

Crude Oil processing and Base Oil production



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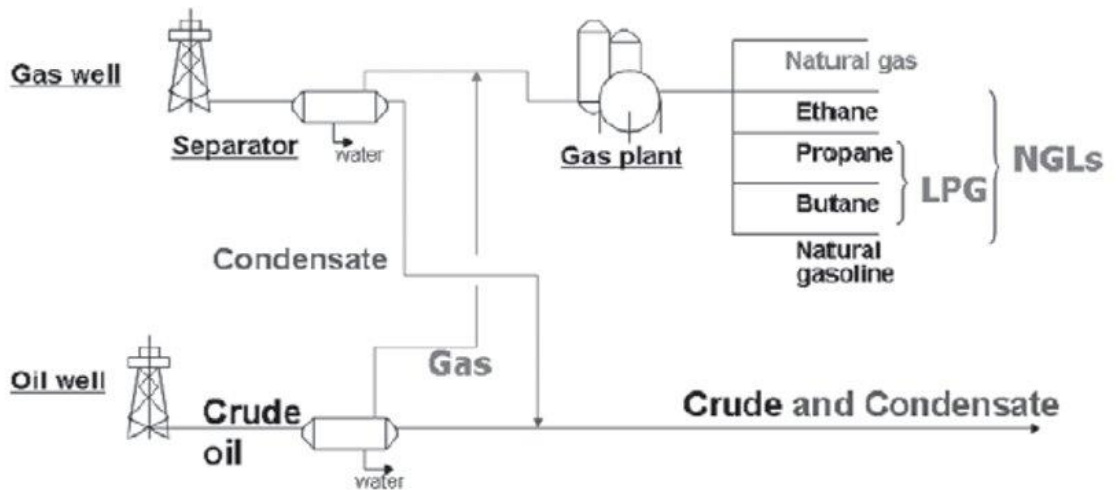
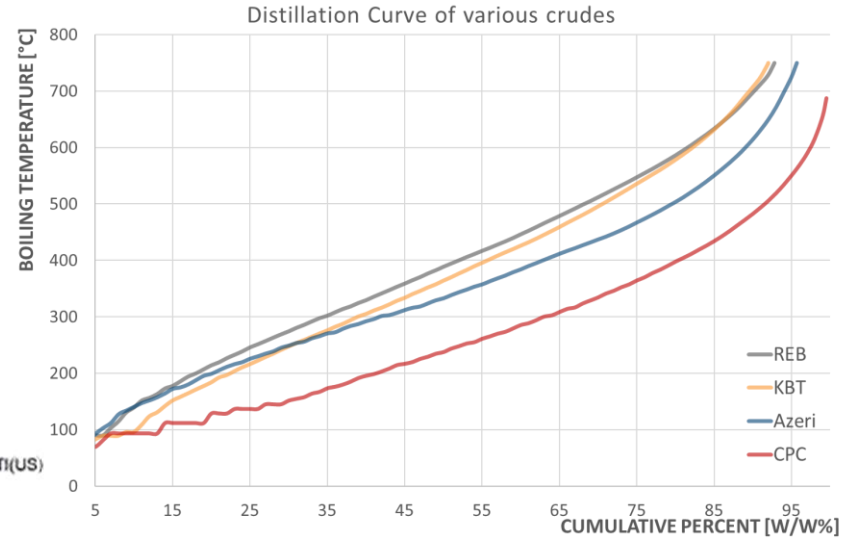
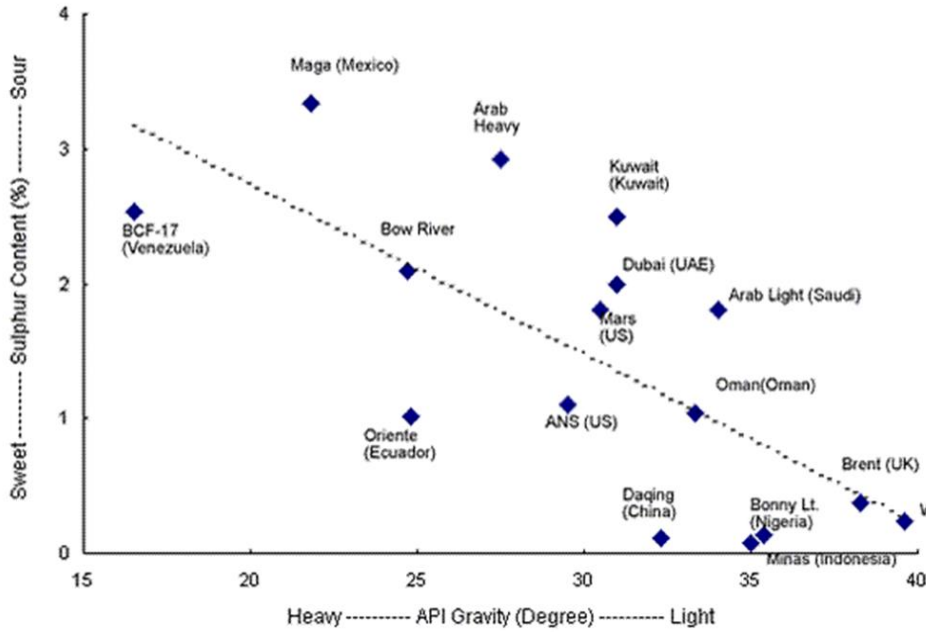
MOL Downstream

Technology Process Development

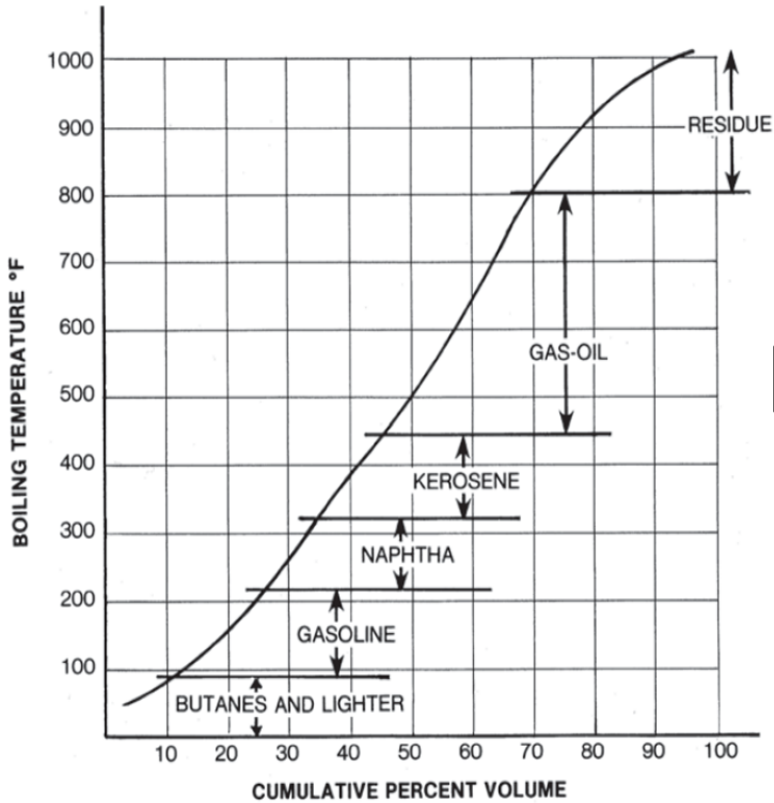


October, 2021

Crude Oil

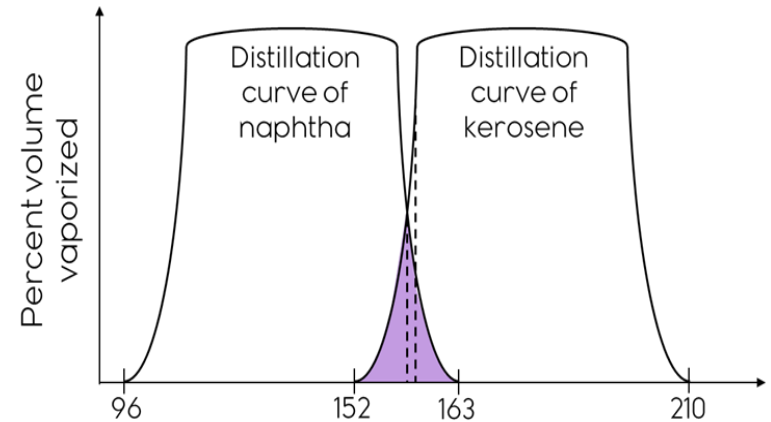


Crude Oil fractions

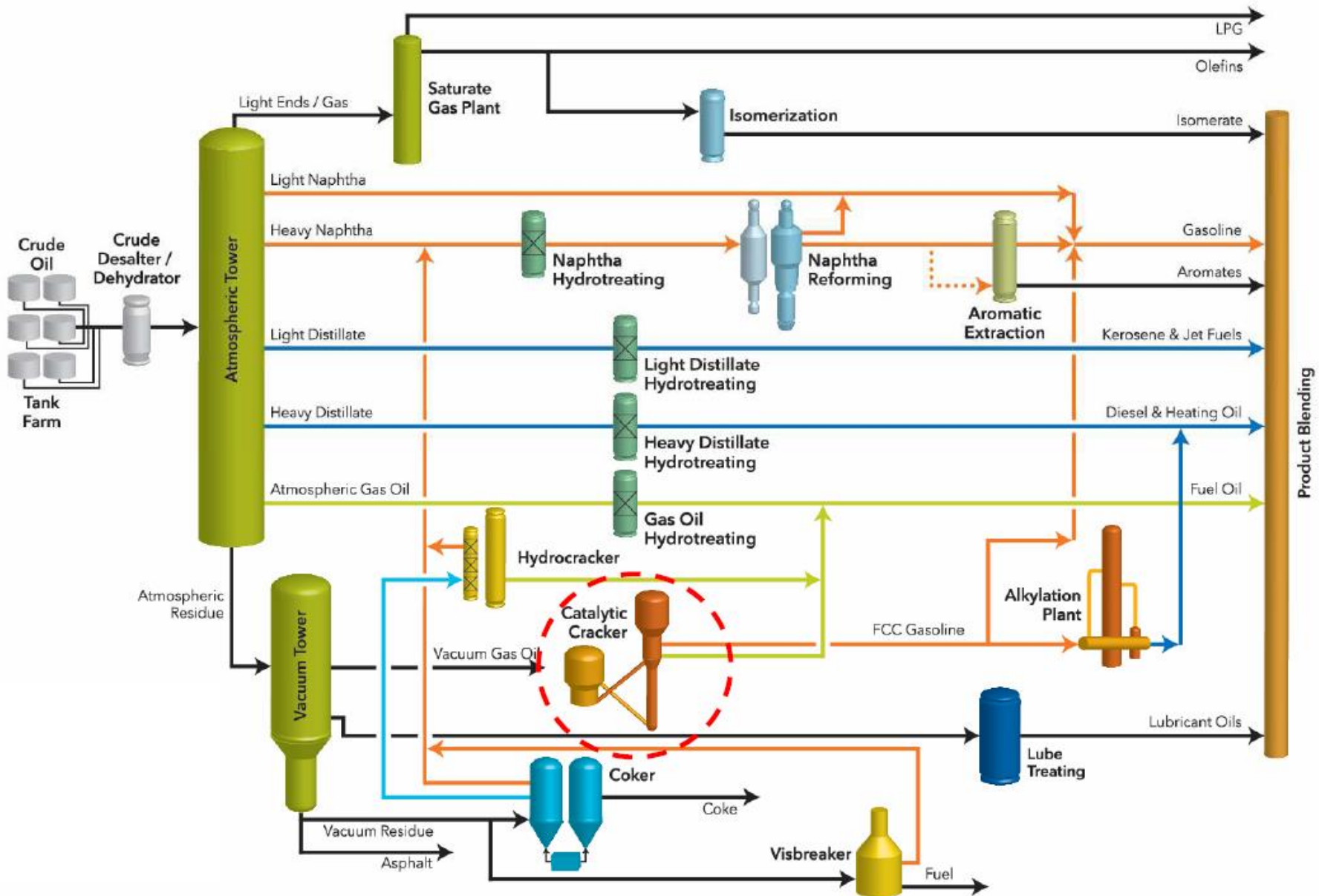


Temperature [°C]	Fractions/Cuts
< 32	Butanes and lighter
32-104	Gasoline
104-157	Naphtha
157-232	Kerosene
232-427	Gas oil
>427	Residue

Fractions – all the compounds that boiling between two given temperatures



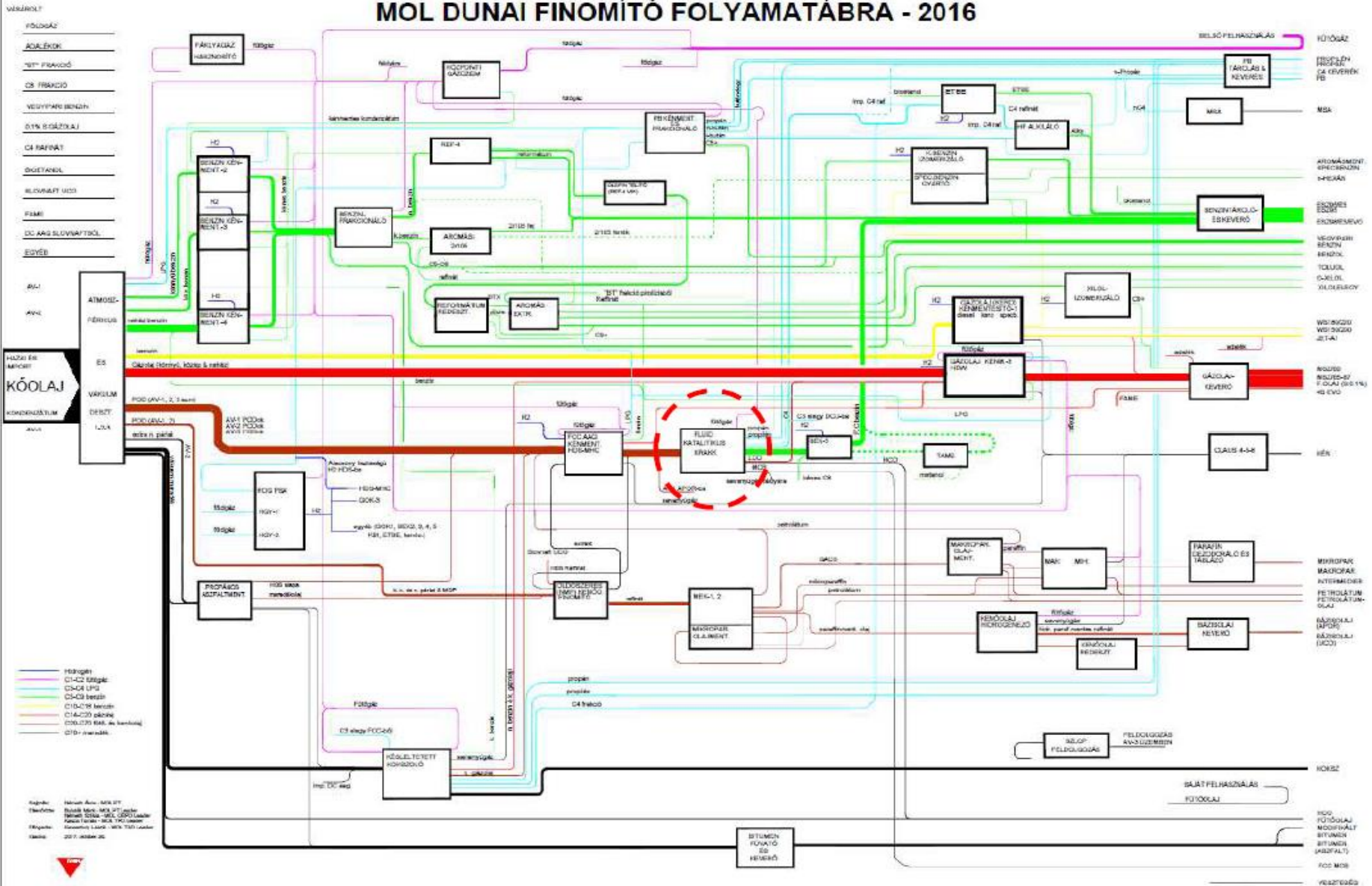
Refinery Overview



Danube Refinery



MOL DUNAI FINOMÍTÓ FOLYAMATÁBRA - 2016



- FORRÁSOK
- ADÁSVÉNYEK
- 10T FRAKCIO
- C8 FRAKCIO
- VEDYFAR BENSZIN
- ÖNY BŐGŐZOLAJ
- C4 FRAKCIÓ
- BIGETÁROL
- ELVONATTI ÜZEM
- FBM
- CC AAG SLOVAFTOL
- EDYSEB
- AV-1
- AV-2

HÁZSI ÉS MÉRŐKÖR
KÖÖLAJ
 KÖZELFOLYÓ
 AV-1

- Hidrogén
- C1-C2 Etilgáz
- C3-C4 LPG
- C4-C5 Naphtha
- C14-C19 Kerosén
- C20-C25 Kerosén és Diesel
- C27+ Ásványolaj

Készítette: ...
 Tervezte: ...
 Székhely: ...
 Működés kezdte: 2017. október 26.

BELSO FELHASZNALAS

FORRÁS
 HŐSÉRŐLŐ
 CA ÉVEKÉN
 FB

MSK

KROKAMÉNTEK
 SPECIFIKUM
 H-FAZIS

ESZMÉSEK
 ESZMÉSEK

VEGYFAR
 BENSZIN
 HÉVŐZOL
 TOLUOL
 GÁZOLAJ
 ALDURISOL

WD 80C
 WD 180C
 WD 240C

ÁRVSZÉNY
 FOLYÓ
 GÉZ (20-5%)
 48 ÉVŐ

HÉN

KEROZIN
 SPECIFIKUM
 H-FAZIS

PARAFIN
 SPECIFIKUM
 H-FAZIS

DIEZELVEZŐ
 H-FAZIS

DIEZELVEZŐ
 H-FAZIS

BAZISOLAJ
 H-FAZIS

KÖZEL FELHASZNÁLÁS

TÁJÉLT FELHASZNÁLÁS

HŐZS

180C
 FOLYÓGÁZ
 BTYONER
 BTYONER
 (KÉZKÖZ)
 FOC MOB

VEZETŐKÖZ

Danube Refinery – Key Figures



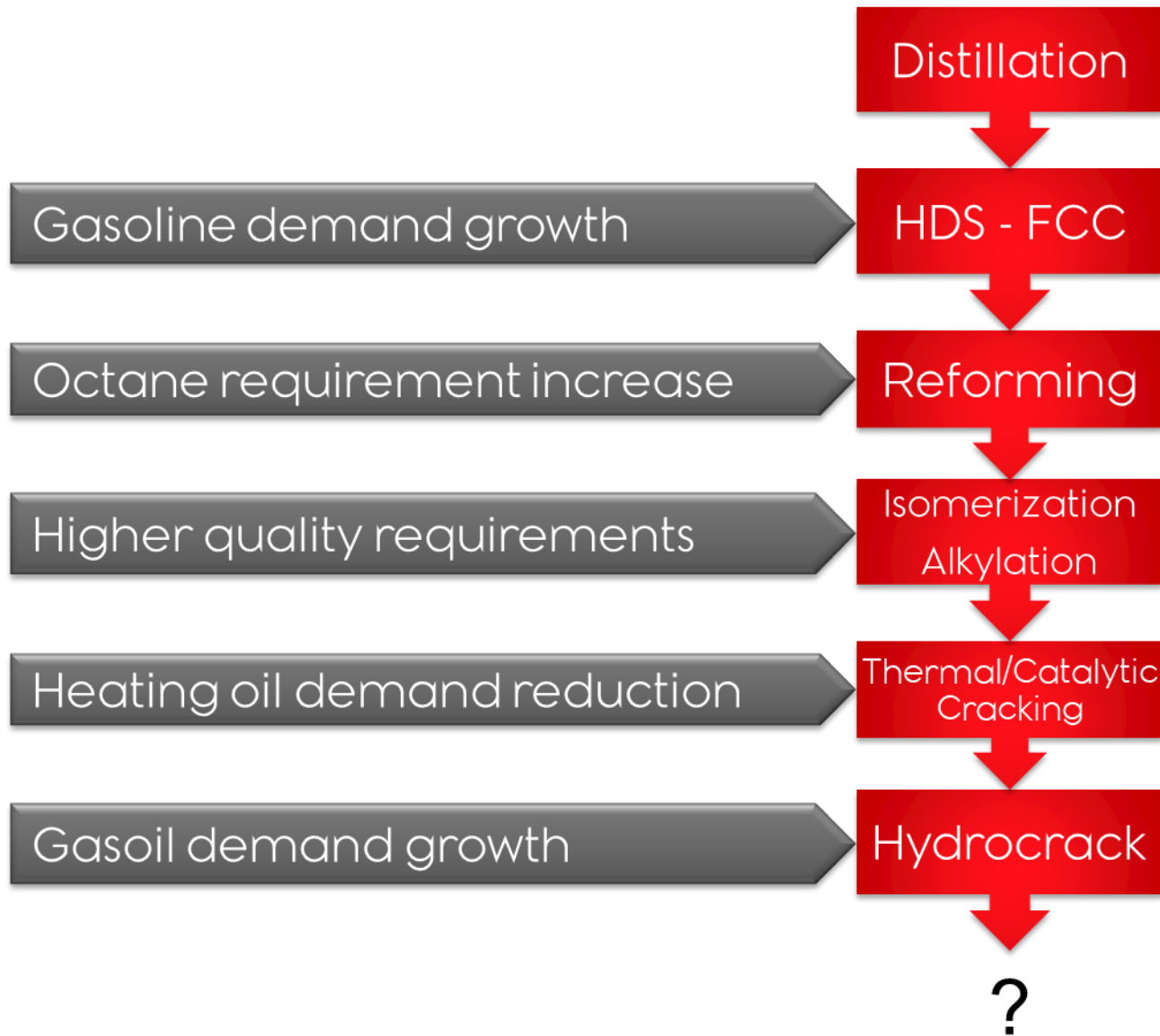
Danube Refinery



Key figures

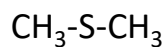
Area:	800 hectares
Distillation capacity:	8.1 Mt/year
Processed crude:	7 Mt/year
Number of plants:	49
Nelson complexity index :	10.6
Number of employees:	cca. 1300

Major Conversion Technologies

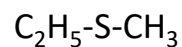


Sulphur containing compounds

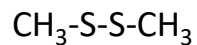
- **H₂S** (hydrogen-sulfide);
- **Mercaptanes:** R-SH (R: <3-30);
- **Mono- and disulfides:** R-S-R' (R, R': alkyl groups);



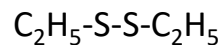
dimethyl-sulfide



ethyl-methyl-sulfide

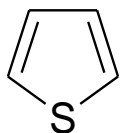


dimethyl-disulfide

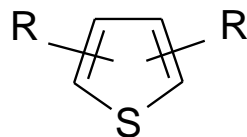


diethyl-disulfide

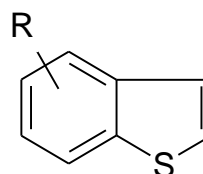
- **Thiophenes**



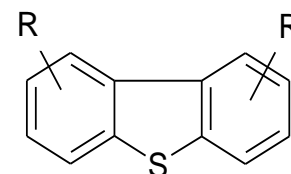
thiophene



alkyl-thiophenes



benzothiophenes



dibenzothiophenes

R: alkyl groups

Product requirements - Gasoline



STANDARD REQUIREMENTS OF GASOLINES

Properties	European Union			
	EN 228 „Euro 2” (1993)	EN 228 „Euro 3” (2000)	EN 228 „Euro 4” (2005)	EN 228 „Euro 5” (2009)
sulphur content, mg/kg, max	500	150	50 / 10¹	10
aromatic content, v/v%, max	-	42	35	35
olefin content, v/v%, max	-	18	18	18
benzene content, v/v%, max	5.0	1.0	1.0	1.0
oxygen content, %, max	-	2.7	2.7	2.7
Reid vapour pressure, kPa	35-100	60/70²	60/70²	45-105²

¹ maximum sulphur content is 50 mg/kg, but 10 mg/kg sulphur content has to be regionally available

² summer / winter quality

- no regulation

Product requirements - Diesel



STANDARD REQUIREMENTS OF DIESEL FUELS

Properties	European Union			
	EN 590:1999	EN 590:2000	EN 590:2005	EN 590:2009 +A1:2010
cetane number, min	48	51	51	51
density at 15°C, kg/m³	820-860	820-845	820-845	820-845
total aromatic content, %, max	-	-	-	-
polyaromatic content, %, max	-	11	11	8
distillation recovery (95%) temperature, °C	370	360	360	360
sulphur content, mg/kg, max	500	350	50.0 / 10.0¹	10.0

¹ maximum sulphur content is 50 mg/kg, but 10 mg/kg sulphur content has to be regionally available
-no limitation

Lubricant Story

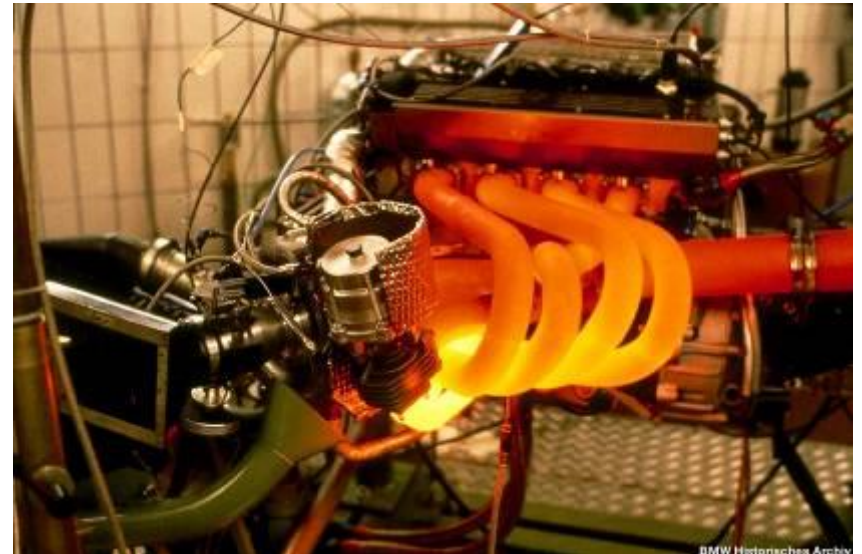


- 1400 BC, beef and mutton fat (tallow) being applied to lubricate chariot axles. Very little changed over the next 3000 years except, that the oils sometimes came from more exotic animals such as whales.
- In 1852 petroleum-based oils first became available. They were not widely accepted at first because they did not perform as well as many of the animal-based products. Raw crude did not make very good lubricant.
- But as the demand for automobiles grew, so did the demand for better lubricants.
- Lubricant manufacturers learned soon which crudes made the best lubricants.
- By 1923 the Society of Automotive Engineers classified engine oils by viscosity: light, medium, and heavy. Engine oils contained no additives and had to be replaced every 800-1000 miles.
- In the 1920s more lubrication manufacturers started “processing” their base oils to improve their performance.
- HC technologies were commercialized for lube production in late '50 and dewaxing was in , '70

Lubes



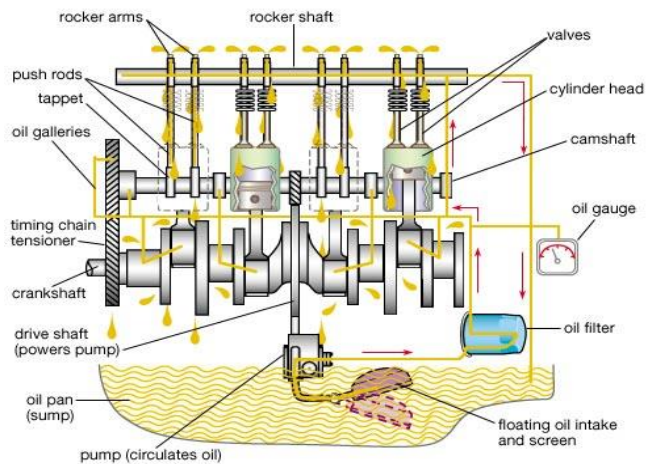
- Automotive: engine oils, automatic transmission fluids (ATF's), gear-oils
- Industrial: machine oils, greases, electrical insulating oils, gas turbine oils
- Pharmacy/cosmetics: white oils, paraffinicum liquidicum
- Provisioning: food grade oils, lining of food containers, cover of food, etc.



Lube Refinery



- ❖ Why beneficial to produce base stocks and waxes?
- ❖ What are the products and which properties are important?
- ❖ Which types of processes?
- ❖ Global market and changes



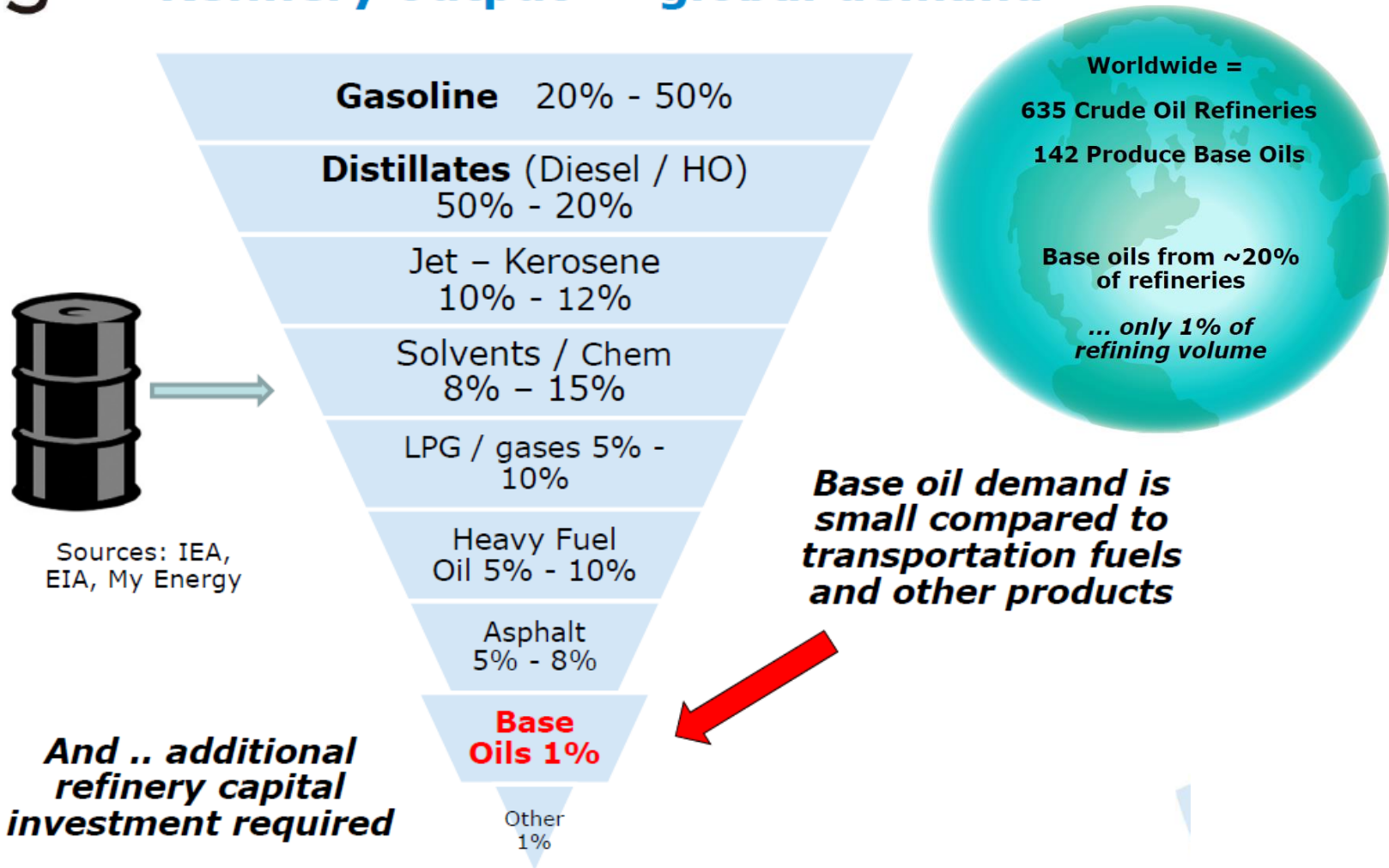
© 2007 Encyclopædia Britannica, Inc.



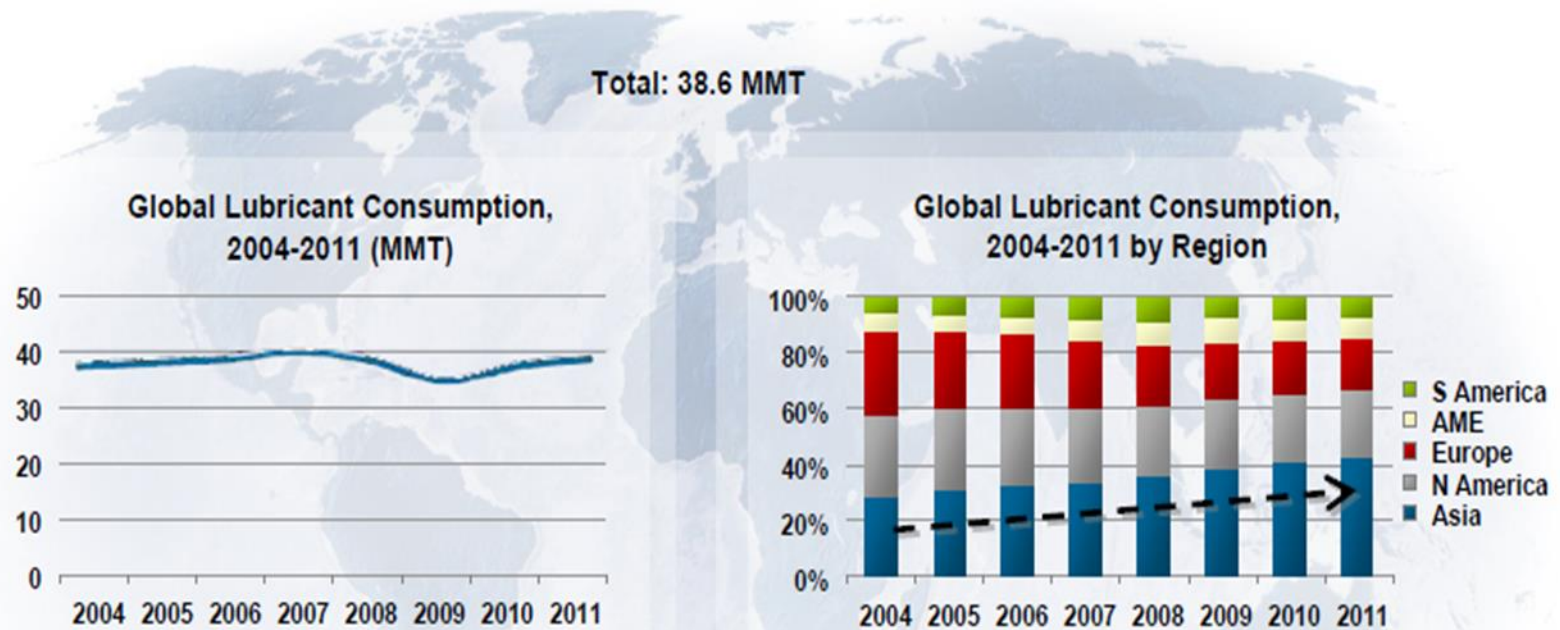
Refinery Outputs



Refinery output = global demand



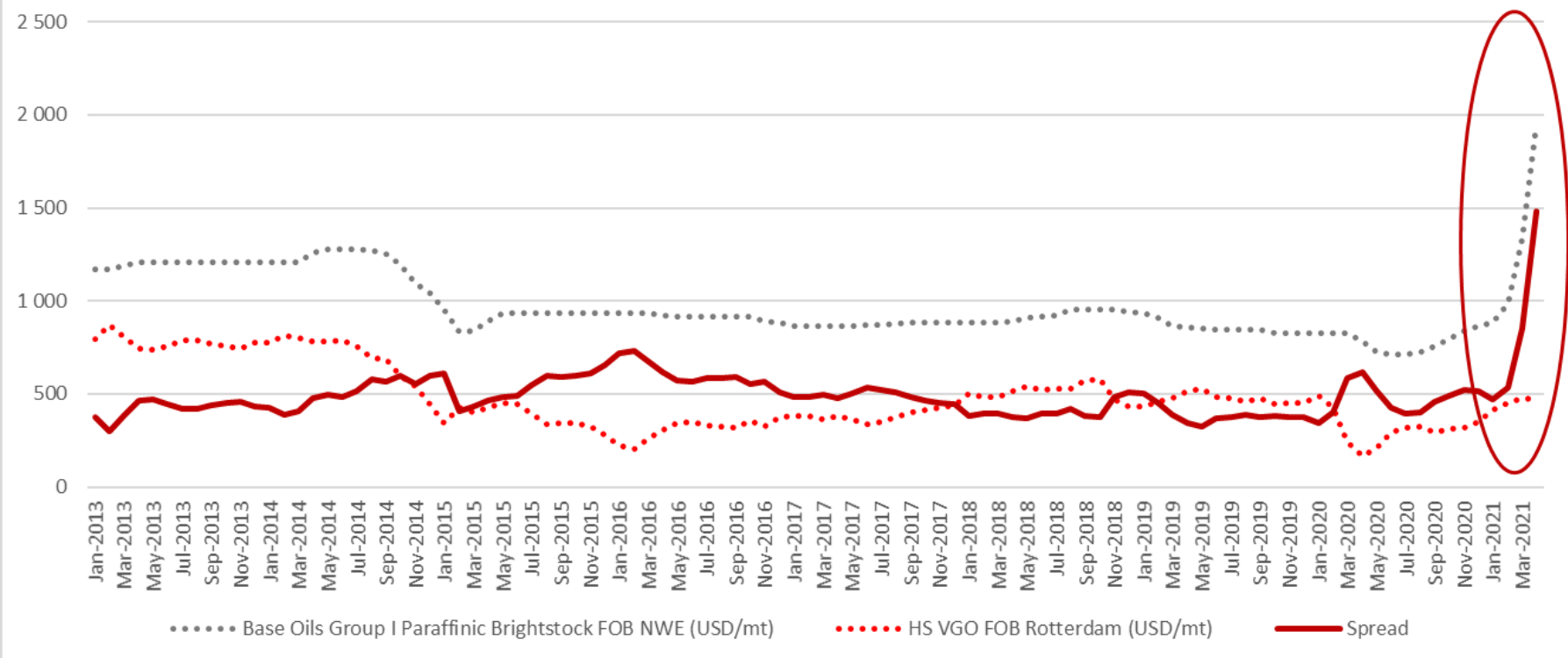
Global Lubricant Consumption by Region



Prices and spread



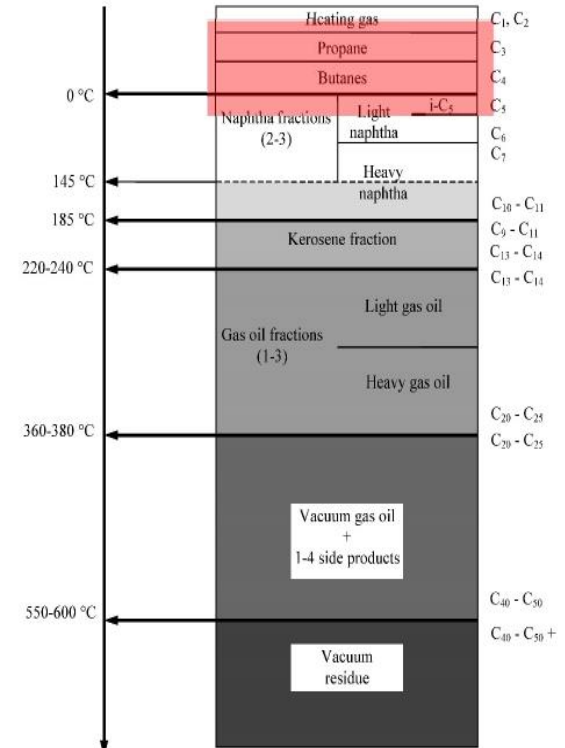
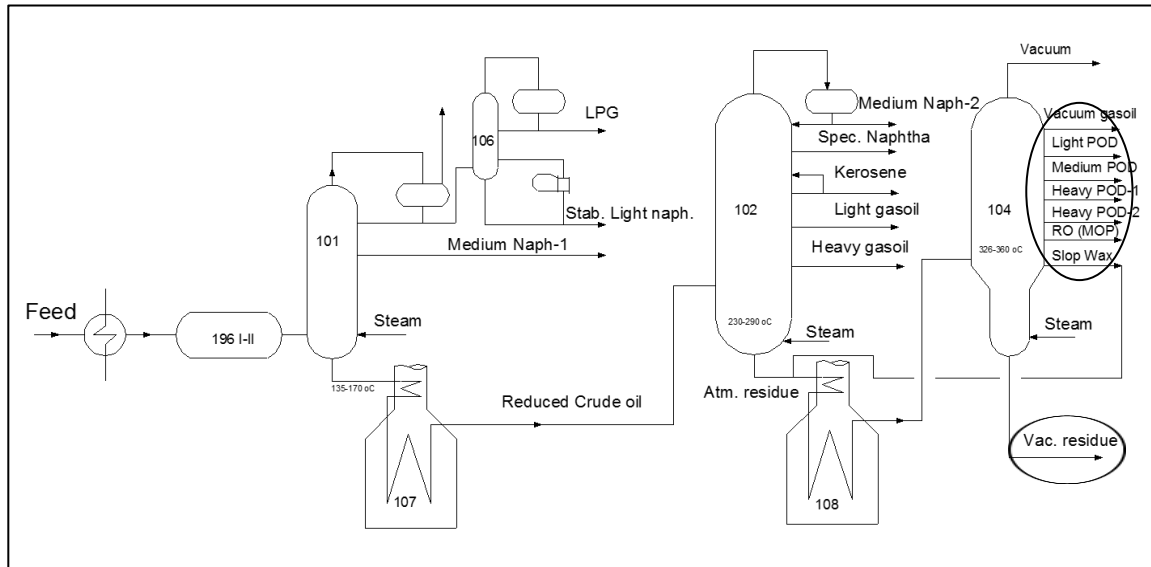
Brightstock - HS VGO Spread



Feedstocks and product portfolio

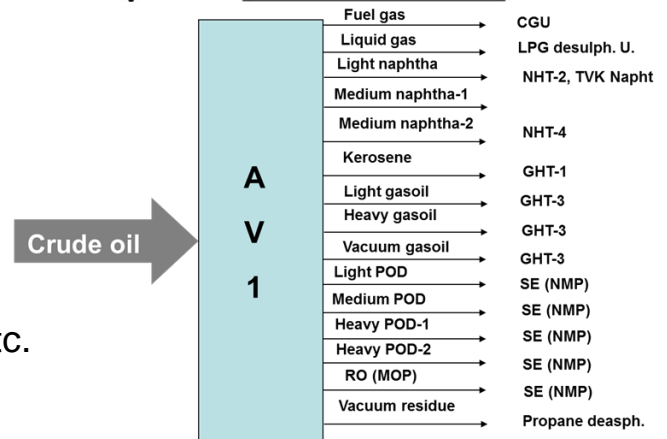


Feedstocks: Vacuum distillates and residues



Products and intermediers:

- Base oils
- Waxes
- Paraffins
- Slack-waxes
- Foots oils
- Others: Side products, solvented distillates, dewaxed distillates, etc.

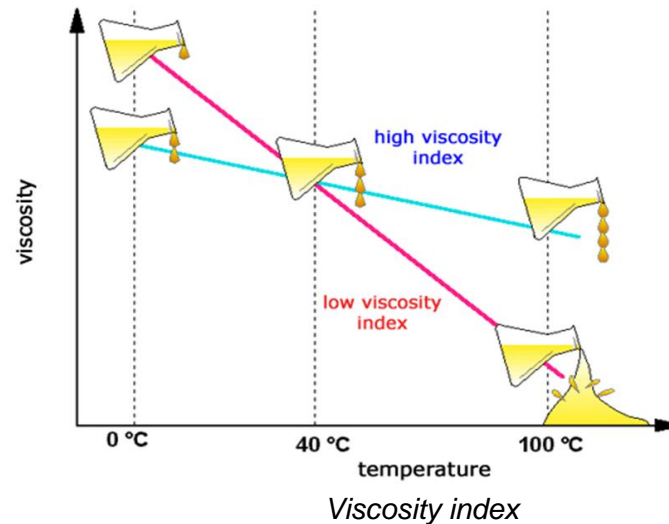


Product properties



Main quality parameters:

- Viscosity
- Volatility (Noack)
- Viscosity index (VI)
- Pour point: the temperature at which the fluid ceases to pour and is nearly a solid (typically the pour point ranges from -6 to -24°C for heavy to light neutrals)
- Cloud point: the temperature at which the first wax crystals appear
- Saturates, aromatics, naphthenes content
- Color (change appearance in presence of light)
- Stability (change appearance in presence of heat)
- Melting point (waxes)



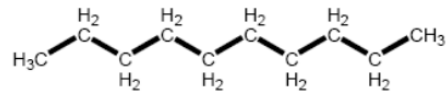
Base Oils API Groups



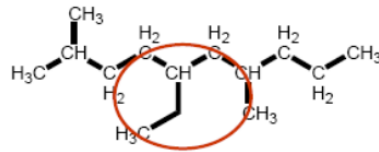
API Group	<u>% saturates</u>	<u>% sulfur</u>	<u>VI</u>
I	< 90 % sats <i>and/or</i>	> 0.03% S	≥ 80 and <120
II	≥ 90 % sats <i>and</i>	≤ 0.03% S	≥ 80 and <120
III	≥ 90 % sats <i>and</i>	≤ 0.03% S	≥ 120
IV	Poly-alpha-olefins (PAO)		
V	Basestocks not included in Groups I – IV		

Source: API 1509 Appendix E

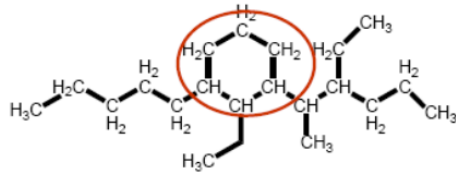
Feedstock composition



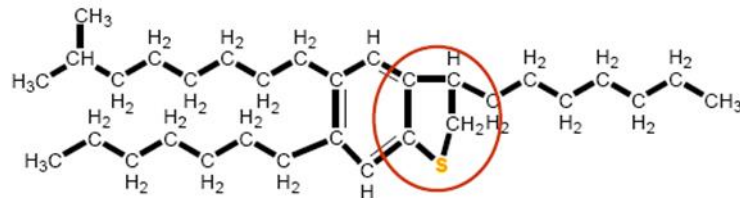
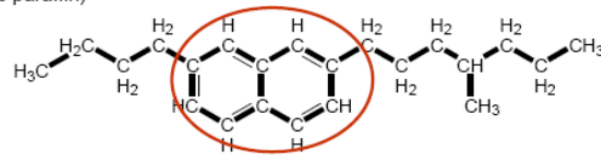
n-Paraffin (straight chain)



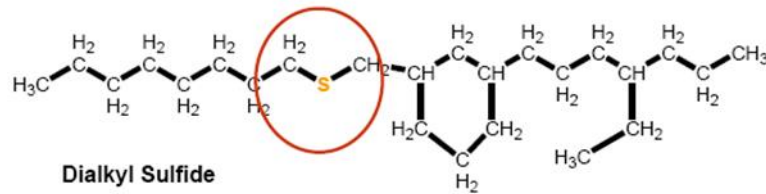
iso-Paraffin (branched chain)



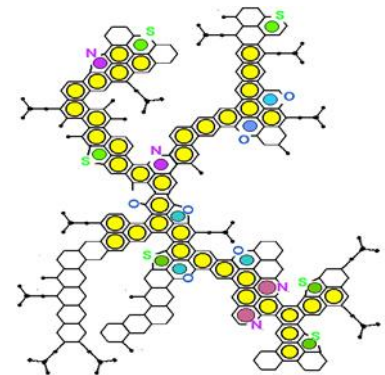
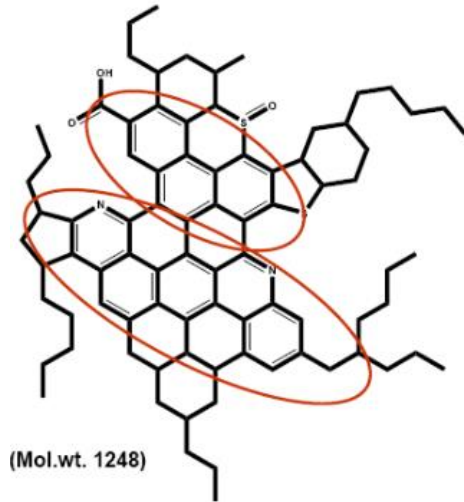
Naphthene (cyclo paraffin)



Benzothiophene (sulfur heterocyclic)



Dialkyl Sulfide



Effect of molecular types



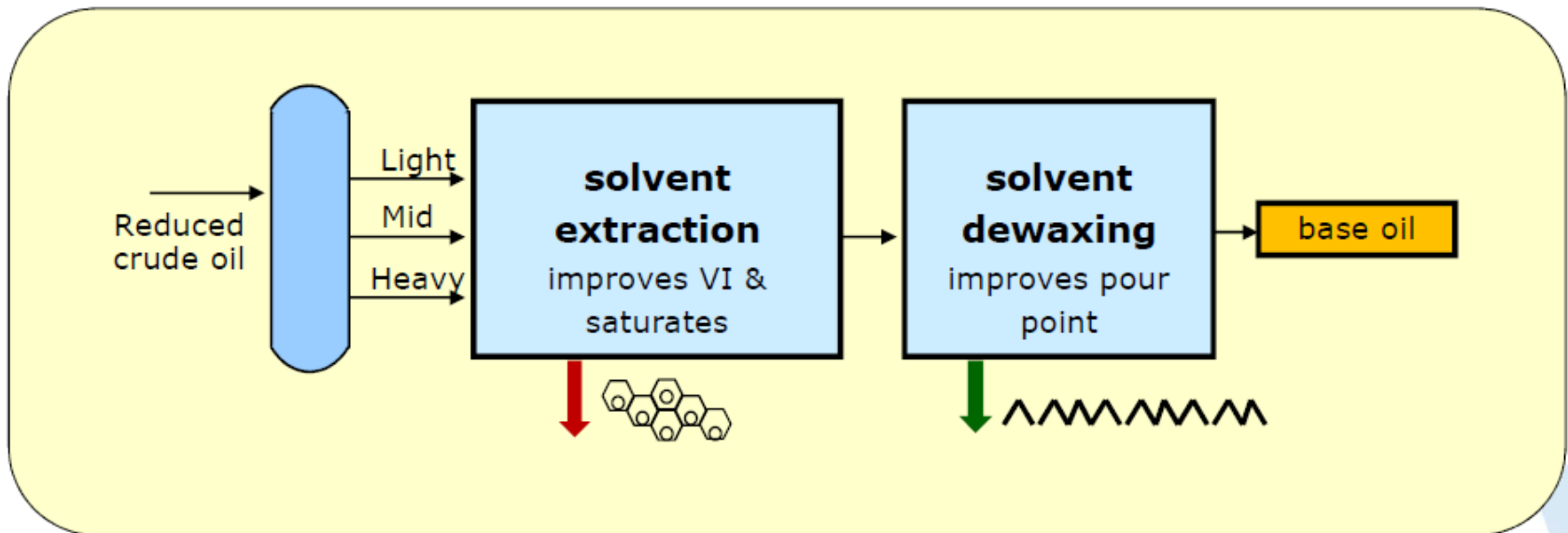
Designation		Viscosity Index	Pour Point	Resistance to Oxidation	Value as Base Oil
<i>n</i> -paraffins		✓ ✓ ✓ ✓	✓	✓ ✓ ✓ ✓	✓ ✓ ✓
iso-paraffins		✓ ✓ ✓	✓ ✓ ✓	✓ ✓ ✓ ✓	✓ ✓ ✓ ✓
Mono-naphthenes		✓ ✓	✓ ✓	✓ ✓ ✓	✓ ✓ ✓
Poly-naphthenes		✓ ✓	✓ ✓ ✓	✓ ✓	Nil
Aromatics		✓	✓ ✓ ✓	✓	Nil

Solvent processes



Main three process steps

- Crude distillation to Light-, Medium- and Heavy feed fractions
- Remove the unwanted aromatics – solvent extraction
- Remove paraffins and waxes – solvent dewaxing



Quality parameter controls

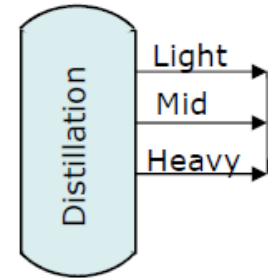


Property

Where controlled

Viscosity

Crude distillation isolates heavy molecules and creates primary viscosity grades



VI

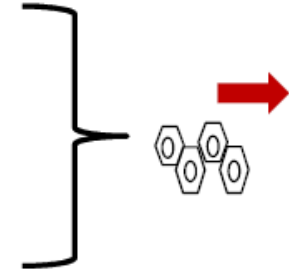
(higher is better)

Solvent extraction (aromatics removal)
+ VI increases as aromatics are removed

Saturates

(higher is better)

Solvent extraction (aromatics removal)
+ Saturates increase as aromatics are removed



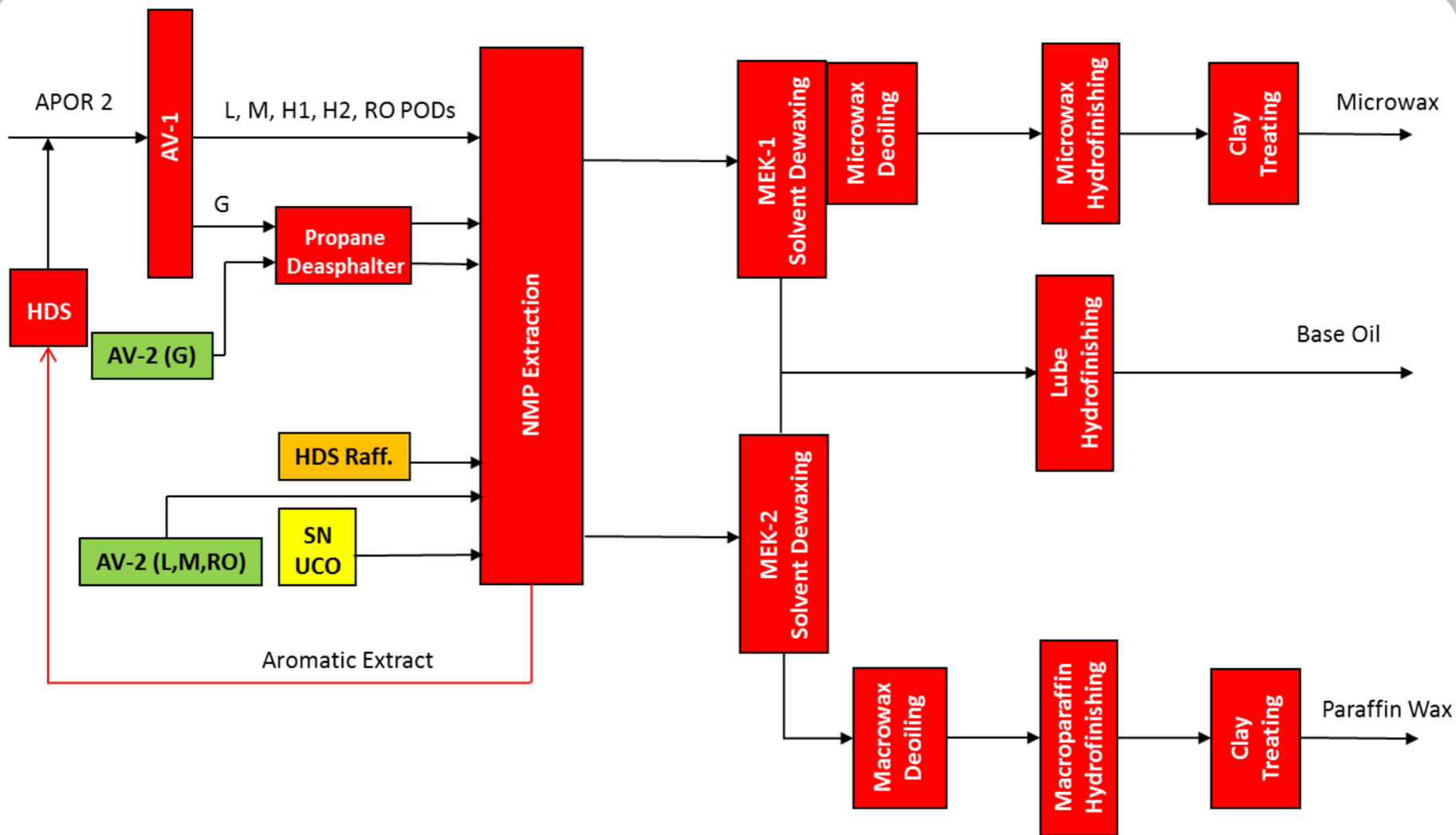
Pour Point

(lower is better)

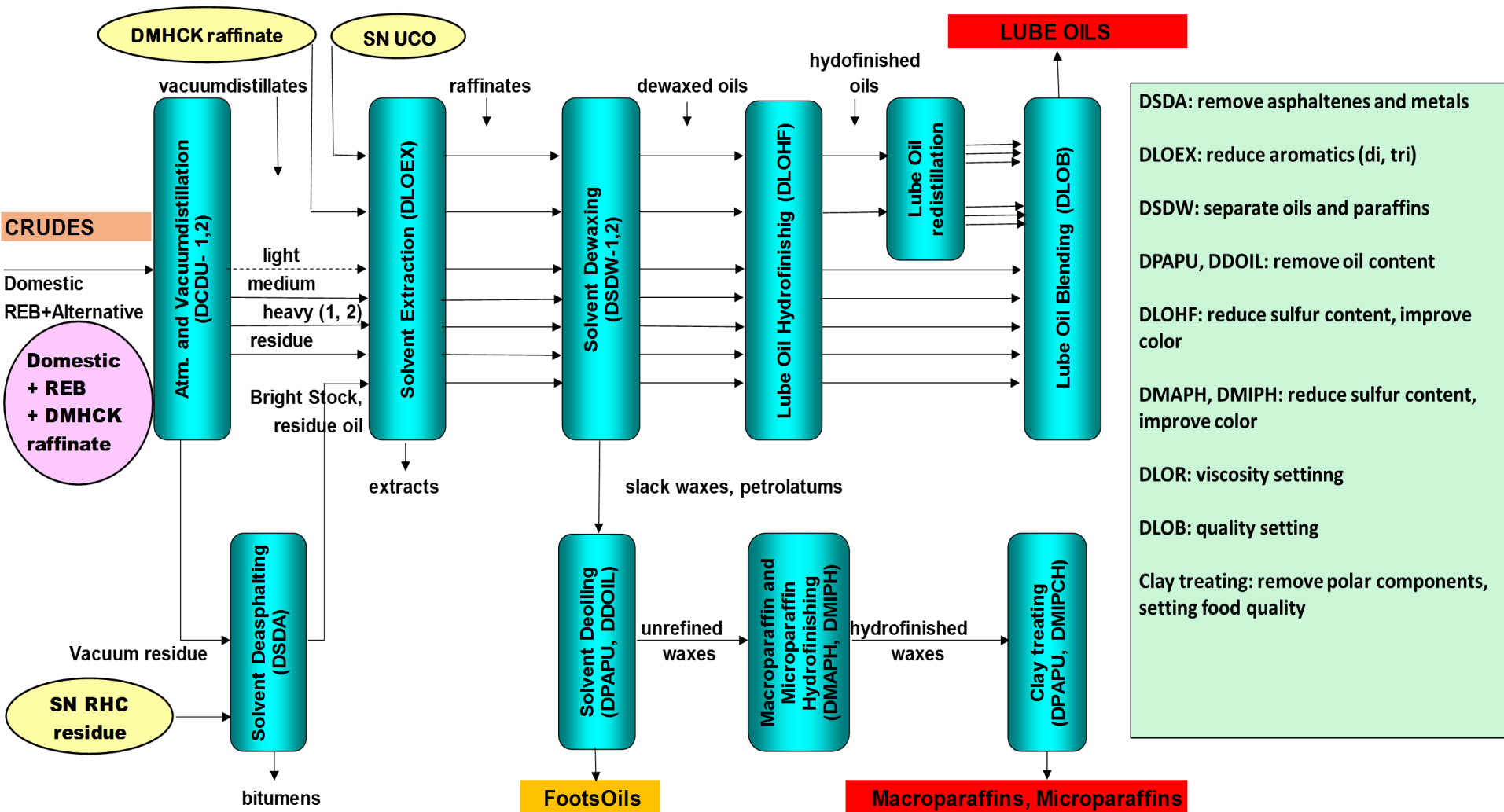
Solvent dewaxing (wax removal)
+ Pour point decreases as wax is removed



Base Oil production in Danube Refinery



Base Oil production in Danube Refinery



Molecules and processes

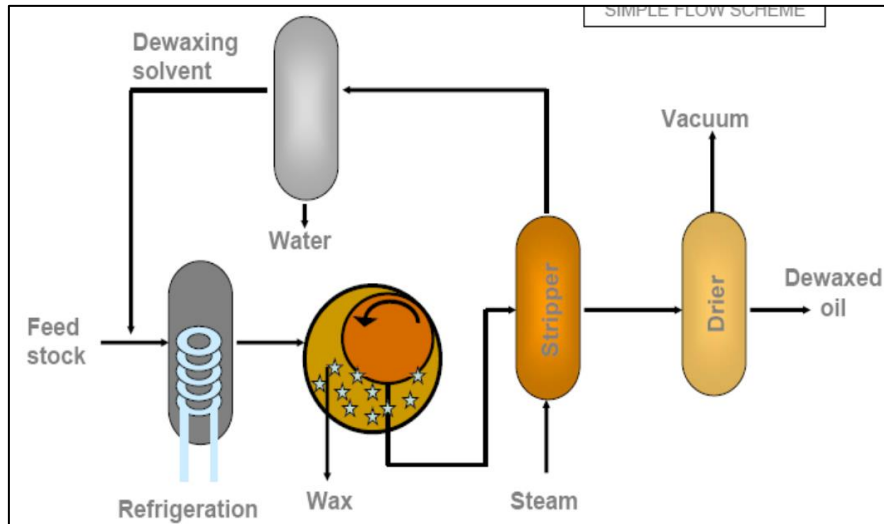


Molecule	Structure	Base Stock Quality Affected	Process Involved
N-Paraffin		High Pour, VI No S and CCR	Dewaxing
I-Paraffin		High VI and Sats Medium Pour	
2-Ring Naphthene		Medium VI, Low Pour, High Acids	Extraction, Hydrofinishing
1-Ring Aromatic		Medium to High VI	Extraction
Multi-Ring Naphthene		Low VI, Low Pour, High Acids	Extraction, Hydrofinishing
Multi-Ring Aromatic		Low VI, Low Pour	Extraction
Organic Sulfur		Good Stability Antioxidant	Hydrofinishing
Organic Nitrogen		Poor Stability	Hydrofinishing
Aliphatic Sulfur and Nitrogen	R-S R-N	Removed by Hydrofinishing	Hydrofinishing
Asphaltenes	Condensed Multi-Rings	High CCR Poor Color	Distillation, Deasphalting

EXTRACTION ↑

↓ **DEWAXING**

Process solvent and ratios



Solvent Dewaxing

Solvent Dewaxing and Deoiling

Solvents: **MEK, Toluene, Acetone**

Typical solvent ratio (MEK-T): 1:3 - 1:5 t/t

Solvent Composition: MEK 40-45%, T: 55-60%

Solvent Deasphalting

Solvents: **Propane** to Heptane $C_3 - C_7$

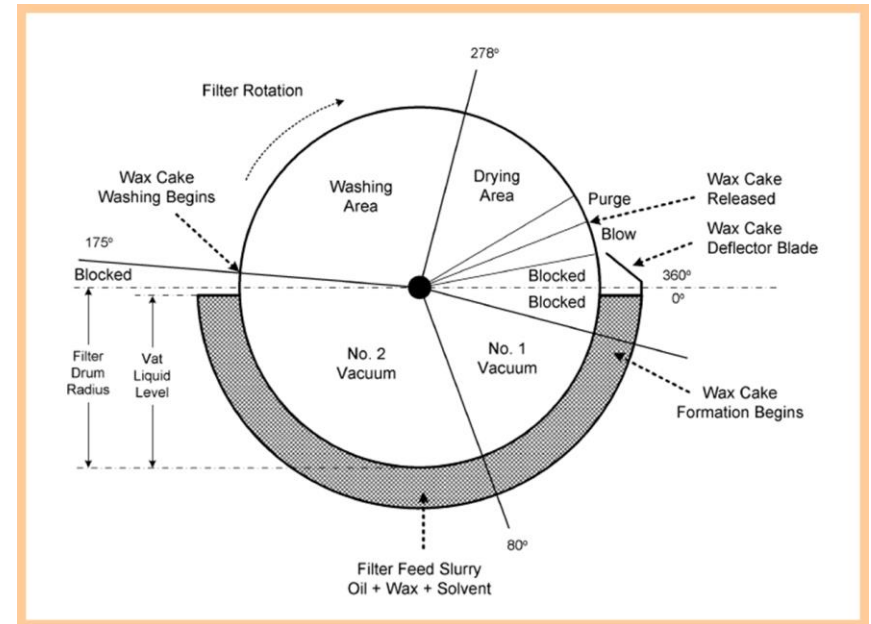
Typical solvent ratio (C_3 case): 1:3,4-3,6 t/t

Solvent Treating (Aromatic removal)

Solvents: Furfural, Phenol,

NMP (N-methyl pyrrolidone)

Typical solvent ratio (NMP case): 1:1,75-2,25 t/t



Wax Filtering

■ Solvent processes

- Vacuum distillation
- Solvent Deasphalting
- Solvent Extraction
- Solvent Dewaxing
- Solvent Deoiling
- Hydrotreating
- Clay treating

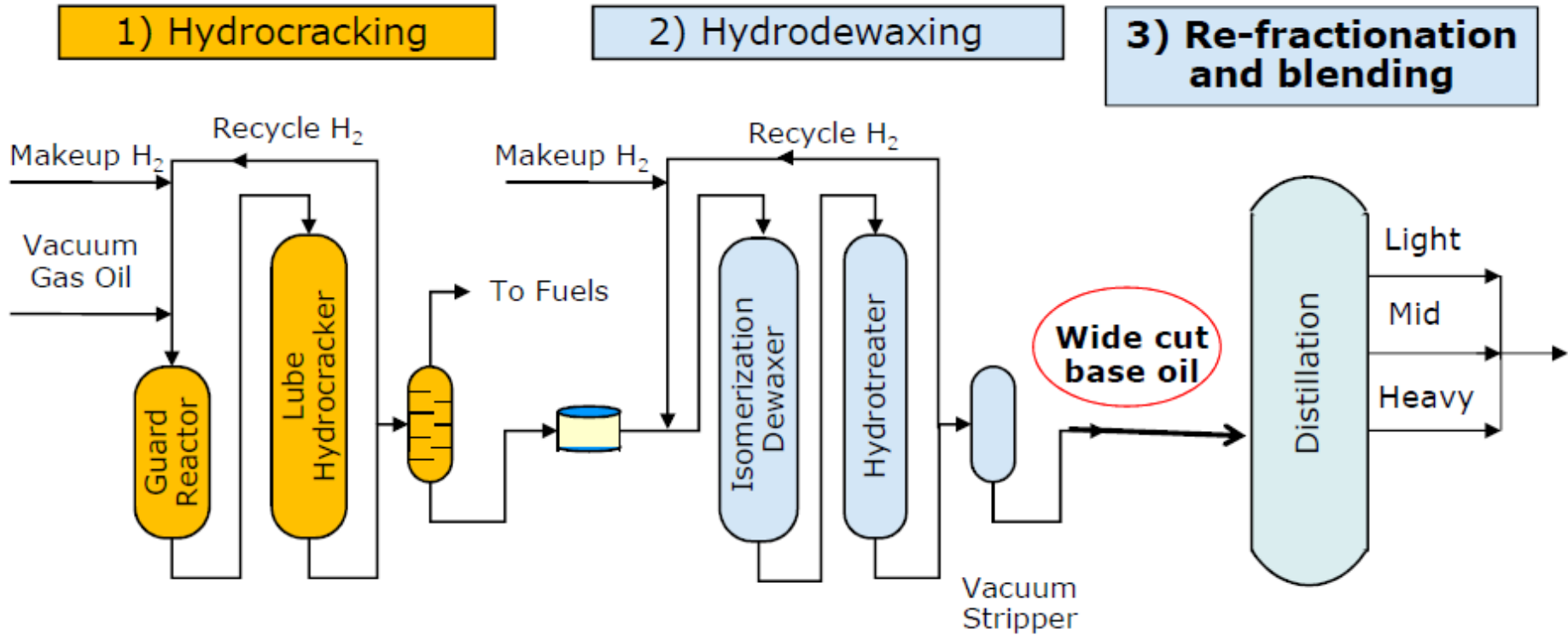
■ Catalytic processes

- Vacuum distillation
- Base Oil Hydrocracking
- Cat. Dewaxing / Isodewaxing
- Hydrotreating

Base Oil Hydrocracking & Isodewaxing



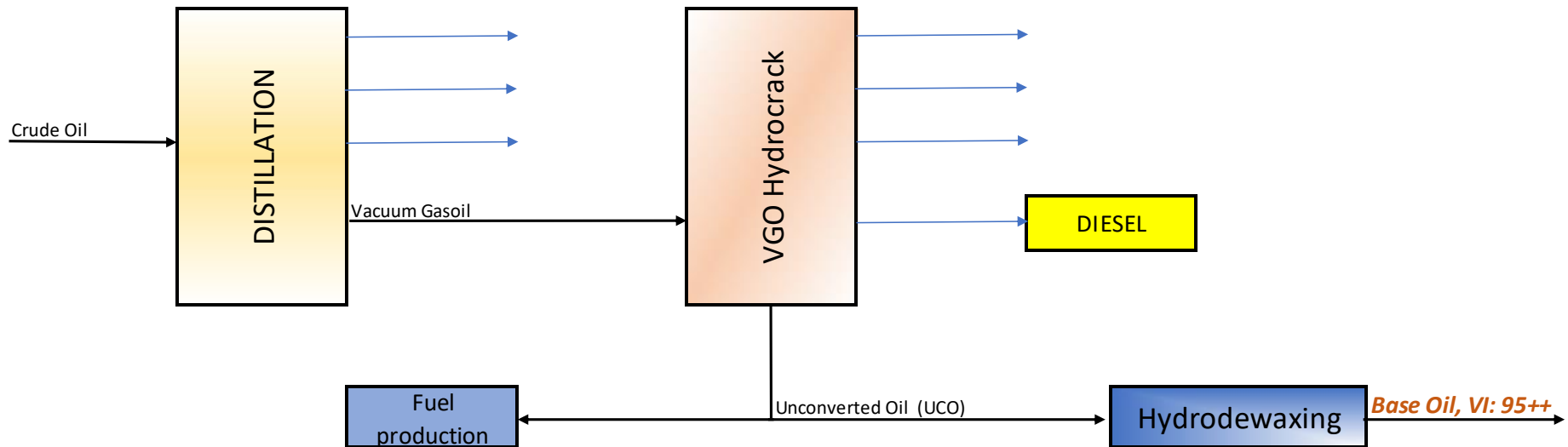
- Catalytic Lube Hydrocracking & Catalytic Dewaxing



Group III production on HCU base



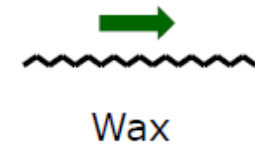
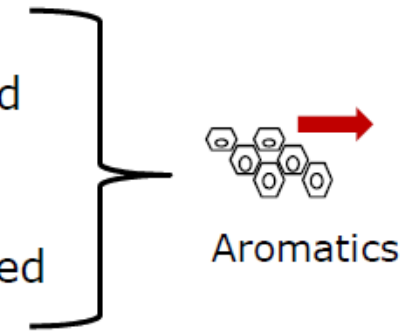
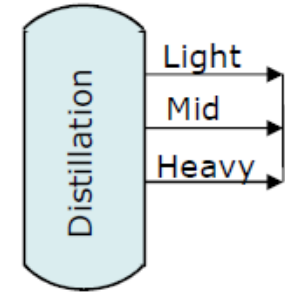
- Base case: VGO Hydrocracker unit (HCU) exists for Diesel production
- Unconverted Oil (HCU Residue) is applicable for Base Oil Production
- Only a Hydrodewaxing unit is needed, Lube Hydrocracker unit is not needed



Catalytic quality parameter controls



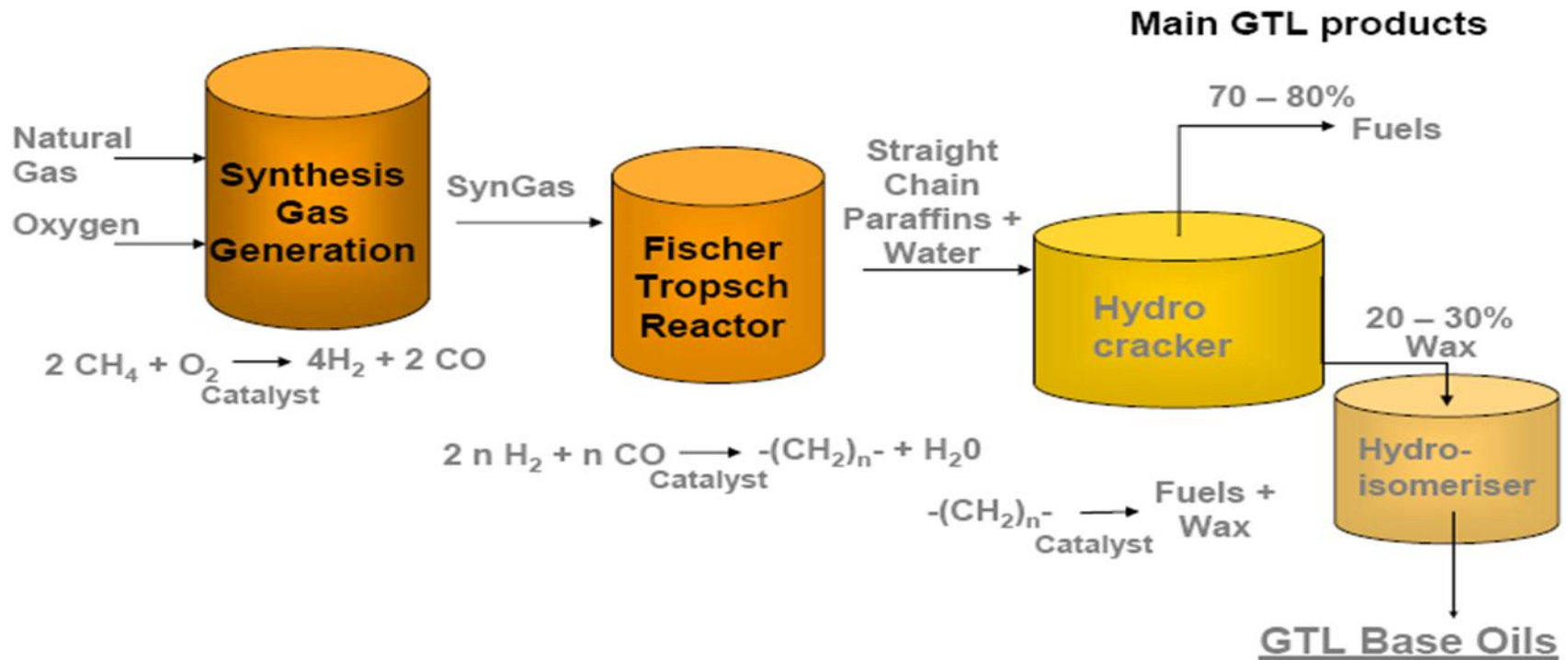
<u>Property</u>	<u>Process where controlled</u>
Viscosity	Crude distillation and back-end re-distillation after hydrocracking / hydrodewaxing
VI	Hydrocracking + VI increases as aromatics are removed
Saturates	Hydrocracking + Sats increase as aromatics are removed
Pour Point	Hydrodewaxing + Pour point decreases as wax is removed



Group III+ production on GTL process



- Fischer-Tropsch process base
- F-T HCs products are a white waxy crude for upgrading
- Group III+ quality Base Oils can be produced next to the fuels



Typical API Group composition



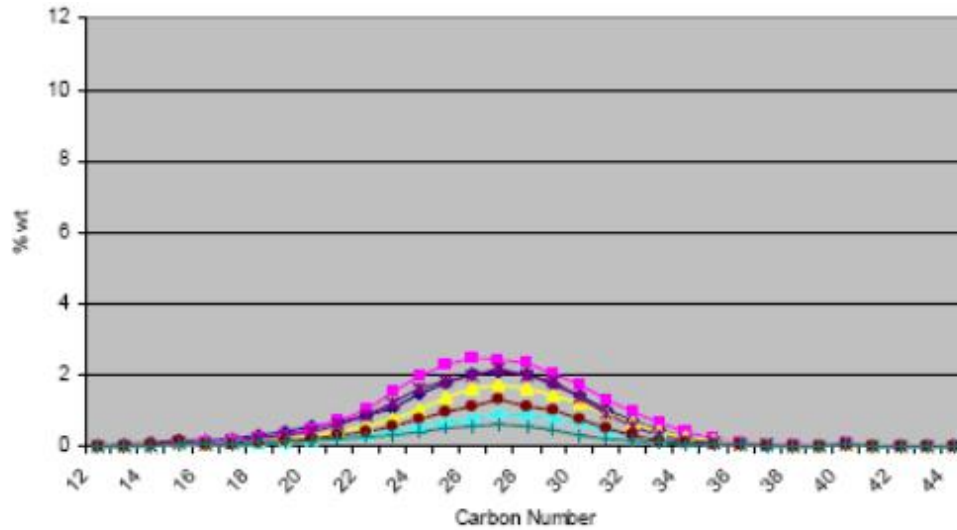
Category	Group I	Group II	Group III
VI	$80 \leq VI < 120$	$80 \leq VI < 120$	$VI \geq 120$
Saturates	$< 90\%$	$\geq 90\%$	$\geq 90\%$
Sulphur	$> 0.03\%$	$\leq 0.03\%$	$\leq 0.03\%$
Composition	iso-paraffins		
Very wide chemical spectrum	naphthenes		
	n-paraffins		
	aromatics		
	polar compounds		

Narrow chemical spectrum

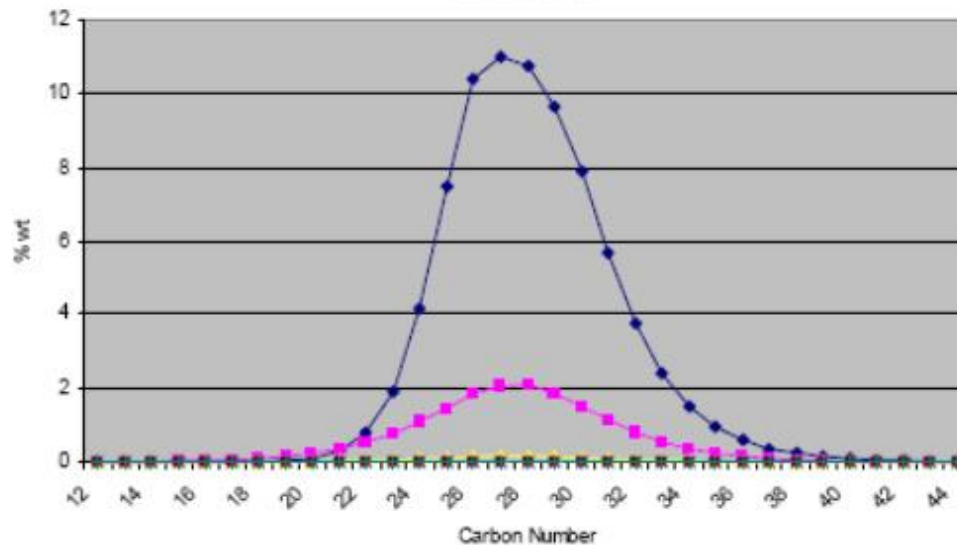
Composition differences



Group I



Group III

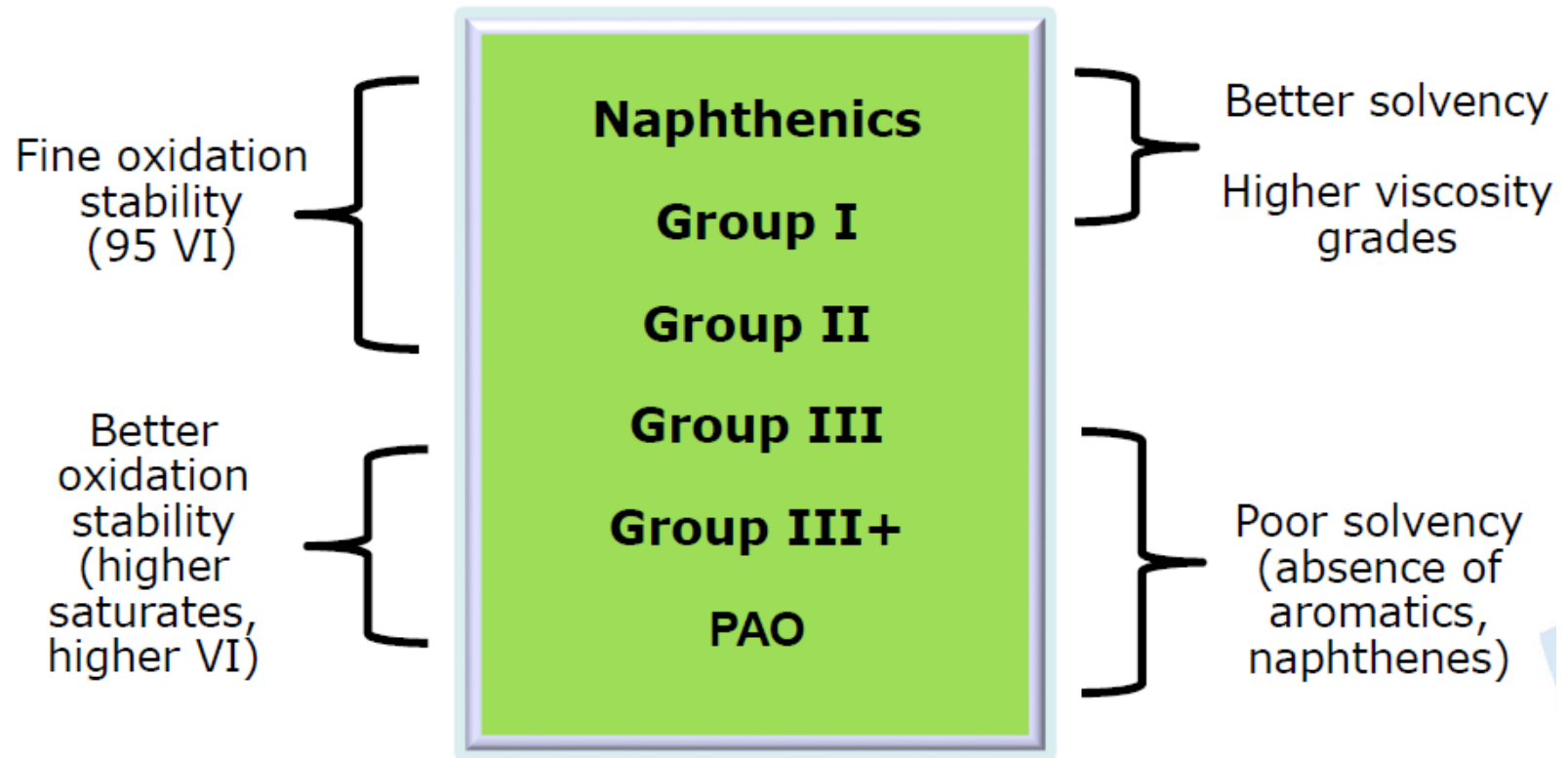


- ◆ paraffins
- mono-naphthenes
- * poly-naphthenes
- poly-naphthenes
-

API Groups - What's better?



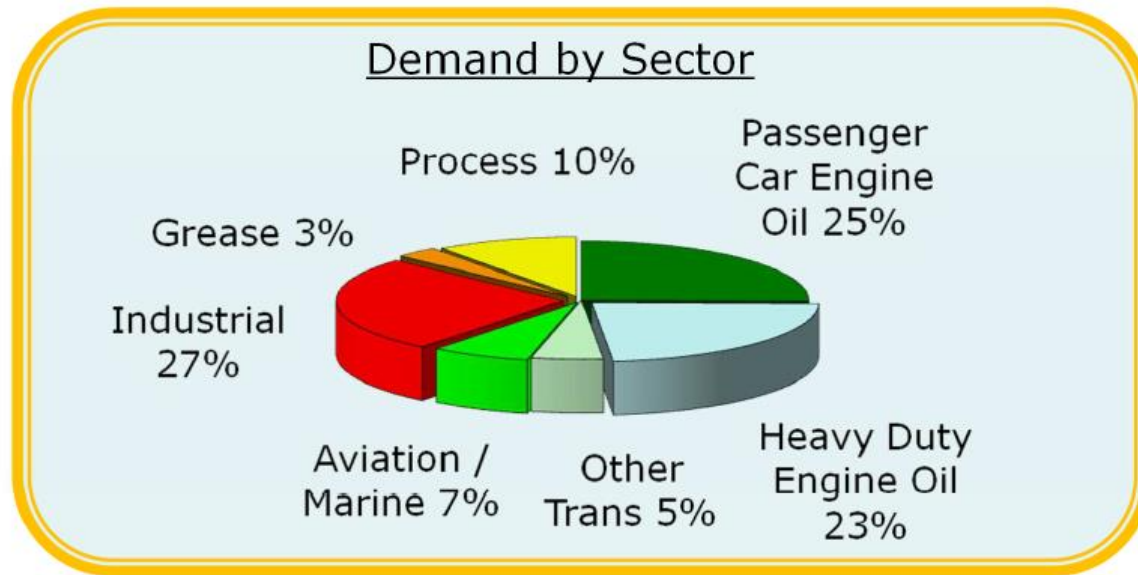
Same Labels, New Perceptions Regarding What's "Better"?



Lubricant market



- **Transportation-related lubrication is largest market at around 60% of global applications**

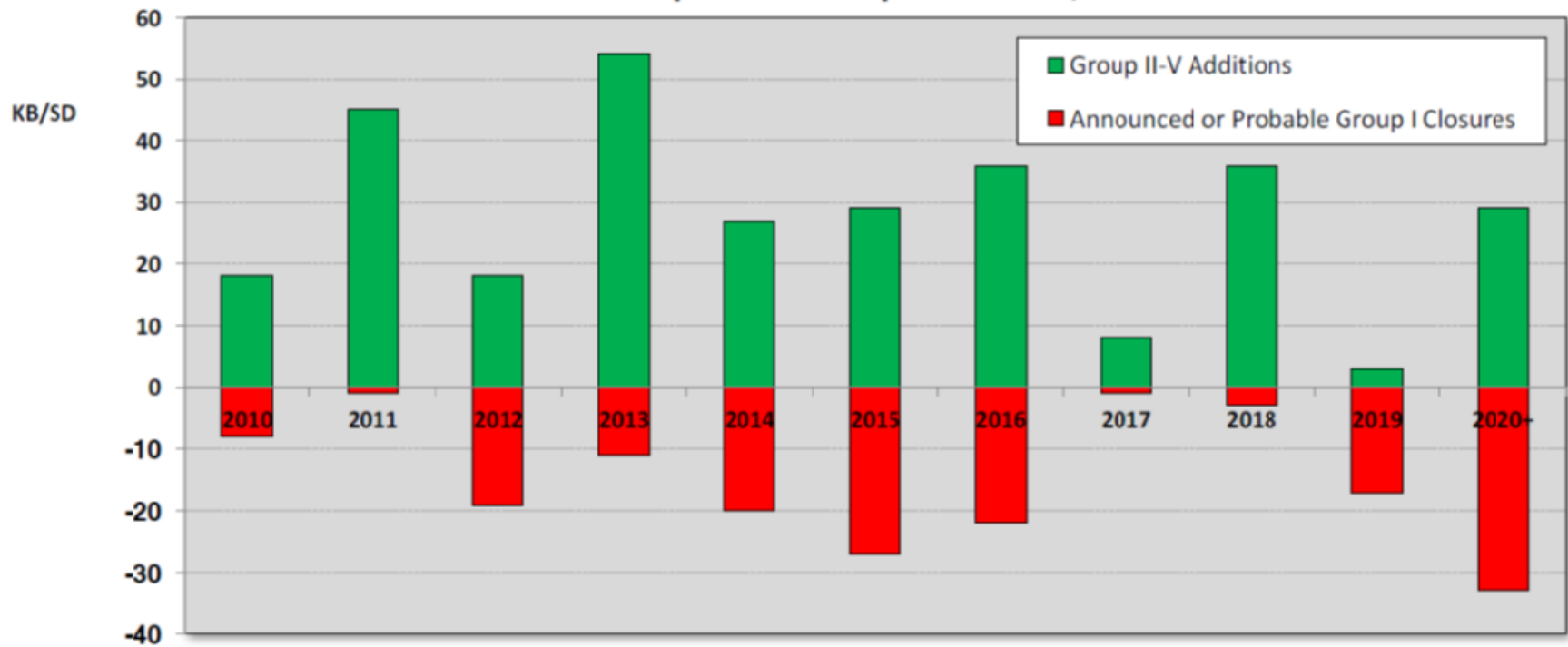


- **Industrial / grease applications are ~ 30%**
- **Non-lubricating applications ("process oils") are ~ 10%**

Group I – Group II/III capacities



Actual and Committed Global Nameplate Base Oil Capacity Additions and Expected Group I Closures, 2010 to 2020



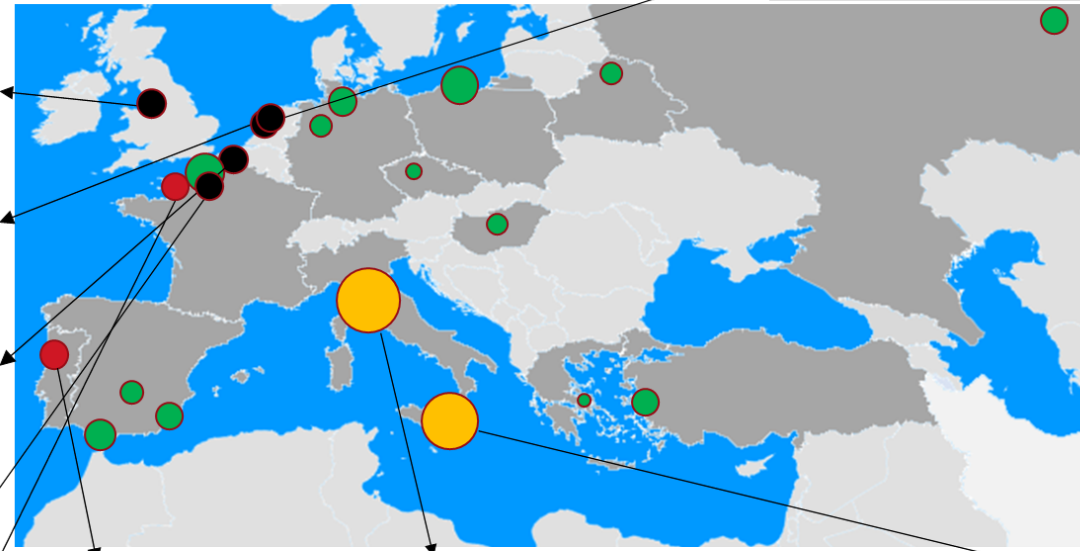
Source: Kline

Nearly 150 KB/D of Group I capacity could be decommissioned during this decade, and another 100-150 KB/D is "At Risk" from low margins/refinery shutdowns by 2030


Base Oil – Changes in global production





CLOSED AND JEOPARTIZED REFINERY IN EUROPE




 **Kuwait Oil, Rotterdam**
shut down in 2016
Base oil capacity: 235 ktpa.


 **Stanlow**
shut down in 2013
Group I base oil capacity: 260 ktpa
To produce base oil requires very specific, light, higher cost crudes. Base oil represents only two percent of the refinery's output but dictates choice of crudes for around 25 percent of total crude intake at Stanlow.

 **Shell, Pernis**
shut down in 2016
Base oil capacity: 370 ktpa.
The causes of closure are continued decline of European demand and new Group II capacity. Without Pernis, it may be that more GTL stocks (from Qatar) will find their way into Shells European lubricant supply chain.


 **Colas, Dunkerque**
shut down in 2015
Capacity: 271 kt Group I + 25 kt Group III
It is a small specialty plant, not a refinery. They bought feed (atm residue) from other refinery.

 **Petroplus, Petit Couronne**
shut down in 2013
Capacity: 320 kt Group I
It is a small specialty plant, not a refinery. They bought feed (atm residue) from other refinery.

 **Gonfreville**
shut down in 2021
Group I base oil capacity: 250 ktpa
Total has decided to permanently close a base oil plant at its refinery in Gonfreville, France. The plant has not produced base oil since a fire damaged the refinery's crude unit in December 2019.

 **PORTO**
shut down in 2021
Base oil capacity: 150 ktpa
Porto has the lowest conversion factor of the 10 refineries on the Iberian Peninsula. The structural changes in oil product demand patterns, driven by the regulatory context in Europe and the effects caused by the Covid-19 pandemic, have led to a significant impact on Galp's downstream industrial activities

 **Livorno**
Base oil capacity: 630 ktpa
The refinery is a low complex one, with a focus on gasoline and lubricants.
Eni confirmed its willingness "to carry out the appropriate assessments for the start of the conversion of the Livorno refinery into a biorefinery

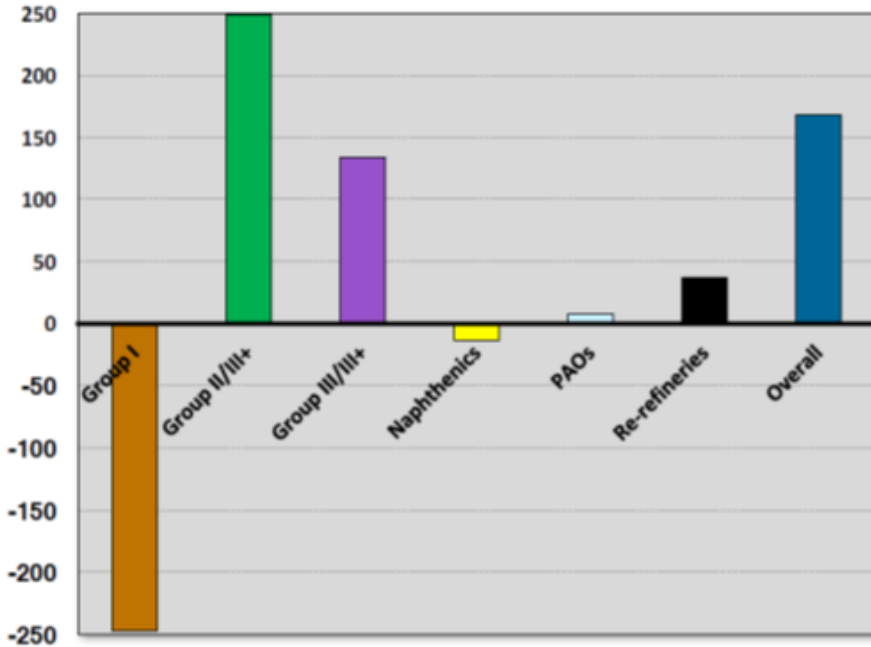
 **Sonatrach, Augusta**
Base oil capacity: 730 ktpa
Augusta was designed for crude oil of medium and heavy grades and not for the light crude oil of the type produced by Algeria.
Sonatrach had made a commitment to ExxonMobil that the Augusta plant would supply the latter with a given volume of base lubricants for a period of ten years.

● jeopardized ● operating ● closed in 2021 ● closed

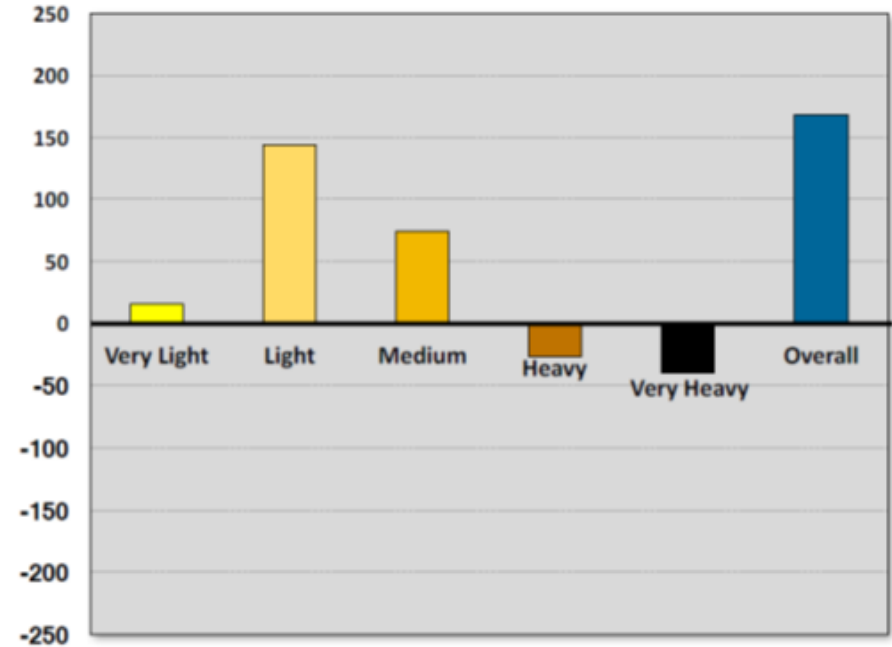
Base Oil – Changes in global production



Changes in Base Oil Capacity by Group, 2000-2017
(KB/SD)

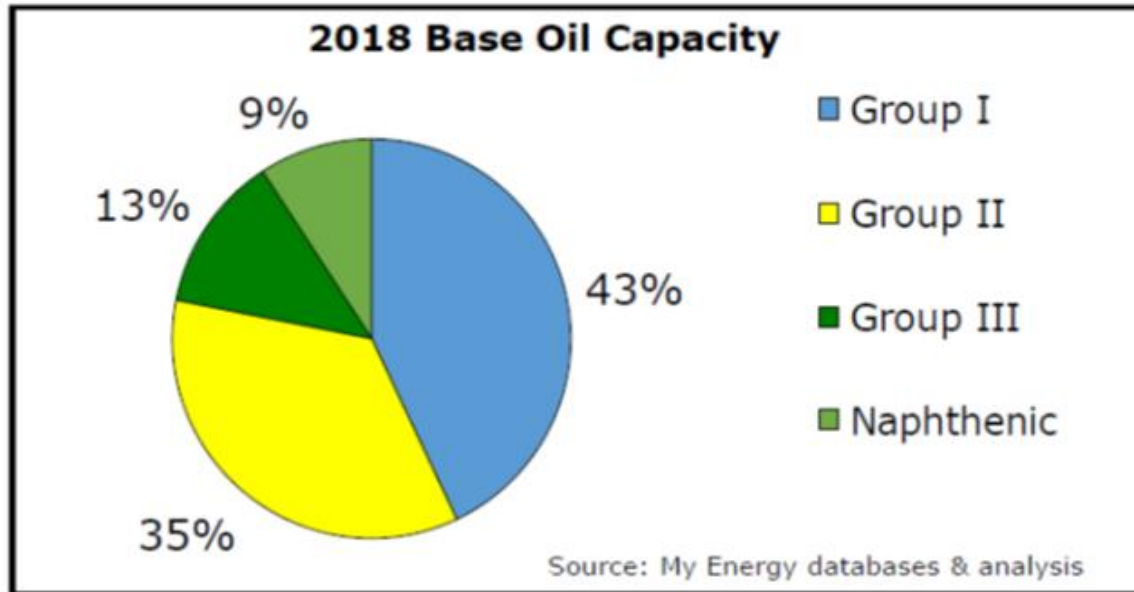


Changes in Base Oil Capacity by Visgrade, 2000-2017
(KB/SD)

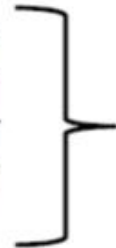


Source: Kline

Base Oil Global Demands



Group I	23500 mT
Group II	19500 mT
Group III	7000 mT
Naphthenic	5000 mT



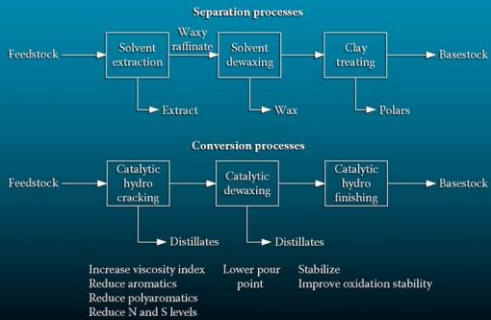
Total ~ 55 MMT
~ 80% avg. global capacity utilization
(supply ~ 44 MMT)

Thank you !



Process Chemistry of Lubricant Base Stocks

CHEMICAL INDUSTRIES/116



Thomas R. Lynch



Thank You for Your Attention !

LUBRICANT BASE OIL AND WAX PROCESSING

Avilino Sequeira, Jr.
Texaco, Inc.
Port Arthur, Texas

Marcel Dekker, Inc.

New York • Basel • Hong Kong

