

As mentioned before phenol is toxic and no more required for the extraction process in the existing or new installations. Also some refiners prefer to replace furfural with NMP and modify the plant accordingly.

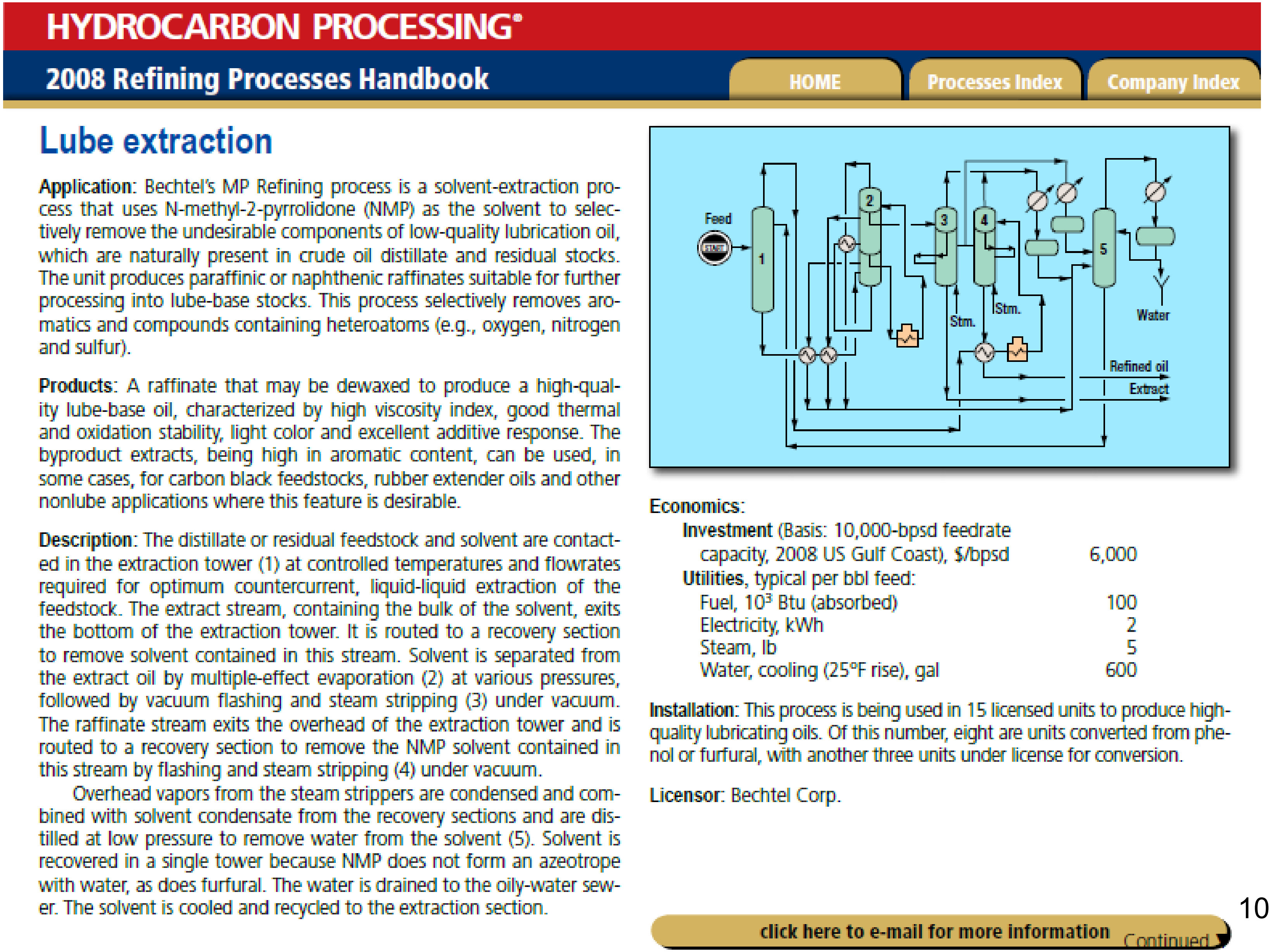
Reasons may include [10]:

- ✓ Significant increase in refining capacity
- ✓ Significant reduction in energy costs
- ✓ Use of marginal quality crudes
- ✓ Reduced maintenance costs
- ✓ Reduced solvent toxicity
- ✓ Reduced solvent losses

Modification of the existing plant

Give your suggestions to modify an existing phenol extraction plant to be replaced by an NMP extraction plant.

NMP extraction [11]



HYDROCARBON PROCESSING®

2008 Refining Processes Handbook

Lube extraction

Application: Bechtel's MP Refining process is a solvent-extraction process that uses N-methyl-2-pyrrolidone (NMP) as the solvent to selectively remove the undesirable components of low-quality lubrication oil, which are naturally present in crude oil distillate and residual stocks. The unit produces paraffinic or naphthenic raffinates suitable for further processing into lube-base stocks. This process selectively removes aromatics and compounds containing heteroatoms (e.g., oxygen, nitrogen and sulfur).

Products: A raffinate that may be dewaxed to produce a high-quality lube-base oil, characterized by high viscosity index, good thermal and oxidation stability, light color and excellent additive response. The byproduct extracts, being high in aromatic content, can be used, in some cases, for carbon black feedstocks, rubber extender oils and other nonlube applications where this feature is desirable.

Description: The distillate or residual feedstock and solvent are contacted in the extraction tower (1) at controlled temperatures and flowrates required for optimum countercurrent, liquid-liquid extraction of the feedstock. The extract stream, containing the bulk of the solvent, exits the bottom of the extraction tower. It is routed to a recovery section to remove solvent contained in this stream. Solvent is separated from the extract oil by multiple-effect evaporation (2) at various pressures, followed by vacuum flashing and steam stripping (3) under vacuum. The raffinate stream exits the overhead of the extraction tower and is routed to a recovery section to remove the NMP solvent contained in this stream by flashing and steam stripping (4) under vacuum.

Overhead vapors from the steam strippers are condensed and combined with solvent condensate from the recovery sections and are distilled at low pressure to remove water from the solvent (5). Solvent is recovered in a single tower because NMP does not form an azeotrope with water, as does furfural. The water is drained to the oily-water sewer. The solvent is cooled and recycled to the extraction section.

Economics:

Investment (Basis: 10,000-bpsd feedrate capacity, 2008 US Gulf Coast), $/bpsd	6,000
Utilities, typical per bbl feed:	
Fuel, 10^3 Btu (absorbed)	100
Electricity, kWh	2
Steam, lb	5
Water, cooling (25°F rise), gal	600

Installation: This process is being used in 15 licensed units to produce high-quality lubricating oils. Of this number, eight are units converted from phenol or furfural, with another three units under license for conversion.

Licensor: Bechtel Corp.

click here to e-mail for more information

Continued

Dewaxing [1, 4]

The straight chain and slightly branched paraffinic compounds tend to crystallize under ordinary temperature conditions. However, at low temperature such as –20 °C, the oil needs to be in a liquid state in the engine crankcase. If crystallize or solidify, it will cause flow problems.

The dewaxing unit is required to lower the cloud and pour points of the oil by eliminating the compounds that crystallize at relatively higher temperature.

Dewaxing [10]

“Although the cold settling-pressure filtration processes and centrifuge dewaxing processes have for the most part been replaced by solvent dewaxing, these older processes are still used to a limited degree.” [10]

Solvent dewaxing

- The solvent reduces the viscosity of the oil and facilitate in pumping and filtration.
- “The most common dewaxing process is based on crystallization with a solvent that modifies the conditions of thermodynamic equilibrium solely by its presence in the liquid. The ideal solvent should dissolve the oil and precipitate all the wax. Additionally, in precipitating the wax crystal structure should be loose so that oil can be filtered through the wax”. [6]

Dewaxing: Solvents [1, 4]

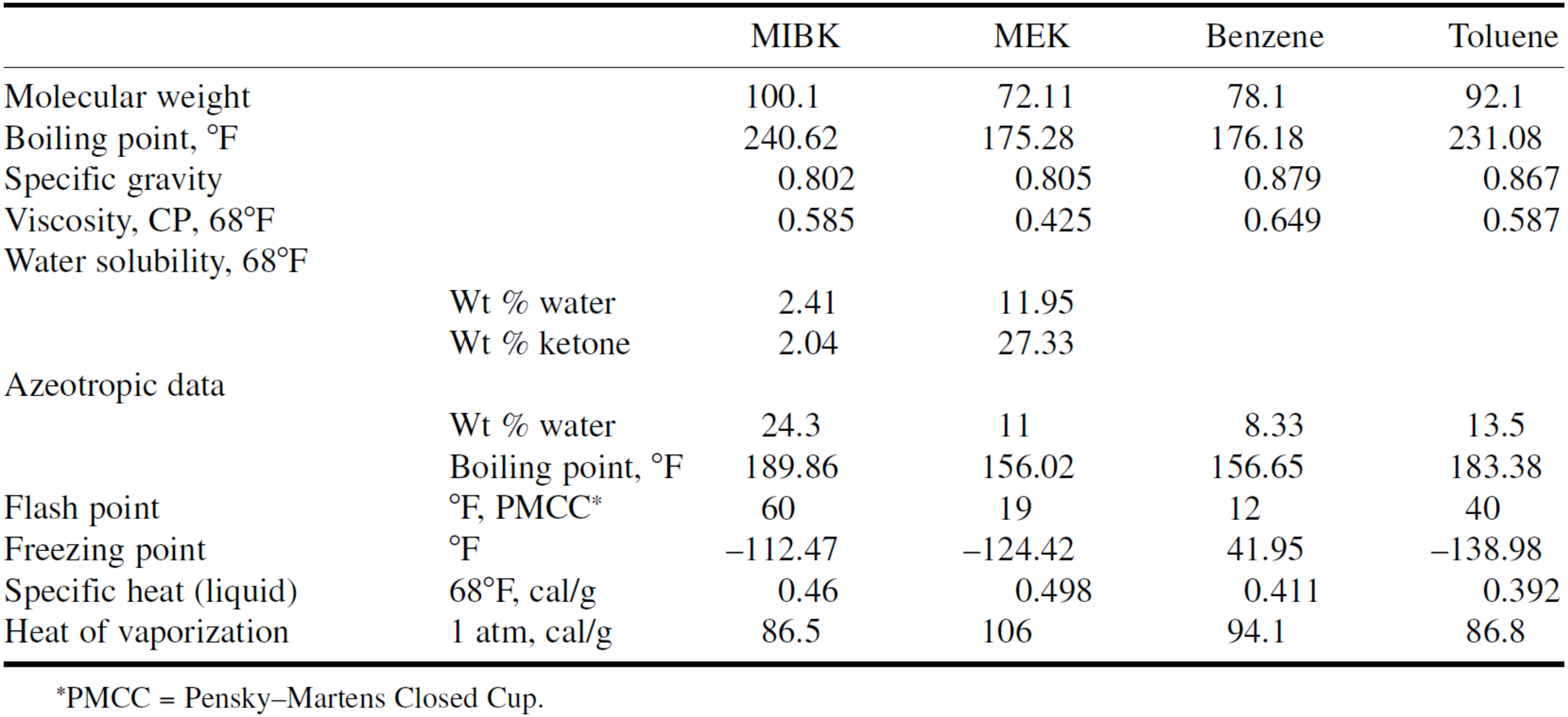
- Mixture of methylethylketone (MEK) and toluene
- Methylisobutylketone (MIBK)
- Dichloromethane
- Trichloroethylene
- Propane
- Mixture of ethylene chloride and benzene
- Mixture of acetone and benzene

Dewaxing: Solvents [1, 4]

- MEK displays low solvent power for paraffinic compounds (and therefore good selectivity)
- Toluene has excellent solvent power for base stocks

The proportions in the mixture of these two solvents can be optimized.

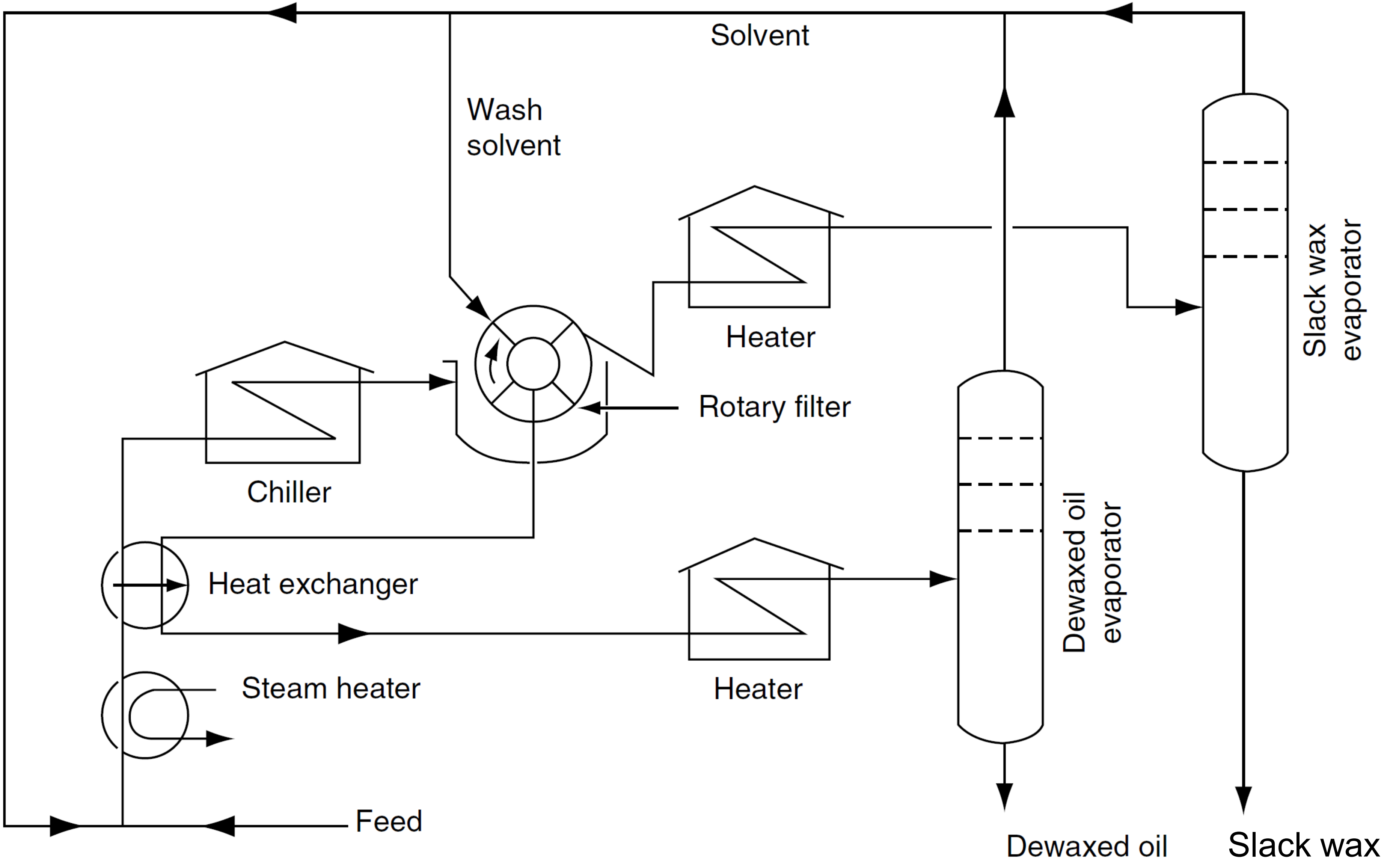
Dewaxing: Solvents [12]



		MIBK	MEK	Benzene	Toluene
Molecular weight		100.1	72.11	78.1	92.1
Boiling point, °F		240.62	175.28	176.18	231.08
Specific gravity		0.802	0.805	0.879	0.867
Viscosity, CP, 68°F		0.585	0.425	0.649	0.587
Water solubility, 68°F					
	Wt % water	2.41	11.95		
	Wt % ketone	2.04	27.33		
Azeotropic data					
	Wt % water	24.3	11	8.33	13.5
	Boiling point, °F	189.86	156.02	156.65	183.38
Flash point	°F, PMCC*	60	19	12	40
Freezing point	°F	–112.47	–124.42	41.95	–138.98
Specific heat (liquid)	68°F, cal/g	0.46	0.498	0.411	0.392
Heat of vaporization	1 atm, cal/g	86.5	106	94.1	86.8

*PMCC = Pensky–Martens Closed Cup.

Simplified dewaxing PFD [4]



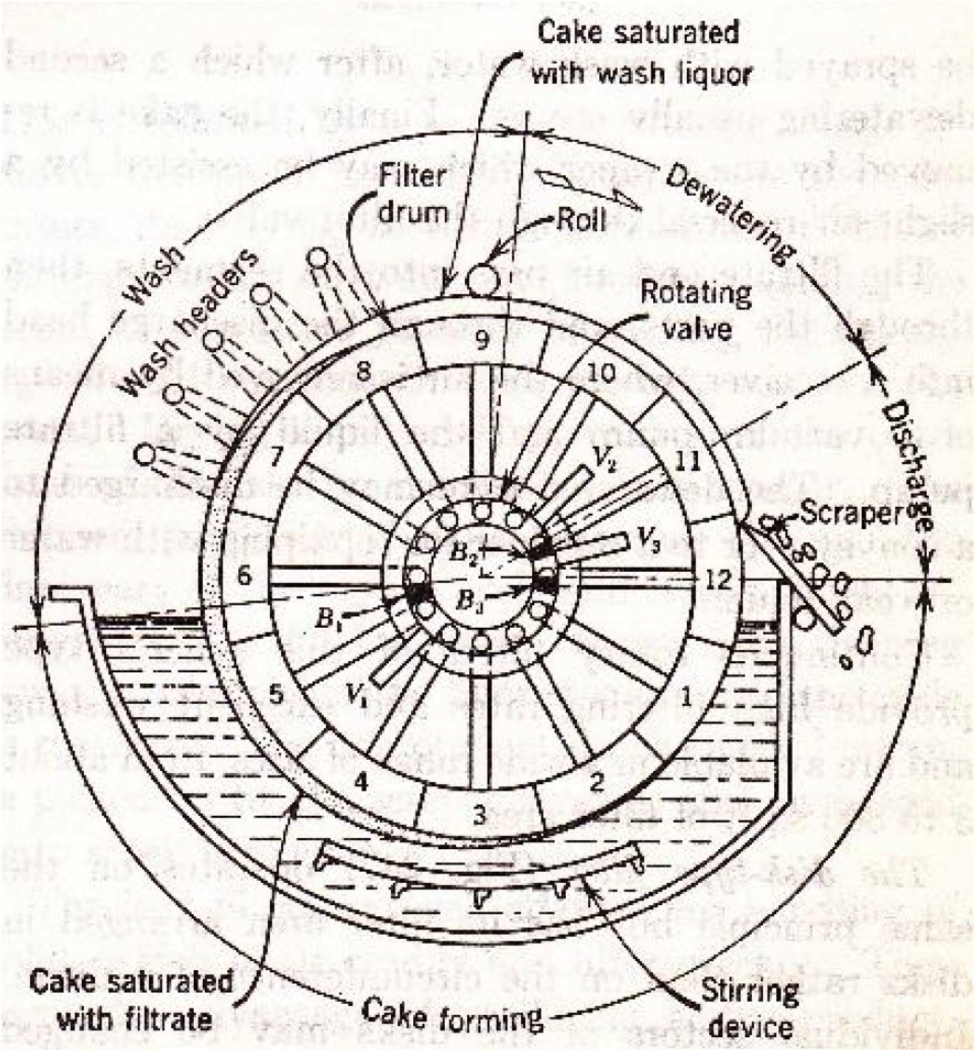
Simplified dewaxing process [4]

- Contacting the solvent with oil
- Crystallization in the presence of the solvent
- Filtration to remove wax from dewaxed oil
- Separation of the solvent from the dewaxed oil and the wax by distillation.

Simplified dewaxing process [4]

- The feedstock is mixed with the solvent such as mixture of MEK and toluene.
- The mixture is heated to make a mixed of oil and solvent.
- The mixture is then cooled and chilled in heat exchanger and chiller system. The chiller is usually a refrigeration system operating at propane.
- The mixture of crystals, oil, and solvent flows to the rotary filters. The cakes are washed with solvent to purify the wax from oil.
- The solvent is recovered in wax and dewaxed oil distillation columns.

Rotary drum vacuum filter [13]



http://www.adelaidecontrolengineering.com/?q=content/rotary-drum-filter
[Accessed on: 17-Aug-2015]

Simplified dewaxing process [10]

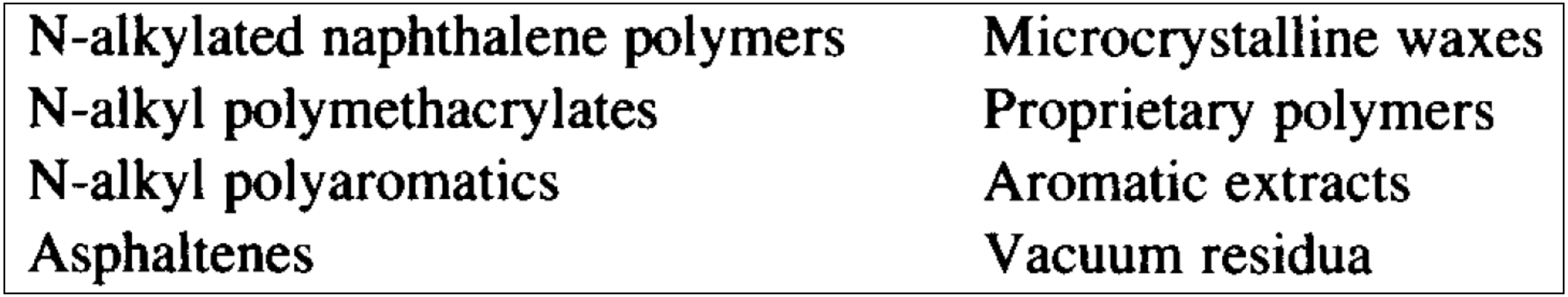
Dewaxing process may be affected by:

- ✓ Nature of the feedstock
- ✓ Type of solvent
- ✓ Solvent to feed ratio
- ✓ Chilling temperature
- ✓ Filtration process (use of filter aids, washing, etc.)
- ✓ Solvent recovery method
- ✓ The final desired pour point

Simplified dewaxing process [10]

What is filter aid?

Types of filter aids used in solvent dewaxing



- N-alkylated naphthalene polymers
- N-alkyl polymethacrylates
- N-alkyl polyaromatics
- Asphaltenes
- Microcrystalline waxes
- Proprietary polymers
- Aromatic extracts
- Vacuum residua

Dewaxing Case Study [12]

Feed	
Cut, °F	840–915
Density	0.8585
Viscosity, cSt, 210°F	5.81
Pour point, °F	134.6
Wax content, Wt %	69

Solvents		MEK + BZ + TOL	MIBK + BZ + TOL	MIBK
Solvent composition:	Vol %			
Methyl ethyl ketone		40		
Benzene		30	30	
Toluene		30	30	
MIBK			40	100
Solvent-to-feed ratio		5/1	5/1	5/1
Dewaxing temperature	°F	–13	–13	–13
Wash solvent-to-feed ratio	V/V	1.5/1	1.5/1	1.5/1
Dewaxed oil				
Yield	Wt %	32.2	23.7	27.4
Pour point	°F	24.8	26.6	6.8
Kinematic viscosity	cSt, 210°F	11	11.4	12.1
Viscosity index		61	67	58
Slack wax				
Yield	Wt %	67.8	73.9	72.6
Conjgealing temperature	°F	144.5	138.56	135.5

Clay treatment [1, 4]

Clay treatment is an adsorption process which is used to remove

- Colored compounds
- Organic acids
- Oxidizable hydrocarbons

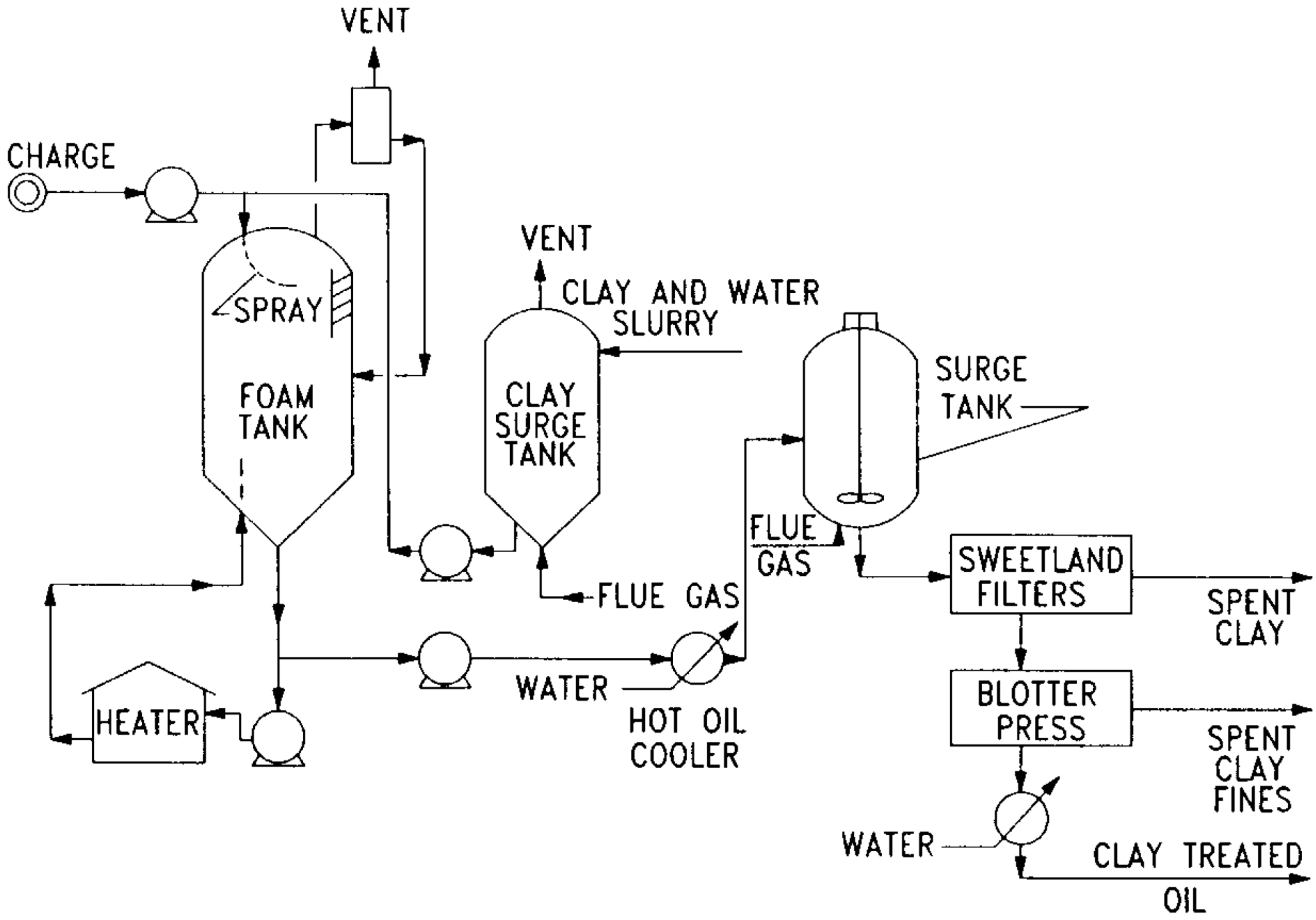
Organic nitrogen compounds importantly affect the color and color stability oil.

Clay treatment [1, 4]

Clay treatment may either be carried out by:

- Contact process (mixing)
- Percolation technique such as flow through a packed particle (adsorbent) bed

Clay treatment: Contact process [10]



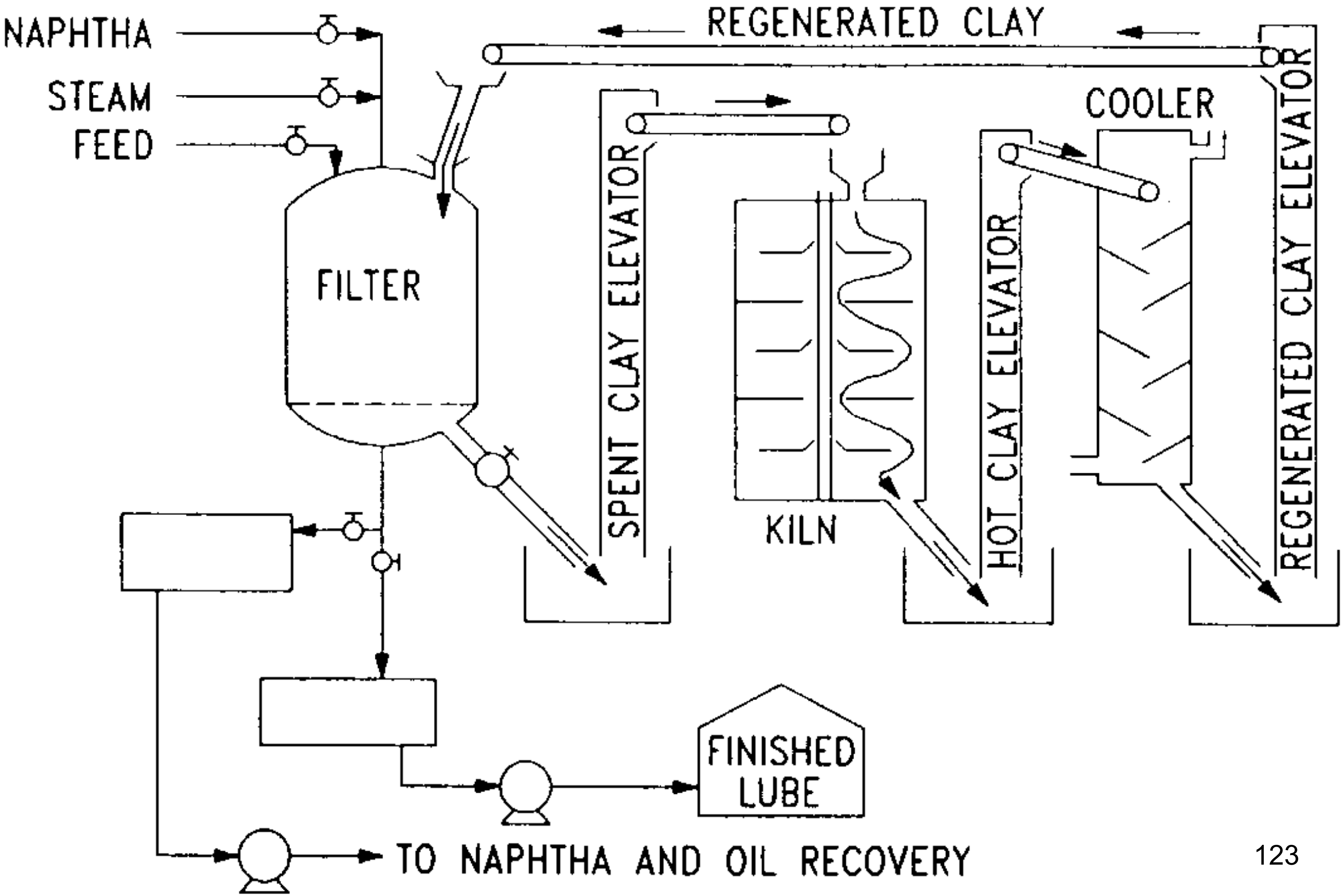
Clay treatment: Contact process [1, 4]

In the contact process the oil and clay are mixed, heated, agitated, and filtered.

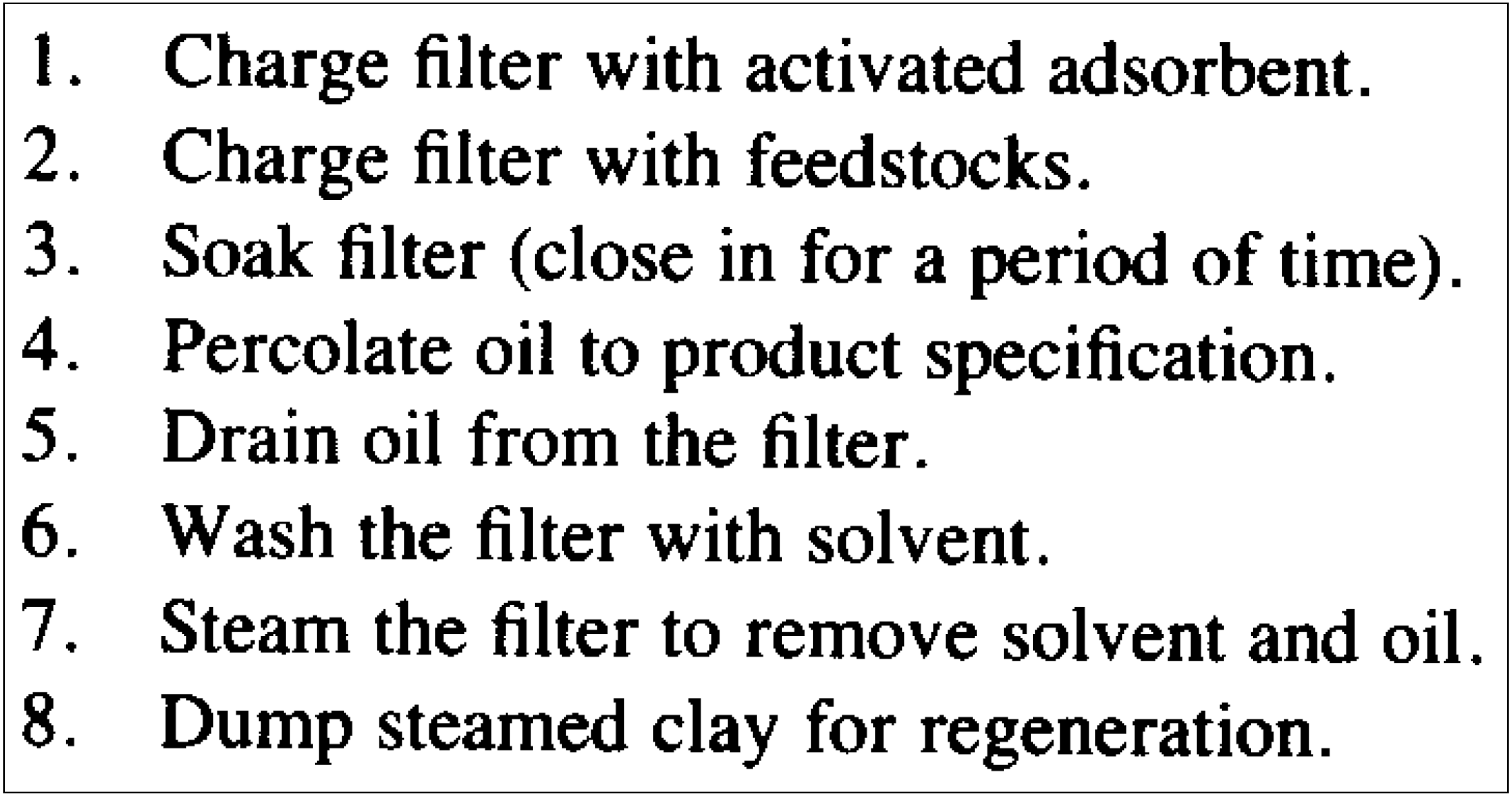
The process is affected by: clay type, clay quantity, and treating temperatures

(300-700 ^{o}F) [10].

Clay treatment: Percolation method [10]



Percolation adsorption cycle [10]

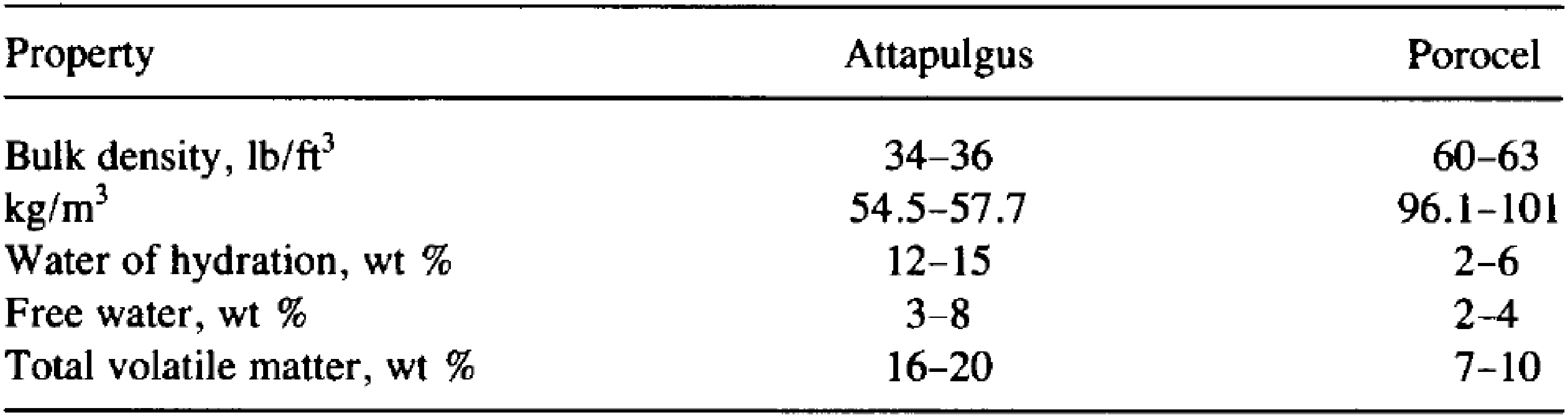


1. Charge filter with activated adsorbent.
2. Charge filter with feedstocks.
3. Soak filter (close in for a period of time).
4. Percolate oil to product specification.
5. Drain oil from the filter.
6. Wash the filter with solvent.
7. Steam the filter to remove solvent and oil.
8. Dump steamed clay for regeneration.

Clay treatment: Clays [10]

Two common types of clays used are: Attapulgus and Porocel. Attapulgus is a hydrous magnesium-aluminum silicate (Fuller's earth) while Porocel is primarily hydrated aluminum oxide (bauxite). Both the clays are activated by heat treatment. Attapulgus clay is tempered at 260-427°C with a residence time of 15-30 min. Porocel clay is tempered for 15-30 min at 371-482°C.

Properties of clays



Property	Attapulgus	Porocel
Bulk density, lb/ft^3	34–36	60–63
kg/m^3	54.5–57.7	96.1–101
Water of hydration, wt %	12–15	2–6
Free water, wt %	3–8	2–4
Total volatile matter, wt %	16–20	7–10

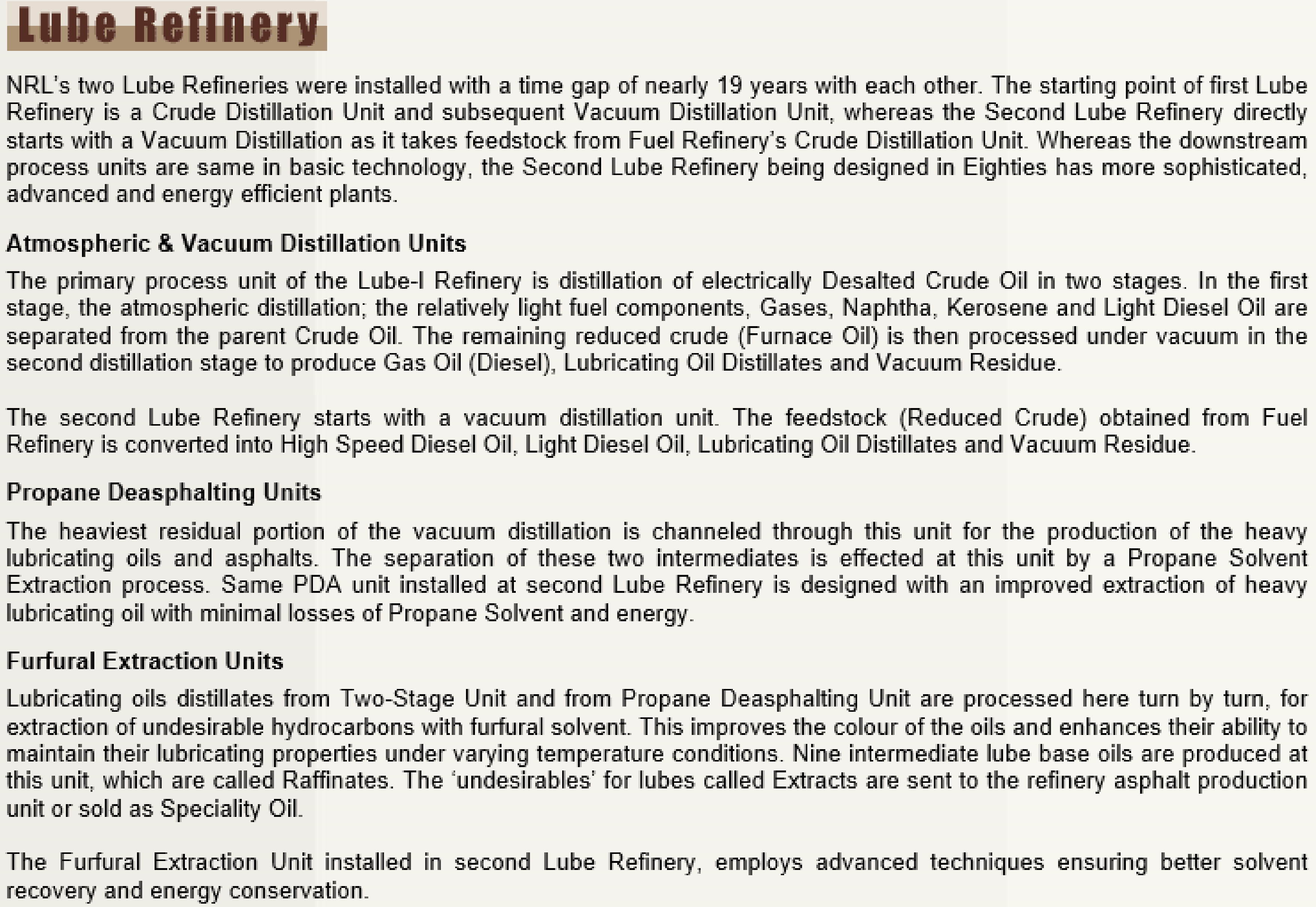
Clay treatment: Clays [1, 4]

Spent clay disposal issues may be one of the major reasons for replacing clay treatment with an increasingly popular hydrogen treatment (hydrofinishing).

Characteristics of some commercial grade lube oils [12]

SAE viscosity grade		15W–40	10W–30
API service classification	Diesel	CH-4, CG-4, CF-4, CF-2, CF	CG-4, CF-4, CF
	Gasoline	SJ	SH
API gravity		27.9	28.9
Specific gravity		0.8877	0.8822
Flash point	ºC	218	210
Pour point	ºC	–33	–33
Viscosity at ºC			
–15	cP	3000	
–20	cP		2840
–25	cP	25,000	
–30	cP		19,500
40	cSt	120.7	73
100	cSt	15.5	11.0
High-temperature/high-shear viscosity	cP, 150ºC	4.4	3.4
Viscosity index		134	141
Zinc	Wt %	0.142	0.142
Nitrogen	Wt %	0.124	0.113
Sulfate ash	Wt %	1.4	1.4
TBN	mg KOH/g	12.2	11.8

National Refinery Limited: A lube oil refinery



Lube Refinery

NRL's two Lube Refineries were installed with a time gap of nearly 19 years with each other. The starting point of first Lube Refinery is a Crude Distillation Unit and subsequent Vacuum Distillation Unit, whereas the Second Lube Refinery directly starts with a Vacuum Distillation as it takes feedstock from Fuel Refinery's Crude Distillation Unit. Whereas the downstream process units are same in basic technology, the Second Lube Refinery being designed in Eighties has more sophisticated, advanced and energy efficient plants.

Atmospheric & Vacuum Distillation Units

The primary process unit of the Lube-I Refinery is distillation of electrically Desalted Crude Oil in two stages. In the first stage, the atmospheric distillation; the relatively light fuel components, Gases, Naphtha, Kerosene and Light Diesel Oil are separated from the parent Crude Oil. The remaining reduced crude (Furnace Oil) is then processed under vacuum in the second distillation stage to produce Gas Oil (Diesel), Lubricating Oil Distillates and Vacuum Residue.

The second Lube Refinery starts with a vacuum distillation unit. The feedstock (Reduced Crude) obtained from Fuel Refinery is converted into High Speed Diesel Oil, Light Diesel Oil, Lubricating Oil Distillates and Vacuum Residue.

Propane Deasphalting Units

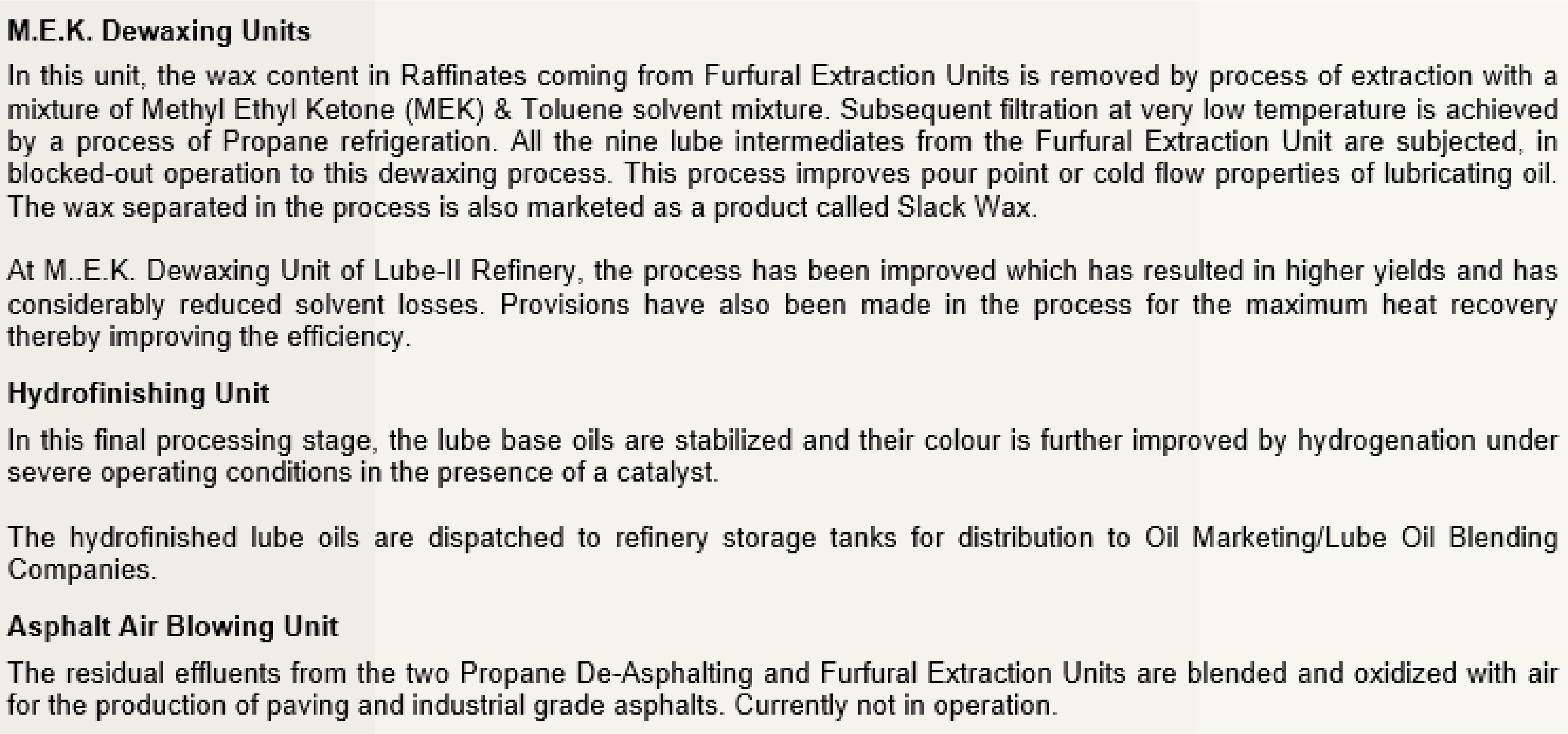
The heaviest residual portion of the vacuum distillation is channeled through this unit for the production of the heavy lubricating oils and asphalts. The separation of these two intermediates is effected at this unit by a Propane Solvent Extraction process. Same PDA unit installed at second Lube Refinery is designed with an improved extraction of heavy lubricating oil with minimal losses of Propane Solvent and energy.

Furfural Extraction Units

Lubricating oils distillates from Two-Stage Unit and from Propane Deasphalting Unit are processed here turn by turn, for extraction of undesirable hydrocarbons with furfural solvent. This improves the colour of the oils and enhances their ability to maintain their lubricating properties under varying temperature conditions. Nine intermediate lube base oils are produced at this unit, which are called Raffinates. The 'undesirables' for lubes called Extracts are sent to the refinery asphalt production unit or sold as Speciality Oil.

The Furfural Extraction Unit installed in second Lube Refinery, employs advanced techniques ensuring better solvent recovery and energy conservation.

National Refinery Limited: A lube oil refinery



M.E.K. Dewaxing Units

In this unit, the wax content in Raffinates coming from Furfural Extraction Units is removed by process of extraction with a mixture of Methyl Ethyl Ketone (MEK) & Toluene solvent mixture. Subsequent filtration at very low temperature is achieved by a process of Propane refrigeration. All the nine lube intermediates from the Furfural Extraction Unit are subjected, in blocked-out operation to this dewaxing process. This process improves pour point or cold flow properties of lubricating oil. The wax separated in the process is also marketed as a product called Slack Wax.

At M..E.K. Dewaxing Unit of Lube-II Refinery, the process has been improved which has resulted in higher yields and has considerably reduced solvent losses. Provisions have also been made in the process for the maximum heat recovery thereby improving the efficiency.

Hydrofinishing Unit

In this final processing stage, the lube base oils are stabilized and their colour is further improved by hydrogenation under severe operating conditions in the presence of a catalyst.

The hydrofinished lube oils are dispatched to refinery storage tanks for distribution to Oil Marketing/Lube Oil Blending Companies.

Asphalt Air Blowing Unit

The residual effluents from the two Propane De-Asphalting and Furfural Extraction Units are blended and oxidized with air for the production of paving and industrial grade asphalts. Currently not in operation.

http://www.nrlpak.com/lube_refinery.html
[Accessed on: 16-Aug-2015]

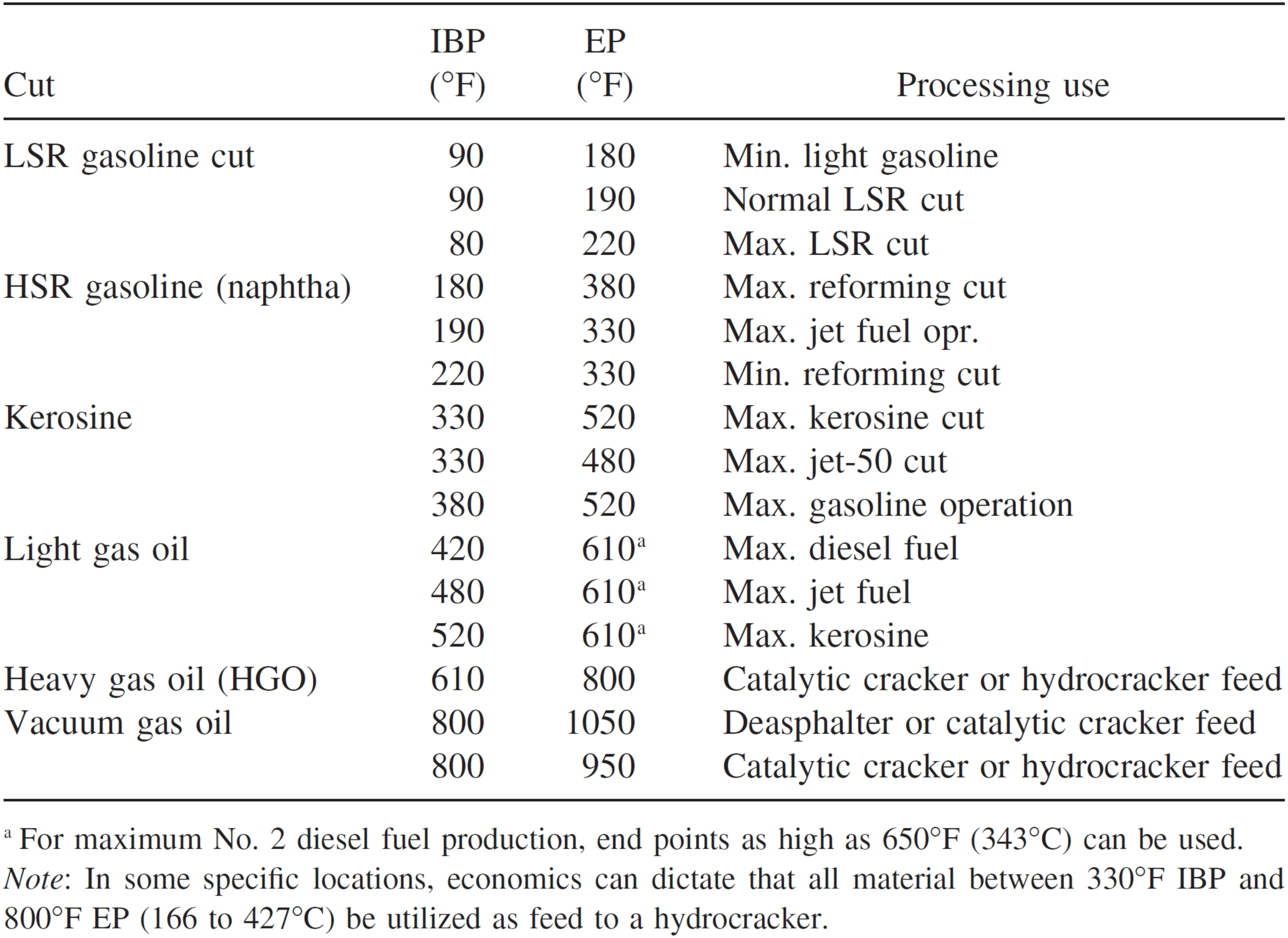
Concept of pseudocomponents

A crude oil or its fraction can be divided into a number of fractions each having a narrow boiling range and called as pseudocomponent. The narrow boiling range of the crude allows one to define an average boiling point of a pseudocomponent as (IBP+EP)/2, which is then called as NBP if the TBP data is at normal pressure. Here, IBP and EP are that of a pseudocomponent.

Why do we need pseudocomponents?

Bring to mind the discussion on undefined and complex mixtures in the class. Read through Fahim or else.

Concept of pseudocomponents [1]

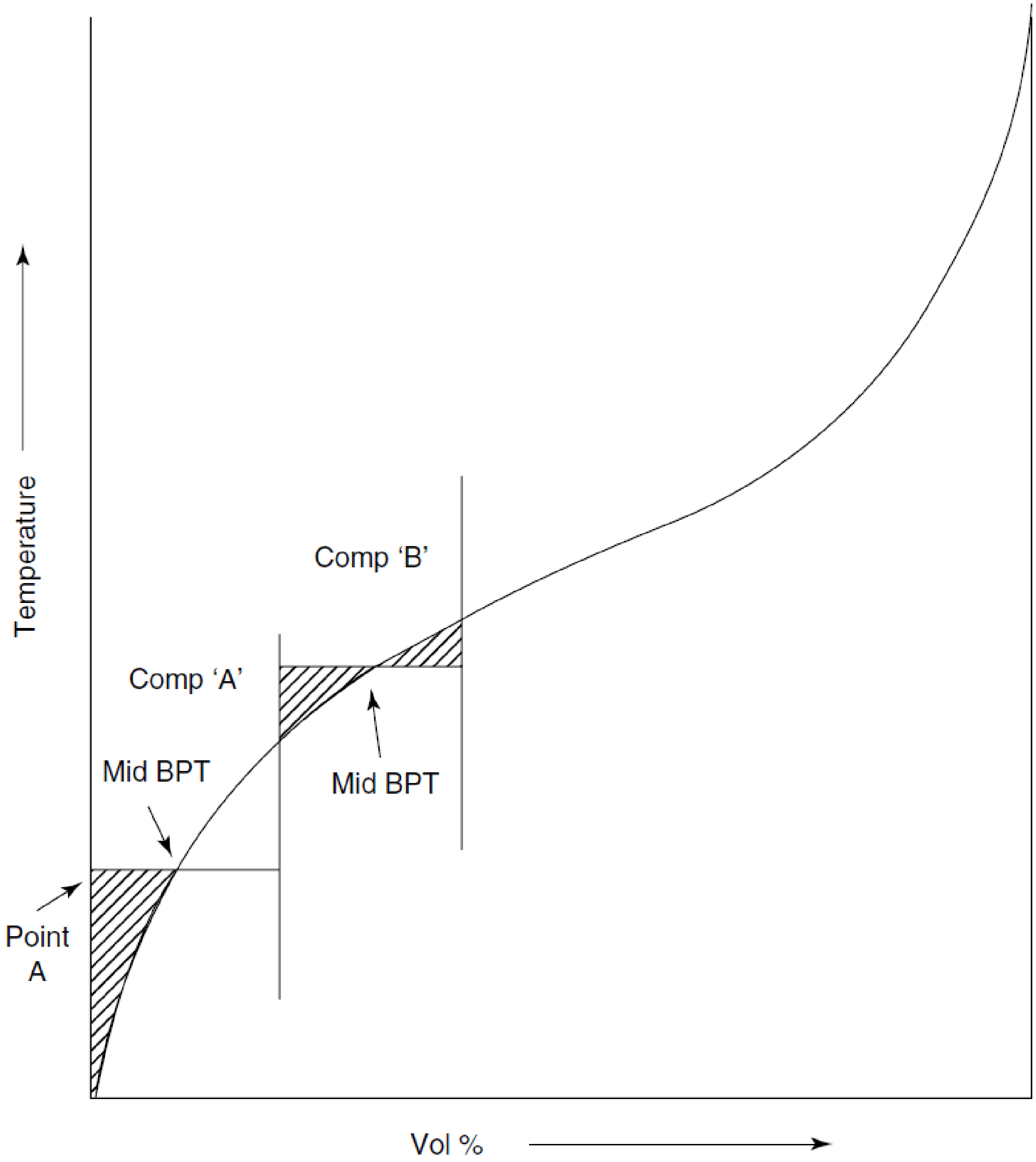


Cut	IBP (°F)	EP (°F)	Processing use
LSR gasoline cut	90	180	Min. light gasoline
	90	190	Normal LSR cut
	80	220	Max. LSR cut
HSR gasoline (naphtha)	180	380	Max. reforming cut
	190	330	Max. jet fuel opr.
	220	330	Min. reforming cut
Kerosine	330	520	Max. kerosine cut
	330	480	Max. jet-50 cut
	380	520	Max. gasoline operation
Light gas oil	420	610[a]	Max. diesel fuel
	480	610[a]	Max. jet fuel
	520	610[a]	Max. kerosine
Heavy gas oil (HGO)	610	800	Catalytic cracker or hydrocracker feed
Vacuum gas oil	800	1050	Deasphalter or catalytic cracker feed
	800	950	Catalytic cracker or hydrocracker feed

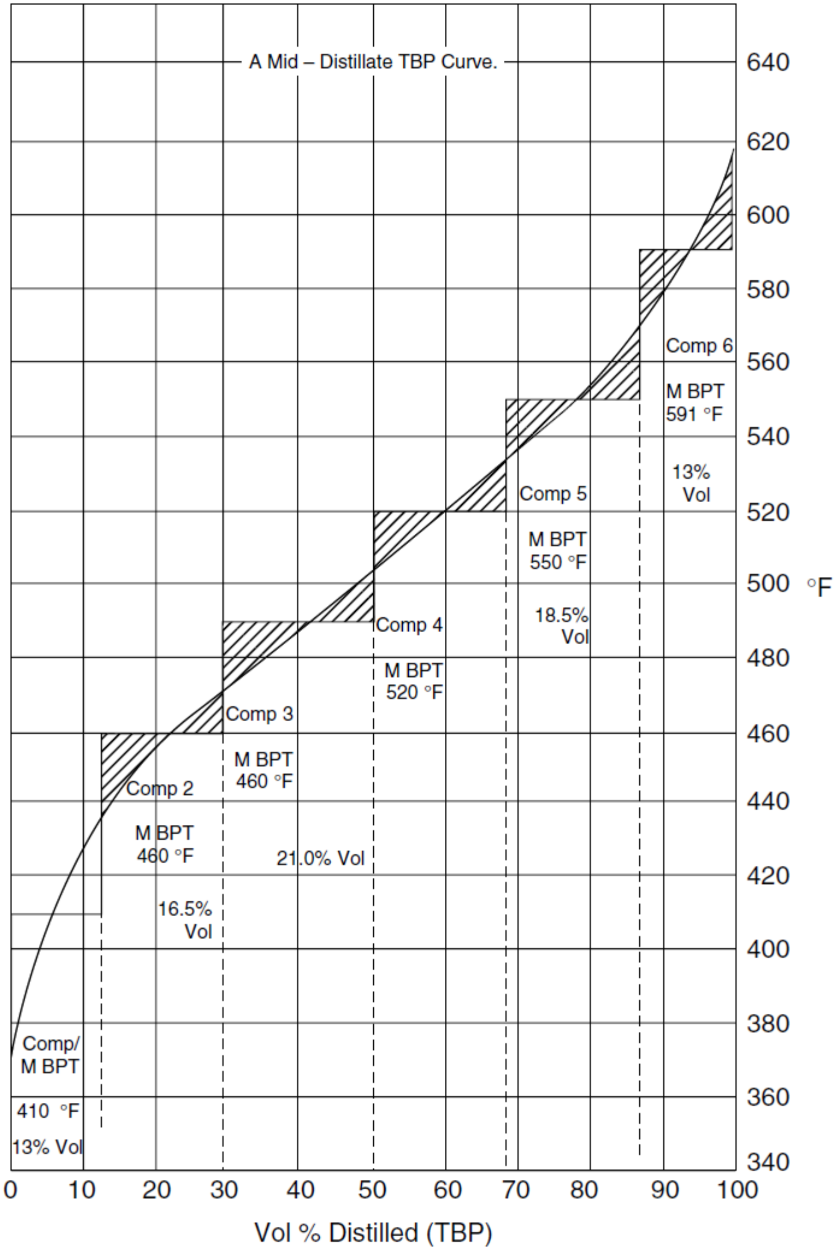
[a] For maximum No. 2 diesel fuel production, end points as high as 650°F (343°C) can be used.

Note: In some specific locations, economics can dictate that all material between 330°F IBP and 800°F EP (166 to 427°C) be utilized as feed to a hydrocracker.

Concept of pseudocomponents [6]



Concept of pseudocomponents [6]



Concept of pseudocomponents

If TBP curve is available, it is further divided into narrow boiling fractions, called pseudocomponents. For these pseudo-components, the average boiling point can be estimated as either mid-boiling point or mid-percent boiling point.

The TBP curve is divided into an arbitrary number of pseudo-components or narrow boiling cuts.

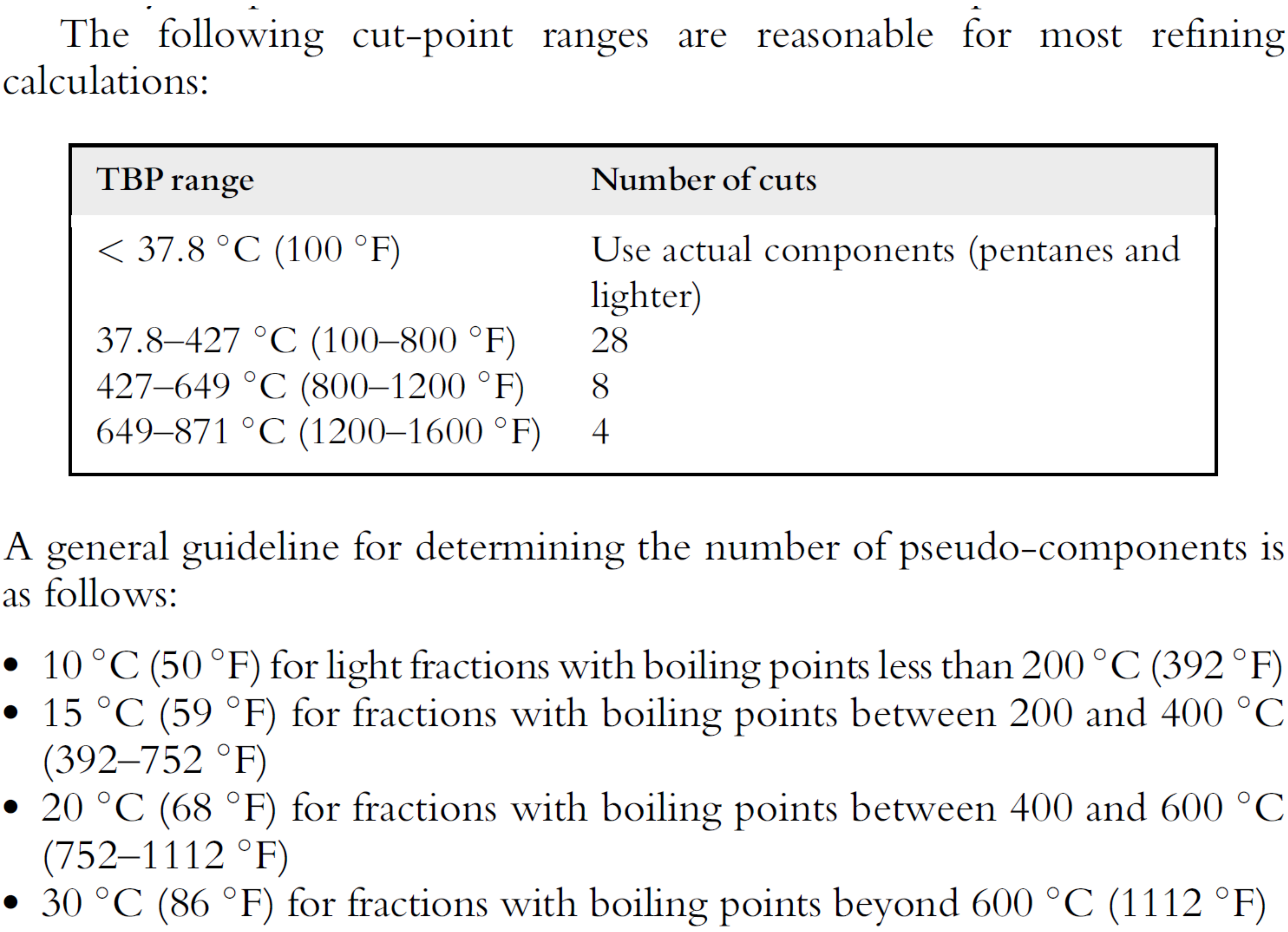
How will you decide about the number of pseudo-components?

Since the boiling range is small, both mid points (mid-boiling point and mid-percent boiling point) are close to each other and can be considered as the MeABP for that pseudo-component.

Concept of pseudocomponents

Each pseudocomponent is characterized by an average normal boiling point, specific gravity, and molecular weight. The first two properties are obtained experimentally from the TBP curve and gravity versus volume percent curve. In some cases, only the overall specific gravity is measured. In such cases, characterization factor of whole crude or given fraction is considered as the characterization factor of each pseudocomponent and specific gravity of each is then measured. The molecular weight is usually calculated through a correlation. Other physico-chemical properties are then calculated.

Concept of pseudocomponents [2]



The following cut-point ranges are reasonable for most refining calculations:

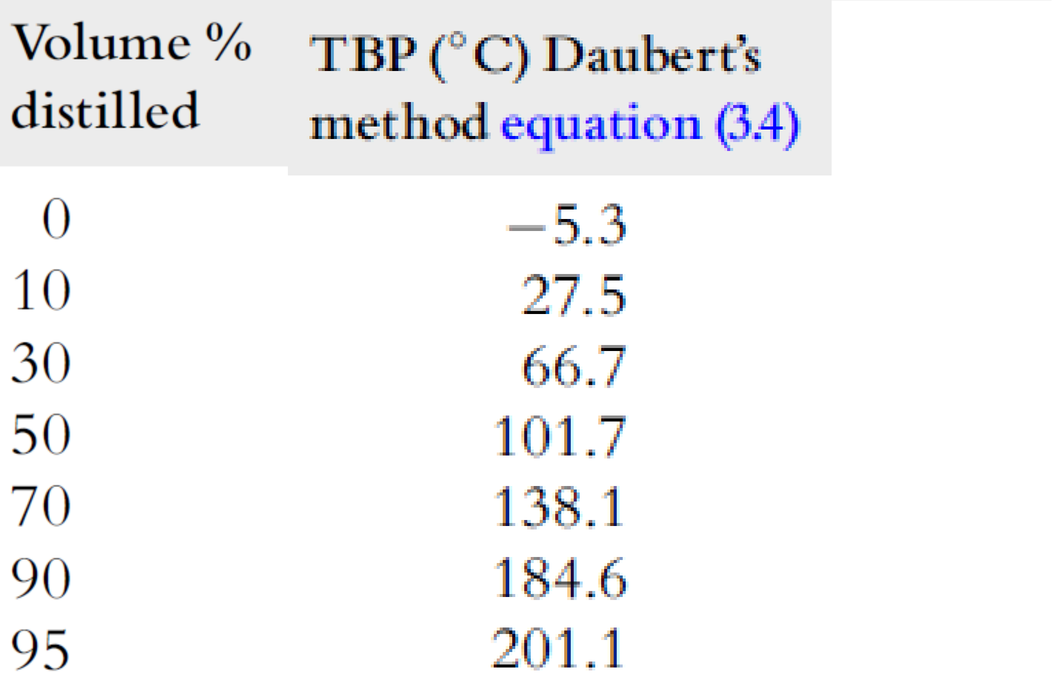
TBP range	Number of cuts
< 37.8 °C (100 °F)	Use actual components (pentanes and lighter)
37.8–427 °C (100–800 °F)	28
427–649 °C (800–1200 °F)	8
649–871 °C (1200–1600 °F)	4

A general guideline for determining the number of pseudo-components is as follows:

- 10 °C (50 °F) for light fractions with boiling points less than 200 °C (392 °F)
- 15 °C (59 °F) for fractions with boiling points between 200 and 400 °C (392–752 °F)
- 20 °C (68 °F) for fractions with boiling points between 400 and 600 °C (752–1112 °F)
- 30 °C (86 °F) for fractions with boiling points beyond 600 °C (1112 °F)

Concept of pseudocomponents

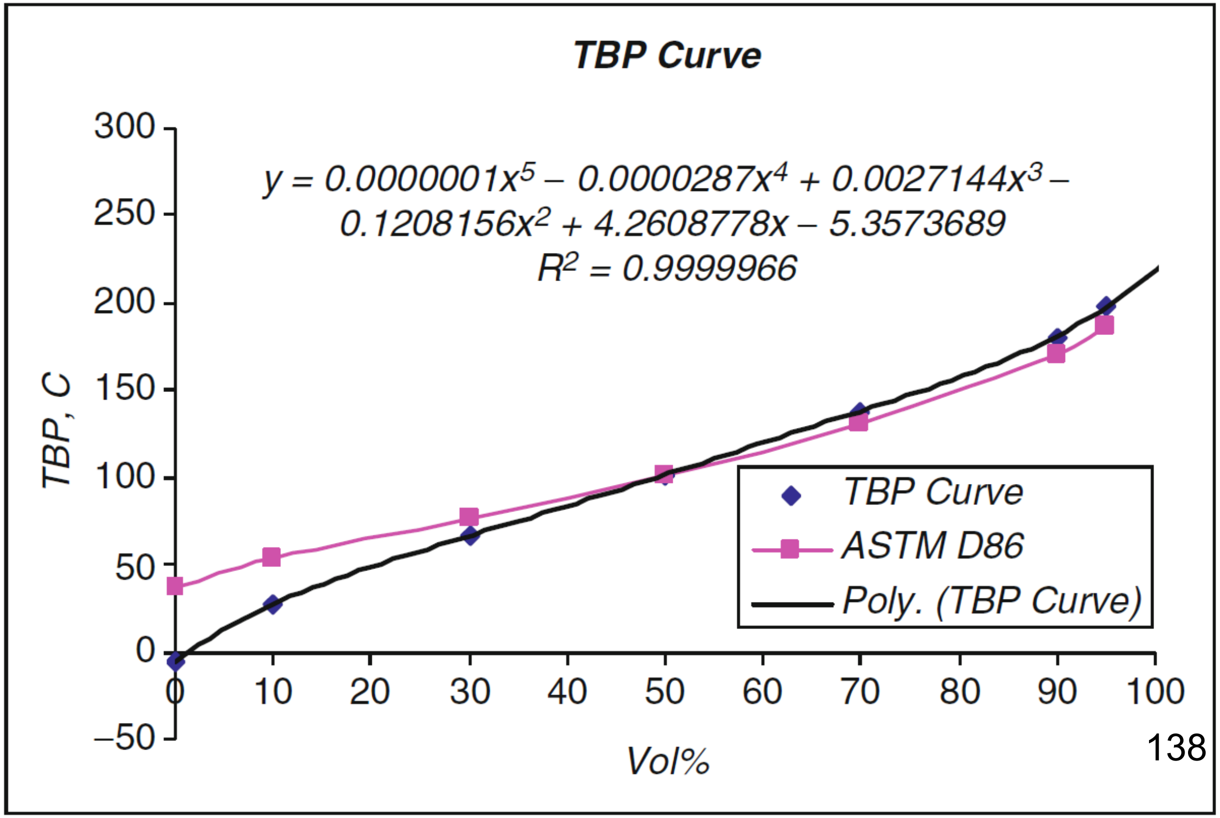
Divide the TBP curve of the petroleum cut as calculated into 20 pseudo-components. Calculate the liquid volume percentage of each pseudo-component. The TBP data is shown below:



Volume % distilled	TBP (°C) Daubert's method equation (3.4)
0	−5.3
10	27.5
30	66.7
50	101.7
70	138.1
90	184.6
95	201.1

Concept of pseudocomponents

The TBP data is drawn in excel and extended by curve fitting to 100% distilled as it is 95% distilled in the TBP apparatus. When using Excel make sure you have reasonable number of significant figures. Try to have nearly 8-10 digits after decimal as shown in the figure below.



Concept of pseudocomponents

Apart from any arbitrary curve fitting (least square), say a polynomial fit, what are the other methods by which a certain TBP curve can be fitted and extended on each side?

Concept of pseudocomponents

The end point is 218.2 and IBP is –5.4 °C. The TBP data is drawn in excel and extended by curve fitting to 100% distilled as it is 95% distilled in the given problem.

As there are 20 pseudocomponents, so each pseudocomponent has a temperature interval of (218.2–(–5.4))/2 or 11.2 °C.

The EBP of the first component is IBP + 11.2 or 5.8 °C.

The average boiling point of the first component is (–5.4+5.8)/2 or 0.2 °C.

The volume percent for the first component is 2.84%.

Note: If not to find directly from the curve by viewing, you may need trial-and-error solution for vol%. You can use Excel Solver (or Goal seek) for finding vol%.

Concept of pseudo-components [2]

EBP of cut (°C)	NBP of cut (°C)	Volume % at end of cut	Cut vol%
5.8	0.2	2.84	2.84
17.0	11.4	6.19	3.36
28.2	22.6	10.22	4.03
39.4	33.8	15.09	4.87
50.5	44.9	20.82	5.73
61.7	56.1	27.15	6.34
72.9	67.3	33.68	6.52
84.1	78.5	40.10	6.42
95.3	89.7	46.36	6.26
106.4	100.8	52.53	6.17
117.6	112.0	58.69	6.16
128.8	123.2	64.89	6.21
140.0	134.4	71.09	6.20
151.1	145.6	77.07	5.98
162.3	156.7	82.53	5.45
173.5	167.9	87.25	4.73
184.7	179.1	91.25	4.00
195.9	190.3	94.63	3.37
207.0	201.5	97.51	2.88
218.2	212.6	100.00	2.49

Concept of pseudocomponents

Calculate the specific gravity and molecular weights of each pseudocomponent of the previous example. The characterization factor is 11.94. Use following correlation for molecular weight in which T_b is the mean average boiling point.

$$M = 42.965[\exp(2.097 \times 10^{-4} T_b - 7.78712\,\mathrm{SG} + 2.08476 \\ \times 10^{-3} T_b \mathrm{SG})] T_b^{1.26007} \mathrm{SG}^{4.98308}$$

Use of Aspen Hysys (Oil Manager) to divide a given TBP curve and to get the cut distribution

For procedural steps, please see class notes.

See the book of Fahim [2].

For tutorial on Aspen HYSYS, see the following website.

http://process-simulations.net/hysys/oil-refining/fractional-distillation-of-crude-oil-hysys#watch-the-tutorial

For exam: You may be asked the questions about the steps, etc., to show how you can use Aspen Hysys for the above mentioned subject.

Use of Aspen Hysys (Oil Manager) to divide a given TBP curve and to get the cut distribution

For procedural steps, please see class notes.

See the book of Fahim [2].

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For exam: You may be asked the questions about the steps, etc., to show how you can use Aspen Hysys for the above mentioned subject.

Course outline

1.Simplified overall crude oil refinery picture

2. Major refinery products and tests: Brief description

3.Separation process: Atmospheric and vacuum distillations, lube oil extraction, dewaxing, deasphalting, and clay treatment.

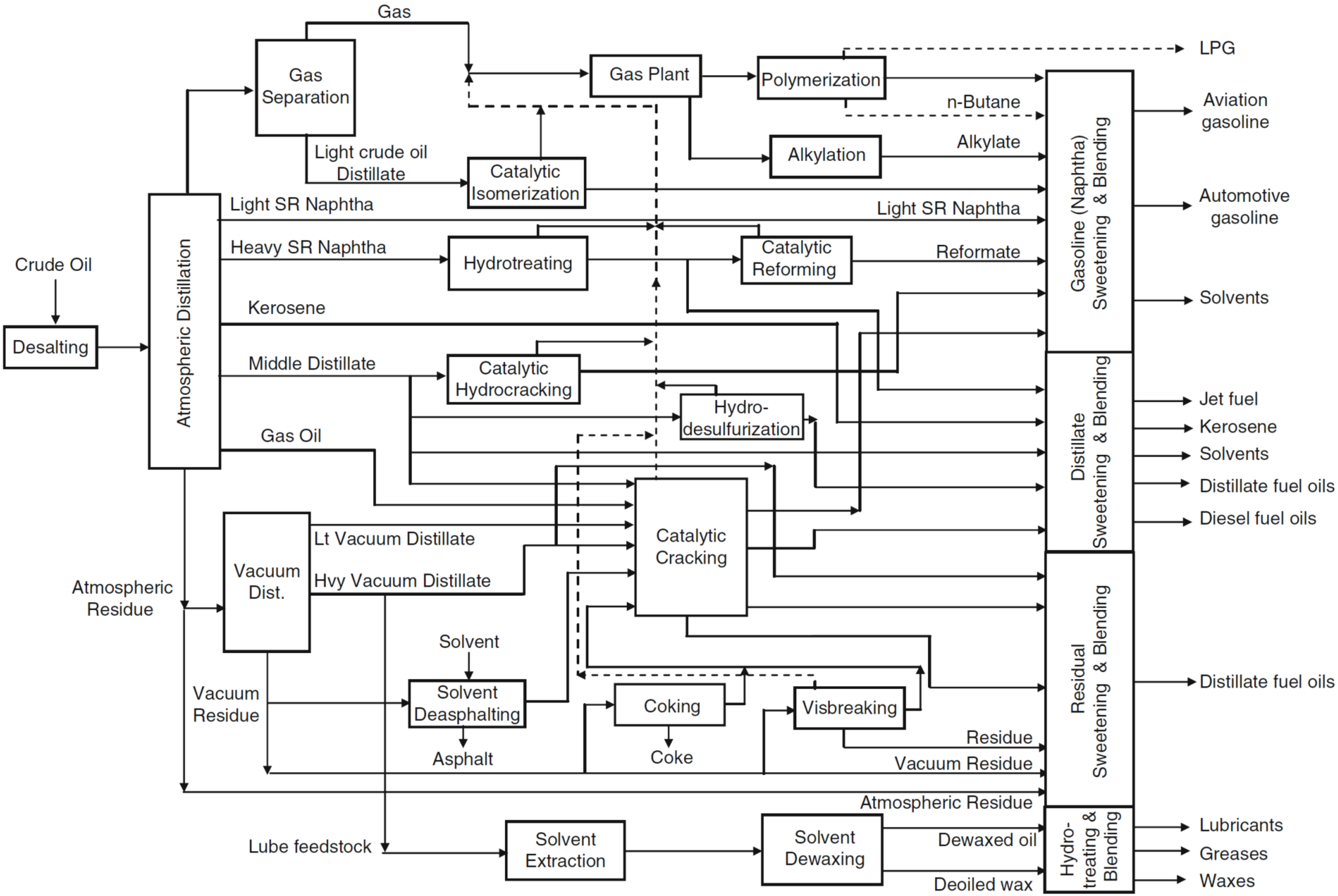
4.Catalysts used in refinery operations

5. Conversion processes: Description of alkylation, polymerization, isomerization of light paraffins, hydrotreating, catalytic reforming, catalytic cracking, hydrocracking, visbreaking of resids, and coking.

5.Material and energy balances for refinery processes (Aspen HYSYS applications)

6.Design guidelines for the selected refinery equipment

Overall refinery flow [2]



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

Conversion processes

We will discuss the following conversion processes:

- Alkylation, polymerization, and isomerization
- Hydrotreating (hydrodesulfurization)
- Catalytic reforming
- Catalytic cracking (fluid catalytic cracking)
- Hydrocracking
- Coking (delayed coking)
- Visbreaking

Alkylation

Alkylation in the petroleum refinery is the reaction of a low molecular weight olefin with an isoparaffin to produce a higher molecular weight isoparaffin.

Usually isobutylene and propylene are used as olefins while isobutane is used as isoparaffin.

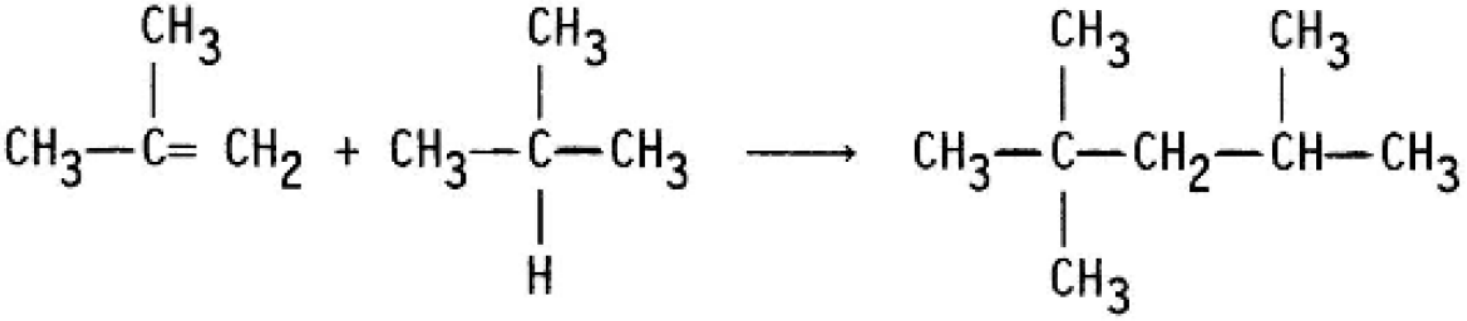
Continuous mixed flow reactors are used.

Hydrofluoric acid or sulfuric acid catalyst is employed.

Temperature of 5 to 21 ^{o}C or lower is used for sulfuric acid process and 38^{o}C or lower for anhydrous hydrofluoric acid process.

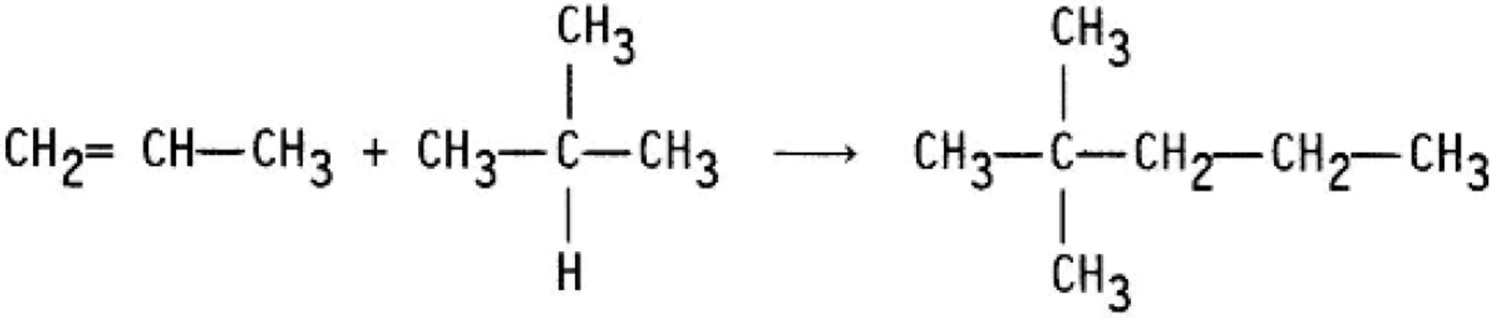
Enough pressure is maintained to keep the hydrocarbons in the liquid state.

Alkylation reactions



$$CH_3-\overset{CH_3}{\overset{|}{C}}=CH_2 + CH_3-\underset{\underset{H}{|}}{\overset{CH_3}{\overset{|}{C}}}-CH_3 \longrightarrow CH_3-\underset{\underset{CH_3}{|}}{\overset{CH_3}{\overset{|}{C}}}-CH_2-\overset{CH_3}{\overset{|}{CH}}-CH_3$$

isobutylene isobutane 2, 2, 4-trimethylpentane (isooctane)



$$CH_2=CH-CH_3 + CH_3-\underset{\underset{H}{|}}{\overset{CH_3}{\overset{|}{C}}}-CH_3 \longrightarrow CH_3-\underset{\underset{CH_3}{|}}{\overset{CH_3}{\overset{|}{C}}}-CH_2-CH_2-CH_3$$

propylene isobutane 2, 2- dimethylpentane (isoheptane)

Alkylation

The volume of catalyst (acid) and liquid hydrocarbon feed are used in equal amounts and isoparaffin to olefin ratios are: 4:1 to 15:1.

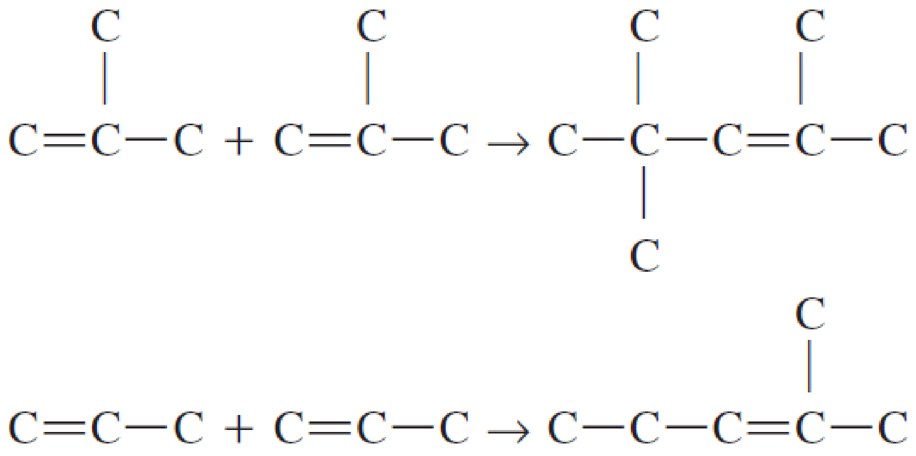
The major sources of olefins are catalytic cracking and coking operations. Olefins can also be produced by the dehydrogenation of paraffins and isobutane may well be cracked commercially to provide alkylation unit feed.

Isobutane is produced in hydrocrackers and catalytic crackers, catalytic reformers, crude distillation, and natural gas processing. In few cases, normal butane is isomerized to produce additional isobutane for the alkylation unit.

Polymerization

Propylenes and butylenes may be polymerized to from a gasoline range product having high octane number. The product itself is an olefin having octane number of 97.

Polymerization reactions are of the following type [1]:



$$\mathrm{C{=}\overset{C}{\overset{|}{C}}{-}C + C{=}\overset{C}{\overset{|}{C}}{-}C \rightarrow C{-}\underset{\underset{C}{|}}{\overset{C}{\overset{|}{C}}}{-}C{=}\overset{C}{\overset{|}{C}}{-}C}$$

$$\mathrm{C{=}C{-}C + C{=}C{-}C \rightarrow C{-}C{-}C{=}\overset{C}{\overset{|}{C}}{-}C}$$

Polymerization

The most widely used catalyst is phosphoric acid on an inert support. This can be in the form of phosphoric acid mixed with kieselguhr (a natural clay) or a film of liquid phosphoric acid on crushed quartz (a natural mineral).

Feed enters the reactor at around 204 ^{o}C. The reaction is highly exothermic and temperature is required to be controlled. Reactor pressure is 3450 kPa.

The polymerized product may need to be hydrogenated before it goes to gasoline pool. Why?

Polymerization [14]

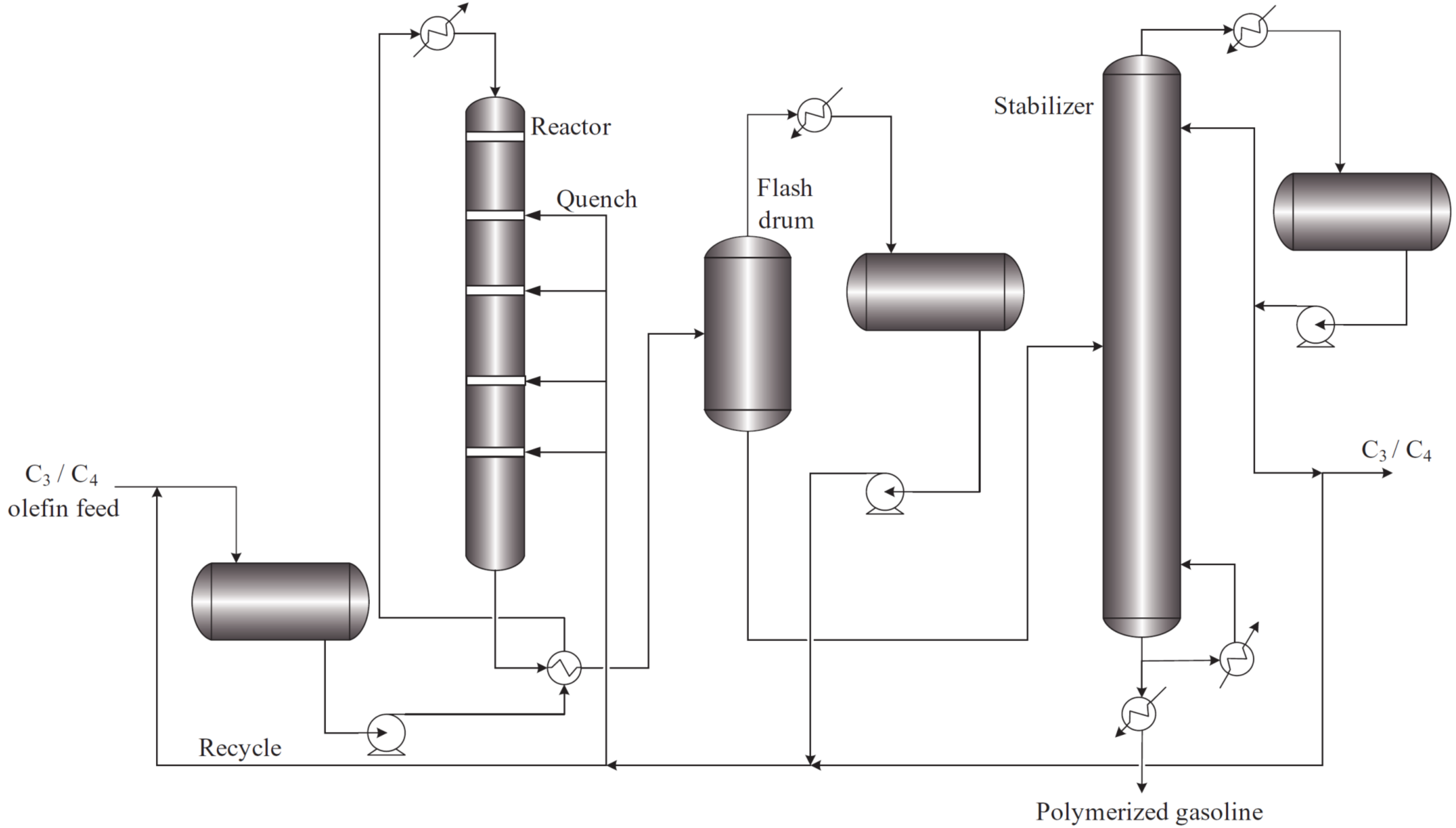


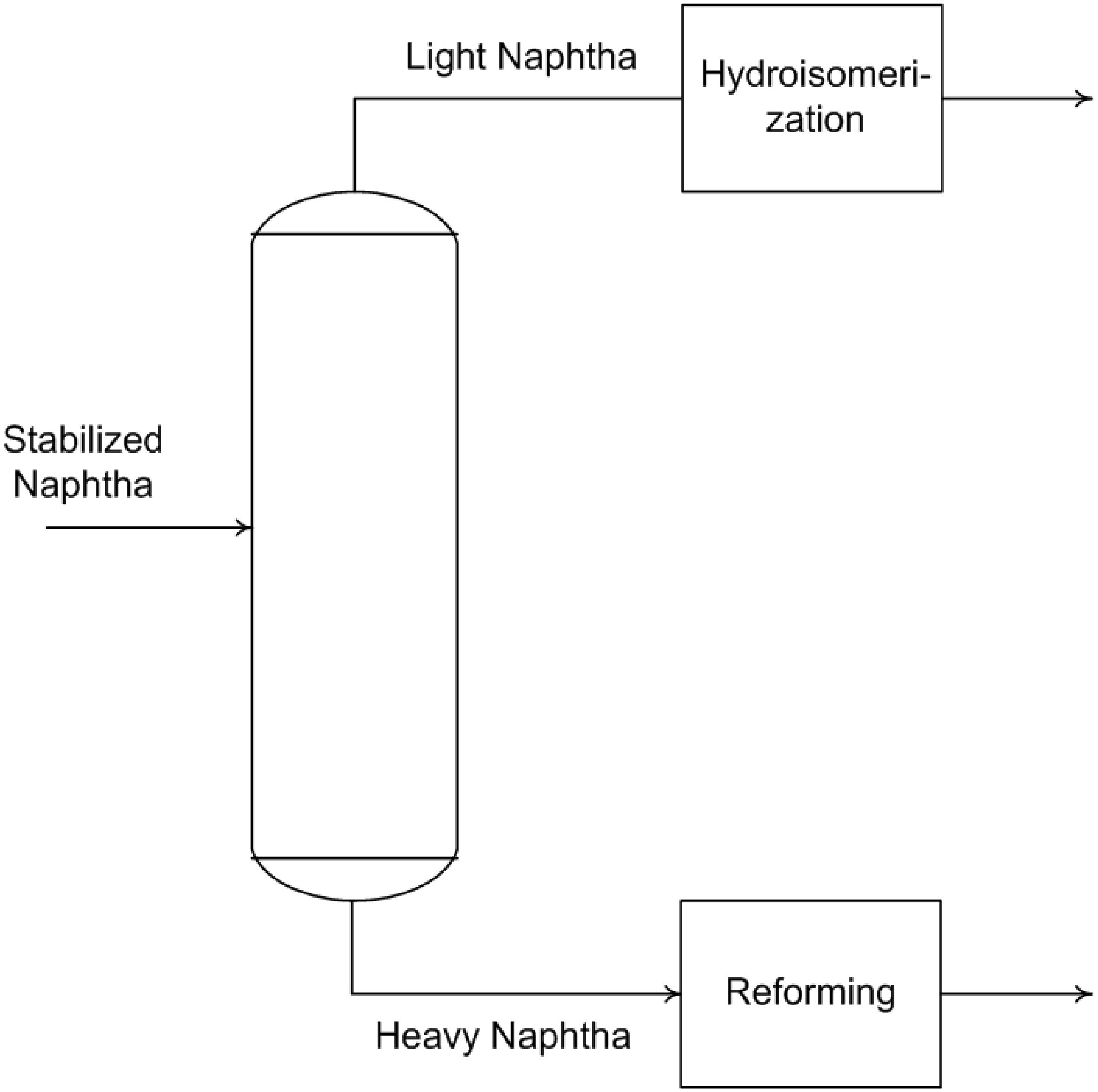
Figure 1.10. Typical process scheme of a polymerization unit.

Isomerization

Benzene is toxic and therefore we do not want benzene in a gasoline. If present in gasoline, the spillage of gasoline and incomplete combustion of gasoline in an engine may add benzene to the atmosphere we breath in.

For a naphtha feed, how can we reduce the concentration of benzene in a gasoline while virtually keeping the same octane rating?

Isomerization



Isomerization

Isomerization is used to improve the octane number of the n-paraffinic feeds by converting them into isoparaffins. As an example, n-pentane has RON (research octane number) of 61.7 while isopentane has a rating of 92.3.

Light straight run naphtha is used as a feed for the isomerization and the following reactor conditions are maintained.

Reaction temperature = 95–205 °C

Reaction pressure = 1725–3450 kPa.

Hydrogen to hydrocarbon molar ratio = 0.05:1.

Catalyst is usually platinum supported on an acidic catalyst such as zeolite or chlorinated metal oxide support.

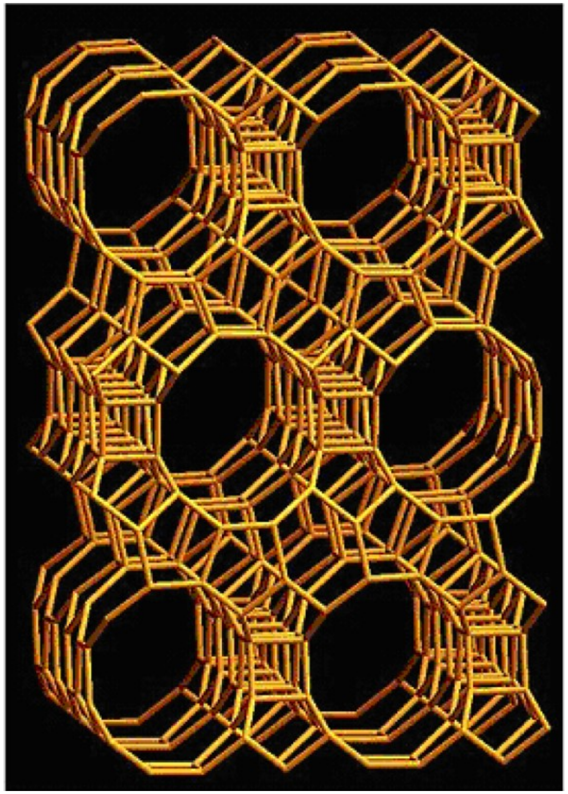
Isomerization

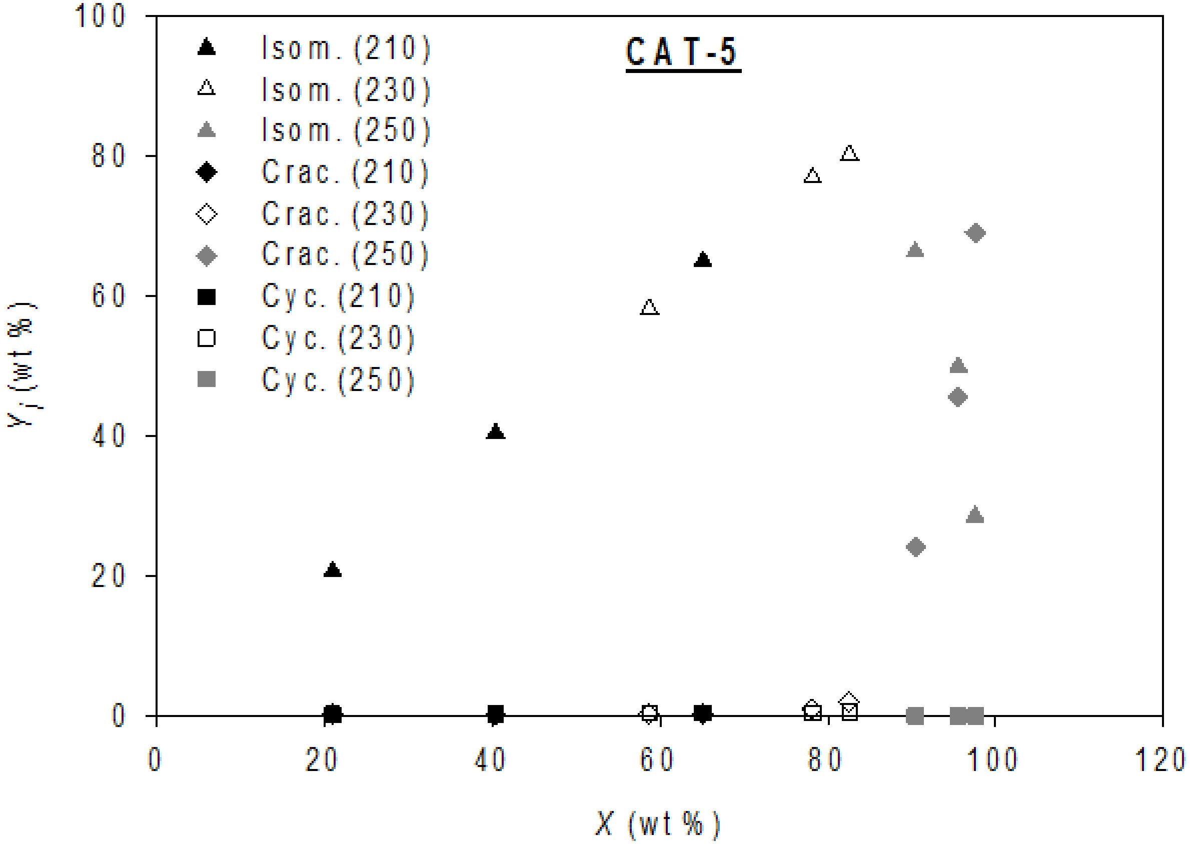
- At elevated temperatures cracking reactions become important and cracked products may increase exponentially and the isomerized products thus become intermediates, i.e., first increase and then decrease with increase in temperature.
- A high hydrogen pressure can lead to reduced coke formation.
- A balance between metal and acidic function may produce better iso/normal ratios.

Isomerization

Catalyst	Catalyst type	Zeolite trade name	Nominal cation form	Post-synthesis modification	Zeolite supplier
CAT-5	1.0 wt% Pt/Beta	CP814E	Ammonium	As received	Zeolyst International

	Si/Al (bulk molar)	N_2-BET (m^2/g)	Pore vol. (cm^3/g)	Pore size (Å)	Pt content (wt%)	Metal dispersion	NH_3-TPD (mmol/g)
	13.21	577.48	0.85	72.70	1.07	0.307	0.63±0.01

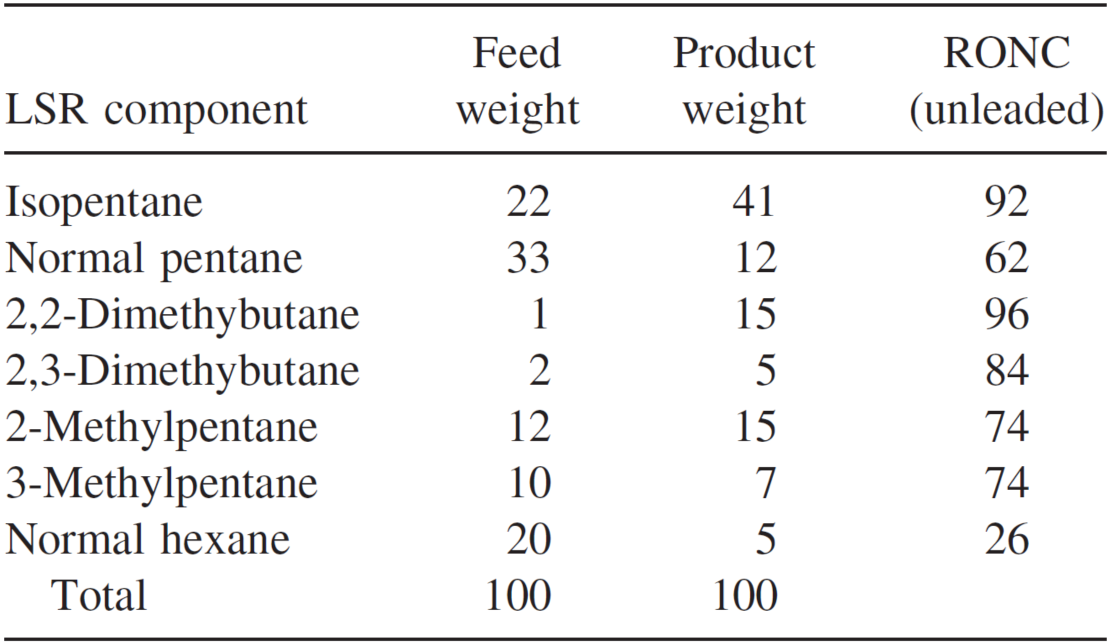




Isomerization

Hydrogen is added to the feed to avoid the deposition of coke on the catalyst surface and consumption of hydrogen is negligible. Due to hydrogen presence in the feed, the process is frequently called as hydroisomerization.

A typical feed and product composition of an isomerization unit is given below [1]:



LSR component	Feed weight	Product weight	RONC (unleaded)
Isopentane	22	41	92
Normal pentane	33	12	62
2,2-Dimethybutane	1	15	96
2,3-Dimethybutane	2	5	84
2-Methylpentane	12	15	74
3-Methylpentane	10	7	74
Normal hexane	20	5	26
Total	100	100	

Isomerization

How can you work out the reaction equilibrium constant and equilibrium conversion of a reaction, if experimental values are lacking?

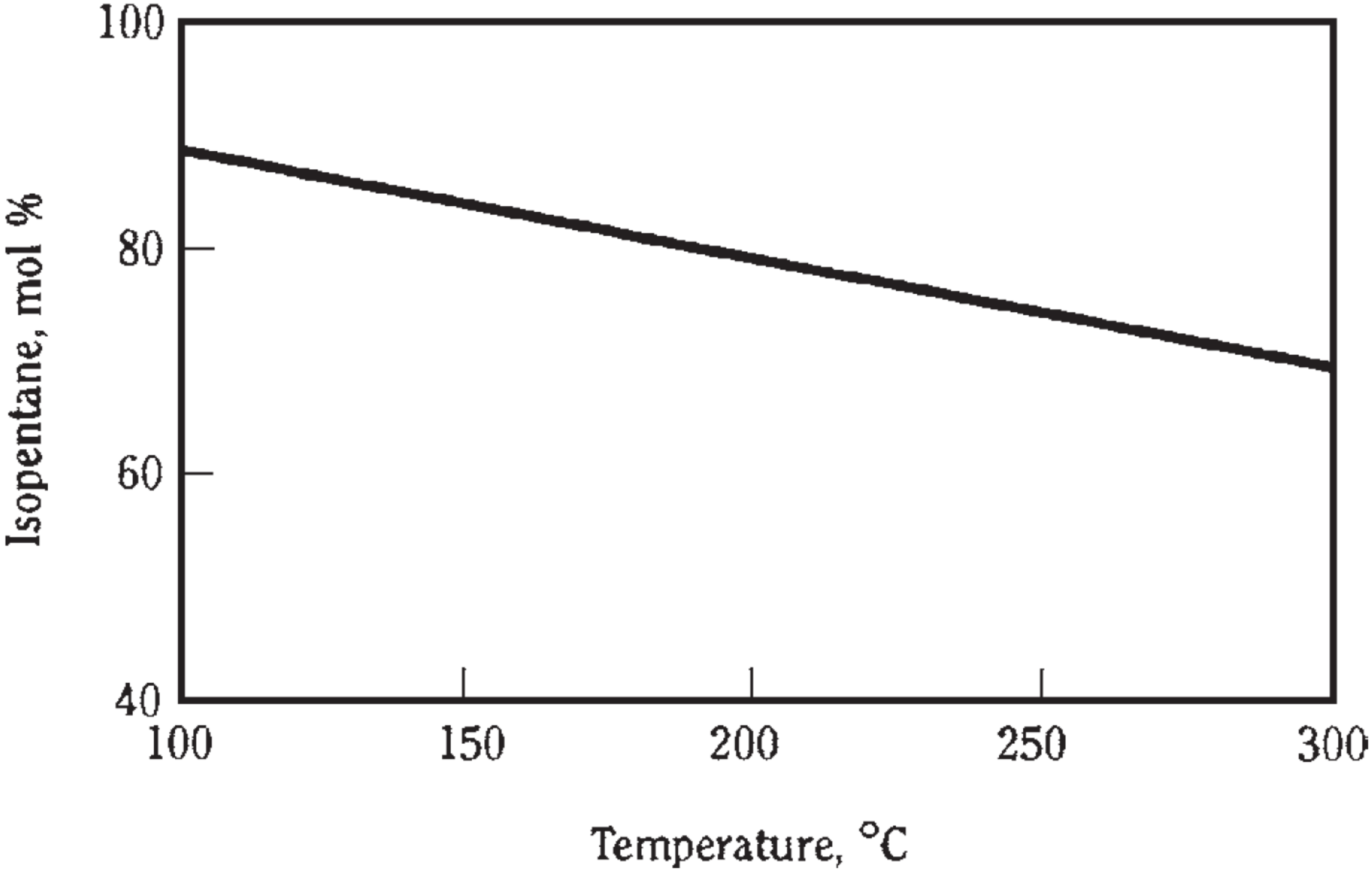
- Using Gibbs free energy of formation and equilibrium constant
- Using Gibbs free energy minimization

Equilibrium conversion of n-pentane

Let’s workout equilibrium conversions and product distribution of n-butane, n-pentane, and n-hexane.

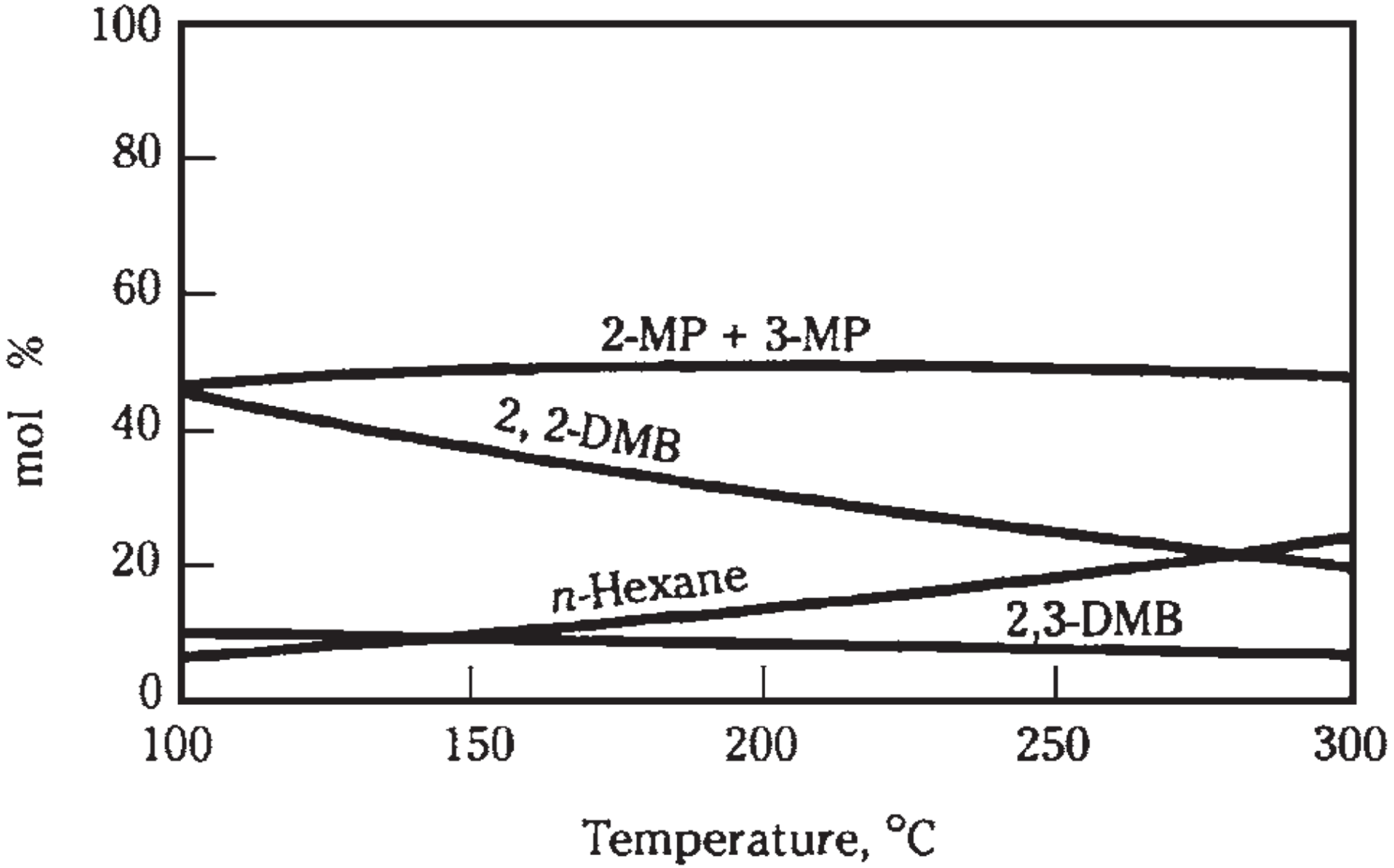
See class notes.

Equilibrium composition of isopentane



n-hexane equilibrium conversion

Workout equilibrium conversions for n-hexane isomerization



Isomerization

AspenHysys can be used to workout equilibrium conversions whether the stoichiometry is known (using equilibrium reactor) or not known (using Gibbs reactor, a Gibbs free energy minimization problem). Standard thermodynamics books give strategy for solving such problems. Let’s proceed to AspenHysys.

Mechanistic steps of isomerization process in the presence of a bifunctional catalyst

1. Adsorption of n-alkane on the catalyst surface
2. Dehydrogenation of n-alkane to the corresponding alkene
3. Protonation of the alkene
4. Isomerization of the protonated alkene to the corresponding protonated iso-alkene
5. Deprotonation of the iso-alkene to the corresponding iso-alkene
6. Hydrogenation of the iso-alkene to the isomerized alkane product
7. Desorption of the isomerized alkane to the gas phase

See also slides regarding cracking and hydrocracking.

Isomerization

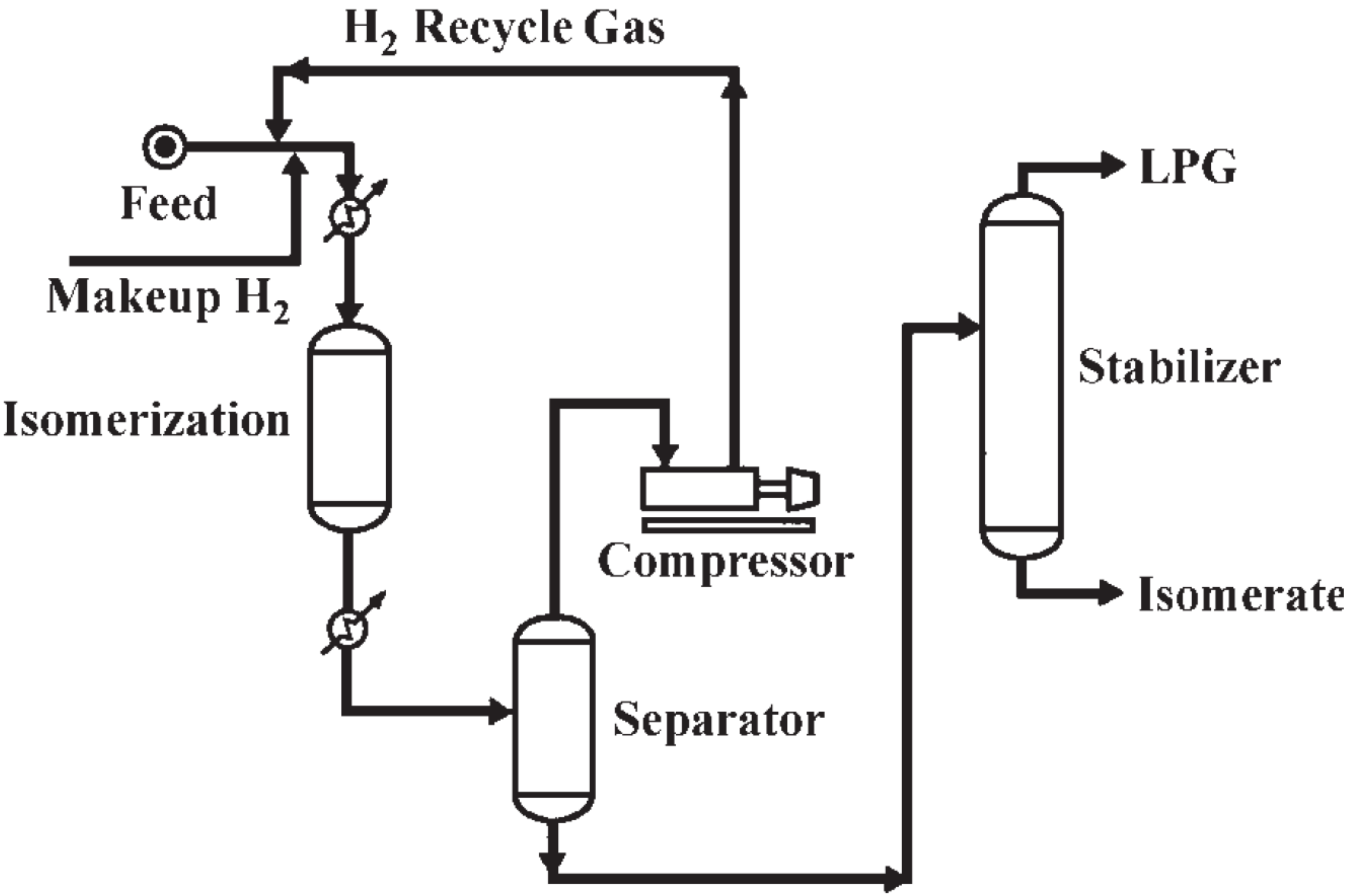
Some refineries do not have hydrocracking facility to supply isobutane for alkylation unit. The required isobutane can be obtained from n-butane using isomerization.

Isomerization

Develop process flow diagram (PFD) for the hydroisomerization process.

(Class activity)

Simplified PFD of a once-through (O-T) isomerization process [5]



Typical performance of O-T process [5]

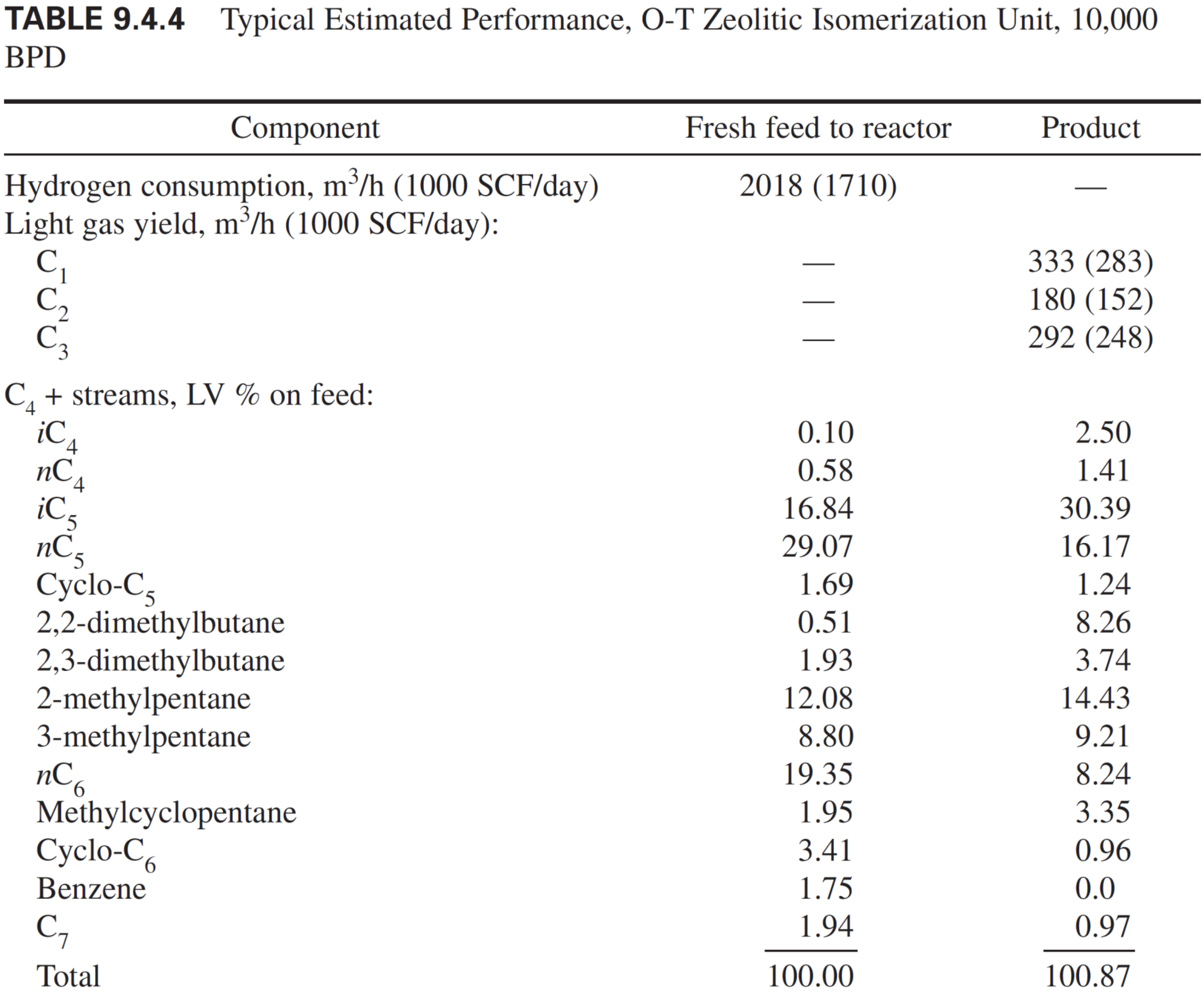
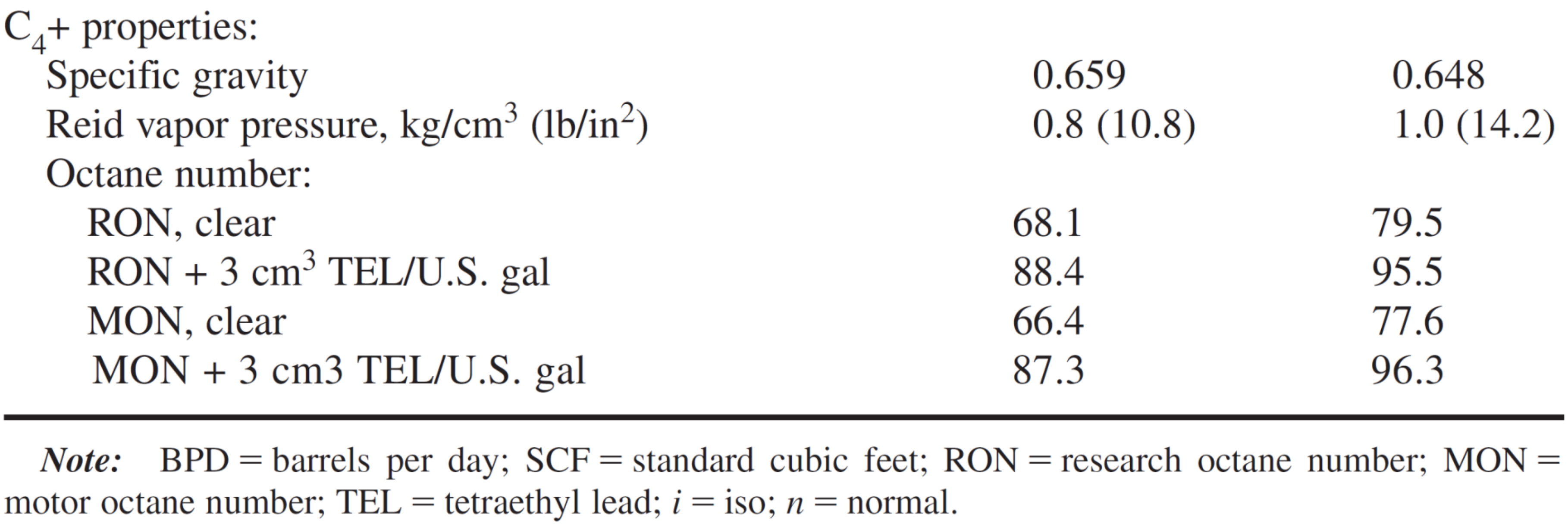


TABLE 9.4.4 Typical Estimated Performance, O-T Zeolitic Isomerization Unit, 10,000 BPD

Component	Fresh feed to reactor	Product
Hydrogen consumption, m^3/h (1000 SCF/day)	2018 (1710)	—
Light gas yield, m^3/h (1000 SCF/day):		
C_1	—	333 (283)
C_2	—	180 (152)
C_3	—	292 (248)
C_4 + streams, LV % on feed:		
iC_4	0.10	2.50
nC_4	0.58	1.41
iC_5	16.84	30.39
nC_5	29.07	16.17
Cyclo-C_5	1.69	1.24
2,2-dimethylbutane	0.51	8.26
2,3-dimethylbutane	1.93	3.74
2-methylpentane	12.08	14.43
3-methylpentane	8.80	9.21
nC_6	19.35	8.24
Methylcyclopentane	1.95	3.35
Cyclo-C_6	3.41	0.96
Benzene	1.75	0.0
C_7	1.94	0.97
Total	100.00	100.87

Typical performance of O-T process (Continued .....) [5]



C_4+ properties:		
Specific gravity	0.659	0.648
Reid vapor pressure, kg/cm^3 (lb/in^2)	0.8 (10.8)	1.0 (14.2)
Octane number:		
RON, clear	68.1	79.5
RON + 3 cm^3 TEL/U.S. gal	88.4	95.5
MON, clear	66.4	77.6
MON + 3 cm3 TEL/U.S. gal	87.3	96.3

Note: BPD = barrels per day; SCF = standard cubic feet; RON = research octane number; MON = motor octane number; TEL = tetraethyl lead; *i* = iso; *n* = normal.

For detail of isomerization process, see ref [5]

Isomerization plant at PRL

14

DAWN MONDAY JULY 27, 2015

DAWN

PRL

PAKISTAN REFINERY LIMITED COMMISSIONS ITS NEW MODULAR ISOMERISATION PLANT

– a first of its kind project undertaken in Pakistan

This plant will convert low value Naphtha into Petrol, a premium product. This initiative doubles Petrol production from 140,000 MT / annum to 280,000 MT / annum, resulting in import substitution and substantial foreign exchange saving.

The new ISOMERISATION plant, with a price tag of USD 50 million, has been built in record time ahead of its schedule. The project execution strategy adopted a modular approach, which comprised of importing 24 fully fabricated modules from the UAE. After overcoming significant inland logistical challenges, these modules were transported from the port to the PRL premises at Korangi and were directly placed onto the foundations.

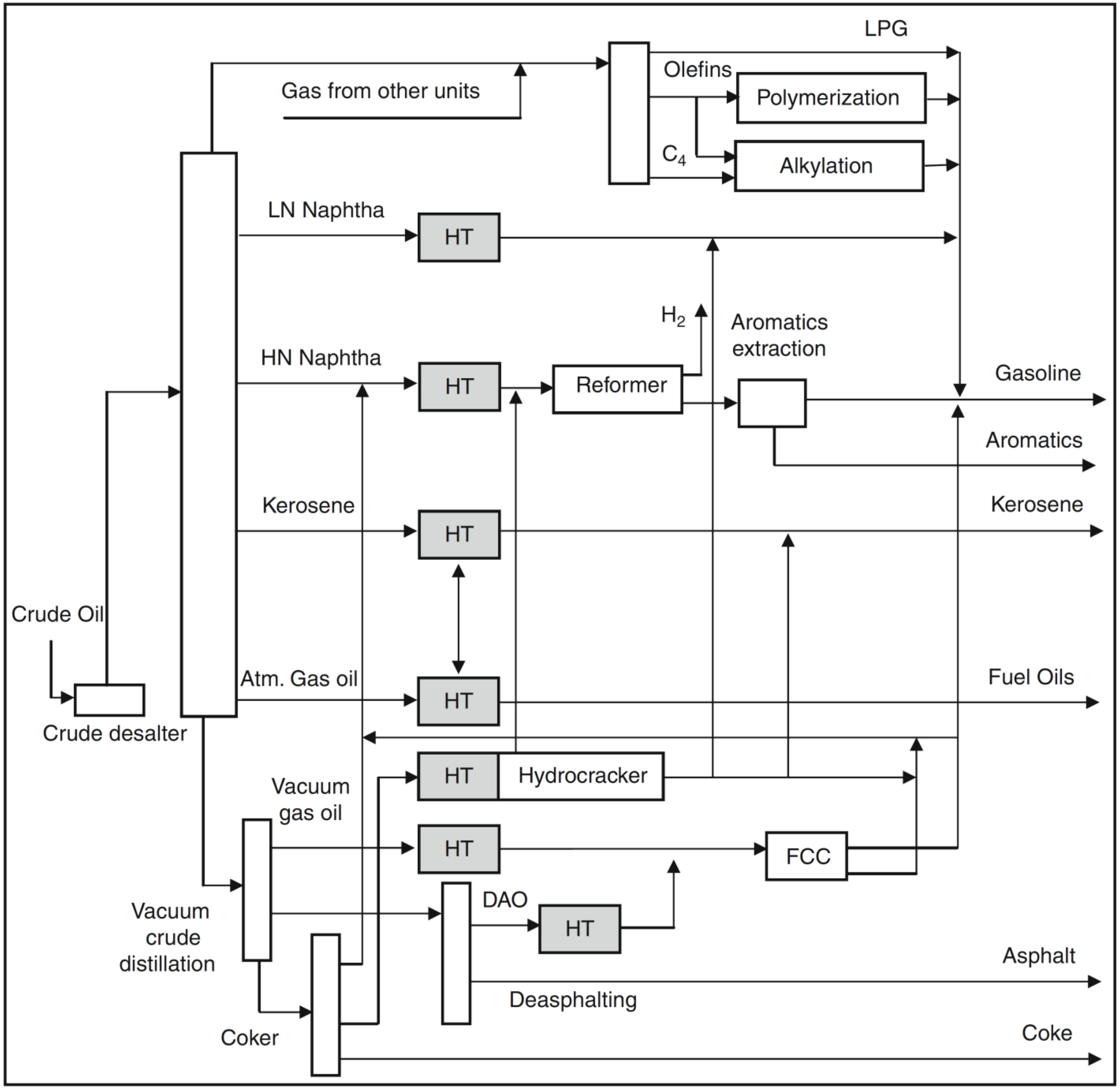
By the Grace of Allah, this entire project from groundbreaking to commissioning has been completed without any lost time incident.

Hydrotreating

Hydrotreating is the removal of impurities from a petroleum fraction. “Hydrotreating refers to a relatively mild operation whose primary purpose is to saturate olefins and/or reduce the sulfur and/or nitrogen content (and not to change the boiling range) of the feed” [1]. The process is used to stabilize (converting unsaturated hydrocarbons such as olefins and diolefins to paraffins) a petroleum fraction and to remove sulfur, nitrogen, oxygen, halides, and trace metals from the petroleum fraction. Hydrotreating is applied to a wide variety of feedstocks. Examples may include:

- Naphtha
- Kerosene
- Diesel (Gas oil)
- Atmospheric resids

Hydrotreating [2]



Hydrotreating

The process is generally carried out at moderately high temperature and pressure and in the presence of a catalyst.

Typical temperature and pressure are 270–340°C and 690–20700 kPag respectively [1].

Nickel/Cobalt and molybdenum oxides on alumina are widely used catalysts.

Hydrotreating catalysts [2]

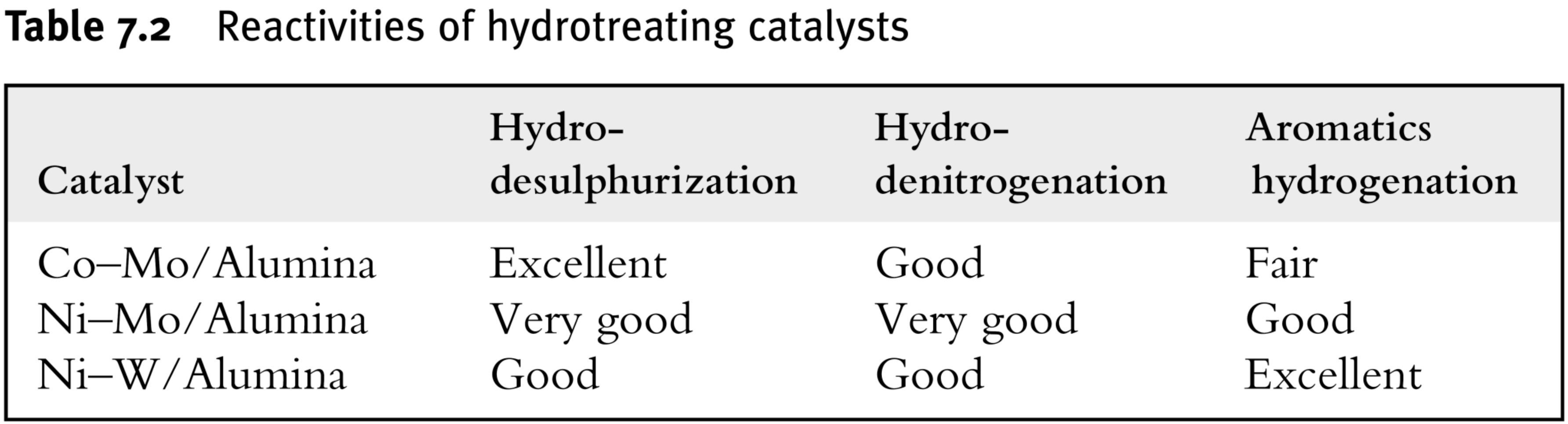


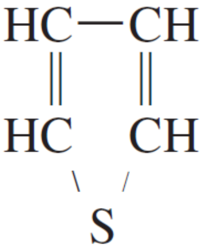
Table 7.2 Reactivities of hydrotreating catalysts

Catalyst	Hydro-desulphurization	Hydro-denitrogenation	Aromatics hydrogenation
Co–Mo/Alumina	Excellent	Good	Fair
Ni–Mo/Alumina	Very good	Very good	Good
Ni–W/Alumina	Good	Good	Excellent

“In the case of a guard reactor, which is used to protect the main catalyst from metal deposition, catalysts with wide pores are chosen and are generally plugged by metal deposition” [Fahim, 2010].

Hydrotreating reactions [2]

1. Desulfurization
   - a. Mercaptans: $RSH + H_2 \rightarrow RH + H_2S$
   - b. Sulfides: $R_2S + 2H_2 \rightarrow 2RH + H_2S$
   - c. Disulfides: $(RS)_2 + 3H_2 \rightarrow 2RH + 2H_2S$
   - d. Thiophenes:



$+ 4H_2 \rightarrow C_4H_{10} + H_2S$

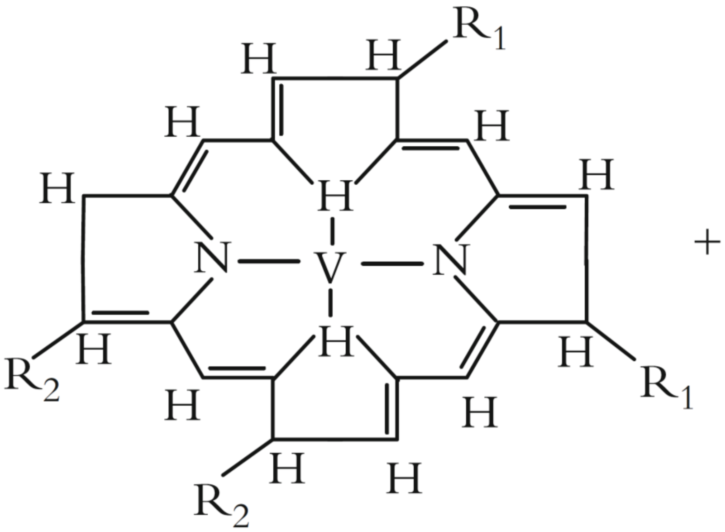
2. Denitrogenation
   - a. Pyrrole: $C_4H_4NH + 4H_2 \rightarrow C_4H_{10} + NH_3$
   - b. Pyridine: $C_5H_5N + 5H_2 \rightarrow C_5H_{12} + NH_3$
3. Deoxidation
   - a. Phenol: $C_6H_5OH + H_2 \rightarrow C_6H_6 + H_2O$
   - b. Peroxides: $C_7H_{13}OOH + 3H_2 \rightarrow C_7H_{16} + 2H_2O$
4. Dehalogenation

   Chlorides: $RCl + H_2 \rightarrow RH + HCl$.
5. Hydrogenation:

   Pentene: $C_5H_{10} + H_2 \rightarrow C_5H_{12}$
6. Hydrocracking: $C_{10}H_{22} + H_2 \rightarrow C_4H_{10} + C_6H_{14}$

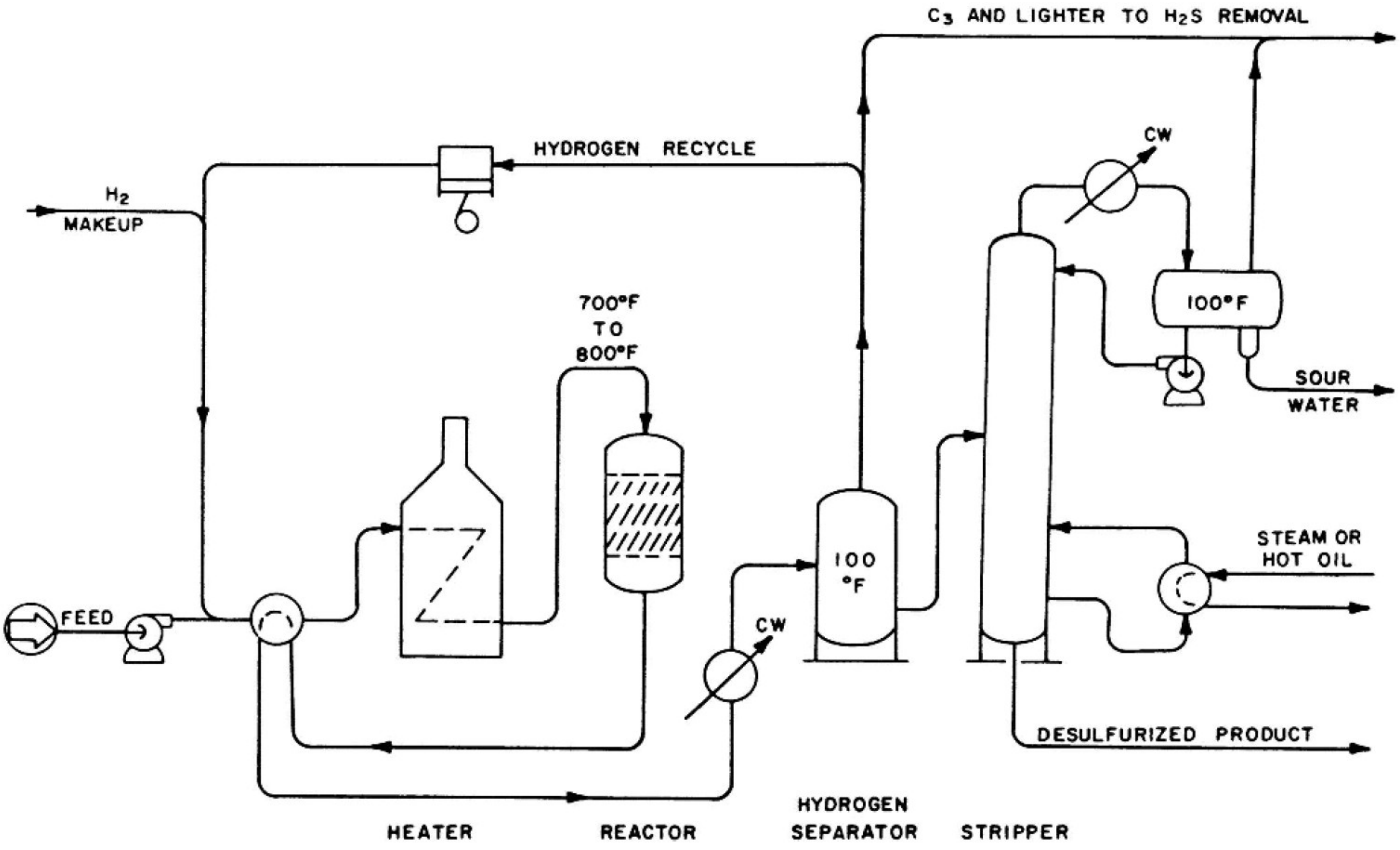
Hydrotreating reactions [2]

7. Hydrogenation of organo-metallic compounds and deposition of metals



$+ \quad H_2 \longrightarrow 2NH_3 + 2R_1H_4 + 2R_2H + V$

Hydrotreating (hydrodesulfurization) [1]



Hydrotreating process parameters [2]

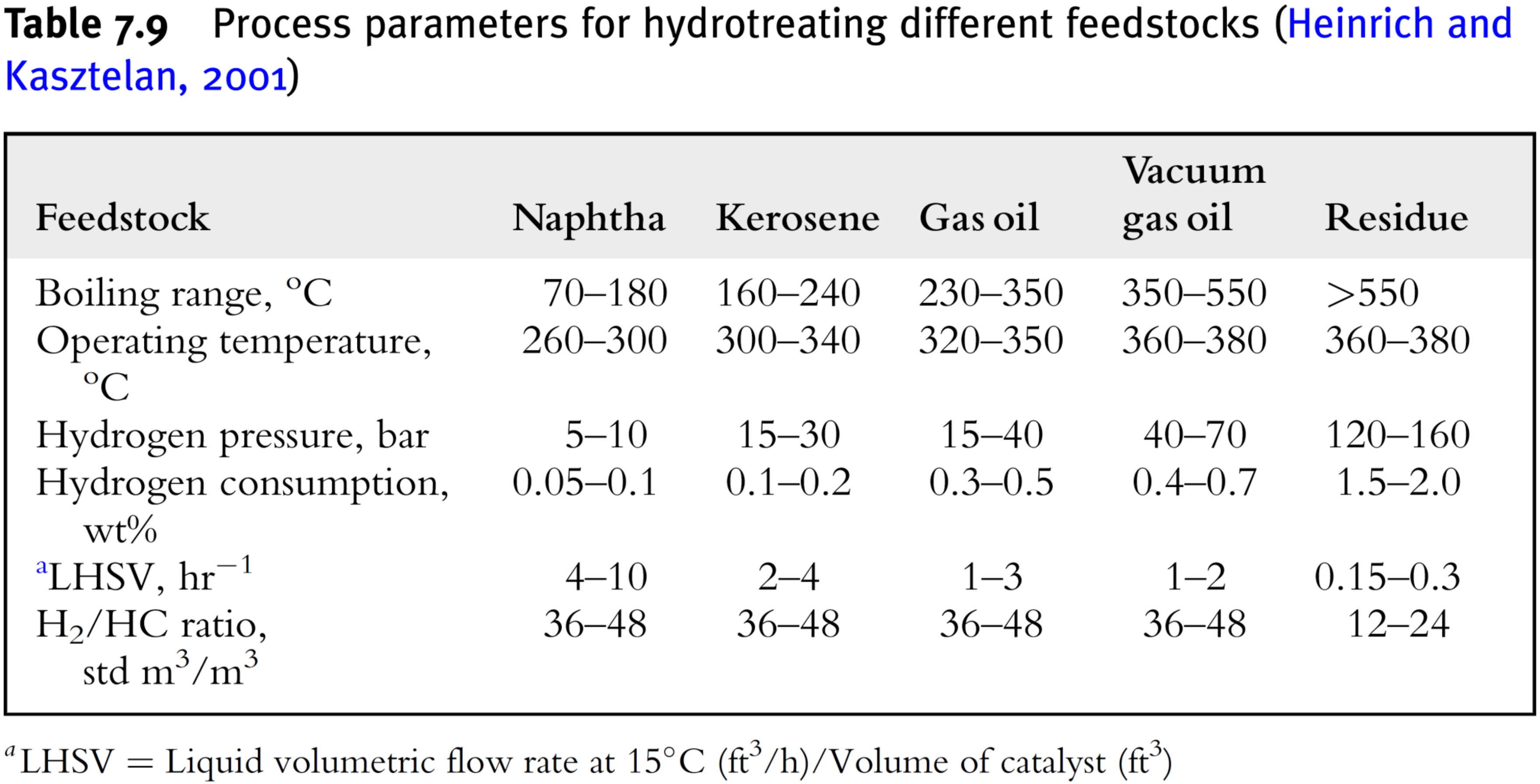


Table 7.9 Process parameters for hydrotreating different feedstocks (Heinrich and Kasztelan, 2001)

Feedstock	Naphtha	Kerosene	Gas oil	Vacuum gas oil	Residue
Boiling range, °C	70–180	160–240	230–350	350–550	>550
Operating temperature, °C	260–300	300–340	320–350	360–380	360–380
Hydrogen pressure, bar	5–10	15–30	15–40	40–70	120–160
Hydrogen consumption, wt%	0.05–0.1	0.1–0.2	0.3–0.5	0.4–0.7	1.5–2.0
[a]LHSV, hr^{-1}	4–10	2–4	1–3	1–2	0.15–0.3
H_2/HC ratio, std m^3/m^3	36–48	36–48	36–48	36–48	12–24

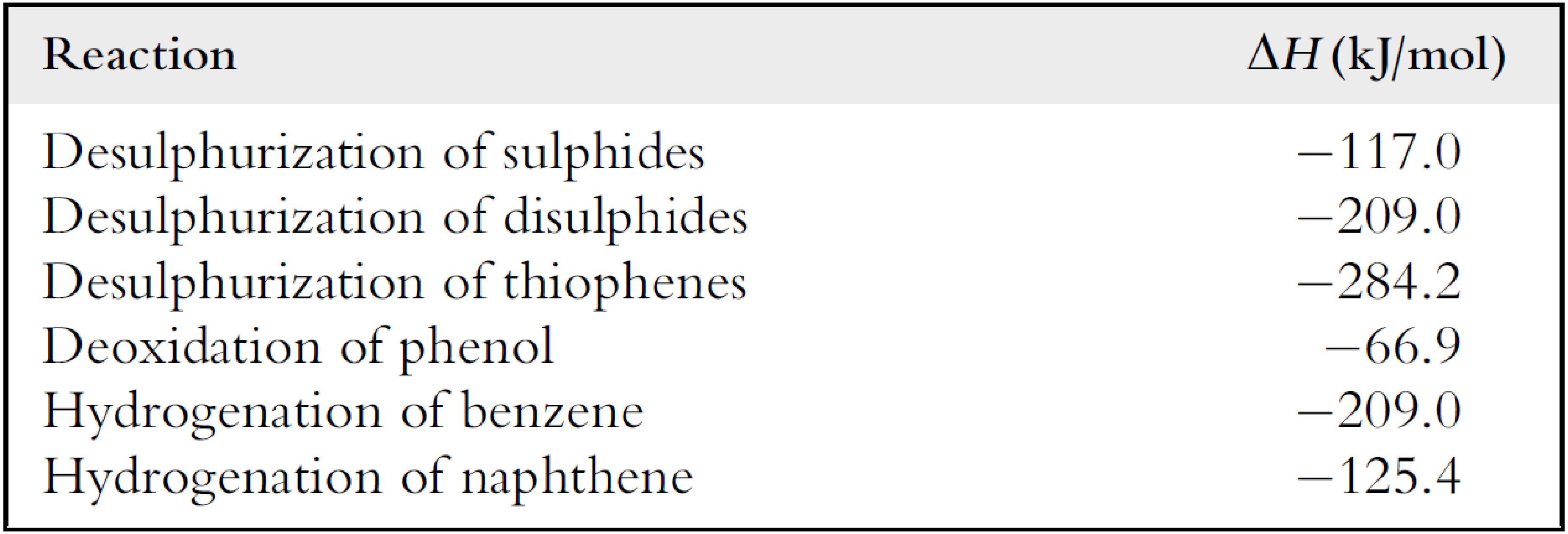
[a] LHSV = Liquid volumetric flow rate at 15°C (ft^3/h)/Volume of catalyst (ft^3)

Thermodynamics of hydrotreating

- Hydrotreating reaction are reversible and highly exothermic.
- “The logarithmic equilibrium constants for several hydrodesulfurization reactions are positive (Gibbs free energy change is negative), indicating that the reaction can virtually proceed to completion if hydrogen is present in the stoichiometric quantity” [Fahim, 2010].
- “Although equilibrium conversions decrease with temperature rise, commercial hydrotreating is run at rather high temperatures to promote the kinetics of these reactions ” [Fahim, 2010].

Thermodynamics of hydrotreating [2]

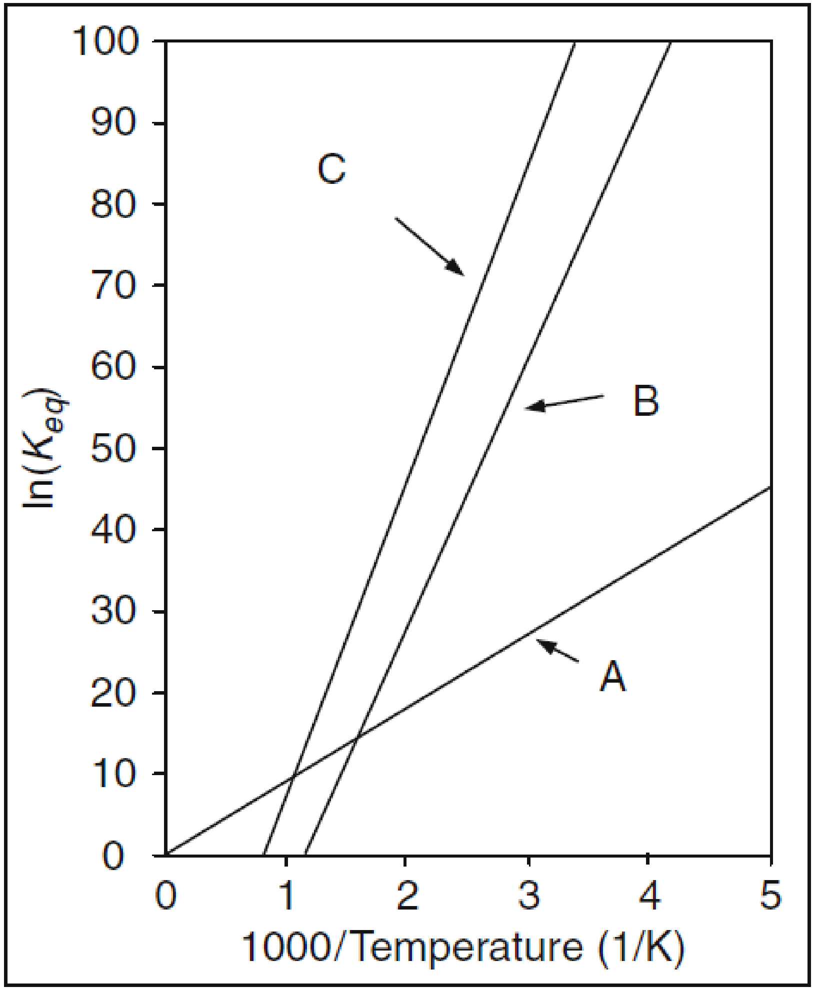
Heats of reactions of some hydrotreating reactions:

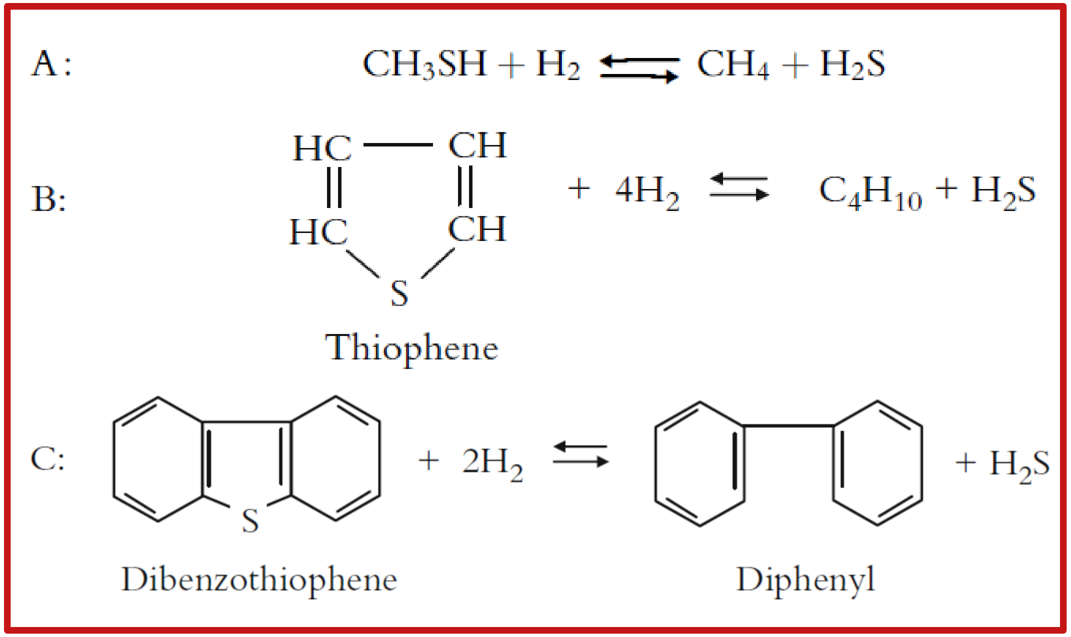


Reaction	ΔH (kJ/mol)
Desulphurization of sulphides	−117.0
Desulphurization of disulphides	−209.0
Desulphurization of thiophenes	−284.2
Deoxidation of phenol	−66.9
Hydrogenation of benzene	−209.0
Hydrogenation of naphthene	−125.4

How can you find heat of reaction?

Thermodynamics of hydrotreating [2]





Thermodynamics of hydrotreating

- Olefin hydrogenation reaction usually goes to completion.
- "An aromatic hydrogenation reaction can reach equilibrium under certain conditions, as in kerosene and gas oil hydrogenation" [2].
- " Hydrodesulfurization can be carried out easier than denitrogenation, while aromatic saturation is the most difficult reaction" [2].

Kinetics of hydrotreating

If the rate of a hydrotreating reaction follows *nth* order mechanism:

$$\boxed{-\frac{dC}{dt} = kC^n}$$

- The $n = 1$ is obtained for the narrow cuts (naphtha and kerosene) [2].
- $n > 1$ is for gas oil and $n = 2.0$ for vacuum gas oil (VGO) or residue [2].

Kinetics of hydrotreating [2]

Example E7.2

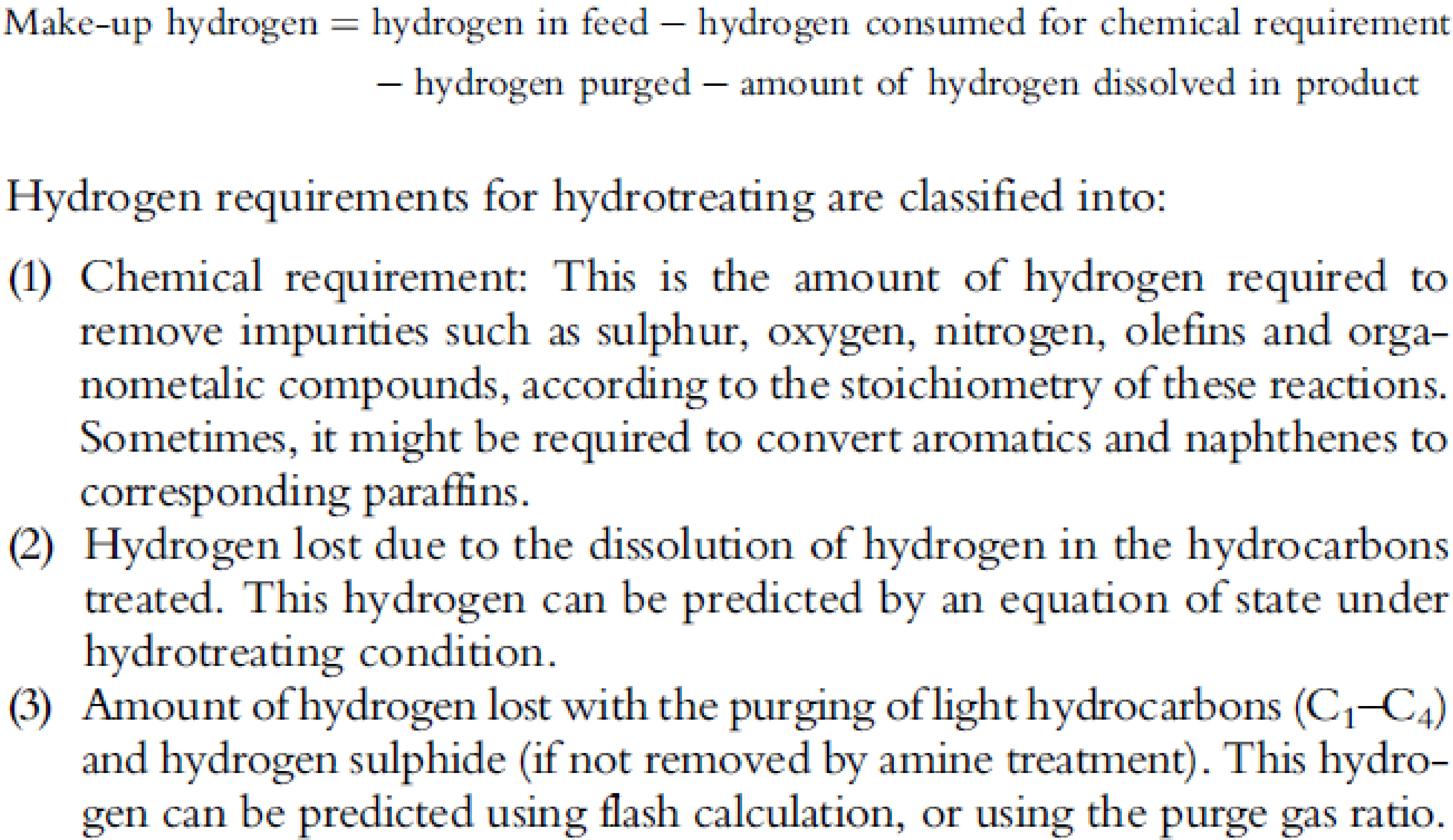
Find the catalyst volume needed for the desulphurization of VGO. The initial sulphur content is 2.3 wt% and the final sulphur content of the product is 0.1 wt%. The reaction rate constant (h^{-1}) can be expressed as:

$$k = 2.47 \times 10^{10} \exp\left(\frac{-14,995}{T}\right)$$

The reaction conditions are $T = 415$ °C and $P = 5.1$ MPa. The order of the reaction was found to be $n = 1.7$. The feed flow rate is 167,500 kg/h and has a density of 910 kg/m^3.

$$\tau = \frac{V}{v_0} = C_{A0} \int_0^{X_{Af}} \frac{dX_A}{-r_A} = -\int_{C_{A0}}^{C_{Af}} \frac{dC_A}{-r_A}$$

Makeup hydrogen for a hydrotreating process [2]



Make-up hydrogen = hydrogen in feed − hydrogen consumed for chemical requirement − hydrogen purged − amount of hydrogen dissolved in product

Hydrogen requirements for hydrotreating are classified into:

(1) Chemical requirement: This is the amount of hydrogen required to remove impurities such as sulphur, oxygen, nitrogen, olefins and organometalic compounds, according to the stoichiometry of these reactions. Sometimes, it might be required to convert aromatics and naphthenes to corresponding paraffins.

(2) Hydrogen lost due to the dissolution of hydrogen in the hydrocarbons treated. This hydrogen can be predicted by an equation of state under hydrotreating condition.

(3) Amount of hydrogen lost with the purging of light hydrocarbons (C_1–C_4) and hydrogen sulphide (if not removed by amine treatment). This hydrogen can be predicted using flash calculation, or using the purge gas ratio.

Hydrotreating correlations: Naphtha and gas oil correlations [2]

The standard cubic foot of hydrogen per barrel of feed (SCFB) required for complete sulphur removal is calculated as:

$$\text{SCFB H}_2 = 191S_f - 30.7$$

where S_f is the sulphur wt% in feed.

The increase in the API gravity of a product is calculated as:

$$\Delta(\text{API})_p = 0.01 \times (\text{SCFB H}_2) + 0.036 \times (\text{API})_f - 2.69$$

where p and f refer to product and feed, respectively.

Hydrotreating correlations: Naphtha and gas oil correlations [2]

Example E7.3

It is required to hydrotreat naphtha which has 1 wt% S and API = 50. Find:

a. How much hydrogen is required to remove all the sulphur in the feed by empirical correlations.
b. How much of this H_2 is used for chemical requirements.

Example E7.4

It is required to remove all S in a feed of atmospheric gas oil (AGO) by hydrotreating. The feed contains 2 wt% S and sulphur compounds distributed is as follows:

Compound	RSH	R_2S	$(RS)_2$	Thiophene (C_4H_4S)
wt %	45	25	20	10

The AGO has an API = 30. Calculate the chemical hydrogen requirement in SCFB.

Naphtha hydrodesulfurization

The hydrotreating process that is specifically employed for the removal of sulfur is called hydrodesulfurization. The principle impurities to be removed in the naphtha are:

- Sulfur
- Nitrogen
- Oxygen
- Olefins
- Metals

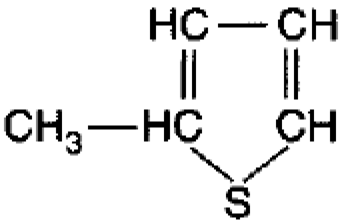
Sulfur impurities

The sulfur containing compounds are mainly:

- Mercaptans
- Sulfides
- Disulfiudes
- Polysulfides
- Thiophenes.

The thiophenes are more difficult to eliminate than most other types.

Example desulphurization reactions [3]



$+ \; 4H_2 \longrightarrow C_5H_{12} \; + \; H_2S$

Methyl thiophene

n pentane

$CH_3{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}SH \; + \; H_2 \longrightarrow C_5H_{12} \; + \; H_2S$

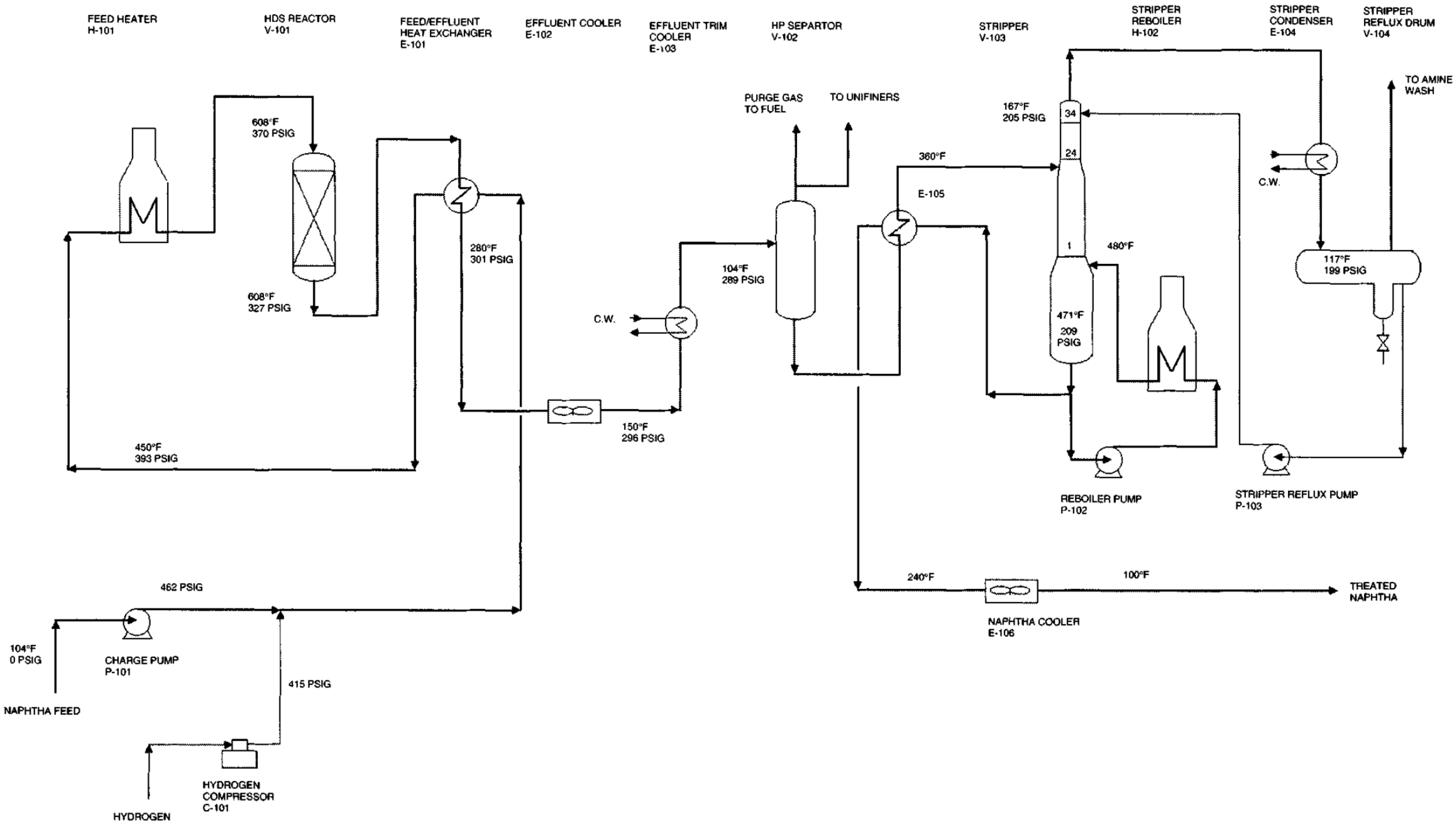
Amyl mercaptan

n pentane

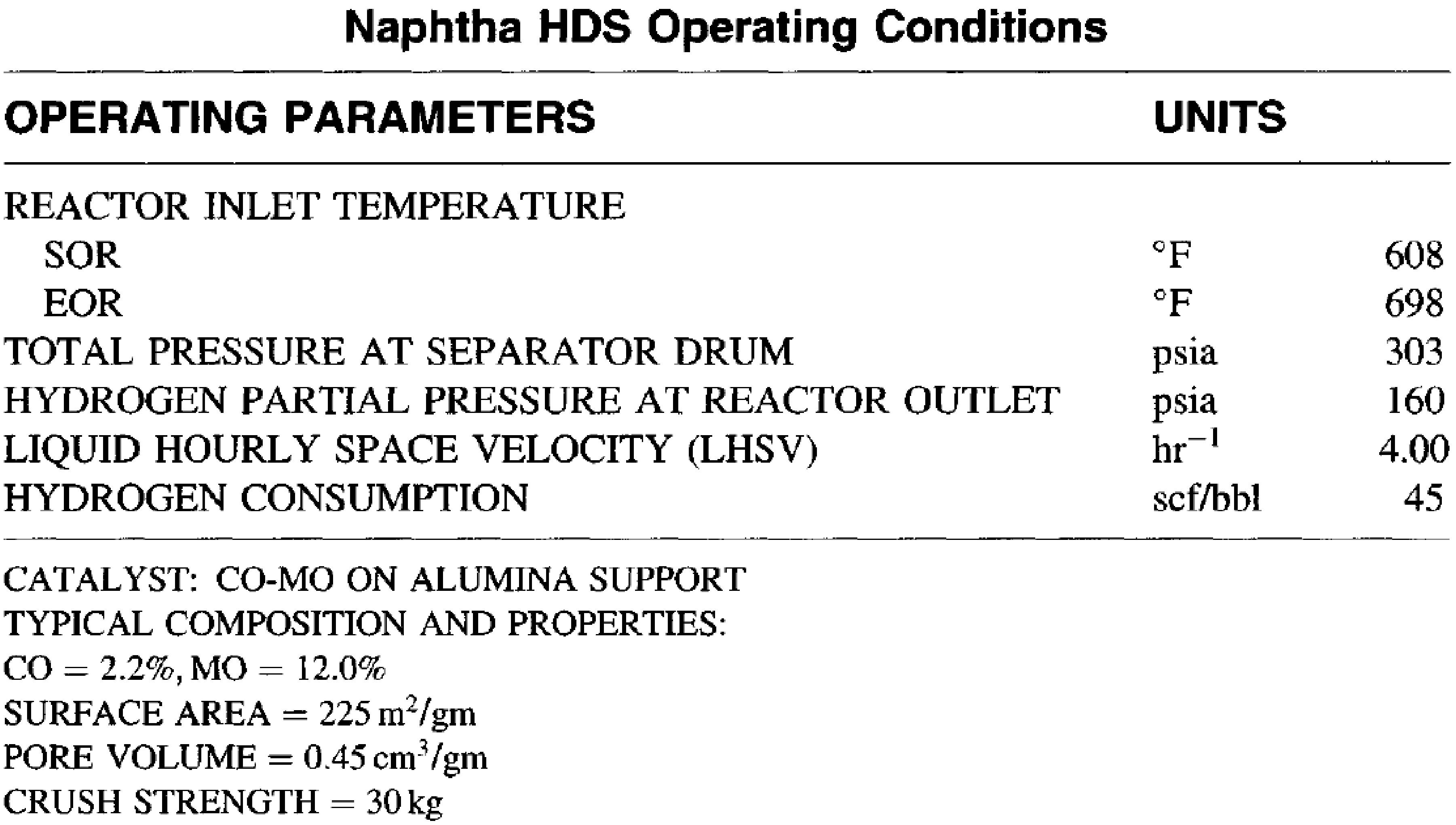
$CH_3{-}CH_2{-}CH_2{-}S{-}S{-}CH_2{-}CH_2{-}CH_3 \; + \; 3H_2 \longrightarrow 2C_3H_8 \; + \; 2H_2S$

Dipropyl disulfide

Desulphurization flow diagram [3]



Desulphurization operating conditions

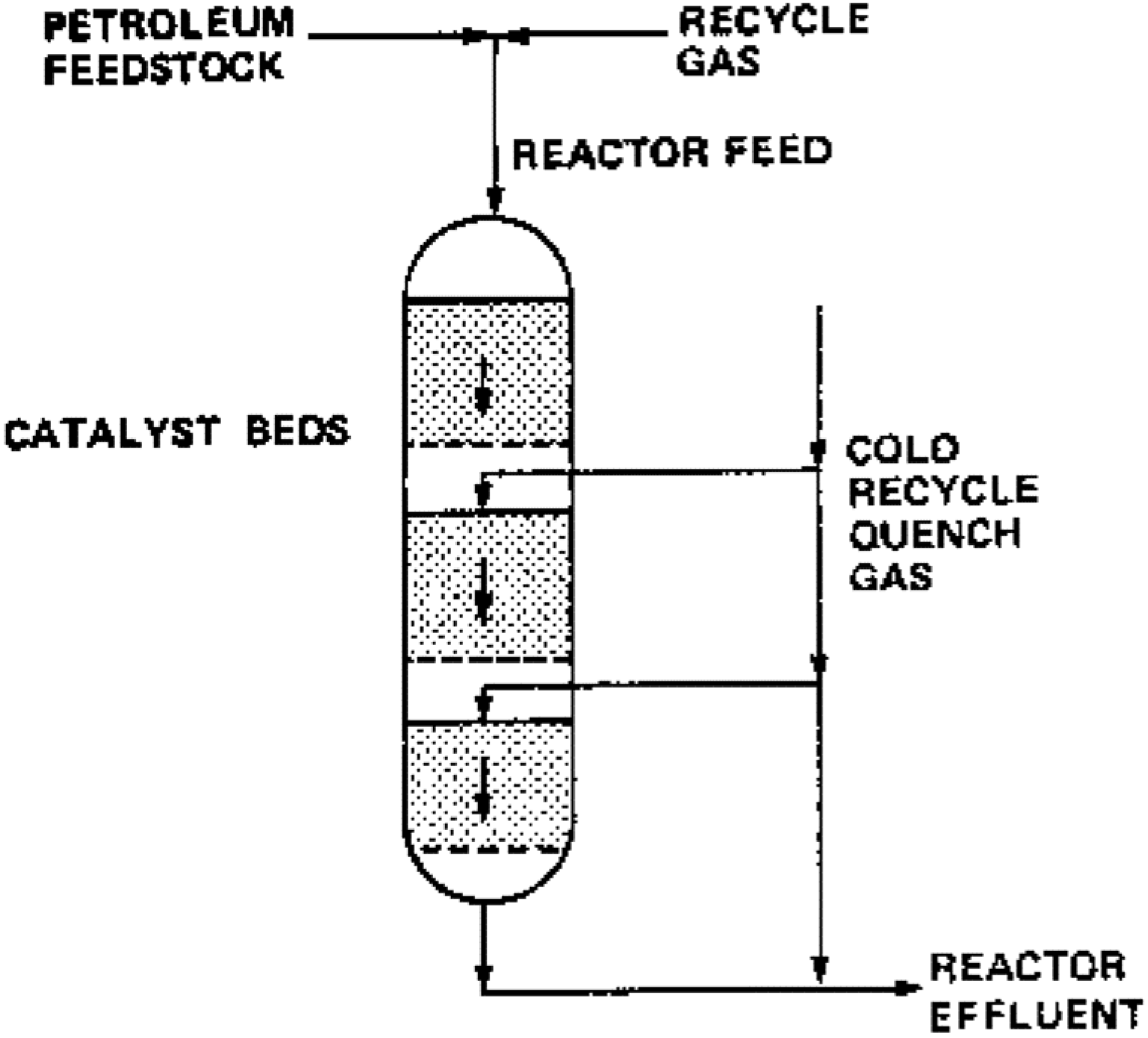


Naphtha HDS Operating Conditions

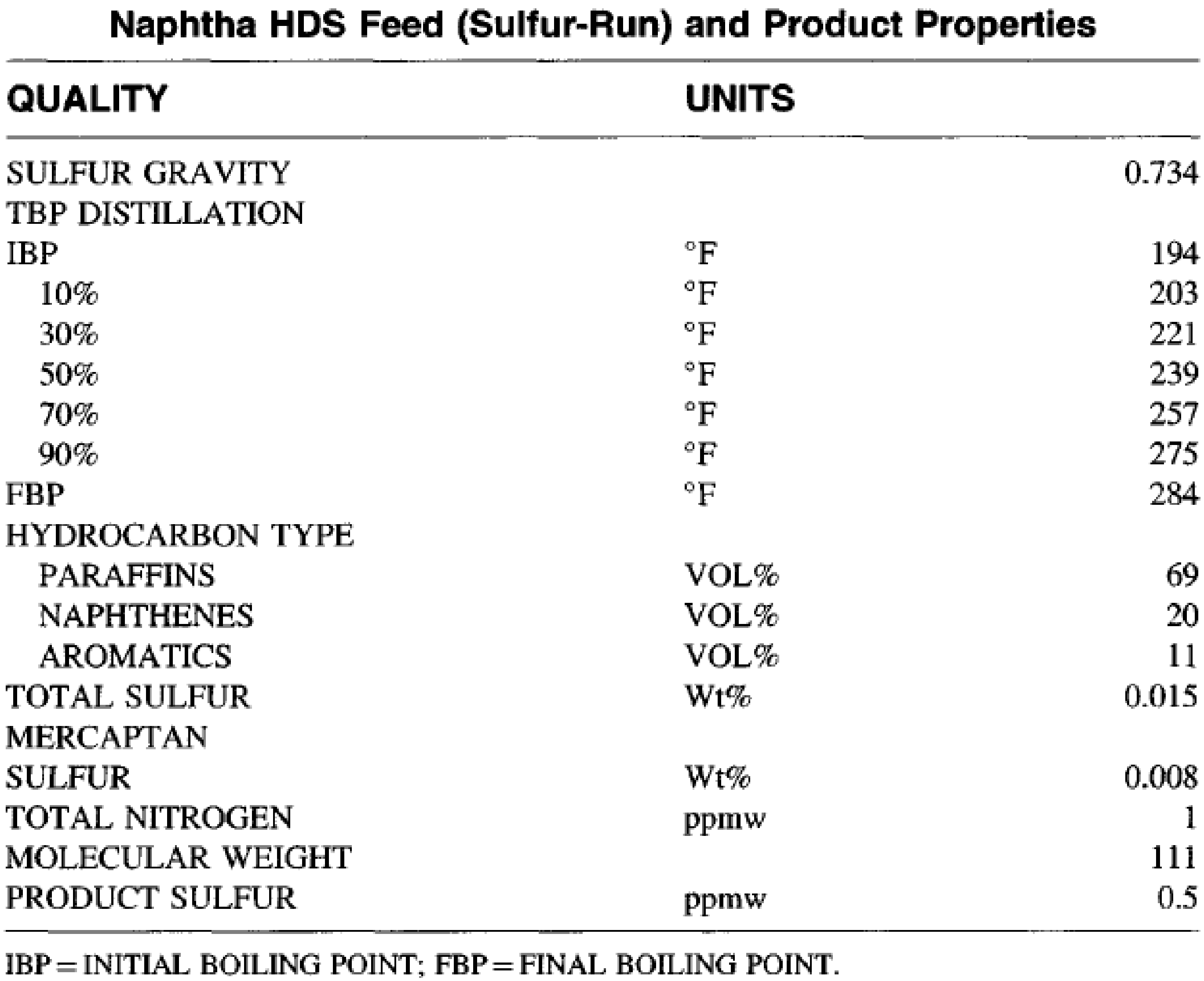
OPERATING PARAMETERS	UNITS	
REACTOR INLET TEMPERATURE		
SOR	°F	608
EOR	°F	698
TOTAL PRESSURE AT SEPARATOR DRUM	psia	303
HYDROGEN PARTIAL PRESSURE AT REACTOR OUTLET	psia	160
LIQUID HOURLY SPACE VELOCITY (LHSV)	hr^{-1}	4.00
HYDROGEN CONSUMPTION	scf/bbl	45

CATALYST: CO-MO ON ALUMINA SUPPORT
TYPICAL COMPOSITION AND PROPERTIES:
CO = 2.2%, MO = 12.0%
SURFACE AREA = 225 m^2/gm
PORE VOLUME = 0.45 cm^3/gm
CRUSH STRENGTH = 30 kg

Desulphurization reactor [3]



Desulphurization results [3]

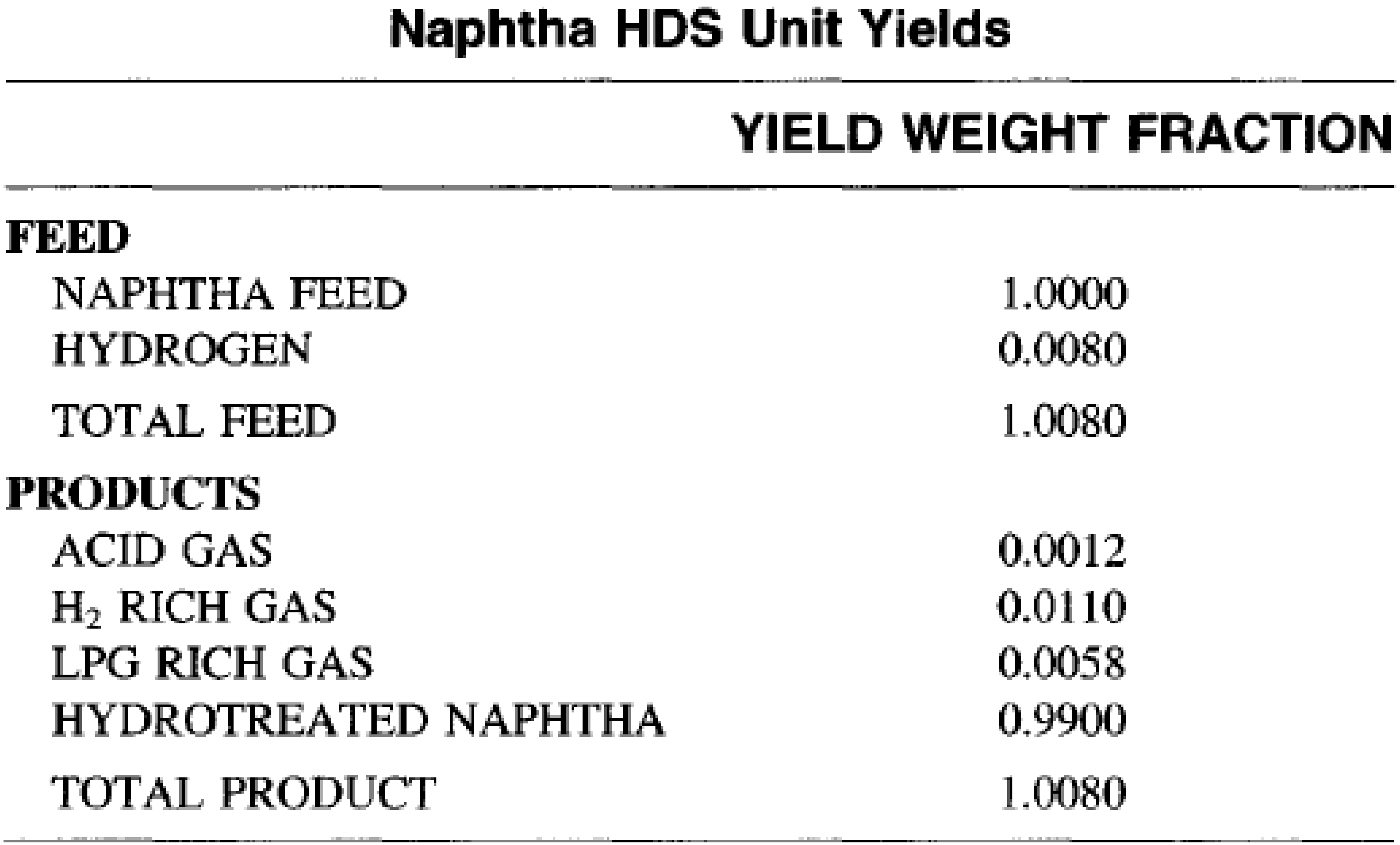


Naphtha HDS Feed (Sulfur-Run) and Product Properties

QUALITY	UNITS	
SULFUR GRAVITY		0.734
TBP DISTILLATION		
IBP	°F	194
10%	°F	203
30%	°F	221
50%	°F	239
70%	°F	257
90%	°F	275
FBP	°F	284
HYDROCARBON TYPE		
PARAFFINS	VOL%	69
NAPHTHENES	VOL%	20
AROMATICS	VOL%	11
TOTAL SULFUR	Wt%	0.015
MERCAPTAN		
SULFUR	Wt%	0.008
TOTAL NITROGEN	ppmw	1
MOLECULAR WEIGHT		111
PRODUCT SULFUR	ppmw	0.5

IBP = INITIAL BOILING POINT; FBP = FINAL BOILING POINT.

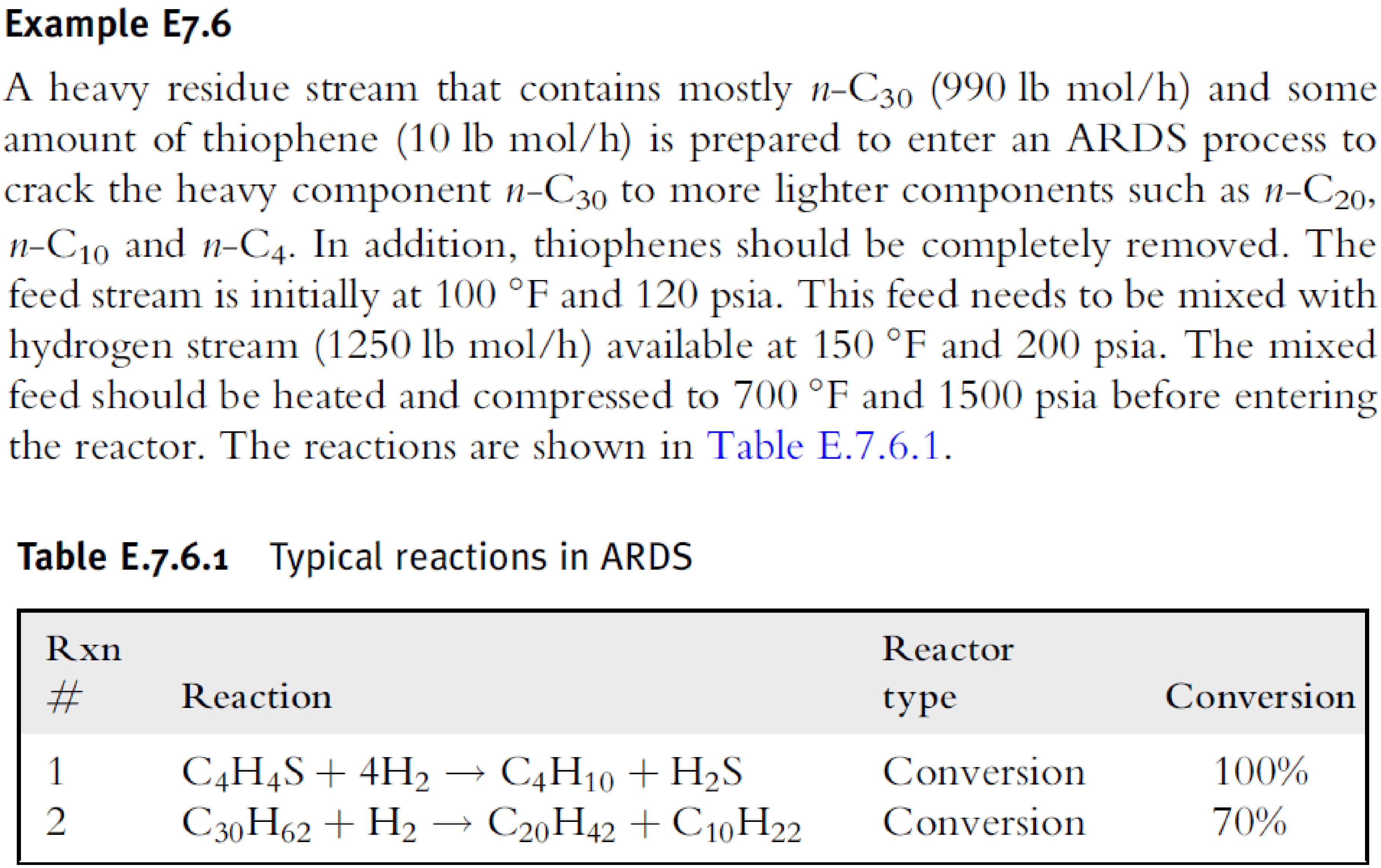
Desulphurization yields [3]



Naphtha HDS Unit Yields

	YIELD WEIGHT FRACTION
FEED	
NAPHTHA FEED	1.0000
HYDROGEN	0.0080
TOTAL FEED	1.0080
PRODUCTS	
ACID GAS	0.0012
H_2 RICH GAS	0.0110
LPG RICH GAS	0.0058
HYDROTREATED NAPHTHA	0.9900
TOTAL PRODUCT	1.0080

Simulation of a hydrotreating process that is accompanied by cracking reaction [2]



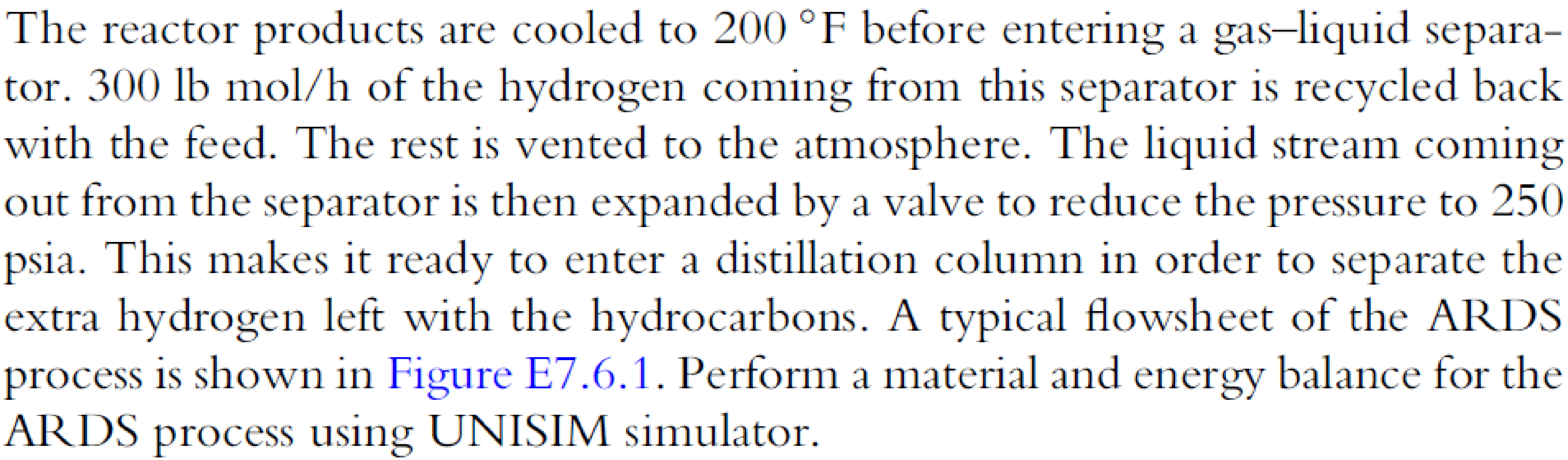
Example E7.6

A heavy residue stream that contains mostly *n*-C_{30} (990 lb mol/h) and some amount of thiophene (10 lb mol/h) is prepared to enter an ARDS process to crack the heavy component *n*-C_{30} to more lighter components such as *n*-C_{20}, *n*-C_{10} and *n*-C_4. In addition, thiophenes should be completely removed. The feed stream is initially at 100 °F and 120 psia. This feed needs to be mixed with hydrogen stream (1250 lb mol/h) available at 150 °F and 200 psia. The mixed feed should be heated and compressed to 700 °F and 1500 psia before entering the reactor. The reactions are shown in Table E.7.6.1.

Table E.7.6.1 Typical reactions in ARDS

Rxn #	Reaction	Reactor type	Conversion
1	$C_4H_4S + 4H_2 \rightarrow C_4H_{10} + H_2S$	Conversion	100%
2	$C_{30}H_{62} + H_2 \rightarrow C_{20}H_{42} + C_{10}H_{22}$	Conversion	70%

Simulation of a hydrotreating process [2]



The reactor products are cooled to 200 °F before entering a gas–liquid separator. 300 lb mol/h of the hydrogen coming from this separator is recycled back with the feed. The rest is vented to the atmosphere. The liquid stream coming out from the separator is then expanded by a valve to reduce the pressure to 250 psia. This makes it ready to enter a distillation column in order to separate the extra hydrogen left with the hydrocarbons. A typical flowsheet of the ARDS process is shown in Figure E7.6.1. Perform a material and energy balance for the ARDS process using UNISIM simulator.

Simulation of hydrotreating of ARDS: Solution [2]

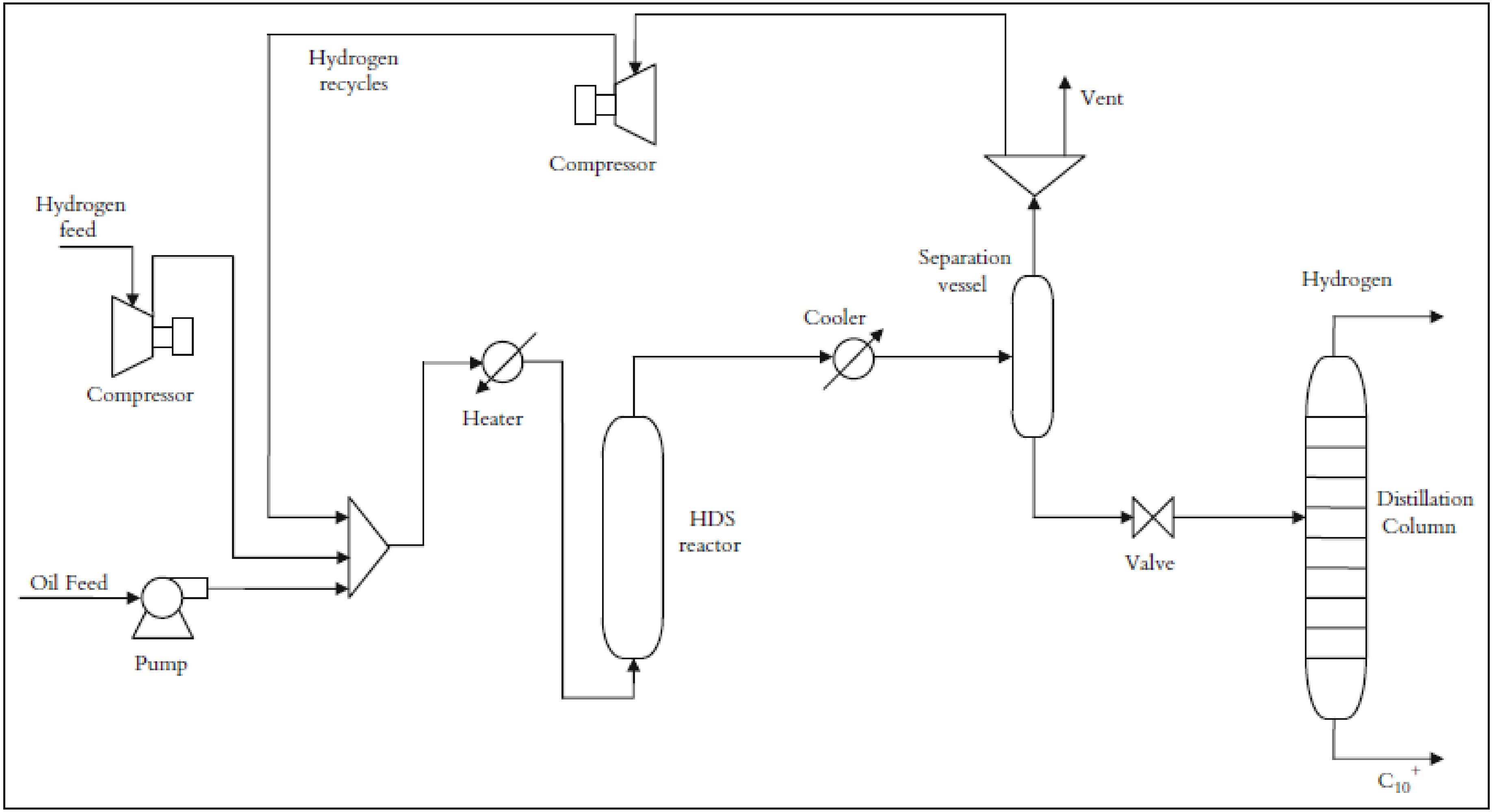
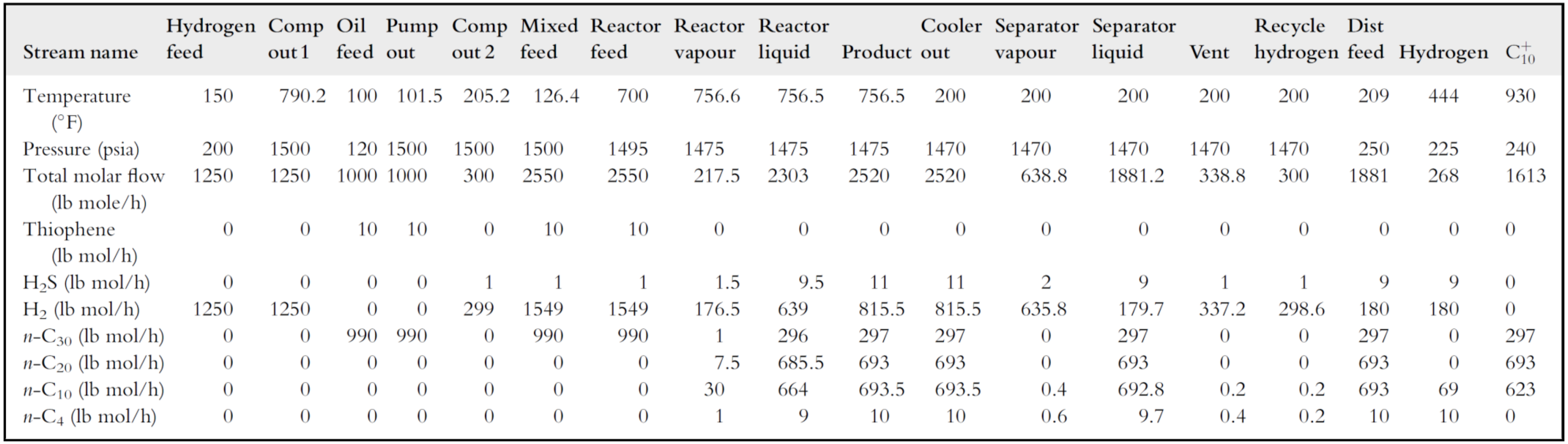


Figure E7.6.1 ARDS process flow chart

Simulation of hydrotreating of ARDS: Solution [2]



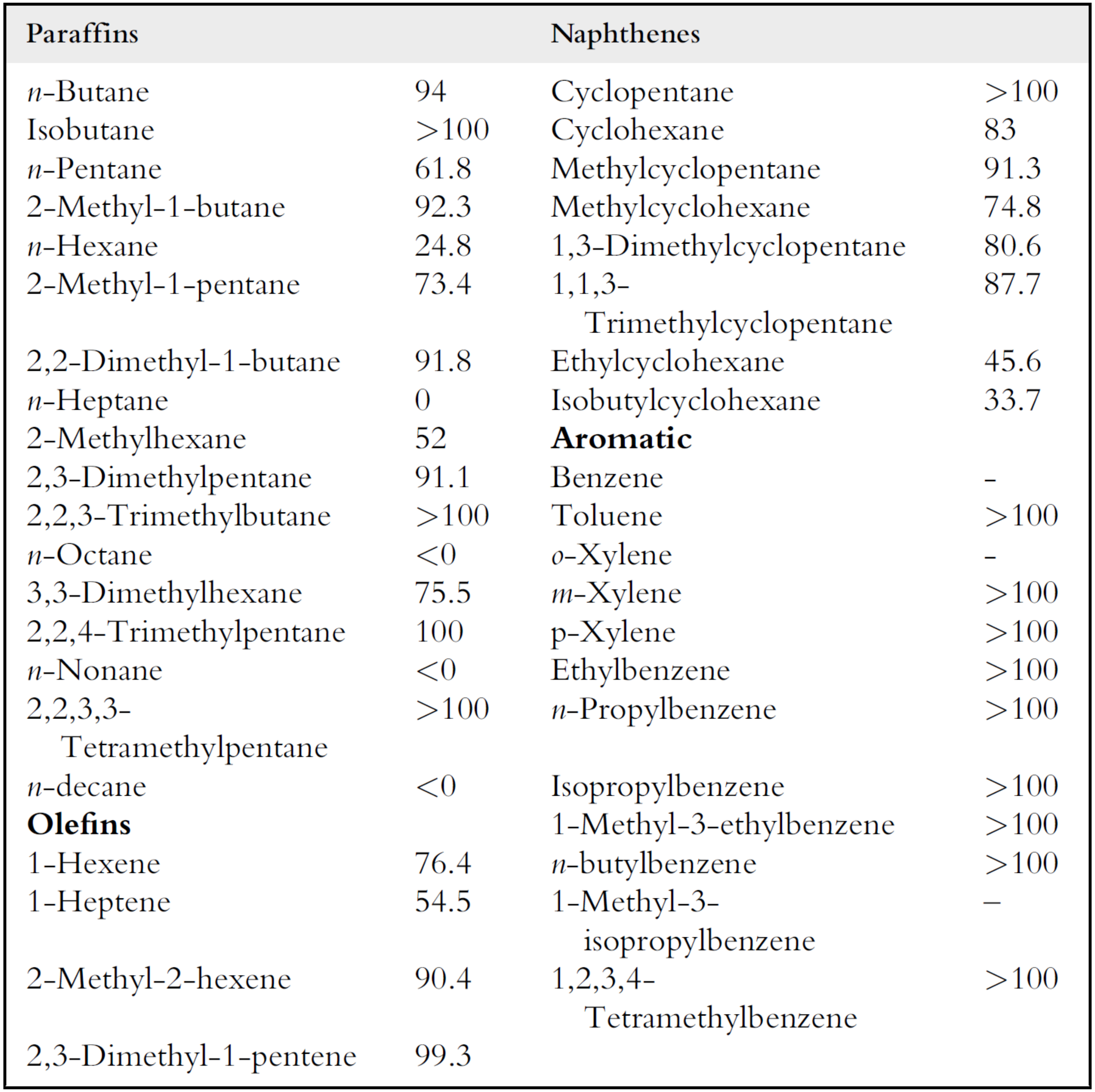
Stream name	Hydrogen feed	Comp out 1	Oil feed	Pump out	Comp out 2	Mixed feed	Reactor feed	Reactor vapour	Reactor liquid	Product	Cooler out	Separator vapour	Separator liquid	Vent	Recycle hydrogen	Dist feed	Hydrogen	C_{10}^{+}
Temperature (°F)	150	790.2	100	101.5	205.2	126.4	700	756.6	756.5	756.5	200	200	200	200	200	209	444	930
Pressure (psia)	200	1500	120	1500	1500	1500	1495	1475	1475	1475	1470	1470	1470	1470	1470	250	225	240
Total molar flow (lb mole/h)	1250	1250	1000	1000	300	2550	2550	217.5	2303	2520	2520	638.8	1881.2	338.8	300	1881	268	1613
Thiophene (lb mol/h)	0	0	10	10	0	10	10	0	0	0	0	0	0	0	0	0	0	0
H_2S (lb mol/h)	0	0	0	0	1	1	1	1.5	9.5	11	11	2	9	1	1	9	9	0
H_2 (lb mol/h)	1250	1250	0	0	299	1549	1549	176.5	639	815.5	815.5	635.8	179.7	337.2	298.6	180	180	0
n-C_{30} (lb mol/h)	0	0	990	990	0	990	990	1	296	297	297	0	297	0	0	297	0	297
n-C_{20} (lb mol/h)	0	0	0	0	0	0	0	7.5	685.5	693	693	0	693	0	0	693	0	693
n-C_{10} (lb mol/h)	0	0	0	0	0	0	0	30	664	693.5	693.5	0.4	692.8	0.2	0.2	693	69	623
n-C_4 (lb mol/h)	0	0	0	0	0	0	0	1	9	10	10	0.6	9.7	0.4	0.2	10	10	0

Catalytic reforming

The objective of catalytic reforming is to convert hydrocarbons of lower octane number to higher octane number gasoline (blend).

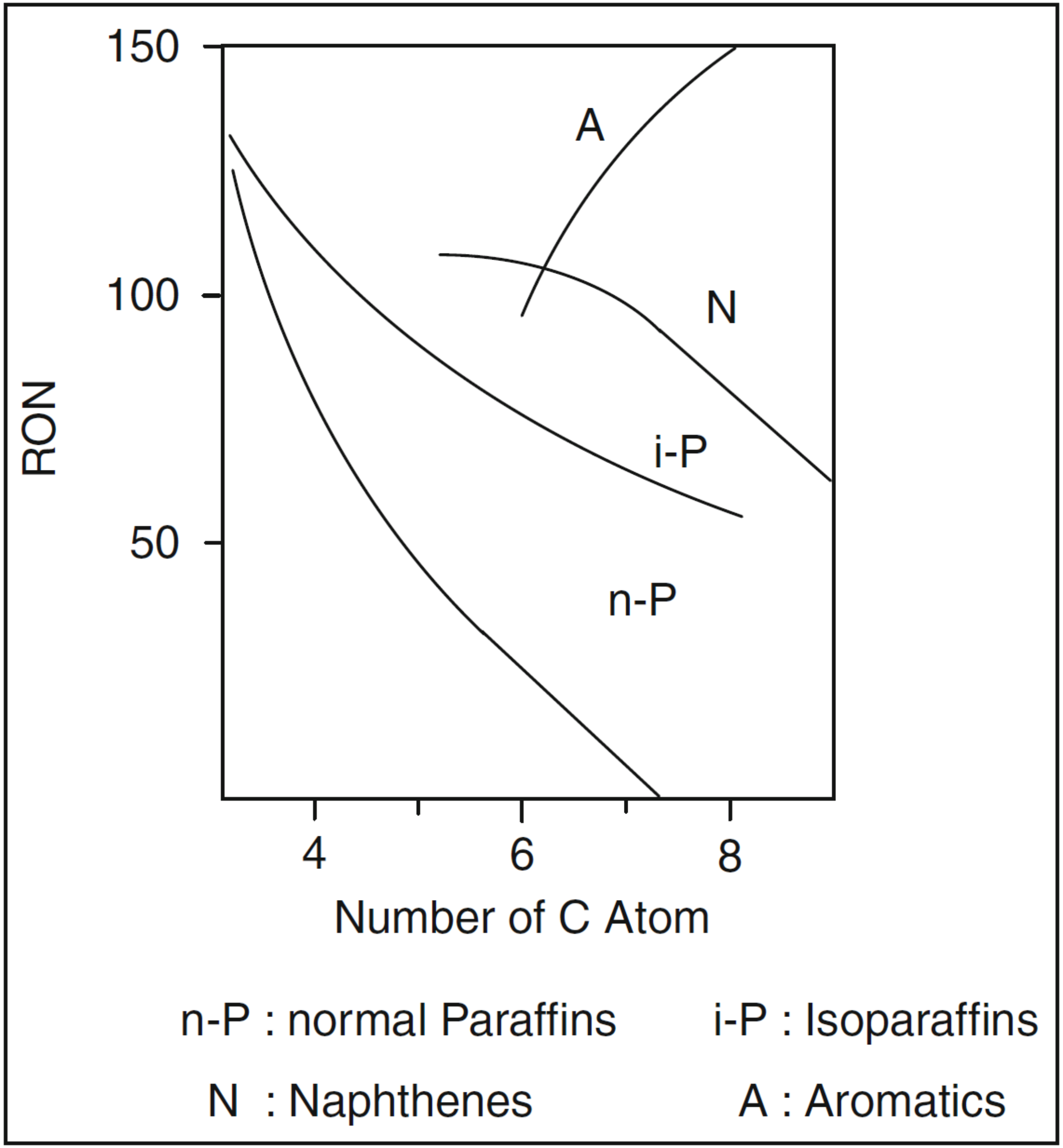
The fact that isoparaffins and aromatics have high octane numbers is the basis of catalytic reforming process.

Octane numbers of various pure compounds [2]



Paraffins		Naphthenes	
n-Butane	94	Cyclopentane	>100
Isobutane	>100	Cyclohexane	83
n-Pentane	61.8	Methylcyclopentane	91.3
2-Methyl-1-butane	92.3	Methylcyclohexane	74.8
n-Hexane	24.8	1,3-Dimethylcyclopentane	80.6
2-Methyl-1-pentane	73.4	1,1,3-Trimethylcyclopentane	87.7
2,2-Dimethyl-1-butane	91.8	Ethylcyclohexane	45.6
n-Heptane	0	Isobutylcyclohexane	33.7
2-Methylhexane	52	**Aromatic**	
2,3-Dimethylpentane	91.1	Benzene	–
2,2,3-Trimethylbutane	>100	Toluene	>100
n-Octane	<0	*o*-Xylene	–
3,3-Dimethylhexane	75.5	*m*-Xylene	>100
2,2,4-Trimethylpentane	100	p-Xylene	>100
n-Nonane	<0	Ethylbenzene	>100
2,2,3,3-Tetramethylpentane	>100	*n*-Propylbenzene	>100
n-decane	<0	Isopropylbenzene	>100
Olefins		1-Methyl-3-ethylbenzene	>100
1-Hexene	76.4	*n*-butylbenzene	>100
1-Heptene	54.5	1-Methyl-3-isopropylbenzene	–
2-Methyl-2-hexene	90.4	1,2,3,4-Tetramethylbenzene	>100
2,3-Dimethyl-1-pentene	99.3		

Octane numbers of various pure compounds [2]



Catalytic reforming

Several technologies are developed by various commercial organizations.

- Platforming by UOP
- Powerforming by Exxon
- Magna forming by Engelhard
- Catalytic eforming by IFP
- Rheniforming by Chevron
- Ultraforming by Amoco.

345–2415 kPa
3–8 mol H_2/mol feed
Reactor inlet: 925–975^{o}F

Catalytic reforming

The feed, generally (C_7-C_{10}) to the catalytic reformer is straight run naphtha or hydrocracker naphtha or coker naphtha that may have an IBP 82 ^oC and final boiling point of 190 ^oC. The feed is the hydrotreated naphtha (through a hydrotreater) to remove sulfur, nitrogen, and other impurities which can poison the reforming catalyst.

Catalytic reforming

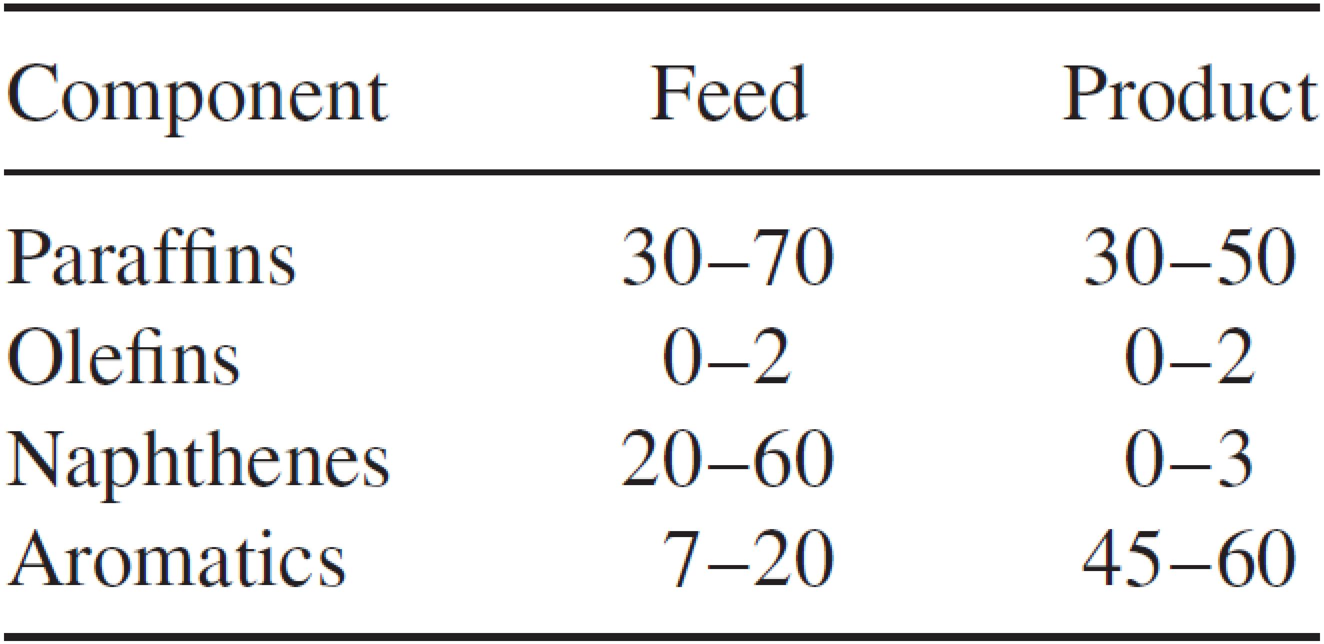
The feed contains four major groups of hydrocarbons:

Paraffins, Olefins, Naphthenes, and Aromatics (PONA).

What is the source of olefins?

Catalytic reforming

Typical feed and product PONA composition in vol% is:



Component	Feed	Product
Paraffins	30–70	30–50
Olefins	0–2	0–2
Naphthenes	20–60	0–3
Aromatics	7–20	45–60

Catalytic reforming catalyst

The catalyst for the reforming process is a bifunctional catalyst Pt/Al_2O_3 with Pt content usually of 0.2 to 0.6% by weight. A bimetallic catalyst using rhenium, tin, or iridium is usually required. For example, rhenium is added along with Pt for stabilization.

The surface area of a typical γ-alumina support is 210 m^2/g.

Catalytic reforming reactions

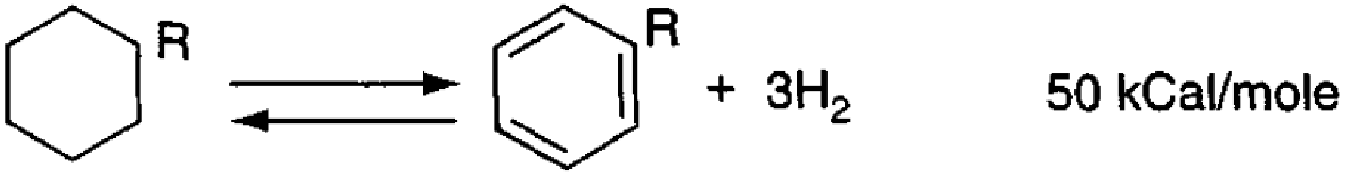
There are four major reactions involved in catalytic reforming:

- Dehydrogenation of naphthenes to aromatics
- Dehydrocyclization of paraffins to aromatics
- Isomerization
- Hydrocracking

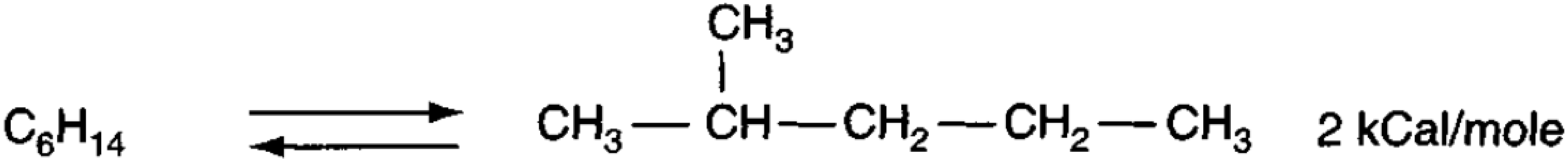
The product contains aromatics and isoparaffins.

Reforming reactions [Parkash, 2003]

(1) Dehydrogenation of napthenes to aromatics with energy absorption



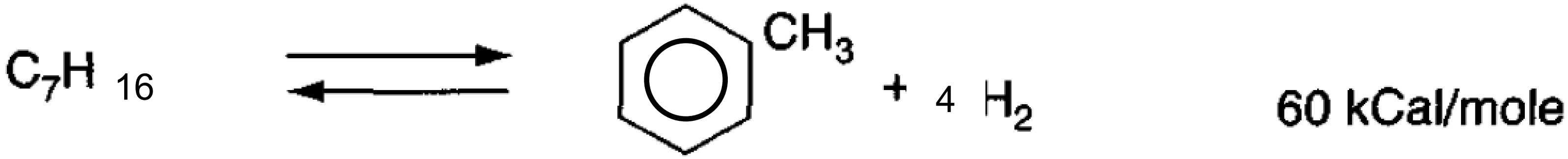
(2) Isomerization of normal paraffins to isoparaffins



$$C_6H_{14} \rightleftharpoons CH_3-\underset{}{\overset{CH_3}{\overset{|}{C}H}}-CH_2-CH_2-CH_3$$

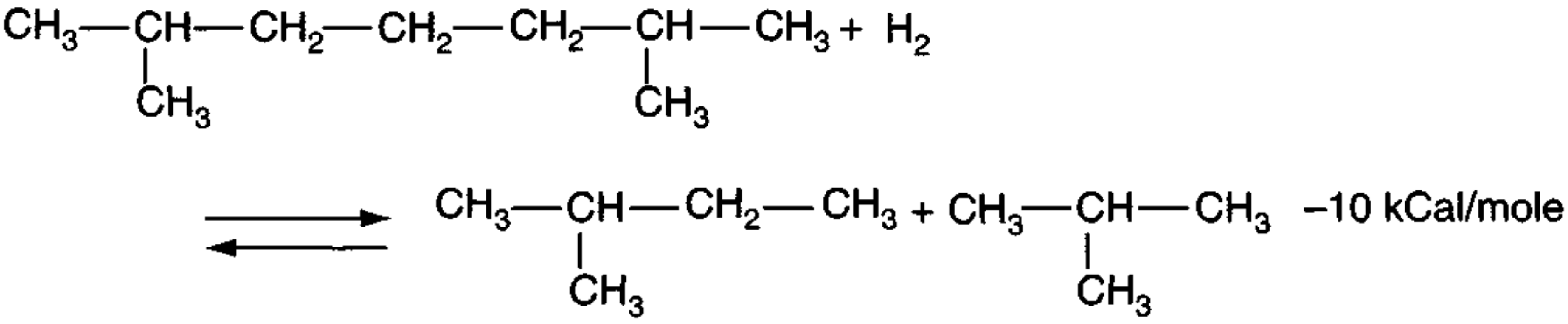
2 kCal/mole

(3) Dehydrocyclization of paraffins



Reforming reactions [Parkash, 2003]

(4) Hydrocracking reactions



$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-CH_2-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3 + H_2 \rightleftharpoons CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-CH_3 + CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3 \quad -10\ \text{kCal/mole}$$

(5) Secondary reactions

Demethanation

$$C_6H_{14} + H_2 \longrightarrow C_5H_{12} + CH_4$$

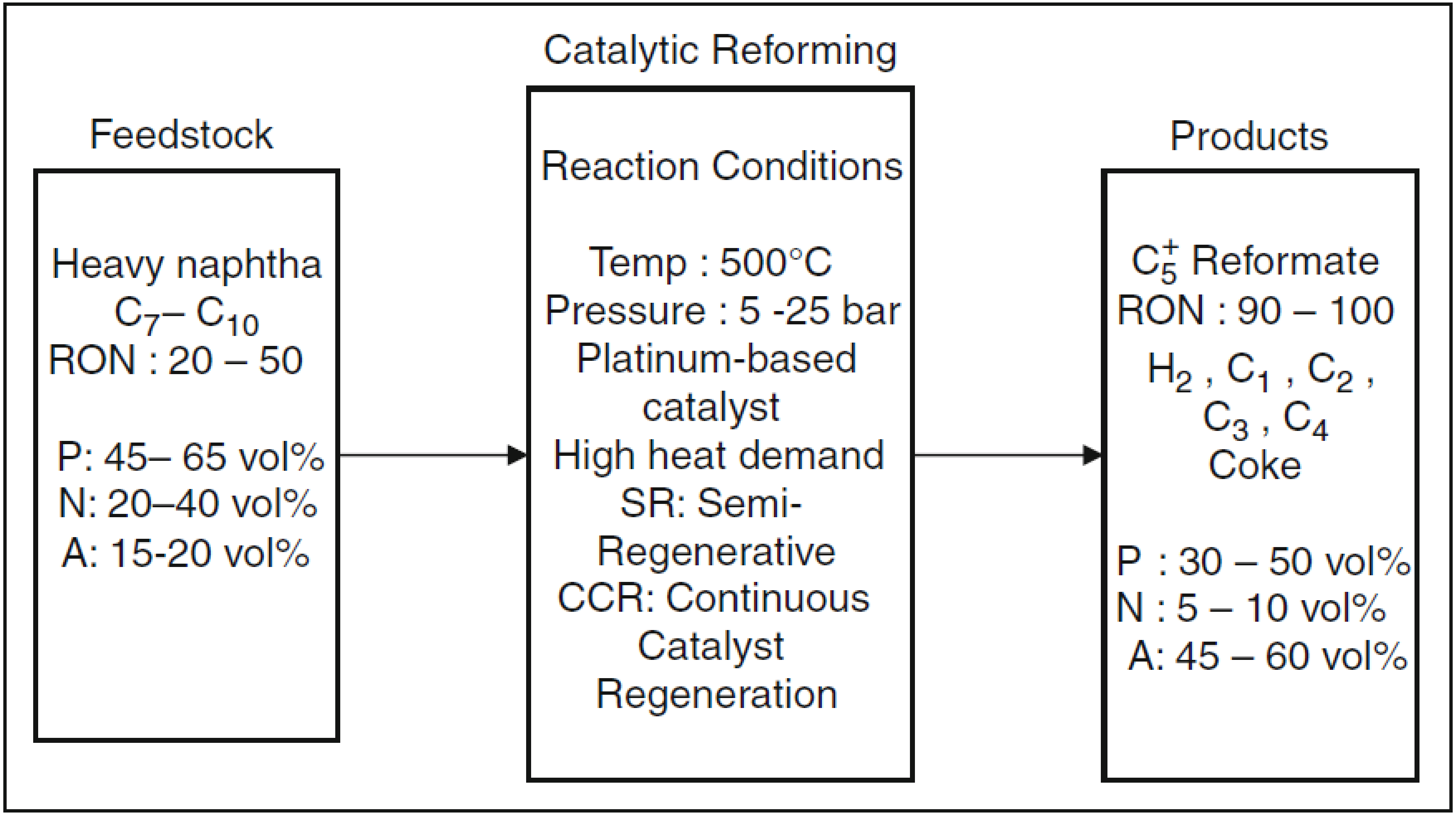
Desulfurisation

$$R\text{–}S\text{–}R + 2H_2 \longrightarrow 2RH + H_2S$$

Denitrification

$$R{=}N\text{–}H + 2H_2 \longrightarrow RH_2 + NH_3$$

An example reforming process [2]



Catalytic Reforming

Feedstock

Heavy naphtha
$C_7 – C_{10}$
RON : 20 – 50

P: 45– 65 vol%
N: 20–40 vol%
A: 15-20 vol%

Reaction Conditions

Temp : 500°C
Pressure : 5 -25 bar
Platinum-based catalyst
High heat demand
SR: Semi-Regenerative
CCR: Continuous Catalyst Regeneration

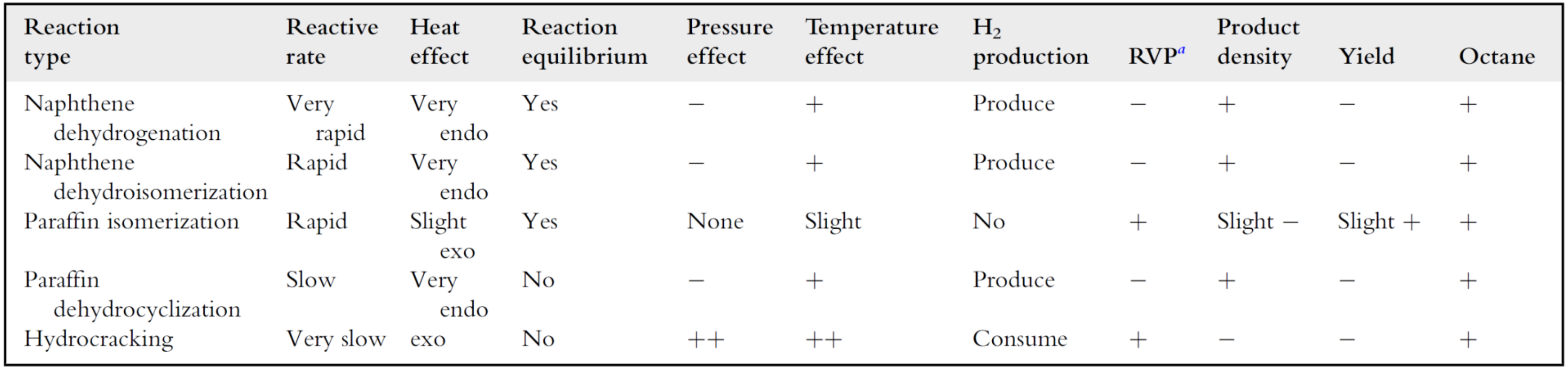
Products

C_5^+ Reformate
RON : 90 – 100
H_2 , C_1 , C_2 , C_3 , C_4
Coke

P : 30 – 50 vol%
N : 5 – 10 vol%
A: 45 – 60 vol%

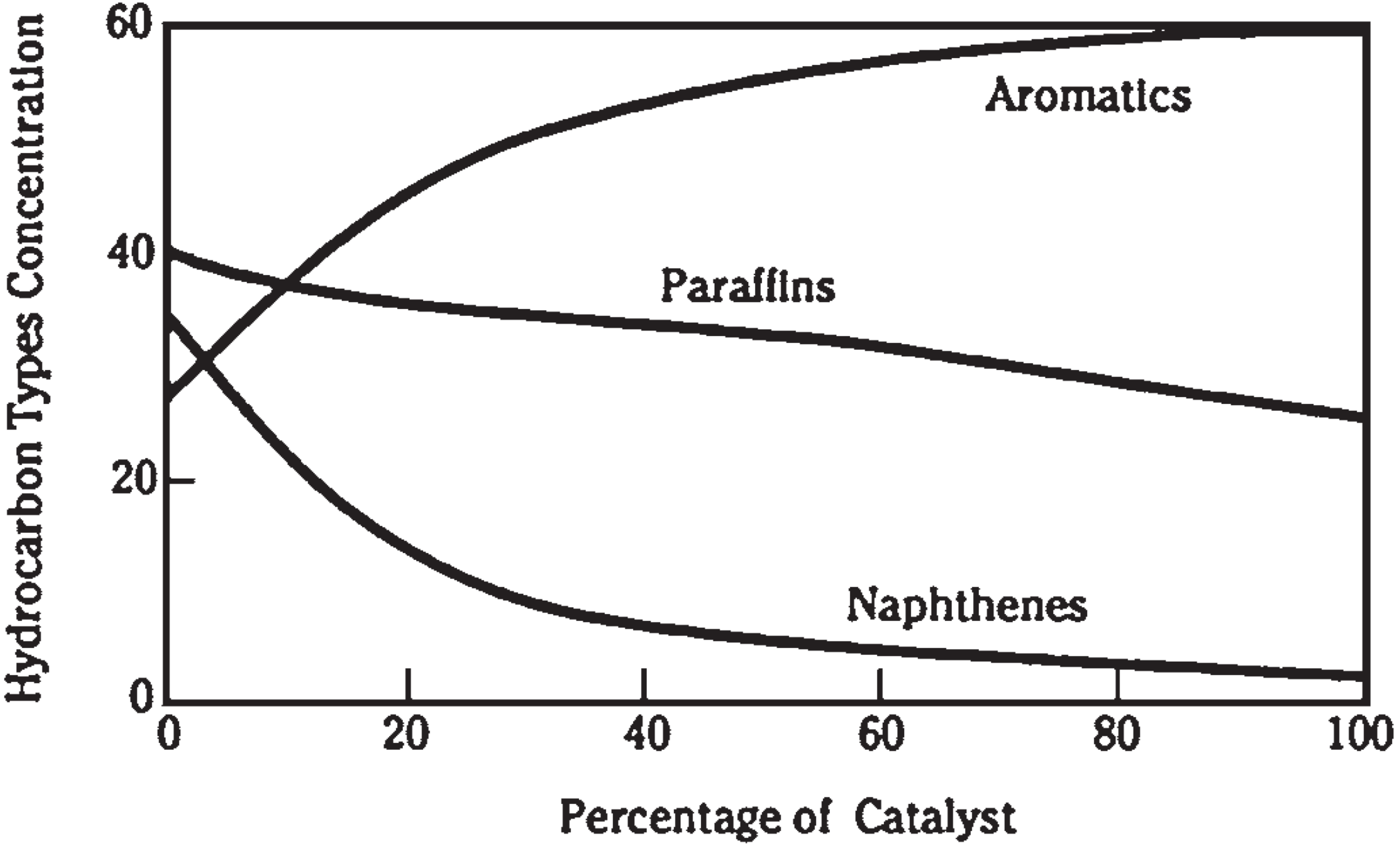
Reforming thermodynamics and kinetics

[2]



Reaction type	Reactive rate	Heat effect	Reaction equilibrium	Pressure effect	Temperature effect	H_2 production	RVP[a]	Product density	Yield	Octane
Naphthene dehydrogenation	Very rapid	Very endo	Yes	−	+	Produce	−	+	−	+
Naphthene dehydroisomerization	Rapid	Very endo	Yes	−	+	Produce	−	+	−	+
Paraffin isomerization	Rapid	Slight exo	Yes	None	Slight	No	+	Slight −	Slight +	+
Paraffin dehydrocyclization	Slow	Very endo	No	−	+	Produce	−	+	−	+
Hydrocracking	Very slow	exo	No	++	++	Consume	+	−	−	+

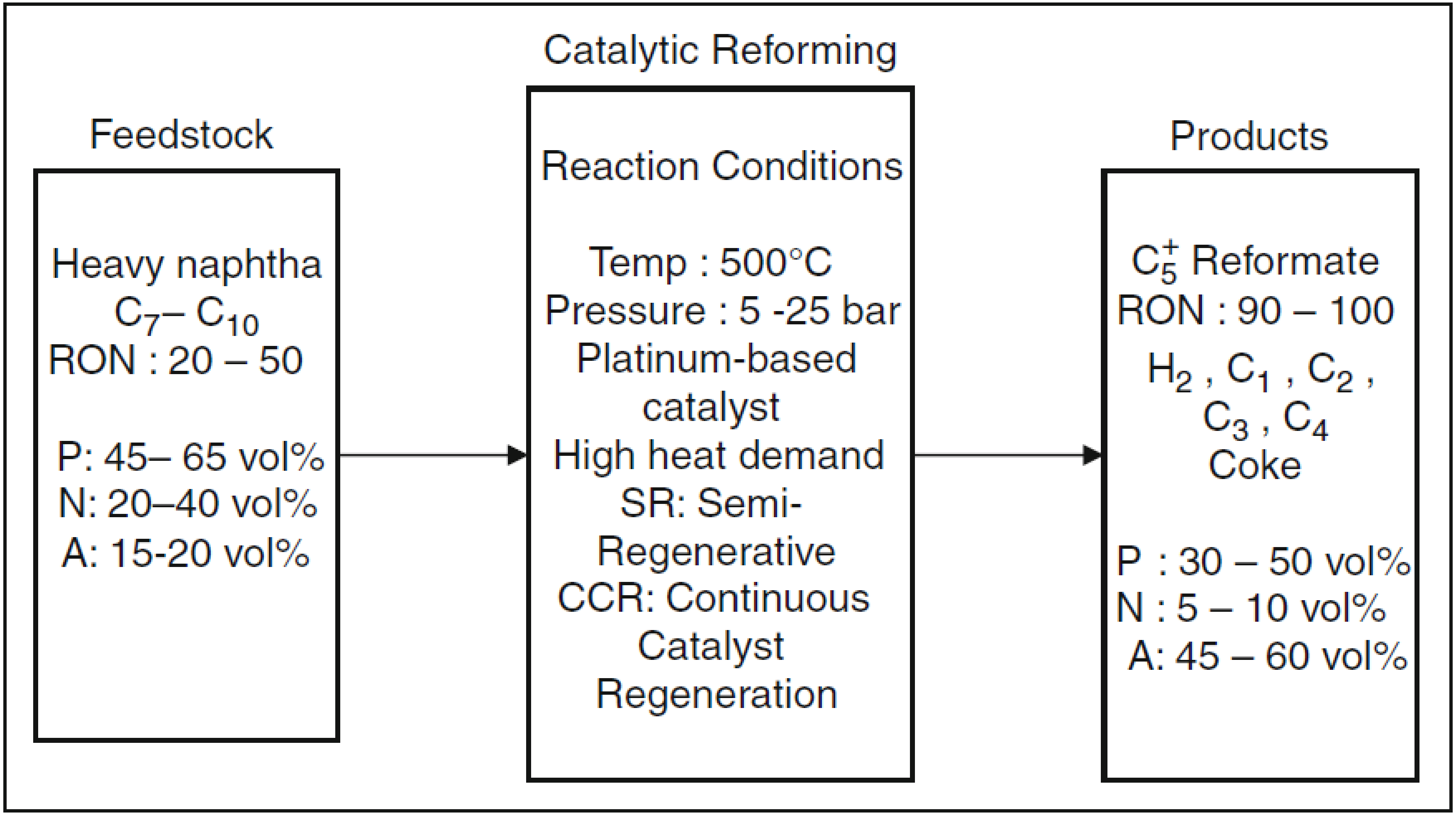
Reforming thermodynamics and kinetics [5]



Effect of pressure

A reduction in pressure leads to increased production of hydrogen and reformate yield and therefore the required temperature for a quality product is decreased, however, coking rate is increased. Why is CCR (to be discussed later) useful over fixed bed operation?

An example reforming process [2]



Catalytic Reforming

Feedstock

Heavy naphtha
$C_7 – C_{10}$
RON : 20 – 50

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A: 15-20 vol%

Reaction Conditions

Temp : 500°C
Pressure : 5 -25 bar
Platinum-based catalyst
High heat demand
SR: Semi-Regenerative
CCR: Continuous Catalyst Regeneration

Products

C_5^+ Reformate
RON : 90 – 100
H_2 , C_1 , C_2 , C_3 , C_4
Coke

P : 30 – 50 vol%
N : 5 – 10 vol%
A: 45 – 60 vol%

Catalytic reforming: Coke deposition

Due to the coke deposited on the active surface, the catalyst is required to be regenerated. The catalyst is regenerated by burning off the coke from the catalyst surface. This is called regeneration of the catalyst.

Catalyst regeneration is an exothermic reaction. A good control is desired.

Reforming processes

Depending upon the catalyst regeneration processing, reforming processes may be:

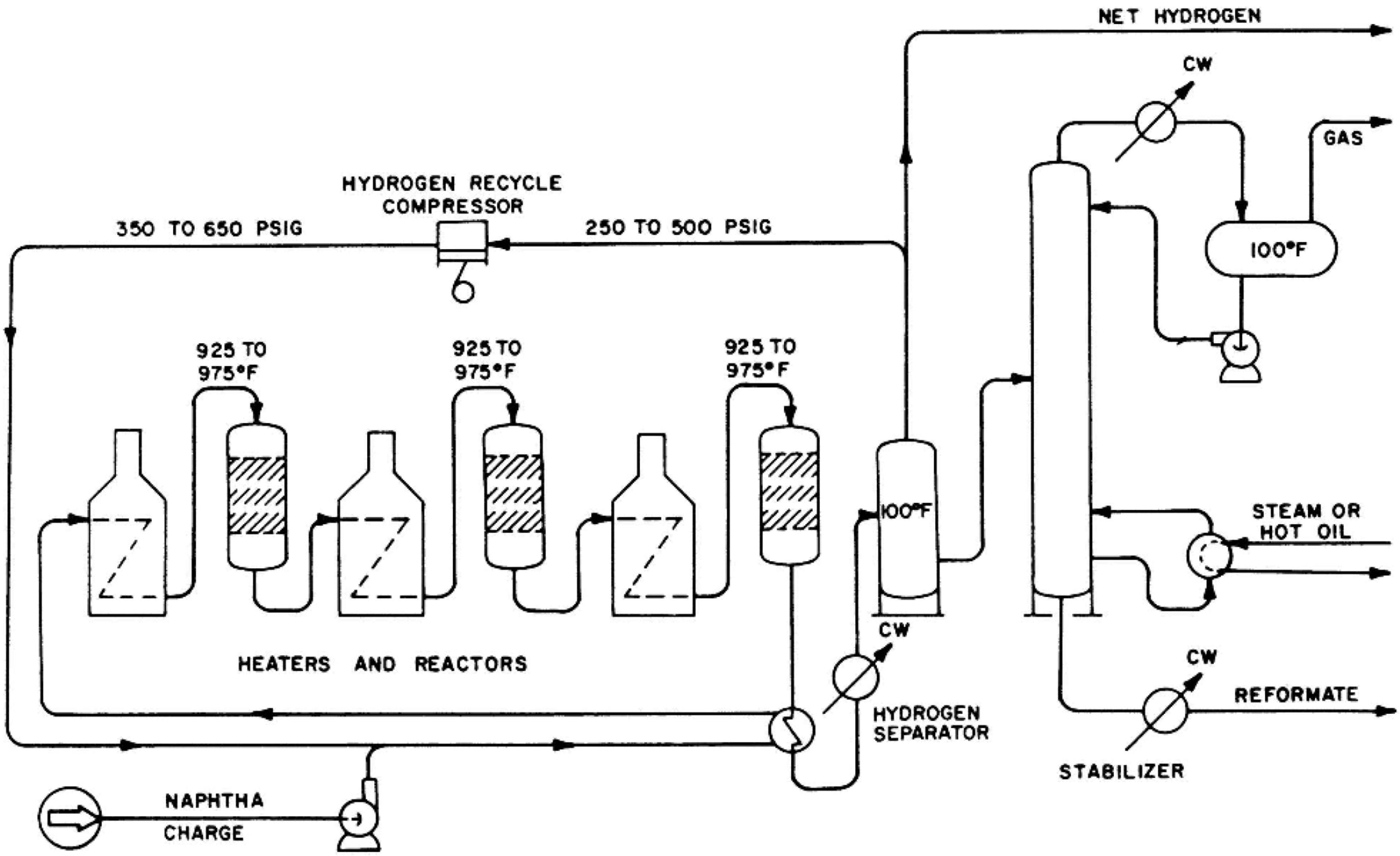
- Semi-regenerative
- Cyclic
- Continuous

95% of new installations are continuous [5].

Reforming processes

- Semi-generative process requires shutdown of the process and then regeneration of the catalyst.
- Cyclic process is a modification of the semi-regenerative process in which an extra reactor is installed and regeneration is carried out in parallel so that the shut down is avoided. Initial cost is higher.
- Continuous regeneration is licensed by UOP under the name UOP CCR platforming. The catalyst flows (in a moving bed fashion) from one reactor to the other under gravity and continuously regenerated in the regenerator. Initial cost is higher. Rather frequent shutdown is avoided so more production.

Semi-regenerative catalytic reforming [1]



Catalytic reforming

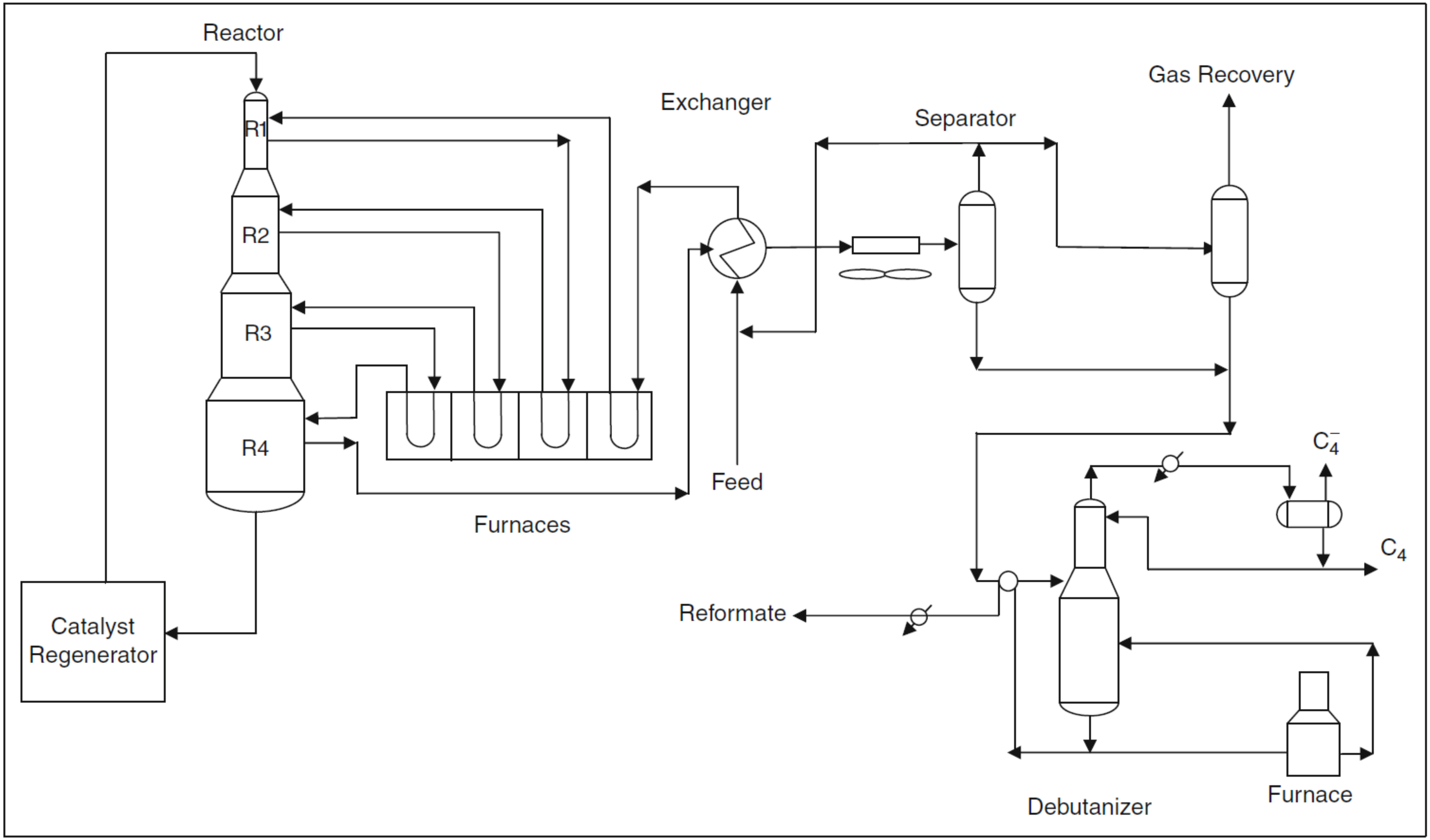
Why hydrogen is required in the feed?

Remember a lot of hydrogen is produced in catalytic reforming and reformer is a principal source of hydrogen in a refinery.

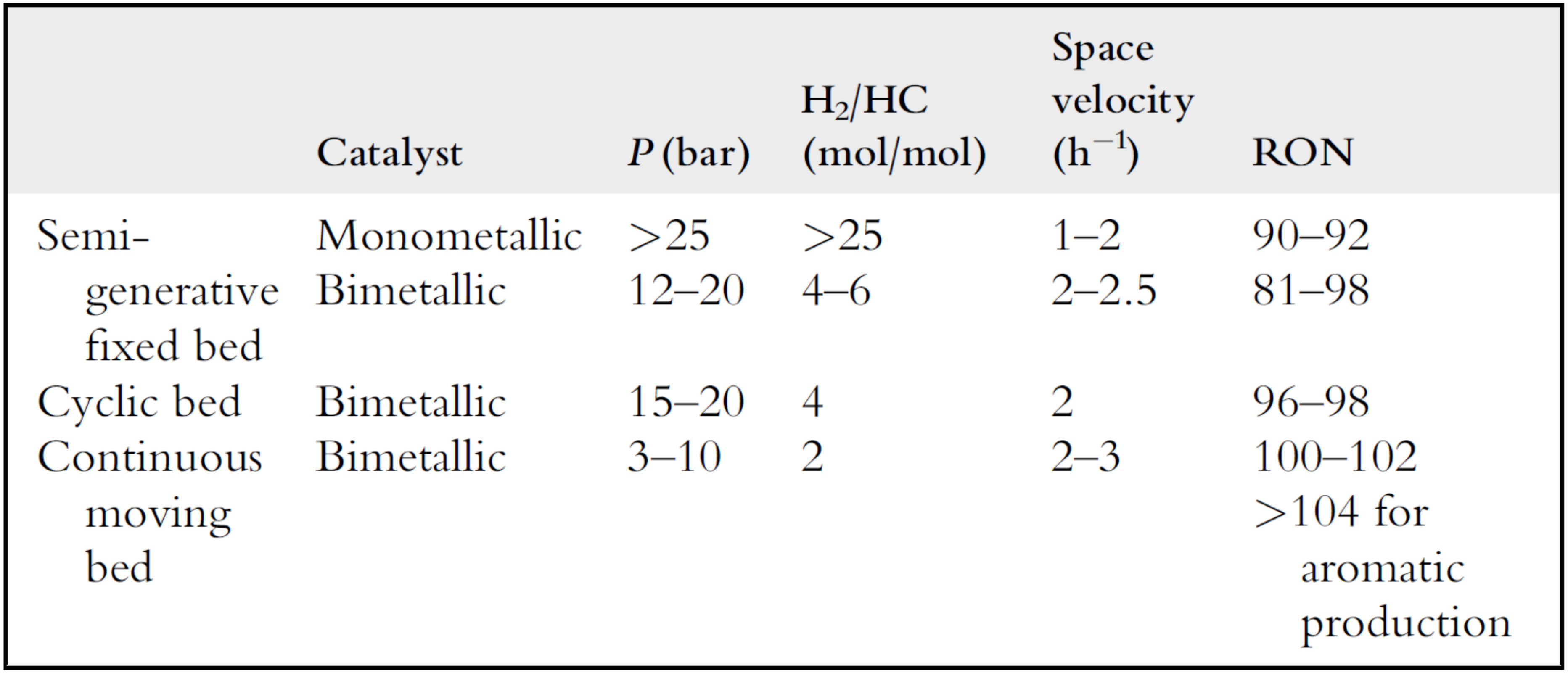
Catalytic reforming

Catalytic reforming is highly endothermic reaction that is why it requires interstage heating.

Continuous catalyst regeneration (CCR) [2]



Continuous catalytic reforming (CCR) [2]



	Catalyst	*P* (bar)	H_2/HC (mol/mol)	Space velocity (h^{-1})	RON
Semi-generative fixed bed	Monometallic	>25	>25	1–2	90–92
	Bimetallic	12–20	4–6	2–2.5	81–98
Cyclic bed	Bimetallic	15–20	4	2	96–98
Continuous moving bed	Bimetallic	3–10	2	2–3	100–102 >104 for aromatic production

Reforming correlations [2]

$$H_2\ \text{wt\%} = -12.1641 + 0.06134 \times C_5^+\ \text{vol \%} + 0.099482 \times \text{RON}_R$$

$$C_1\ \text{wt\%} = 11.509 - 0.125 \times C_5^+\ \text{vol \%}$$

$$C_2\ \text{wt\%} = 16.496 - 0.1758 \times C_5^+\ \text{vol \%}$$

$$C_3\ \text{wt\%} = 24.209 - 0.2565 \times C_5^+\ \text{vol \%}$$

$$\text{Total } C_4 = 27.024 - 0.2837 \times C_5^+\ \text{vol \%}$$

wt%

$$nC_4\ \text{wt\%} = 0.585 \times \text{total } C_4\ \text{wt\%}$$

$$iC_4\ \text{wt\%} = 0.415 \times \text{total } C_4\ \text{wt\%}$$

$$C_5^+\ \text{vol\%} = -0.03806 \times \text{RON}_R^2 + 6.292793 \times \text{RON}_R - 14.4337 \times K$$

$$C_5^+\ \text{vol\%} = 132.2483 + 0.66472 \times \text{RON}_R + 0.297921 \times \text{RON}_F$$

$$C_5^+\ \text{vol\%} = 142.7914 - 0.77033 \times \text{RON}_R + 0.219122 \times (N + 2A)_F$$

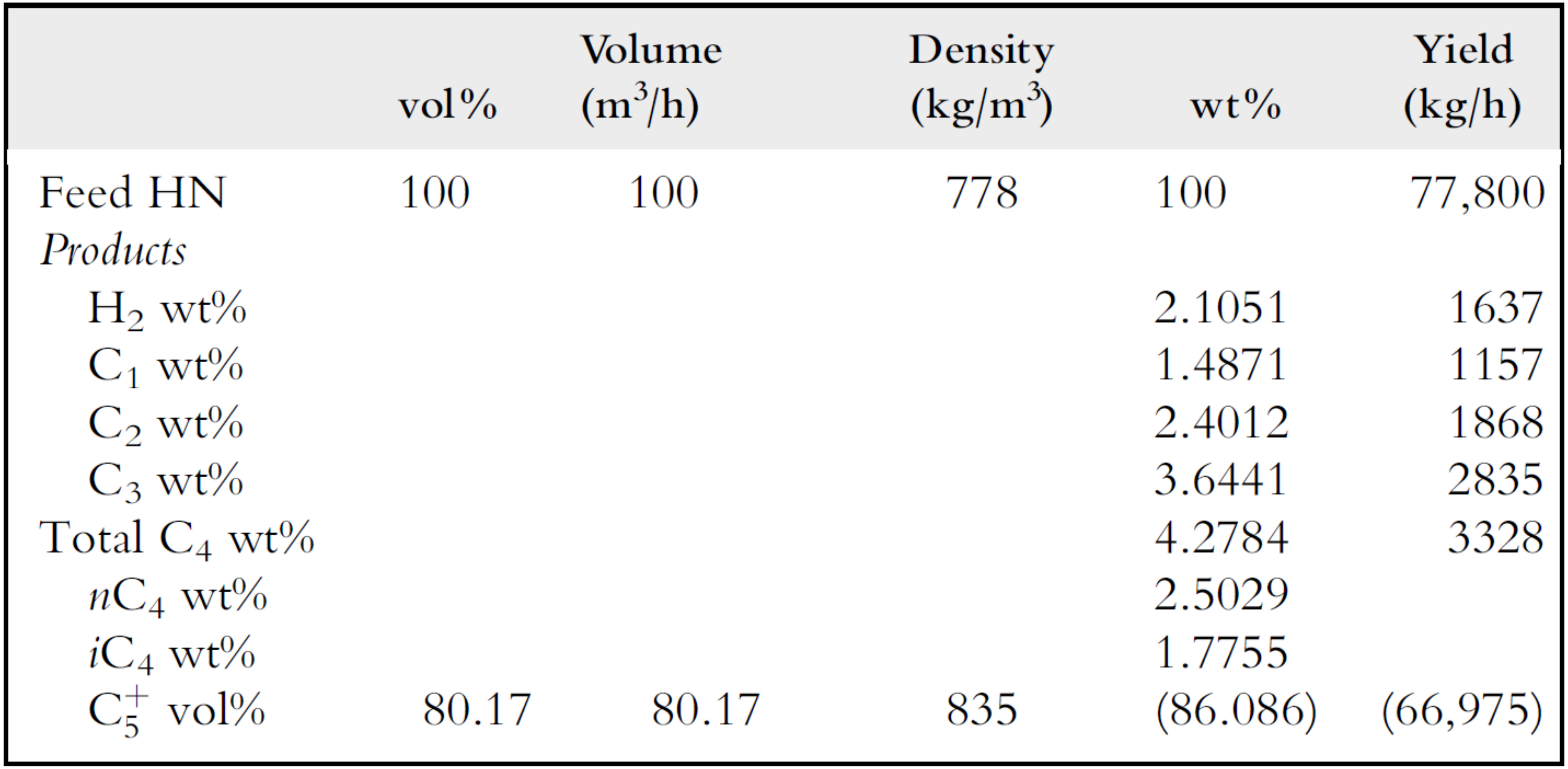
$$\text{SCFB } H_2 = 0.0002 + 0.48848\ H_2\ \text{wt\%}$$

RON_F = research octane number of feed; RON_R = research octane number of reformate;C_5^+ vol% = volume percent of reformate yield; SCFB H_2 = standard cubic foot of H_2 produced/barrel of feed; K = characterization factor $(T_B)^{1/3}/\text{SG}$; T_B = absolute mid-boiling of feed, °R; SG = specific gravity of feed; N = napthenes vol % and A = aromatics vol %.

Example [2, p. 108]

100 m^3/h of heavy naphtha (HN) with specific gravity of 0.778 has the following composition: $A = 11.5$ vol%, $N = 21.7$ vol% and $P = 66.8$ vol% is to be reformed to naphtha reformate of RON = 94. Calculate the yields of each product for that reformer.

Example [2, p. 108]

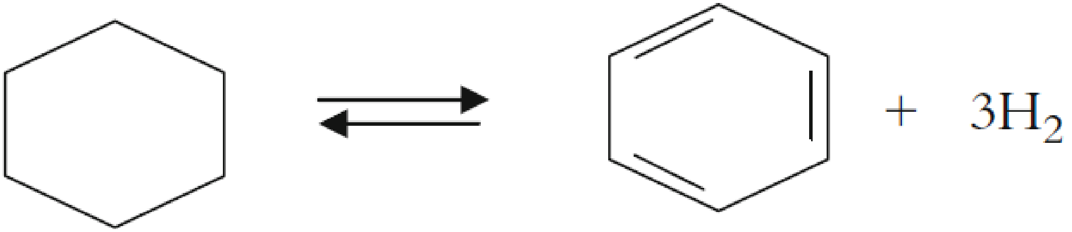


	vol%	Volume (m^3/h)	Density (kg/m^3)	wt%	Yield (kg/h)
Feed HN	100	100	778	100	77,800
Products					
H_2 wt%				2.1051	1637
C_1 wt%				1.4871	1157
C_2 wt%				2.4012	1868
C_3 wt%				3.6441	2835
Total C_4 wt%				4.2784	3328
nC_4 wt%				2.5029	
iC_4 wt%				1.7755	
C_5^+ vol%	80.17	80.17	835	(86.086)	(66,975)

Thermodynamics of reforming [2]

Example E7.1

Consider the following dehydrogenation reaction:



Cyclohexane (CH) Benzene (BZ) Hydrogen

Determine and plot the equilibrium conversion as a function of temperature and pressure, given the following data:

The free energy $\Delta G = 200,100 - 396T$

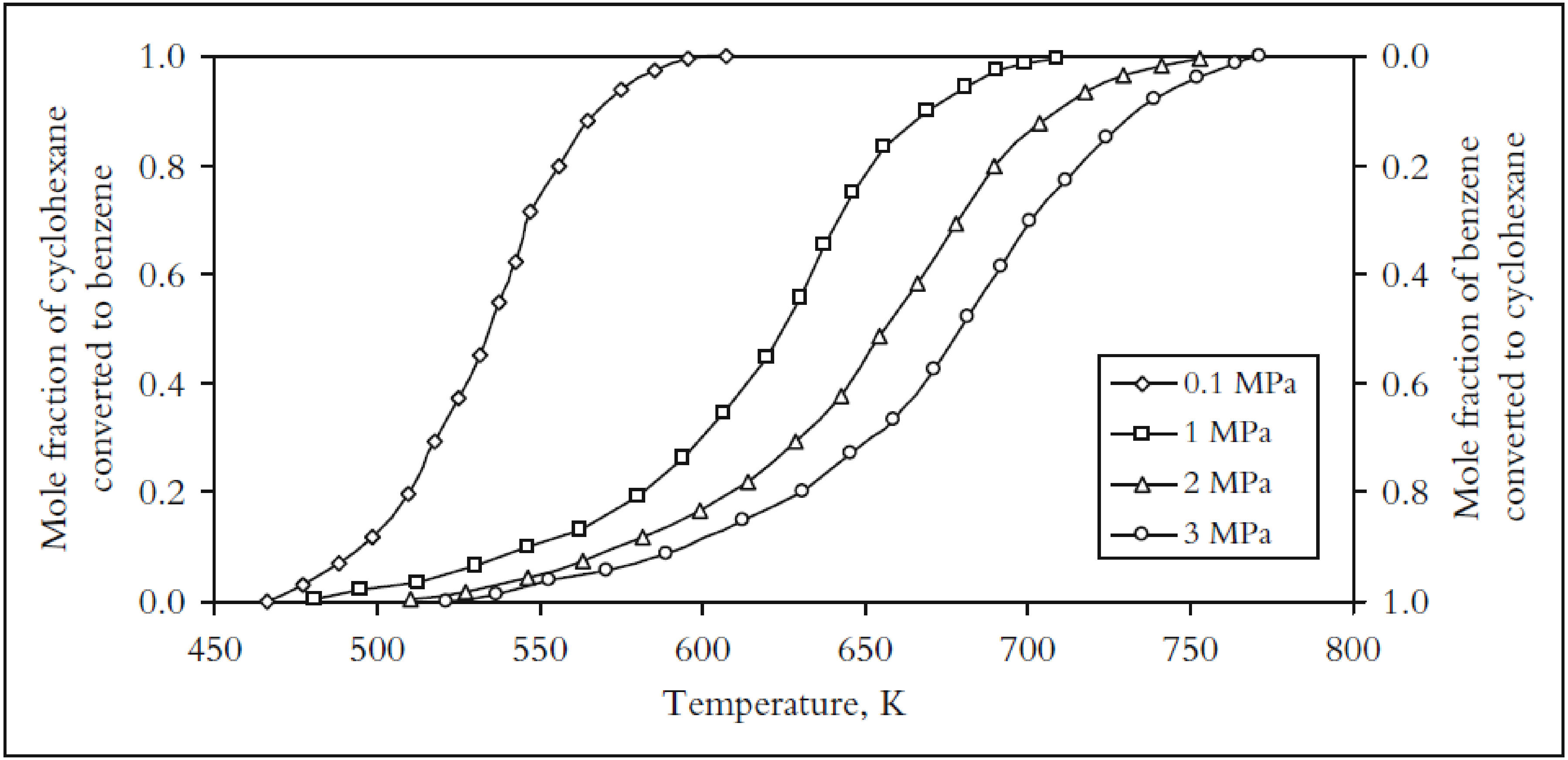
where ΔG is in J/mol and T is in Kelvin

The equilibrium constant, K_{eq}, is related to the free energy as follows:

$$\Delta G = -RT \ln K_{\text{eq}}$$

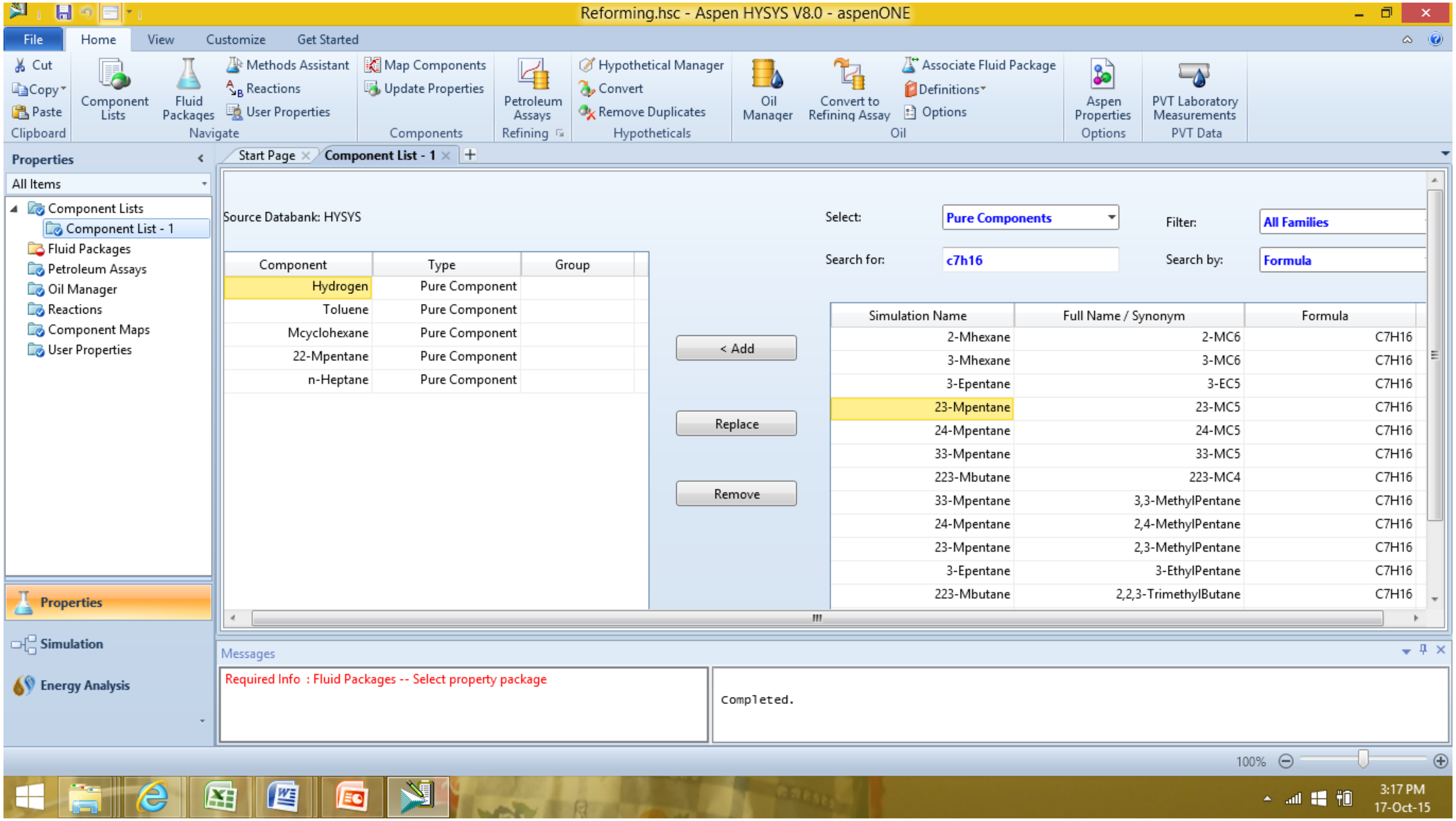
where R is the gas law constant.

Thermodynamics of reforming [2]



Catalytic reforming: Simulation

Simulation of catalytic reforming using a few model components.



Source Databank: HYSYS

Component	Type	Group
Hydrogen	Pure Component	
Toluene	Pure Component	
Mcyclohexane	Pure Component	
22-Mpentane	Pure Component	
n-Heptane	Pure Component	

Select: Pure Components

Filter: All Families

Search for: c7h16

Search by: Formula

Simulation Name	Full Name / Synonym	Formula
2-Mhexane	2-MC6	C7H16
3-Mhexane	3-MC6	C7H16
3-Epentane	3-EC5	C7H16
23-Mpentane	23-MC5	C7H16
24-Mpentane	24-MC5	C7H16
33-Mpentane	33-MC5	C7H16
223-Mbutane	223-MC4	C7H16
33-Mpentane	3,3-MethylPentane	C7H16
24-Mpentane	2,4-MethylPentane	C7H16
23-Mpentane	2,3-MethylPentane	C7H16
3-Epentane	3-EthylPentane	C7H16
223-Mbutane	2,2,3-TrimethylButane	C7H16

Required Info : Fluid Packages -- Select property package

```
Completed.
```

Go to Fahim et al., 2010 [2] Chapter No. 5 and see Example 5.5 for more rigorous simulation of a reforming unit.

Catalytic cracking

Catalytic cracking is used to convert heavy fractions such as vacuum gas oil to gasoline range and lighter products.

Catalytic cracking has advantages over thermal cracking as more gasoline having higher octane rating and less heavy fuel oils and light gases are produced. Also light gases contain more olefins.

Catalytic cracking

Cracking is generally carried out in either a

1. Moving bed reactor, or
2. Fluidized bed reactor

The fluid catalytic cracking (FCC) is a fluidized bed cracking system and is widely acceptable more than moving bed reactor system.

Catalytic cracking

The role of catalytic cracking is to take heavy desulfurized feedstock and crack it into lighter, mainly high octane gasoline. The FCC also produces olefins and LPG.

Catalytic cracking

Feed to FCC:

The gas oil from vacuum column and conversion processes boiling between 316 ^{o}C and 566 ^{o}C is used [2]. The gas oil can be considered a mixture of aromatics, naphthenic, and paraffinic hydrocarbons.

Atmospheric residue and vacuum residue may also be used.

FCC products:

Gasoline and lighter products, i.e., FCC is used to produce gasoline, olefins, and LPG. Olefins produced can be used for alkylation and polymerization.

Catalytic cracking reactions

- 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

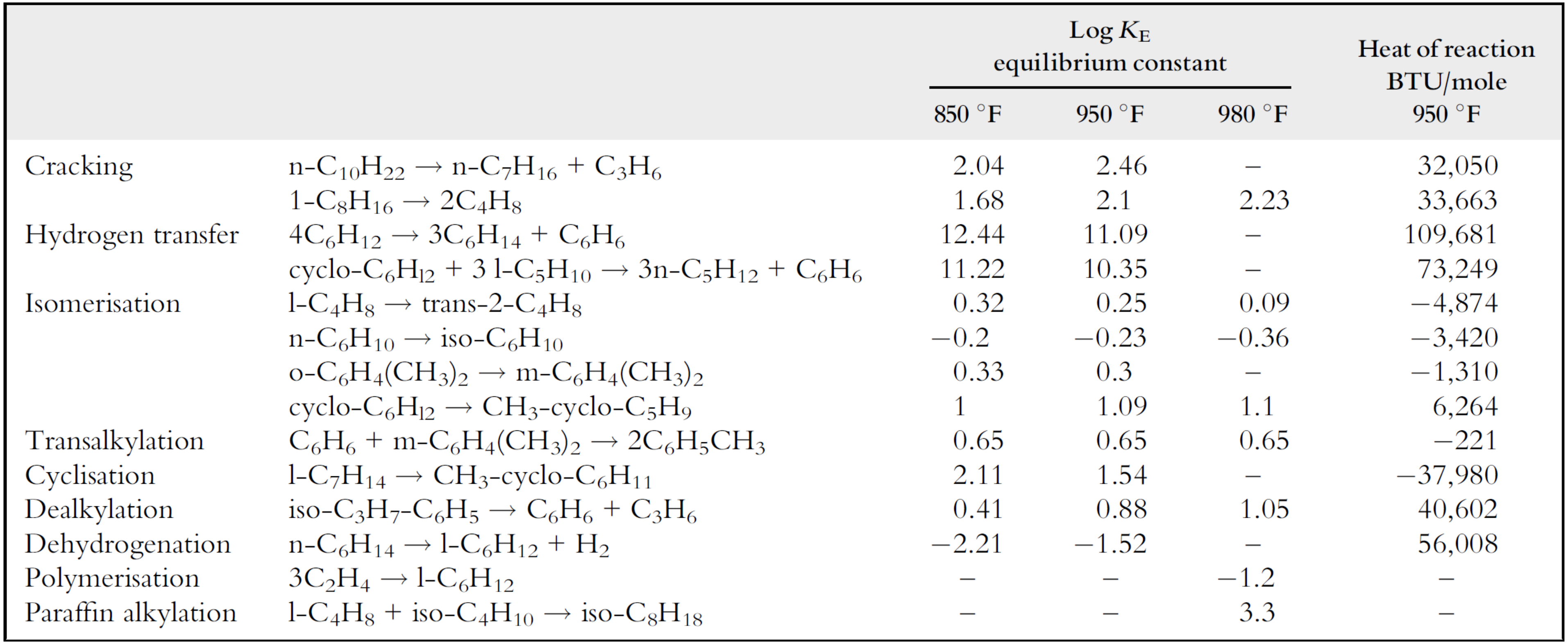
  Naphthene isomerisation → Restructured naphthenes
- Aromatics

  Aromatics (side chain) → Aromatics + Olefins

  Aromatic transalkylation → Alkylaromatics

  Aromatic dehydrogenation → Polyaromatics → Coke

Catalytic cracking thermodynamics [2]



		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	–

Overall catalytic cracking is quite endothermic and the heat of reaction is provided by combustion of coke in the regenerator.

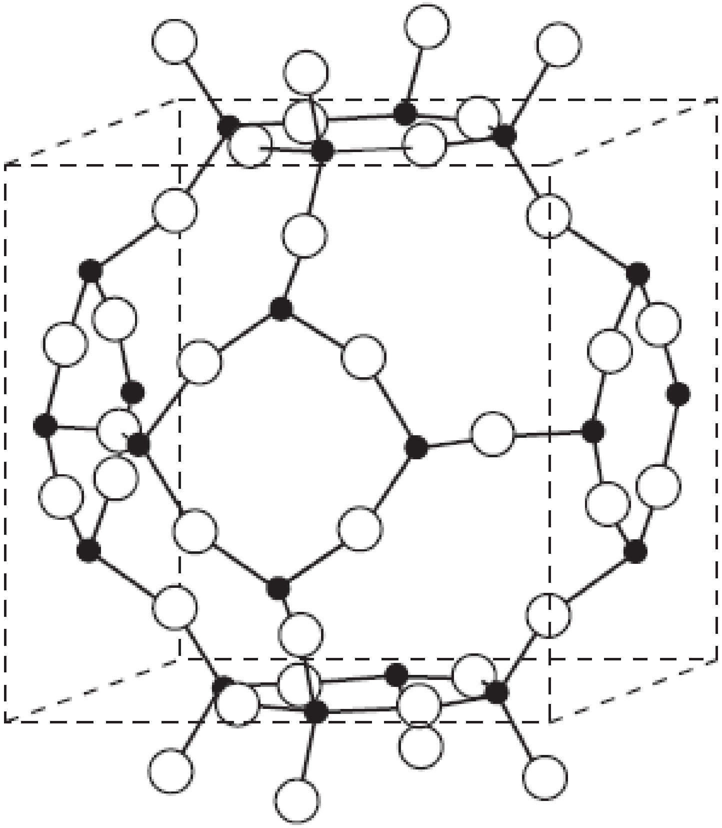
Catalytic cracking catalyst

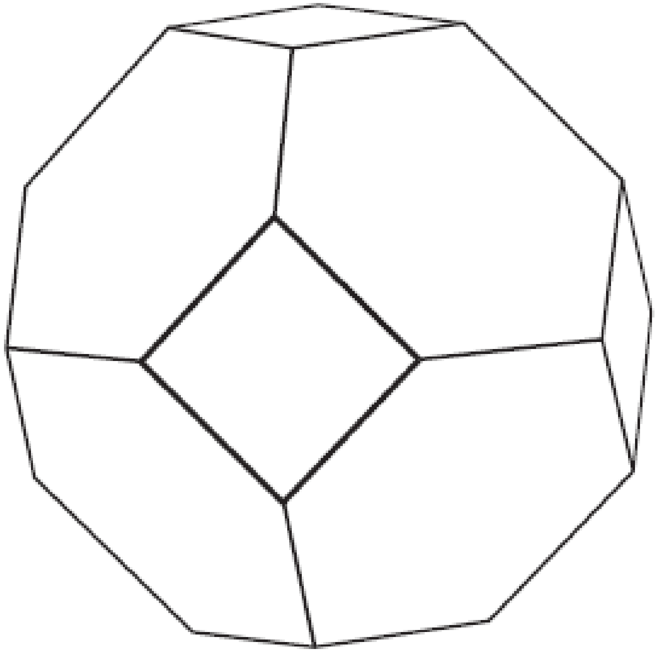
The FCC catalyst is a powder with an average particle size of 75 μm. It is zeolite (crystalline aluminosilicates) type catalyst. Y-zeolite and ZSM-5 zeolite are common in catalytic cracking.

Catalytic cracking catalyst

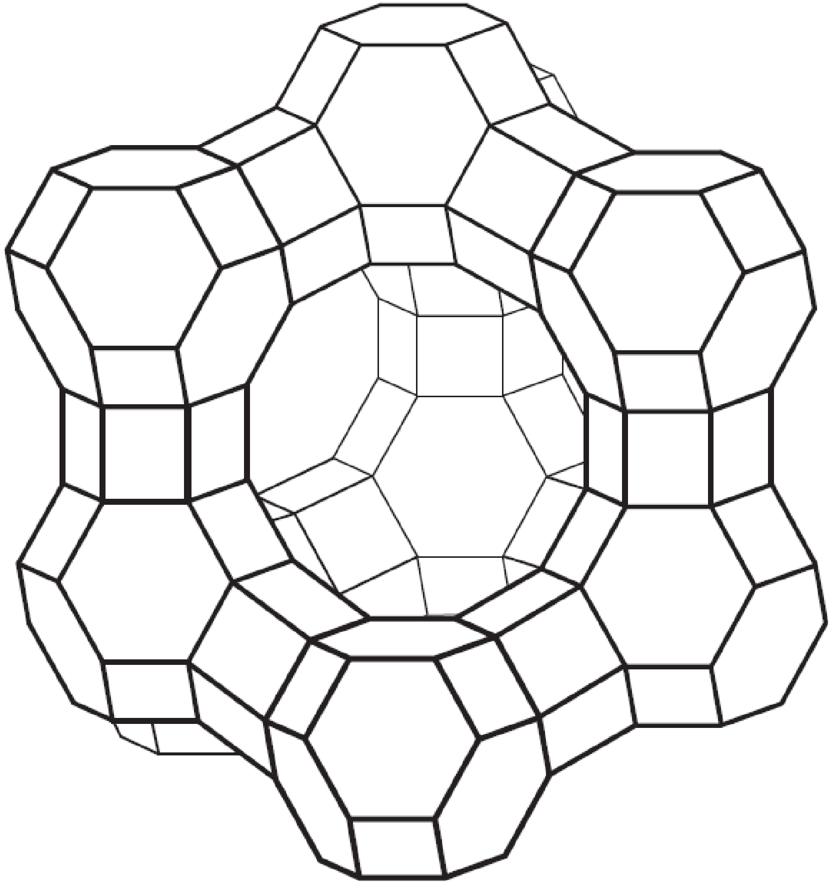
Zeolites are aluminosilicate crystalline structures. They consist of SiO_4 and AlO_4^- tetrahedra that are linked through common oxygen atoms and give a three dimensional network. In the interior of the structure there are water molecules and mobile alkali metal ions such as of sodium that are capable of being ion exchanged with other cations such as that of Pt.

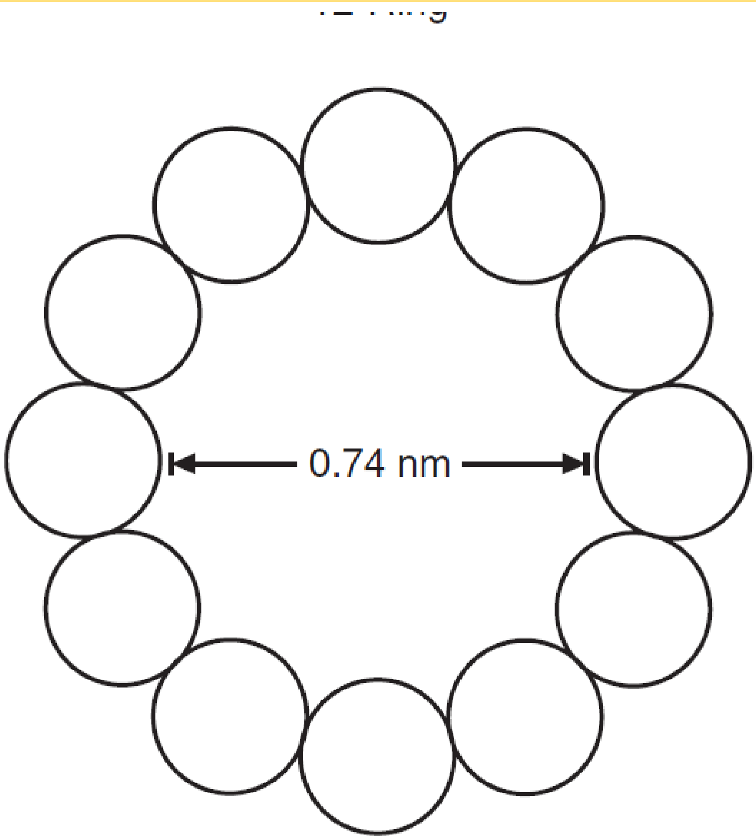
Sodalite unit (*β*-cage) [15]





Zeolite Y structure [15]



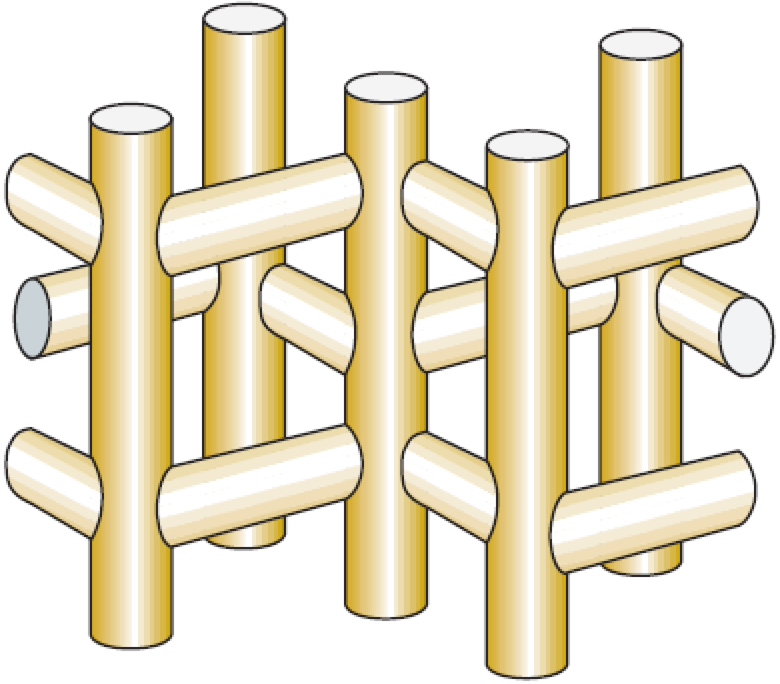


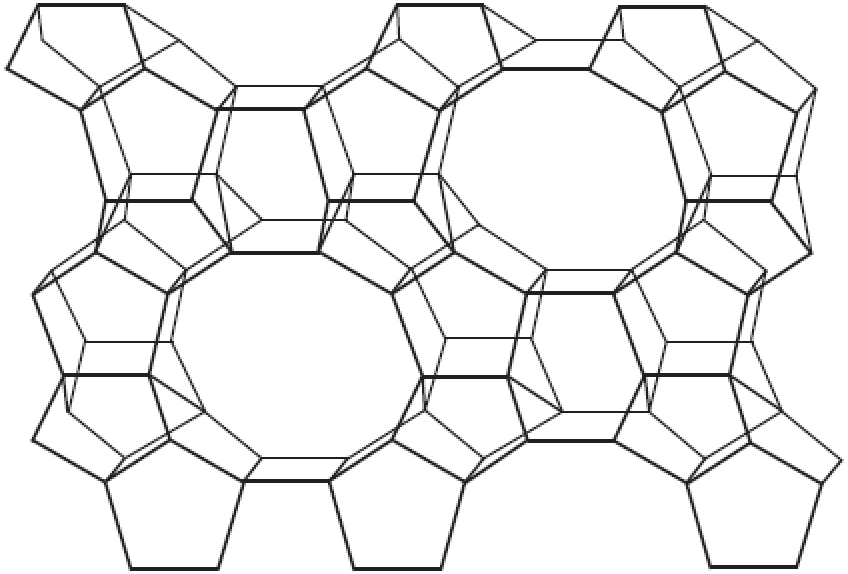
Y-zeolite contains a faujasite structure and has a large pore size and allows large size molecules.

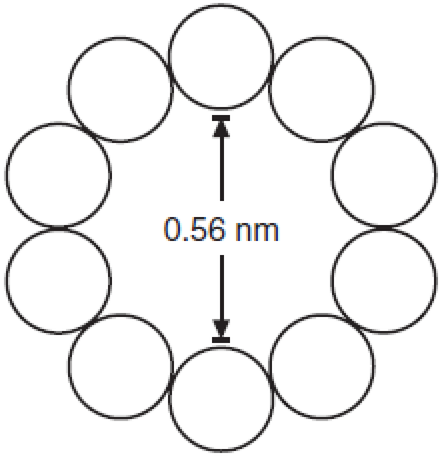
Zeolite ZSM-5

In the cracking of long chain paraffins, ZSM-5 is used. ZSM-5 allows normal alkane such as n-heptane and isomerizes to improve octane rating. Branched and cyclic compounds are not allowed to enter and hence are not cracked.

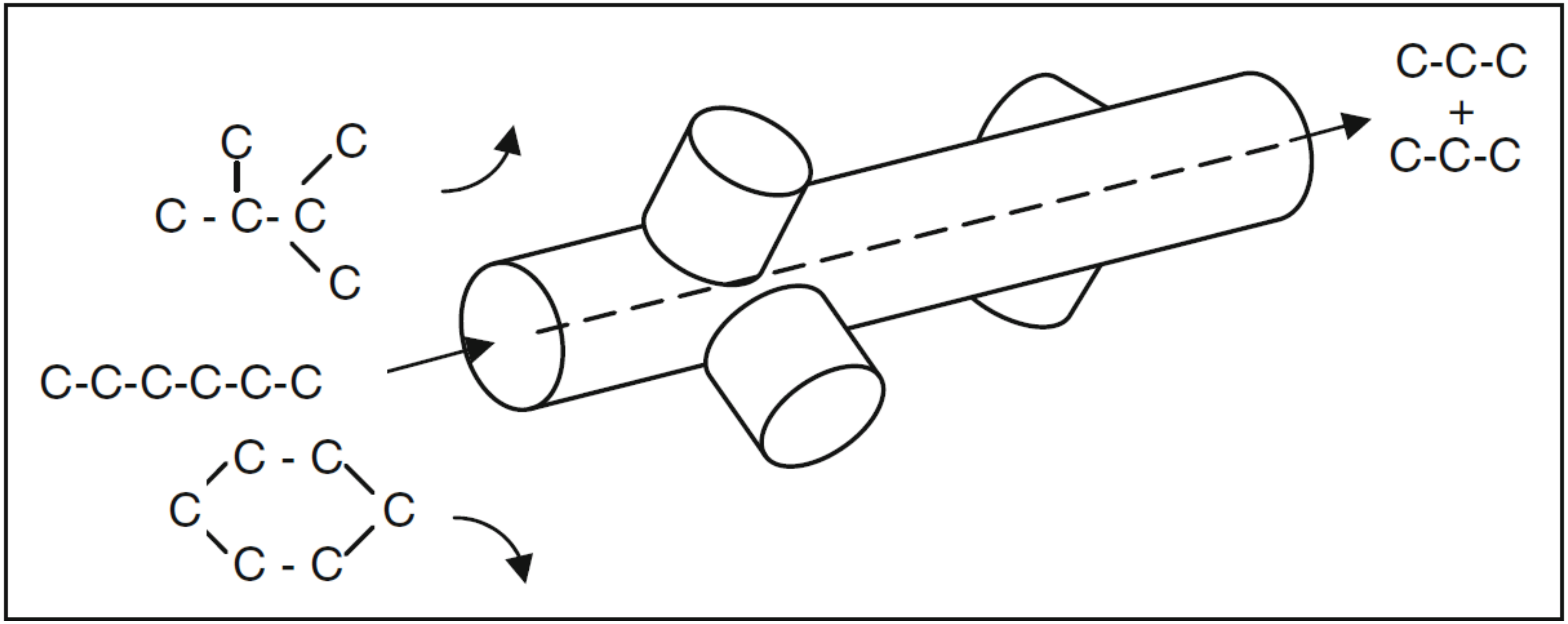
Zeolite ZSM structure: Pentasil unit [15]







Shape selectivity of ZSM-5 [2]



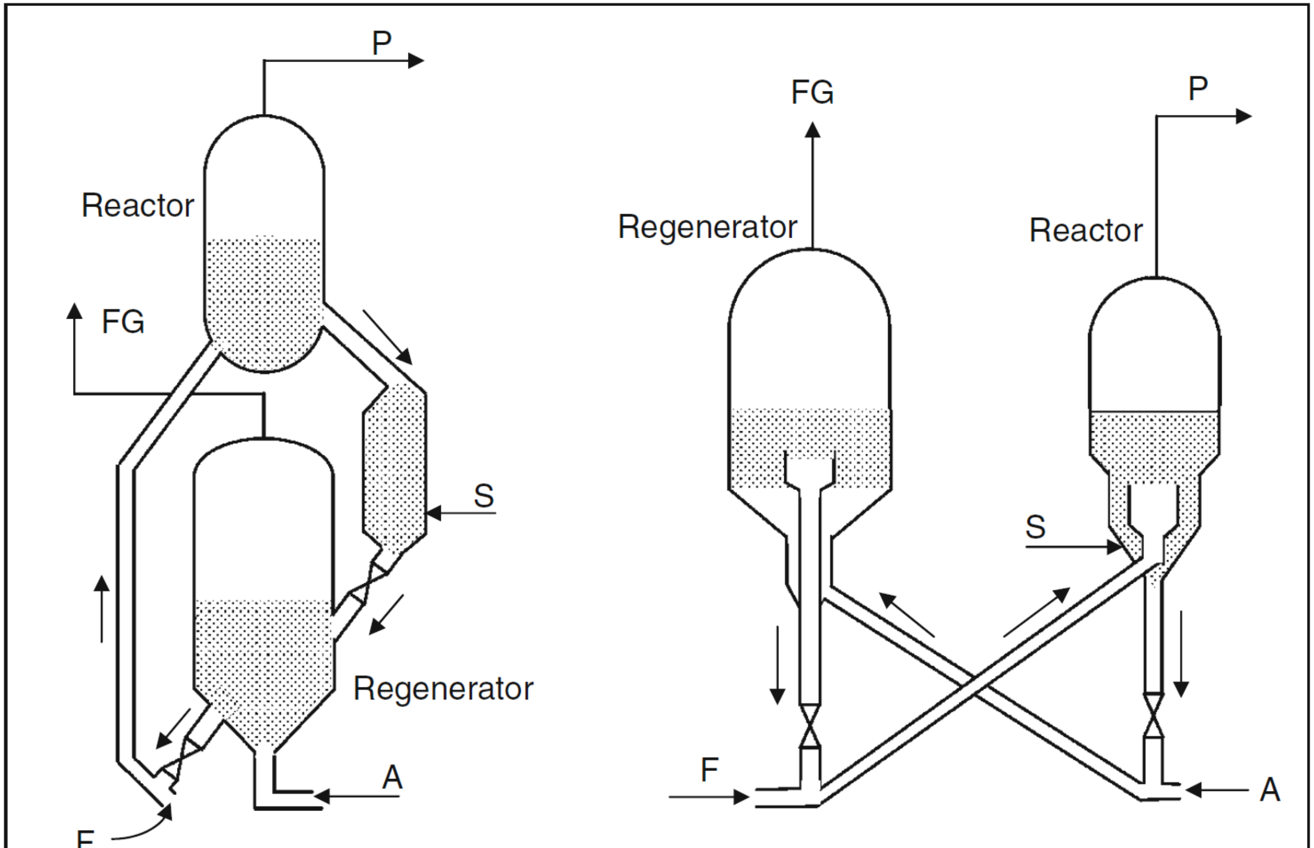
Fluid catalytic cracking

The FCC unit mainly depends on circulating a zeolite catalyst with the vapor of the feed into a riser-reactor for a few seconds. The cracked products are disengaged from the solids and taken out to a distillation column for the separation of the desired products. The catalyst is circulated back into the regenerator where coke is burned and the catalyst is regenerated. The combustion of the coke generates the heat required to carry out the generally endothermic reaction in the riser.

Fluid catalytic cracking

Two basic types of FCC units are used today.

1. Side-by-side, 2. Stacked



Stacked type

Side–by–Side type

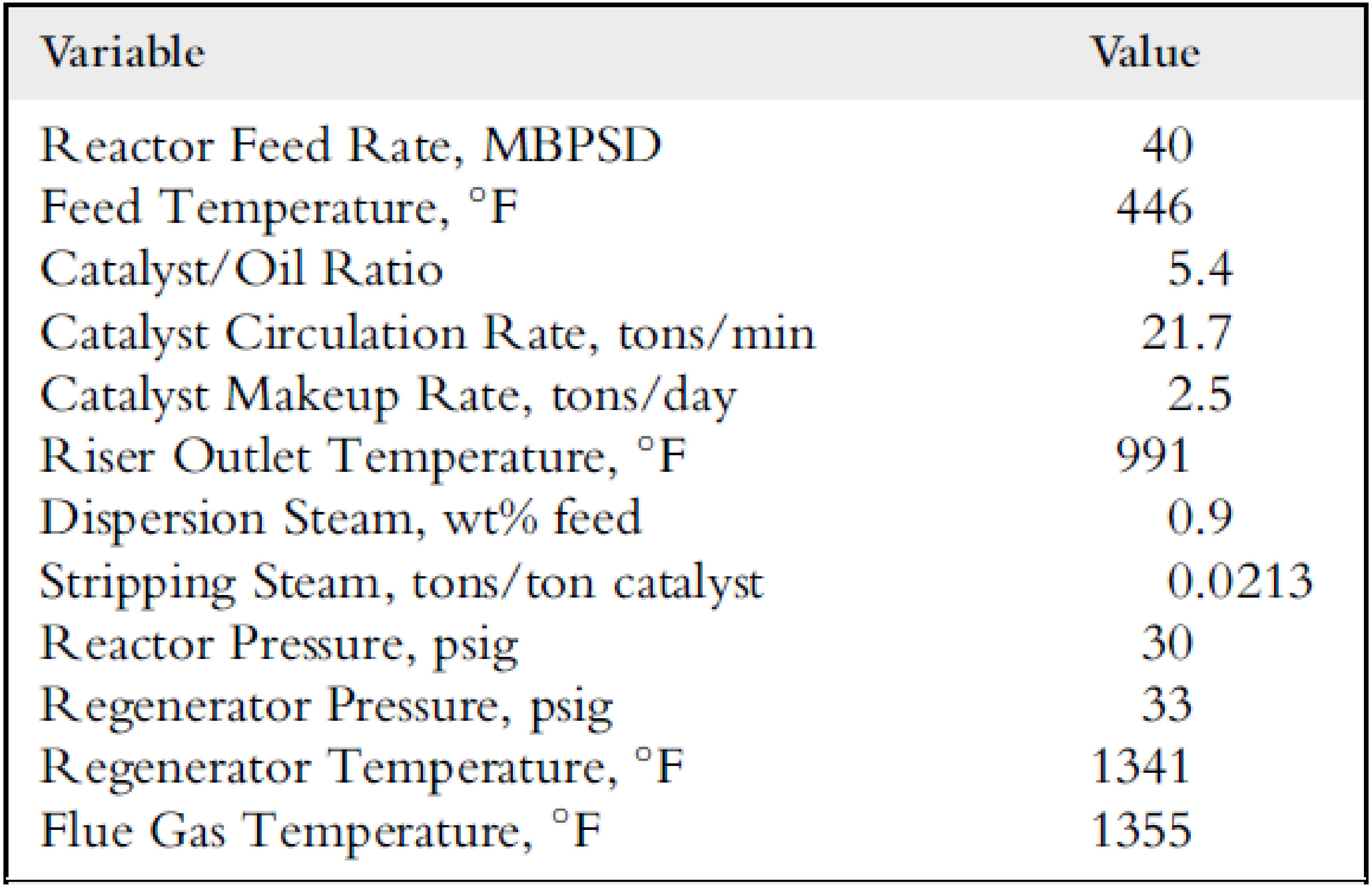
F = Feed, P = Products, S = Steam, FG = Flue gas, A = Air

Fluid catalytic cracking: Operating conditions

“The high volume of products caused by the cracking of larger molecules requires low operating pressure (1-5 bar). The high endothermic nature of cracking reactions requires that the reactor operates at high temperatures 480-550 ^{o}C” [2]

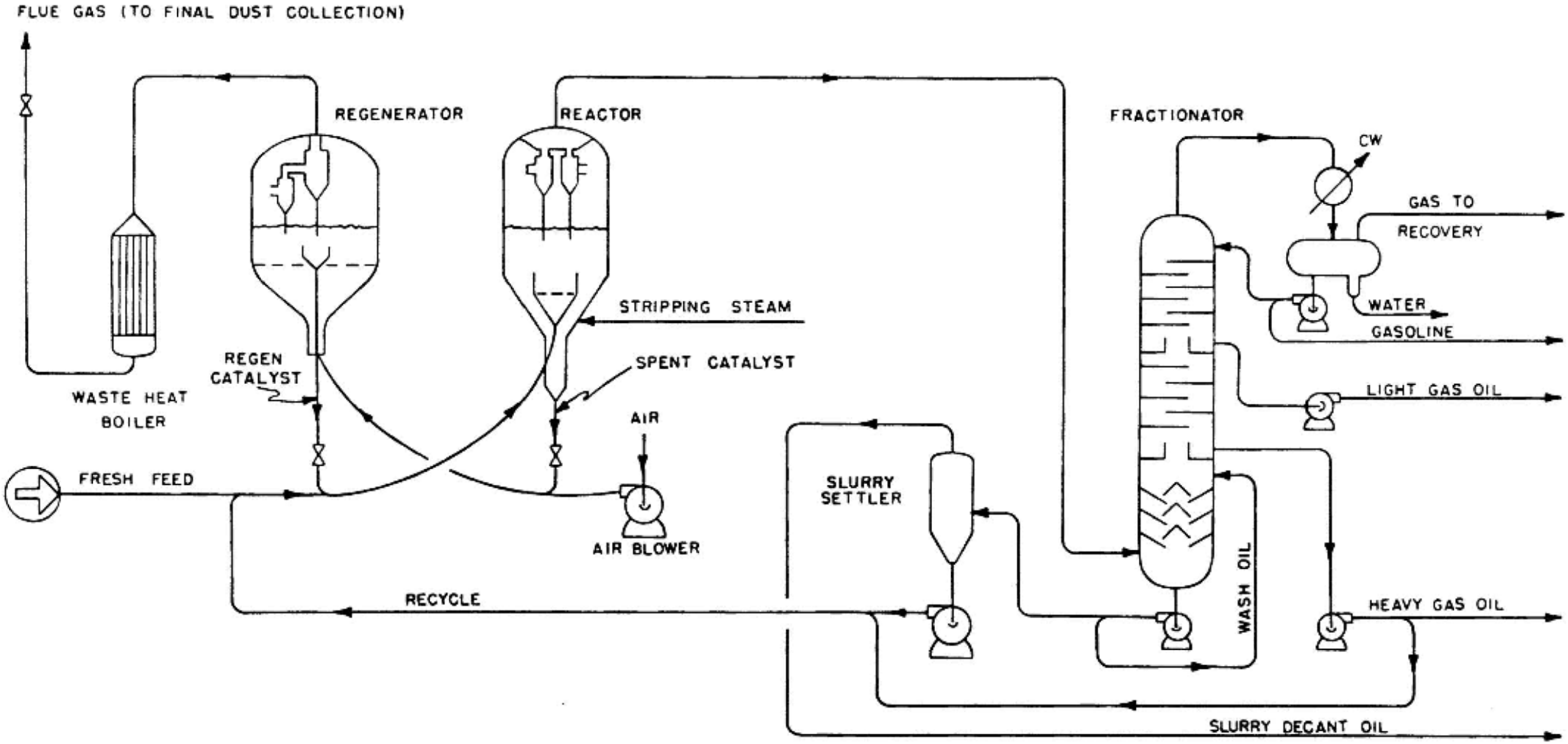
Fluid catalytic cracking

Reactor and regenerator operating conditions



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

Fluid catalytic cracking (FCC) [1]



Fluid catalytic cracking (FCC) [1]

http://dwe.man.eu/energy-related-engineering/refinery-technology/galp-refinery-sines

Catalytic cracking: Simulation

Go to Fahim et al., 2010 Chapter No. 8 and see Example 8.5 of simulation of a catalytic cracking unit.

Hydrocracking

Hydrocracking is a catalytic hydrogenation process in which high molecular weight feedstocks are converted and hydrogenated to lower molecular weight products. Cracking will break bonds, and the resulting unsaturated products are consequently hydrogenated into stable compounds. Hydrogenation also removes impurities such as sulfur, nitrogen, and metals in the feed.

Hydrocracking

It is mainly used to produce kerosene and diesel range products.

Vacuum gas oil is the feedstock for hydrocrackers, however a variety of feedstocks may be applied and variety of products may be obtained.

The catalyst used in hydrocracking is a bifunctional catalyst.

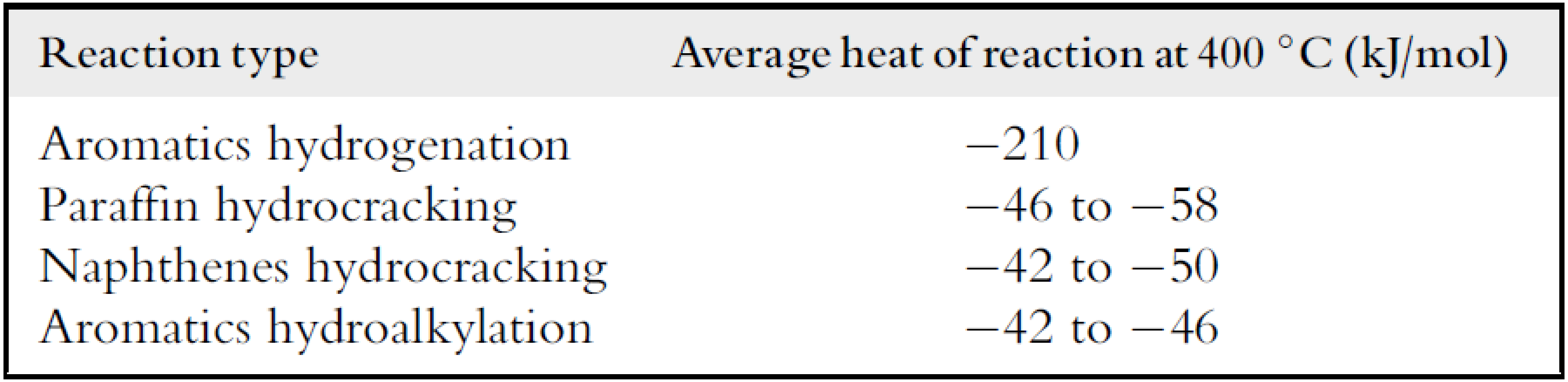
Hydrocracking reactions

Hydrocracking involves hydrotreating and cracking (hydrocracking) reactions. The hydrocracking reactions produce lower molecular weight products. An example hydrocracking reaction is

$$RCH_2CH_2CH_2CH_3 + H_2 = RCH_3 + CH_3CH_2CH_3$$

The reactions such hydrodealkylation, aromatics saturation, dehydrocyclization, etc., also occur during the coarse of hydrocracking.

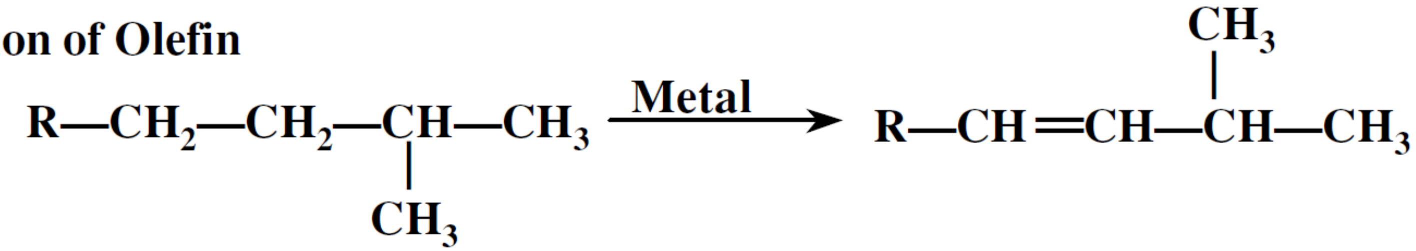
Heat of reactions of hydrocracking reactions [2]



Reaction type	Average heat of reaction at 400 °C (kJ/mol)
Aromatics hydrogenation	−210
Paraffin hydrocracking	−46 to −58
Naphthenes hydrocracking	−42 to −50
Aromatics hydroalkylation	−42 to −46

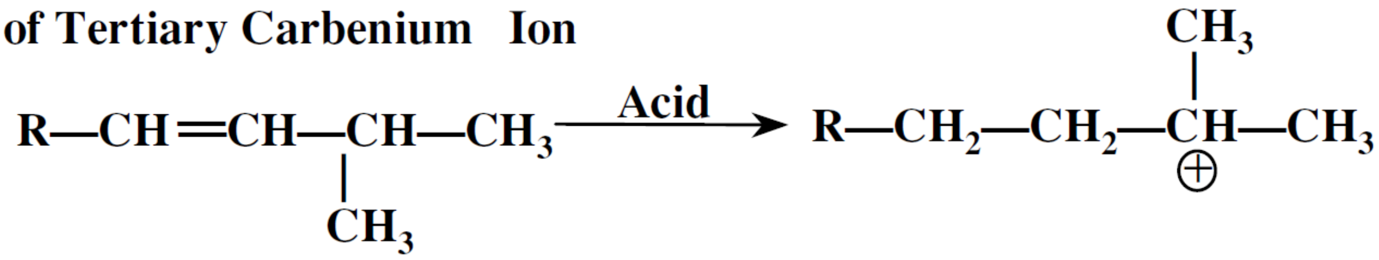
Hydrocracking reaction mechanism

(A) Formation of Olefin



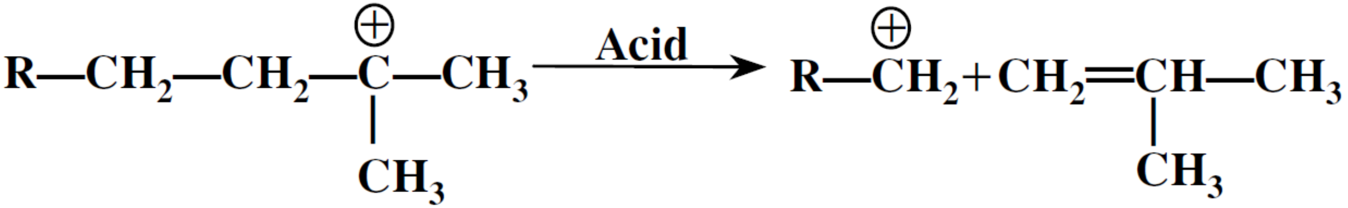
$$\mathrm{R{-}CH_2{-}CH_2{-}\underset{\displaystyle CH_3}{\underset{|}{C}H}{-}CH_3} \xrightarrow{\text{Metal}} \mathrm{R{-}CH{=}CH{-}\overset{\displaystyle CH_3}{\overset{|}{C}H}{-}CH_3}$$

(B) Formation of Tertiary Carbenium Ion



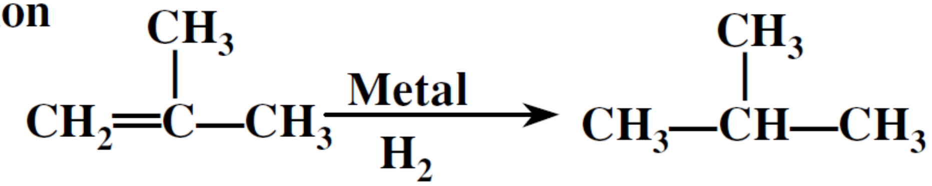
$$\mathrm{R{-}CH{=}CH{-}\underset{\displaystyle CH_3}{\underset{|}{C}H}{-}CH_3} \xrightarrow{\text{Acid}} \mathrm{R{-}CH_2{-}CH_2{-}\underset{\oplus}{\overset{\displaystyle CH_3}{\overset{|}{C}H}}{-}CH_3}$$

(C) Isomerization and Cracking



$$\mathrm{R{-}CH_2{-}CH_2{-}\underset{\displaystyle CH_3}{\underset{|}{\overset{\oplus}{C}}}{-}CH_3} \xrightarrow{\text{Acid}} \mathrm{R{-}\overset{\oplus}{C}H_2 + CH_2{=}\underset{\displaystyle CH_3}{\underset{|}{C}H}{-}CH_3}$$

(D) Olefin Hydrogenation



$$\mathrm{CH_2{=}\overset{\displaystyle CH_3}{\overset{|}{C}}{-}CH_3} \xrightarrow[\mathrm{H_2}]{\text{Metal}} \mathrm{CH_3{-}\overset{\displaystyle CH_3}{\overset{|}{C}H}{-}CH_3}$$

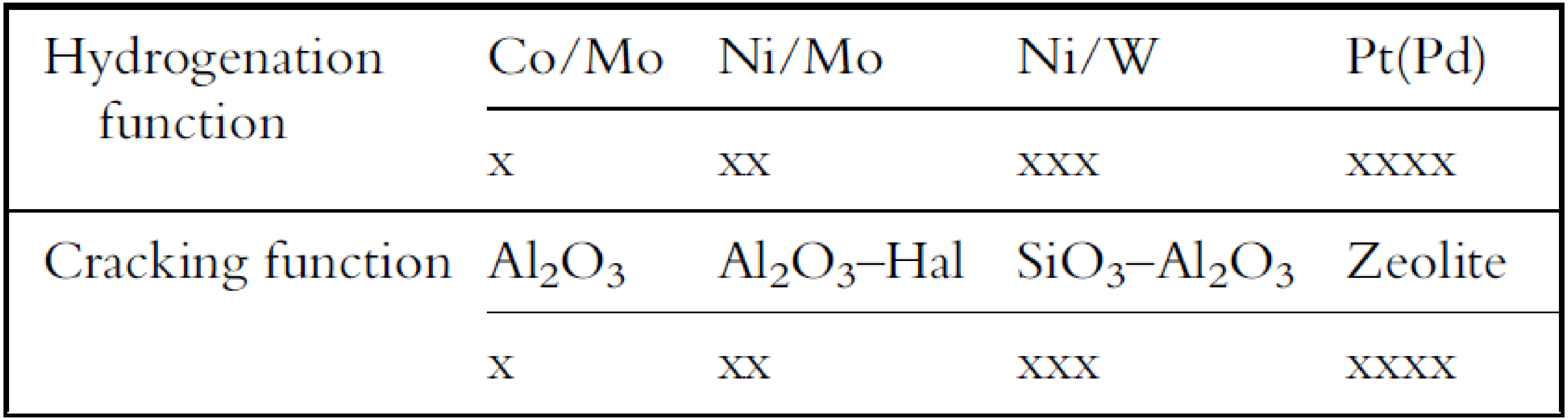
Hydrocracking operating conditions

The hydrogen partial pressure ranges between 85-170 bar and reactor temperature 300-450 ^{o}C.

Hydrocracking catalyst

The catalyst used in hydrocracking is a bifunctional or dual function catalyst. It is composed of a metallic part, which promotes hydrogenation (and dehydrogenation), and an acid part (support), which promotes hydrocracking, hydroisomerization, and dehydrocyclization reactions.

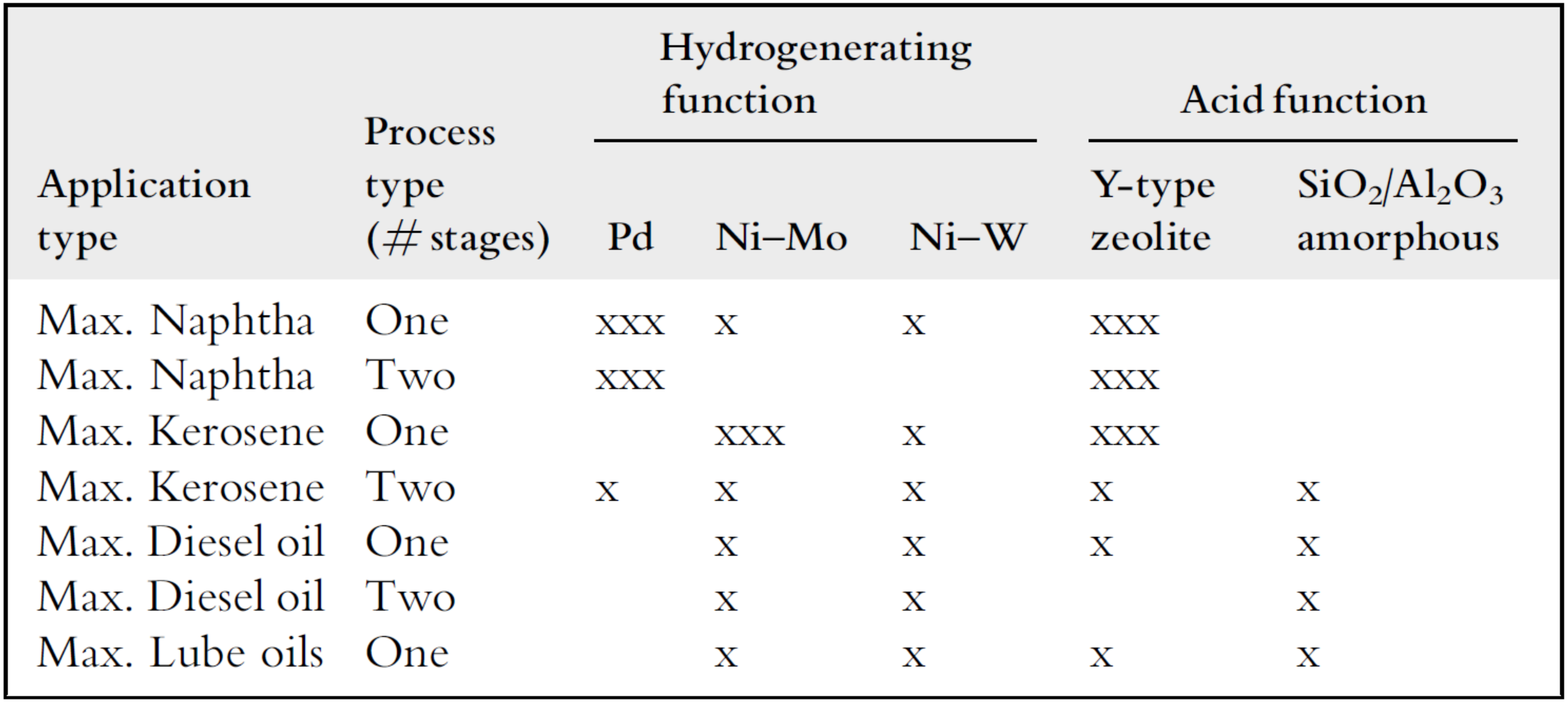
Hydrocracking catalyst [2]



Hydrogenation function	Co/Mo	Ni/Mo	Ni/W	Pt(Pd)
	x	xx	xxx	xxxx
Cracking function	Al_2O_3	Al_2O_3–Hal	SiO_3–Al_2O_3	Zeolite
	x	xx	xxx	xxxx

x represents order of strength

Hydrocracking catalyst [2]

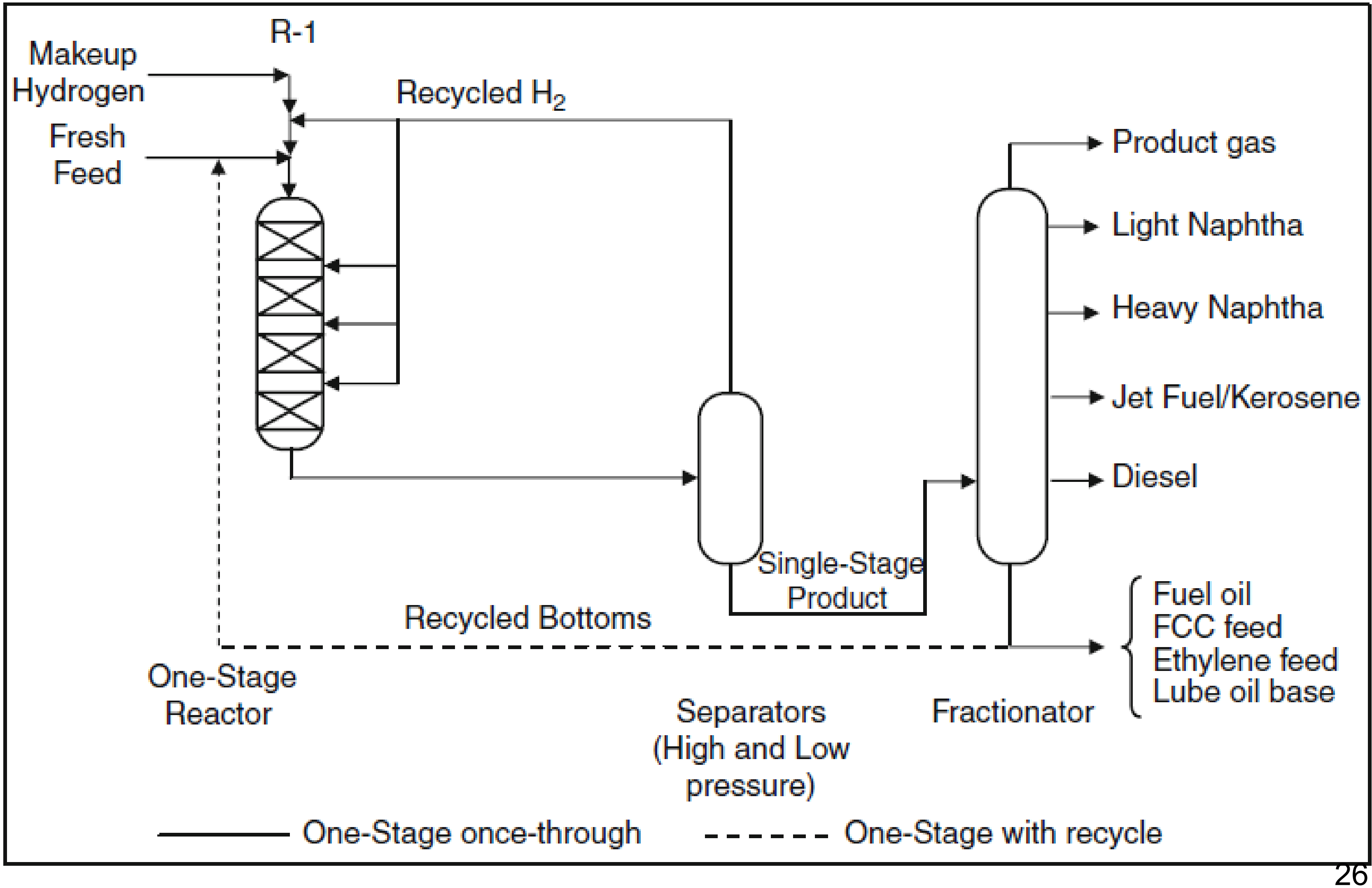


Application type	Process type (# stages)	Hydrogenerating function			Acid function	
		Pd	Ni–Mo	Ni–W	Y-type zeolite	SiO_2/Al_2O_3 amorphous
Max. Naphtha	One	xxx	x	x	xxx	
Max. Naphtha	Two	xxx			xxx	
Max. Kerosene	One		xxx	x	xxx	
Max. Kerosene	Two	x	x	x	x	x
Max. Diesel oil	One		x	x	x	x
Max. Diesel oil	Two		x	x		x
Max. Lube oils	One		x	x	x	x

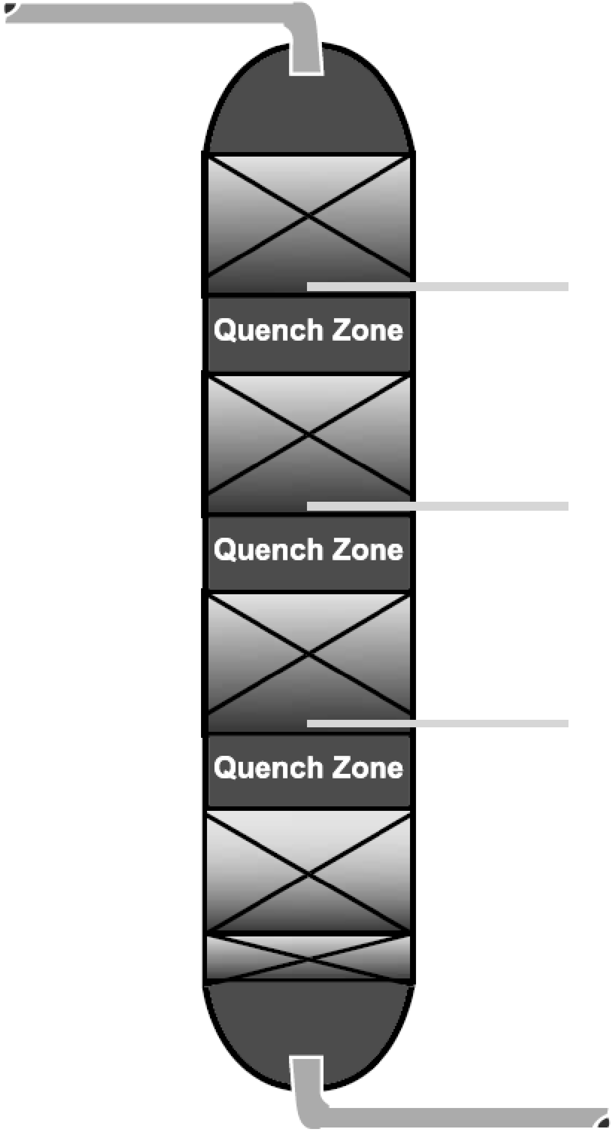
Hydrocracking catalyst

The acidic function is provided by the support which is usually a amorphous oxide such as silica-alumina, zeolite. Silica-alumina is support is common. The metal function for hydrocracking may be obtained from a combination of Group VIA (Mo, W) and Group VIIIA (Co, Ni) metal sulfides.

A single-stage with recycle hydrocracking process [2]



Typical hydrocracking reactor configuration [6]



Thermal cracking processes

1. **Coking**
2. **Visbreaking**

Coking

Coking is a severe thermal cracking process which is carried out to convert heavy fractions into solid coke and lighter hydrocarbons.

Coking

Coking is typically employed for treating mostly vacuum residues to prepare feed for the catalytic cracking/hydrocracking units and thereby decreasing the amount of low priced heavy fuel oils.

"The deposited coke contains most of the asphaltenes, sulfur, and metals present in the feed, and the products are unsaturated gases (olefins) and highly aromatic liquids." [2]

Applications of petroleum coke

Coke may be used

- as a fuel
- to make anodes for the electrolytic cells
- to manufacture graphite, and
- in the production of chemicals.

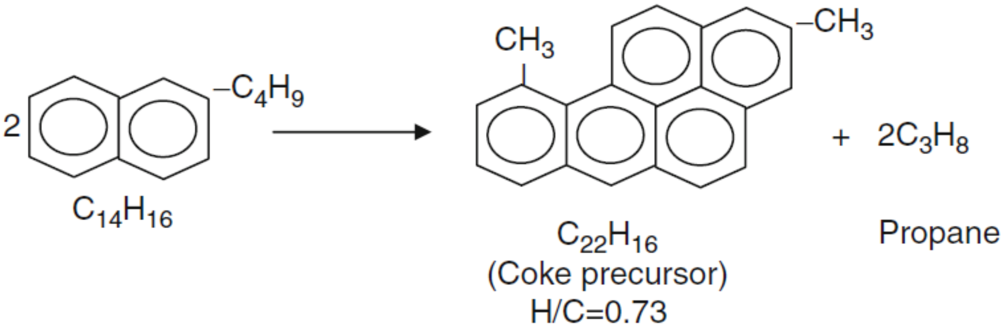
Petroleum coke is different from coke from coal and not suitable for metallurgical processing.

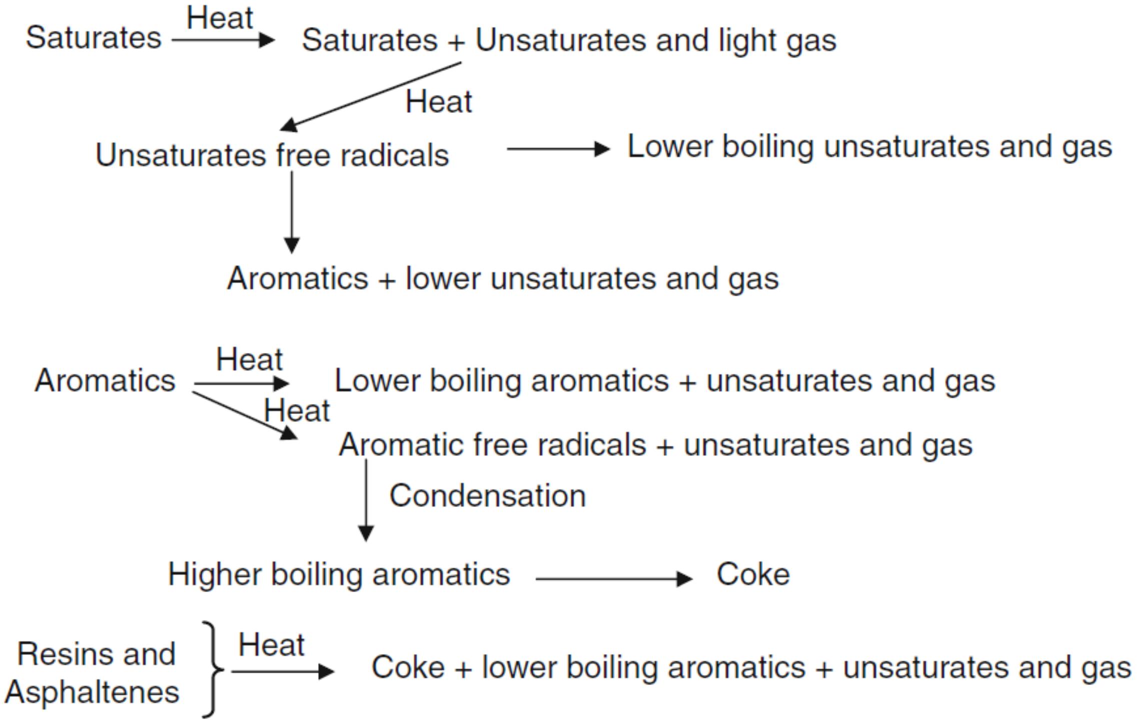
Coking

The feed for the coking process is usually vacuum residue, however, FCC residue and visbreaker residue may also be subjected to a coking process.

The products of a coker are typically light gases (e.g. unsaturarted C_1-C_4 and *i*-butane), coker naphtha (may be sent reforming or sent directly to gasoline blending unit), light and heavy gas oils. Light gas oil may be blended with kerosene [2].

Coke formation





Saturates $\xrightarrow{\text{Heat}}$ Saturates + Unsaturates and light gas

Saturates + Unsaturates and light gas $\xrightarrow{\text{Heat}}$ Unsaturates free radicals

Unsaturates free radicals → Lower boiling unsaturates and gas

Unsaturates free radicals → Aromatics + lower unsaturates and gas

Aromatics $\xrightarrow{\text{Heat}}$ Lower boiling aromatics + unsaturates and gas

Aromatics $\xrightarrow{\text{Heat}}$ Aromatic free radicals + unsaturates and gas

Aromatic free radicals + unsaturates and gas $\xrightarrow{\text{Condensation}}$ Higher boiling aromatics

Higher boiling aromatics → Coke

Resins and Asphaltenes $\xrightarrow{\text{Heat}}$ Coke + lower boiling aromatics + unsaturates and gas

Dehydrogenation of methylcyclohexane leading to coke formation

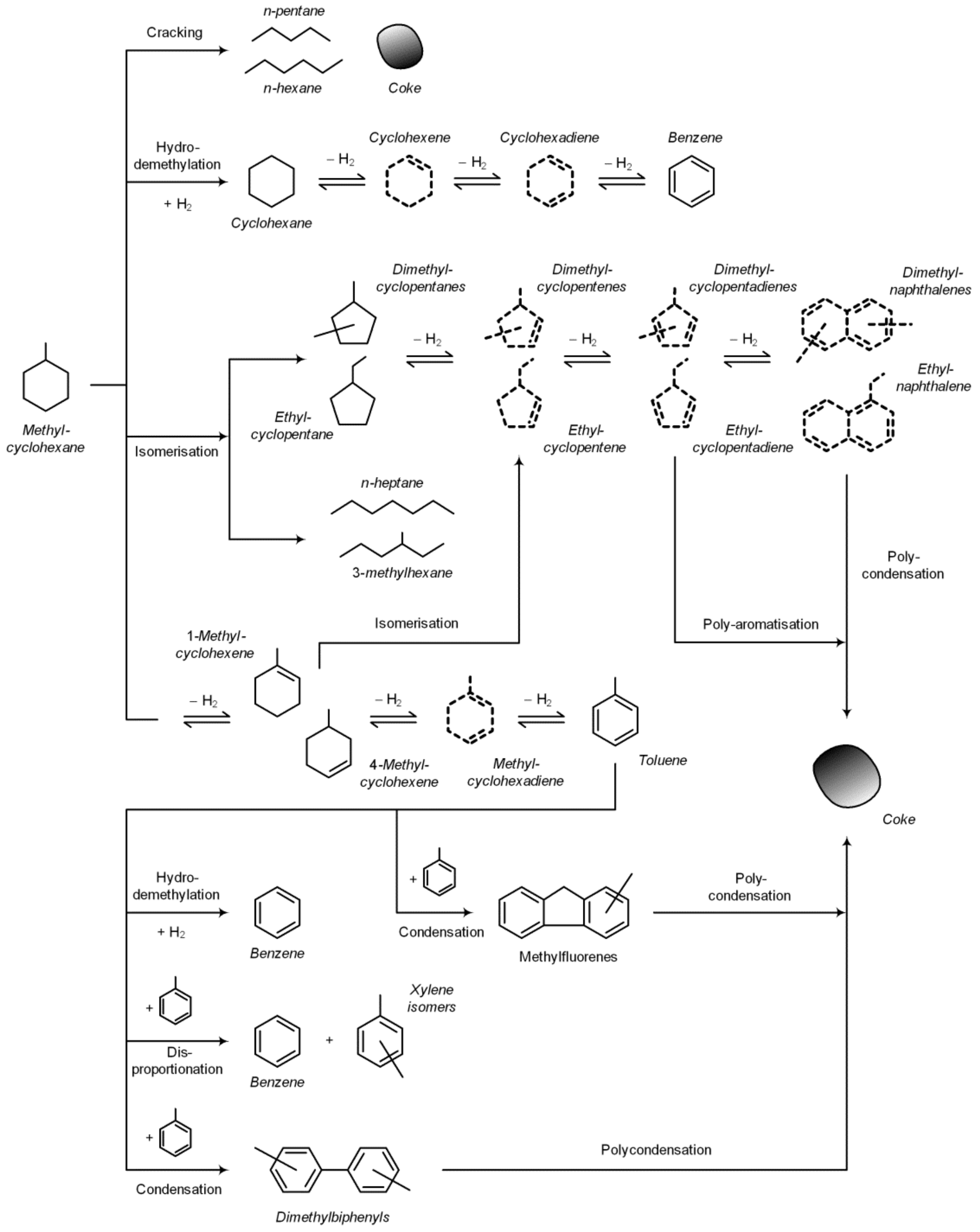


Fig. 1

Coking processes

Delayed coking is the most widely used process to carry out a coking operation.

A high velocity of oil in the furnace tubes prevents significant coking in the furnace even above the coking conditions. Sufficient time is then given in the coke drums for coking reactions to take place. That is why the process is called delayed coking.

Fluid coking is a continuous process compared to delayed coking. Flexicoking also uses fluid coking process but a gasification reactor is also there.

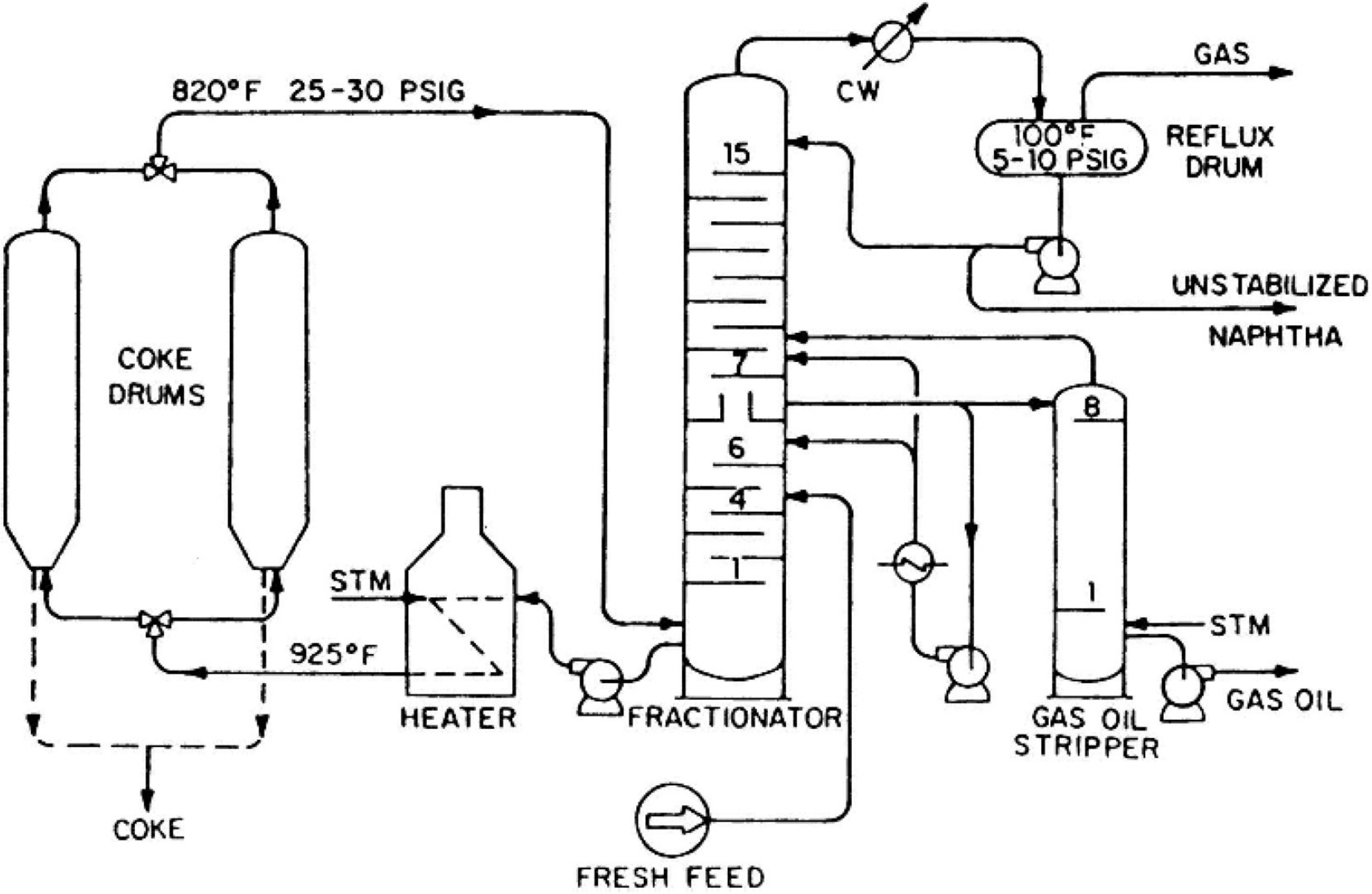
Delayed coking

Steam is injected in the furnace to inhibit the coke formation. The feed is heated higher than 900 ^{o}F (482 ^{o}C) and a vapor-liquid mixture leaving the furnace flows to the coking drum. The coking reactions take place in the drum and the vapors issuing from the coking drum are quenched in the fractionator by the liquid feed to prevent further coking. Moreover, it simultaneously condense a part of heavy ends which are then recycled.

Delayed coking: Effect of pressure

“Increasing pressure will increase coke formation and slightly increase gas yield. However, refinery economics require operating at minimum coke formation. New units are built to work at 1 bar gauge (15 psig), while existing units work at 2.4 bar gauge (35 psig). In a case of production of needle coke, a pressure of 150 psig is required”. [Fahim]

Delayed coking [1]



Delayed coking

When a coke drum is filled, the heater output is switched to the second drum and the coke is collected.

Usually two coke drums are employed however, four drums are also used.

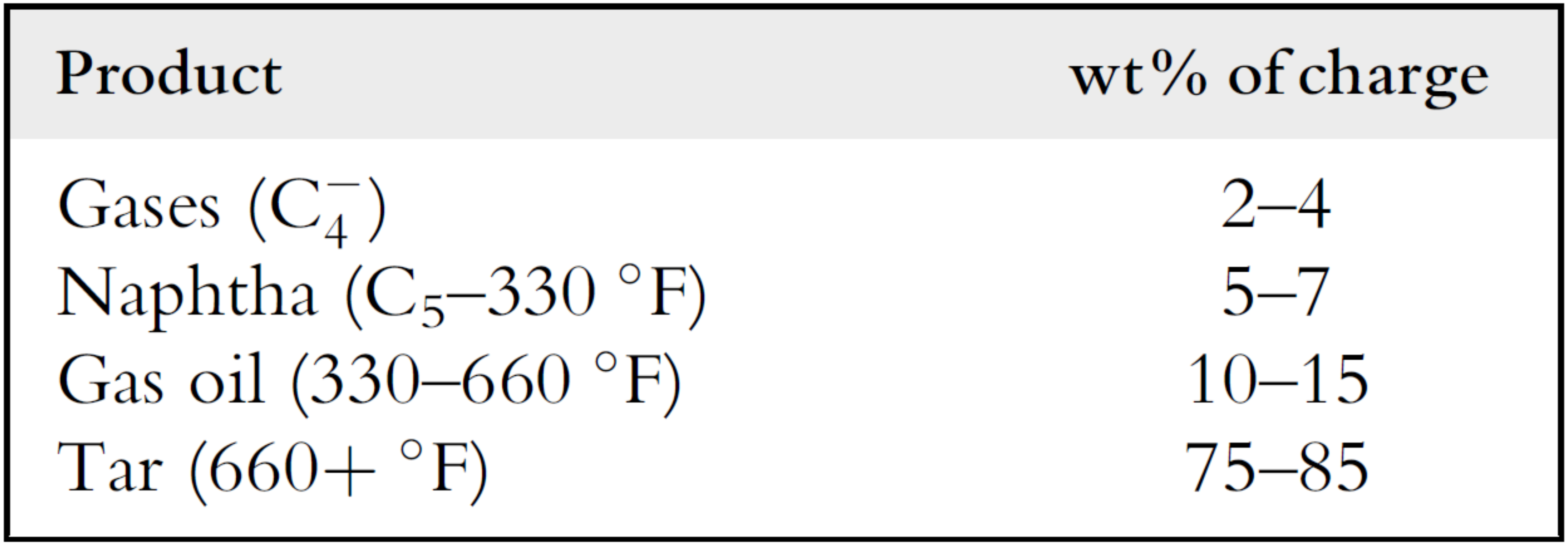
Visbreaking

Visbreaking is a mild thermal cracking carried out to reduce the viscosities and pour points of atmospheric and vacuum tower bottoms. The objective is to produce a fuel oil stock of improved viscosity characteristics.

The visbreaking product yields are dependent upon the reaction temperature and the residence time.

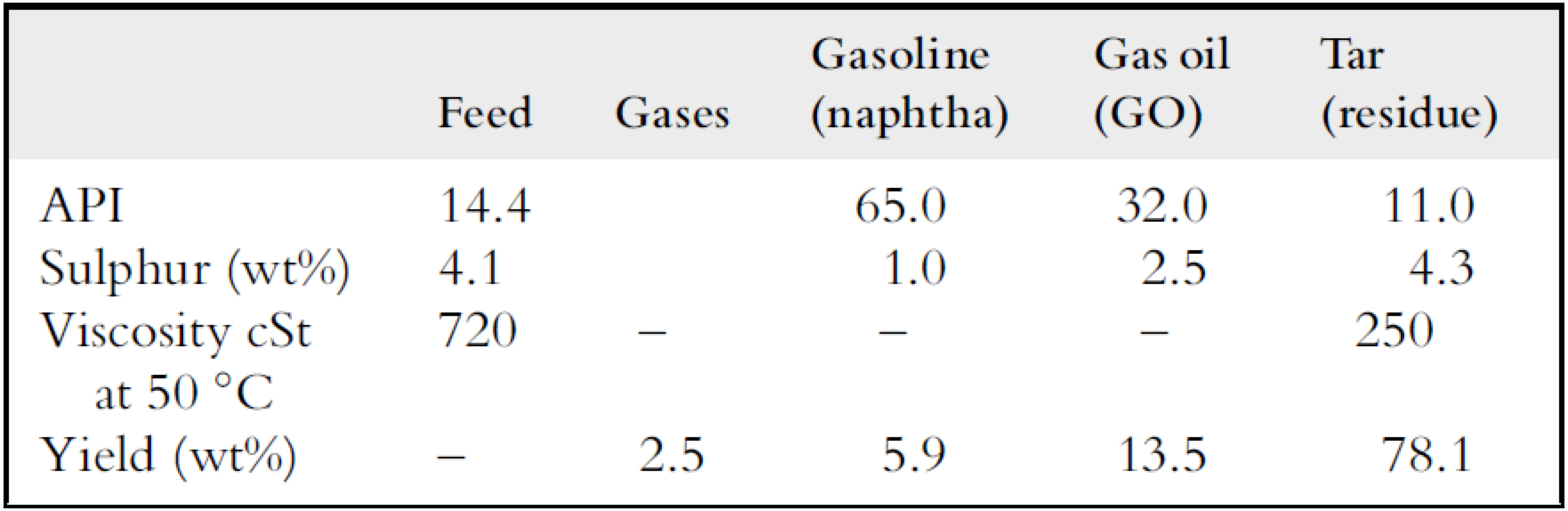
Visbreaking: Typical product yields [2]

The products of visbreaking include light gases, naphtha (gasoline), gas oil, and residue (main product).



Product	wt% of charge
Gases (C_4^-)	2–4
Naphtha (C_5–330 °F)	5–7
Gas oil (330–660 °F)	10–15
Tar (660+ °F)	75–85

Visbreaking: Kuwait oil product yields [2]

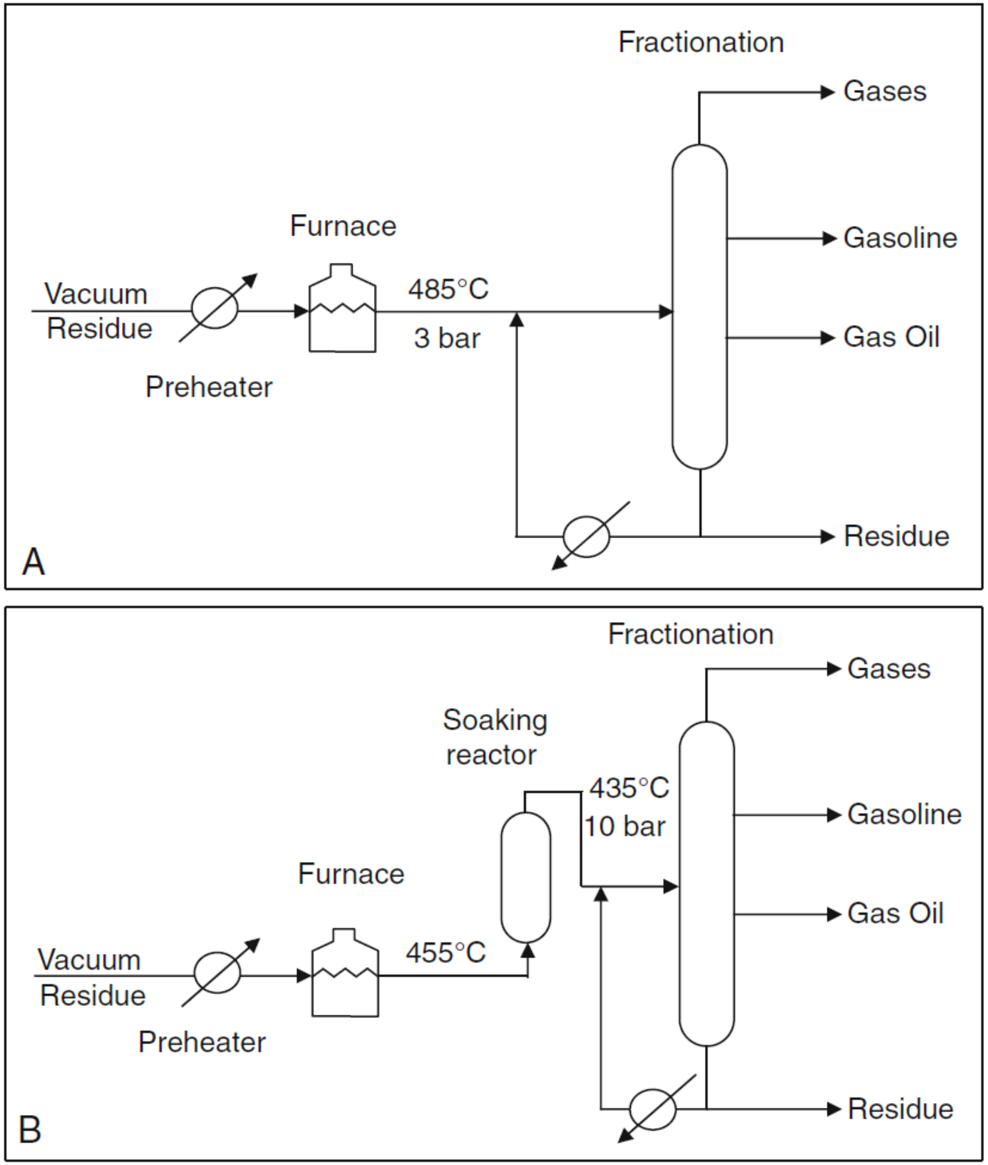


	Feed	Gases	Gasoline (naphtha)	Gas oil (GO)	Tar (residue)
API	14.4		65.0	32.0	11.0
Sulphur (wt%)	4.1		1.0	2.5	4.3
Viscosity cSt at 50 °C	720	–	–	–	250
Yield (wt%)	–	2.5	5.9	13.5	78.1

Visbreaking types

Visbreaking is either coil breaking when the resid is broken in the furnace coil and soaker breaking when soaked in the reactor for few minutes.

Visbreaking [2]



(A) Coil type visbreaker. (B) Soaker type visbreaker

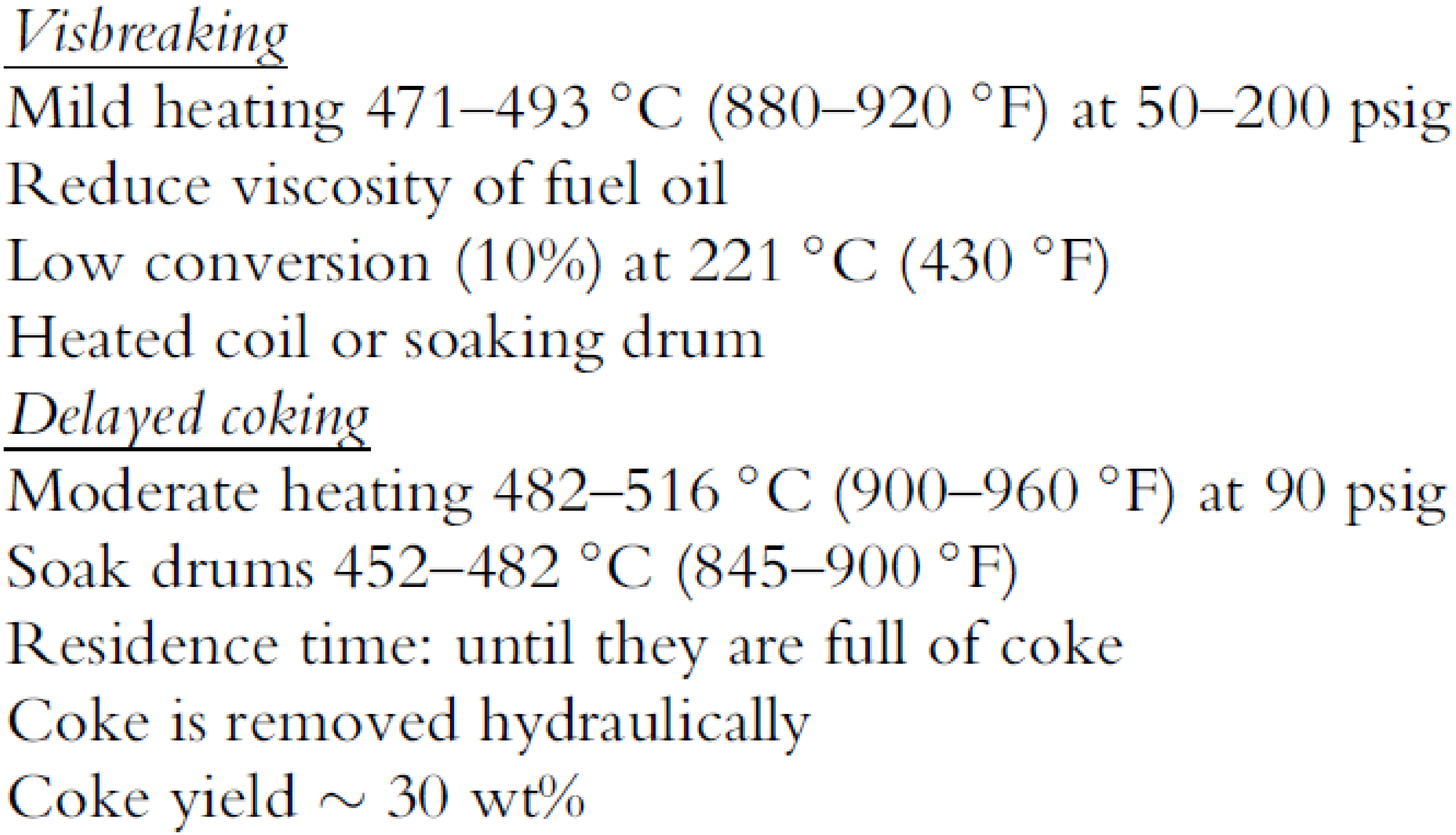
Coil visbreaking

The feed residue feedstock is heated and then mildly cracked in the visbreaker furnace. Reaction temperature range from 850 to 900 ^{o}F and operating pressures vary from as low as 3 bar to as high as 10 bar. Coil furnace visbreaking is used and the visbroken products are immediately quenched to stop the cracking reaction. The quenching step is essential to prevent coking in the fractionation tower. The gas oil and the visbreaker residue are the most commonly used as quenching streams.

Comparison of coil and soaker visbreakings

"Coil cracking is described as a high temperature, short residence time route whereas soaker cracking is a low temperature, long residence time route. The yields achieved by both options are in principle the same, as are also the properties of the products. Both process configurations have their advantages and applications. Coil cracking yields a slightly more stable visbreaker products, which are important for some feedstocks and applications. It is generally more flexible and allows the production of heavy cuts, boiling in the vacuum gas oil range. Soaker cracking usually requires less capital investment, consumes less fuel and has longer on-stream times." [2]

Comparison of visbreaking and delayed coking [2]



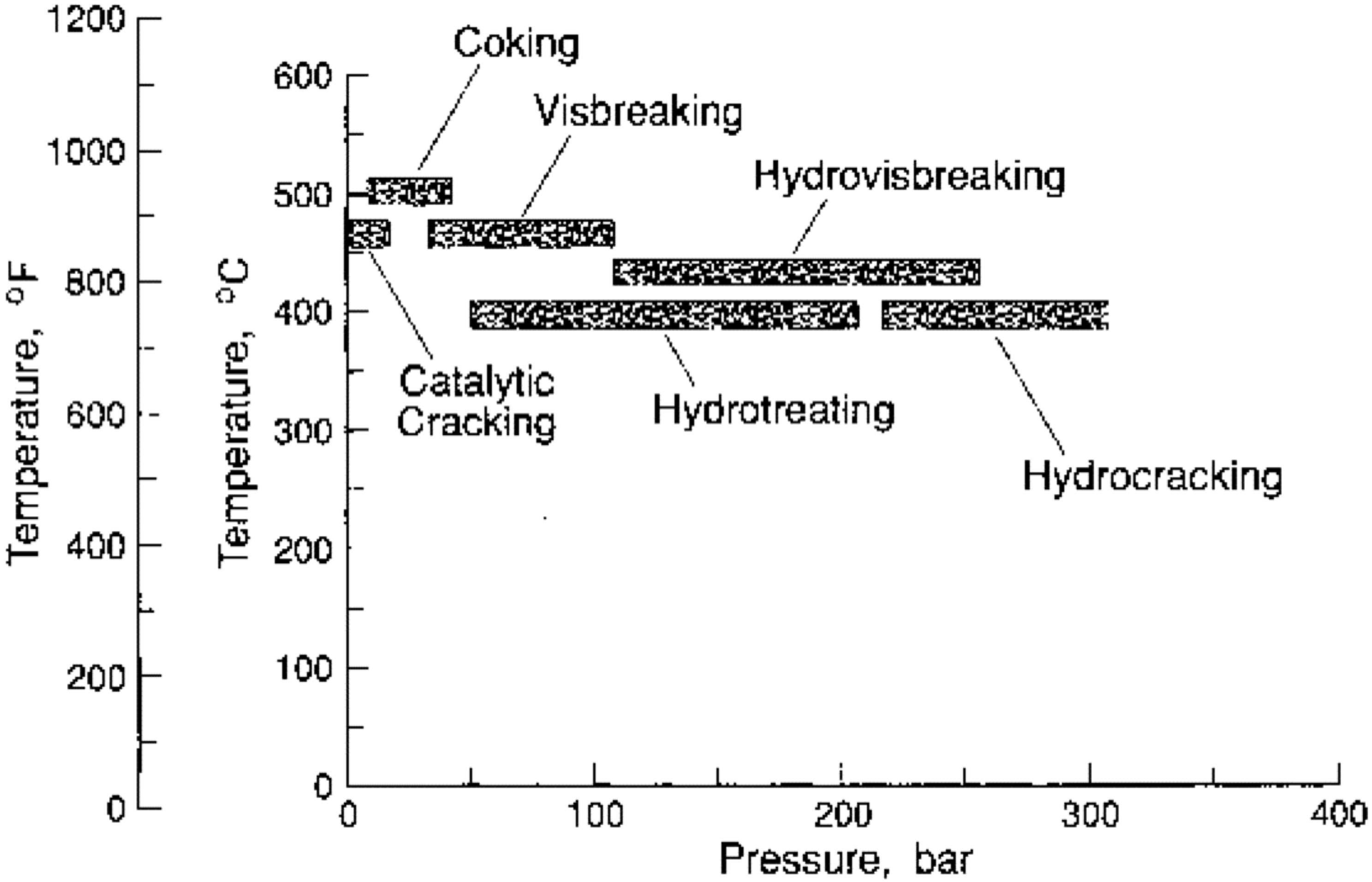
Visbreaking

Mild heating 471–493 °C (880–920 °F) at 50–200 psig
Reduce viscosity of fuel oil
Low conversion (10%) at 221 °C (430 °F)
Heated coil or soaking drum

Delayed coking

Moderate heating 482–516 °C (900–960 °F) at 90 psig
Soak drums 452–482 °C (845–900 °F)
Residence time: until they are full of coke
Coke is removed hydraulically
Coke yield ~ 30 wt%

Temperature and pressure conditions of various conversion processes



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