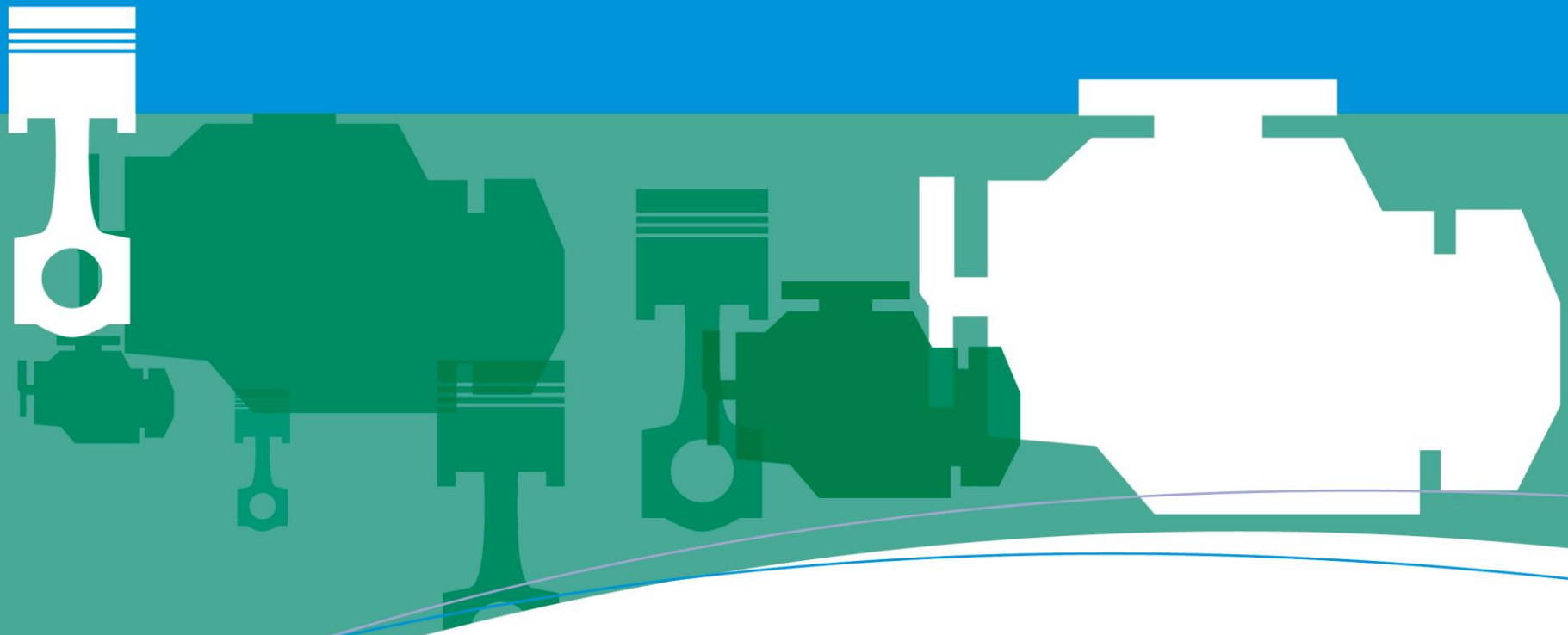
Performance you can rely on.

Lubricant base stocks



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What's in the bottle?

=

- Viscosity Modifier → This morning
- Pour Point Depressant → Video
- Base Stocks → NOW!
- Performance Additives → This afternoon

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Outline

- What are base stocks?
  - Why are base stock important?
  - Key properties of base stocks
- Refining processes
  - Overview
  - Major base stock types
    - Solvent Extraction (SE)
    - Hydrocracking (HC)
    - Synthetics
    - Others
- API base oil groups
- Names and definitions
- Measurements and typical targets
- Recent trends

Lubricant base stocks

- A lubricant component
  - Roughly 80-99+% of petroleum products
    - Usually doesn't have all required properties
    - Additives are used to enhance and customize properties
- Mineral oil base stocks
  - Refined from crude oil
    - Petroleum = "Petra-oleum" = "Rock Oil"
  - Common processes
    - Solvent extraction
      - Separate "good" from "bad" molecules
    - Hydrocracking
      - Convert "bad" molecules into "good" molecules
    - Synthesis
      - "Built" from chemical reactions
- Animal and vegetable oils also used

Found in minerals, not made of minerals

Most of the starting materials come from crude oil

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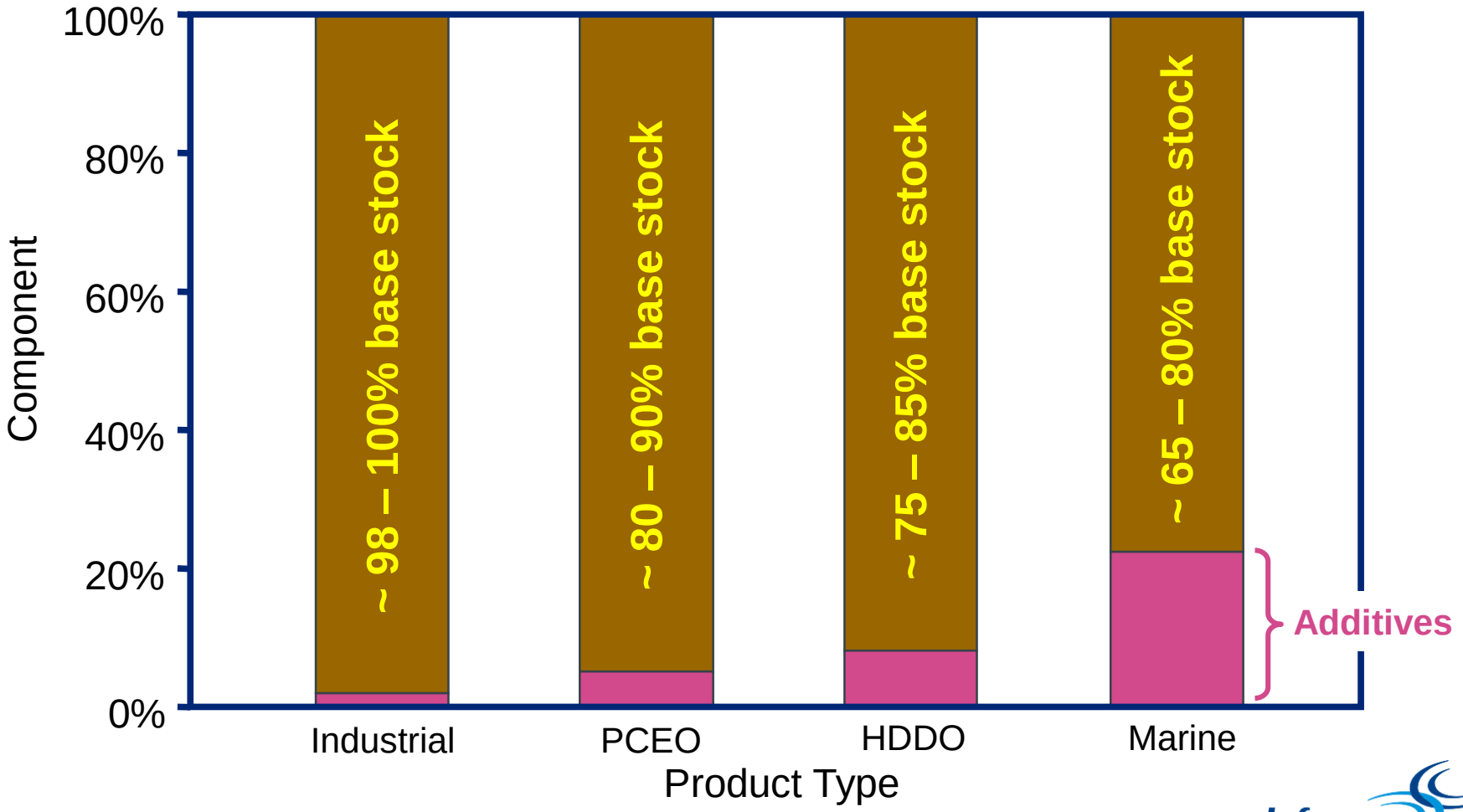
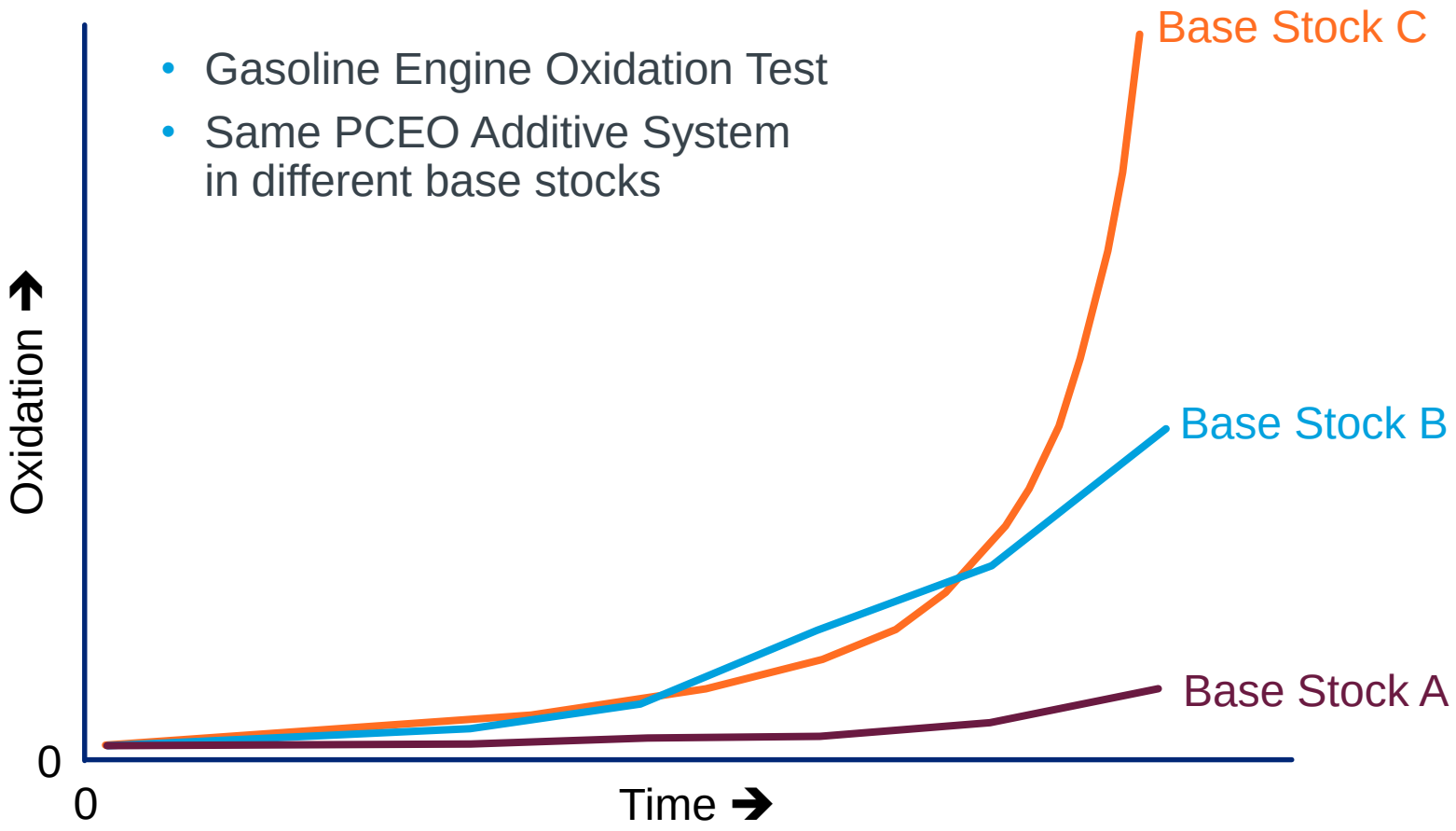
Why are base stocks important?

1. They are the major component in lubricants



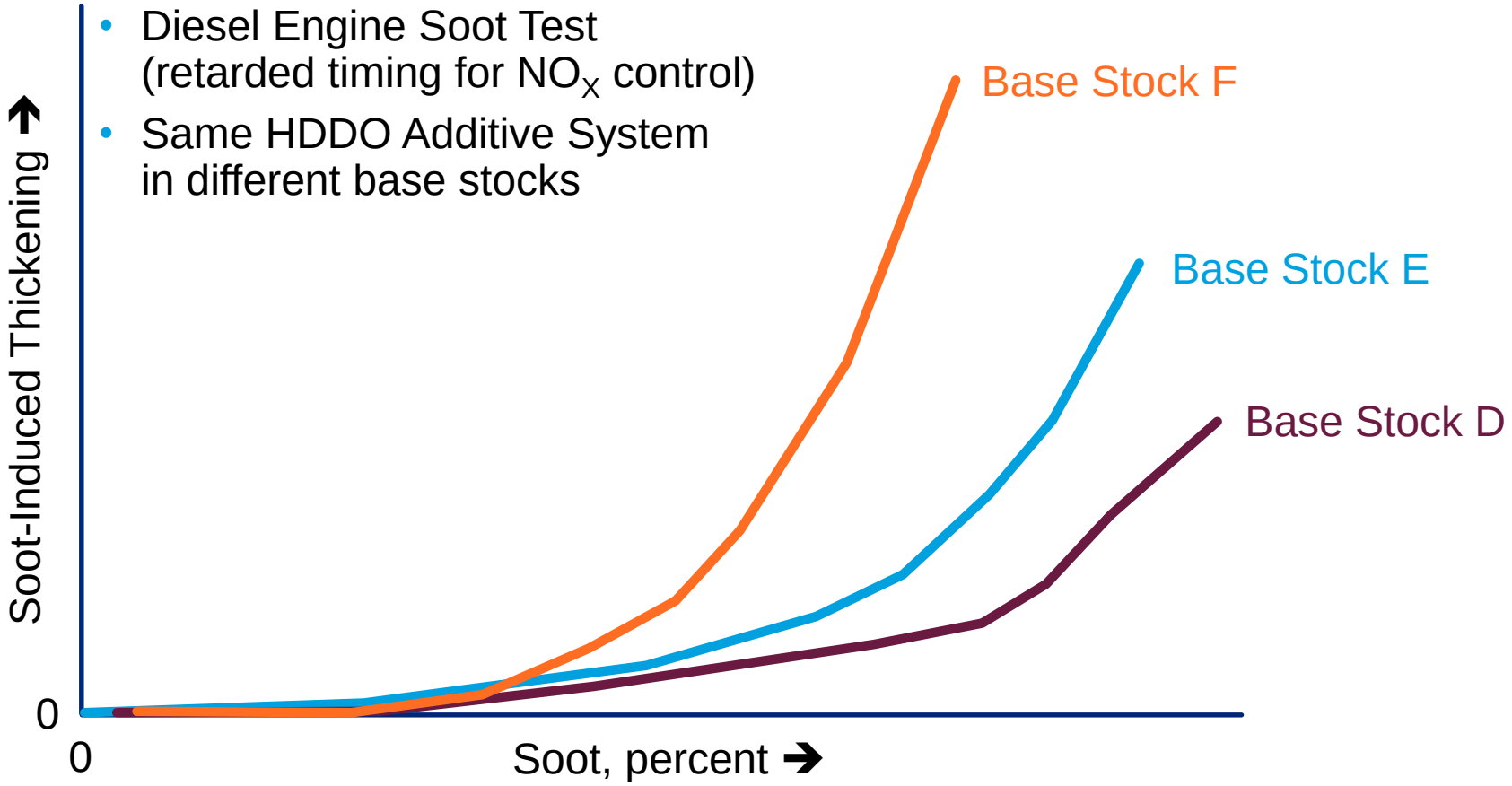
Why are base stocks important?

2. They have a major effect on performance (oxidation)



Why are base stocks important?

3. They have a major effect on performance (soot-handling)



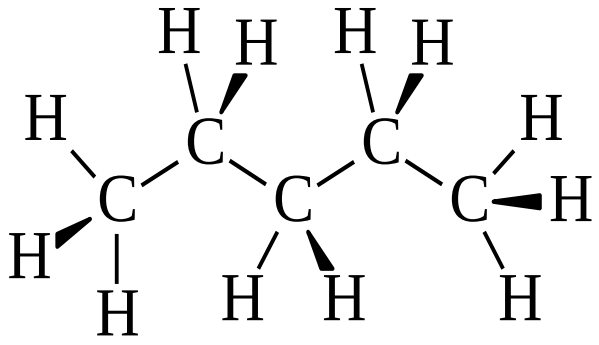
Lubricant properties affected by base stocks

- Viscometrics
  - SAE viscosity grade (*e.g.*, SAE 5W-30)
  - Viscosity Index
  - Pour point and low temperature fluidity
  - Fuel economy
  - Wear protection
- Oxidation
  - Viscosity increase
  - Acid formation, that leads to corrosion
  - Deposit control
- Dispersancy and solvency
  - Soot control (HDD)
  - Viscosity increase and filter plugging
  - Sludge
  - Deposit control
- Foaming and air entrainment
  - Cavitation and oxidation
- Volatility (evaporation)
  - Oil Consumption and Flash Point

What are base stocks?

- Base stocks are primarily hydrocarbons
  - Hydrocarbon = molecule containing hydrogen and carbon
  - Sometimes generalized to molecules with other elements
- Equivalent chemical symbols:

C_5H_{12} (pentane) =



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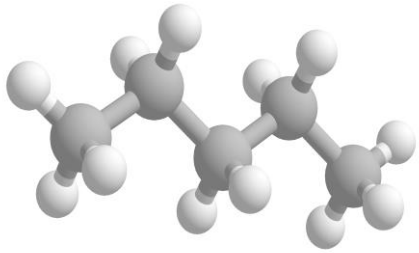

(three-dimensional)

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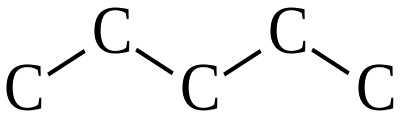

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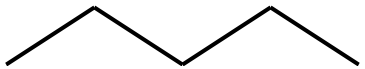
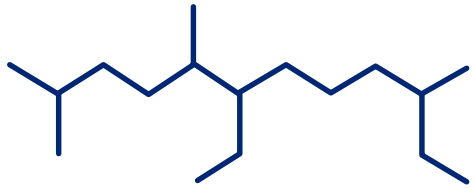
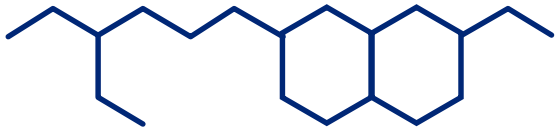


Base stock molecules – hydrocarbons

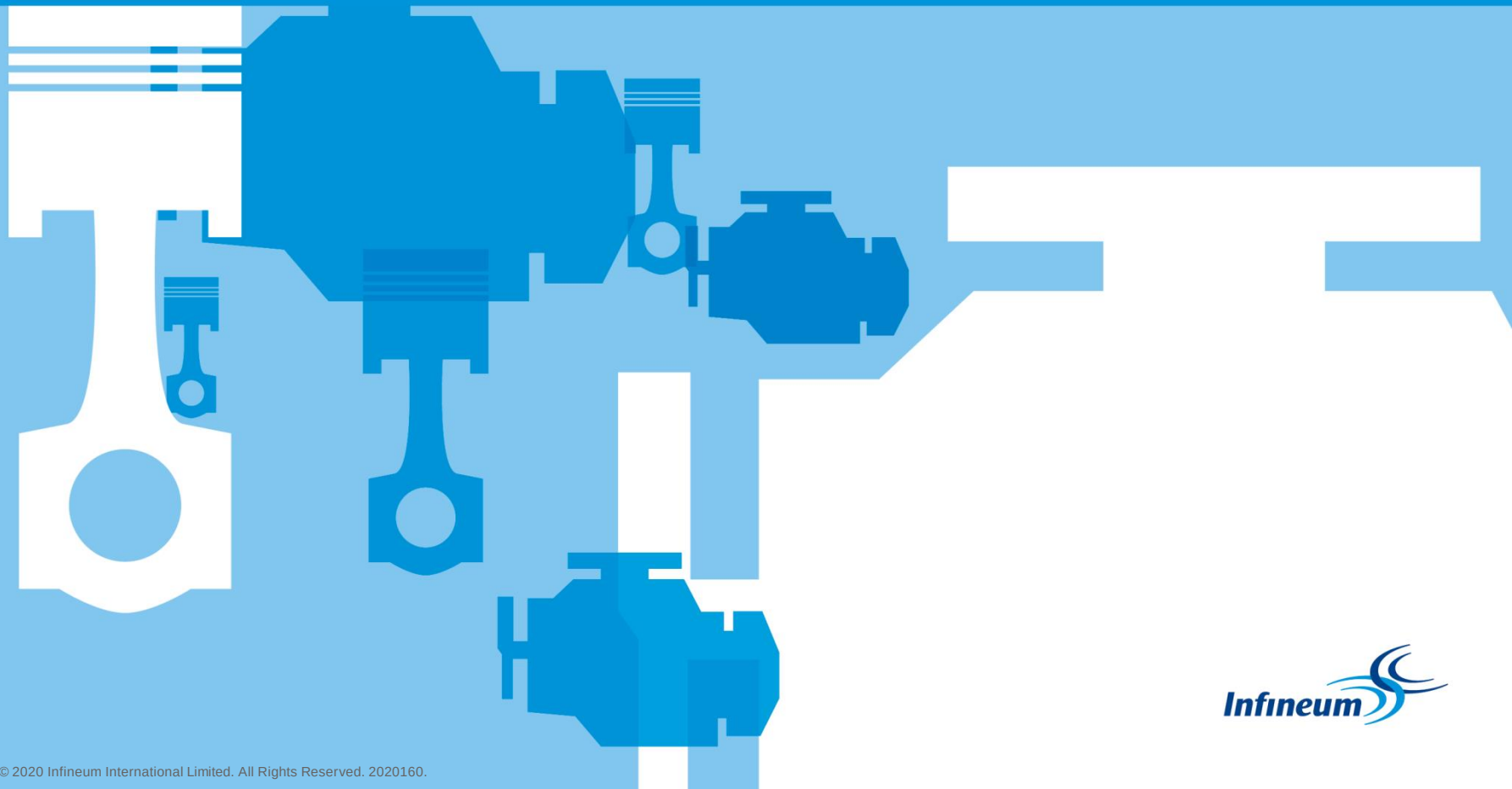
Type	Structure	Properties
• Saturates		
• Paraffins (no rings)		
• Straight chain		Very high VI (~175) Excellent oxidation Low volatility Very high pour point
Best lube molecules • Branched chain		High VI (~100-150) Good oxidation Medium pour point
• Naphthenes (rings)		Medium VI (~60-110) Poor oxidation Low pour point
• Aromatics (unsaturated rings)		Low VI (<60) Very poor oxidation Low pour point

- Polars
  (atoms other than carbon and hydrogen: sulphur, nitrogen, etc.)

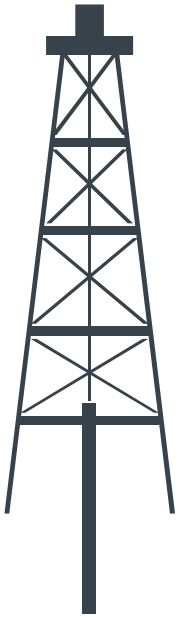
Key base stock properties

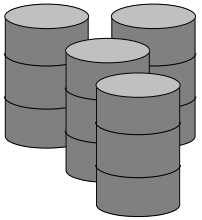
- Viscosity (D445)
  - Sometimes kinematic viscosity at 100°C: HC 4, HC 6, HC 12
  - Sometimes “Neutral Number”: S150N, S600N
  - ISO Grade for Industrial Oils – related to kinematic viscosity (mm^2/s) at 40°C
  - Low temperature: CCS (D5293), MRV (D4684), SBV (D5133), Pour Point (D97)
- Viscosity Index (D2270)
  - Rate of change of viscosity with temperature
  - Arbitrary scale defined by ASTM “Table Look-up”
- Saturates (D2007)
  - Measure of “stable” vs. “reactive” molecules
  - Intended as an approximation of oxidative stability – Not perfect
- Sulfur (D4294)
  - Corrosive and poison to exhaust catalysts
- Volatility (D5800)
  - Evaporation
- Chemical properties are also very important
  - More difficult to measure and specify

Base stock refining



Refinery overview

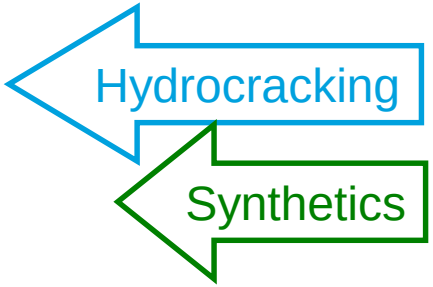




Crude oil → Refinery processes → Refined Petroleum products

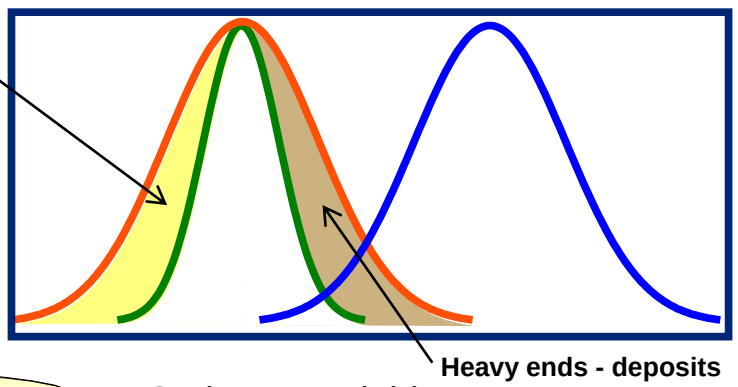
Refining in a nutshell

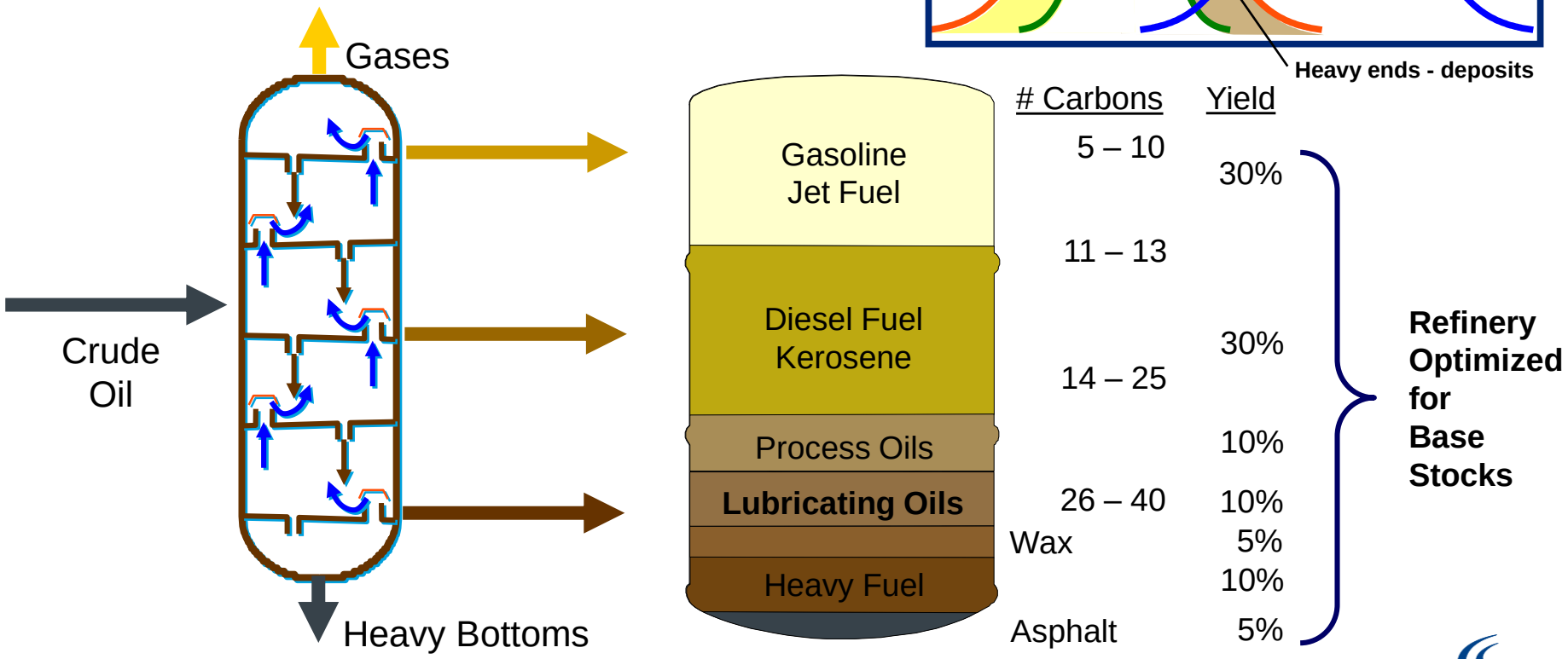
- Start
  - Crude oil
  - Mixtures of **GOOD** and **BAD** molecules
- Goal
  - **REDUCE** the Proportion of **BAD** molecules
  - **INCREASE** the Proportion of **GOOD** molecules
- Using Refining processes:
  - Separation
    - Remove the **BAD** molecules
      - Throw them away?
      - Use them for something else!
  - Conversion
    - Change **BAD** molecules into **GOOD** molecules
  - Synthesis
    - Build **GOOD** molecules from small ones
- Other processing steps involved
  - Not covered today



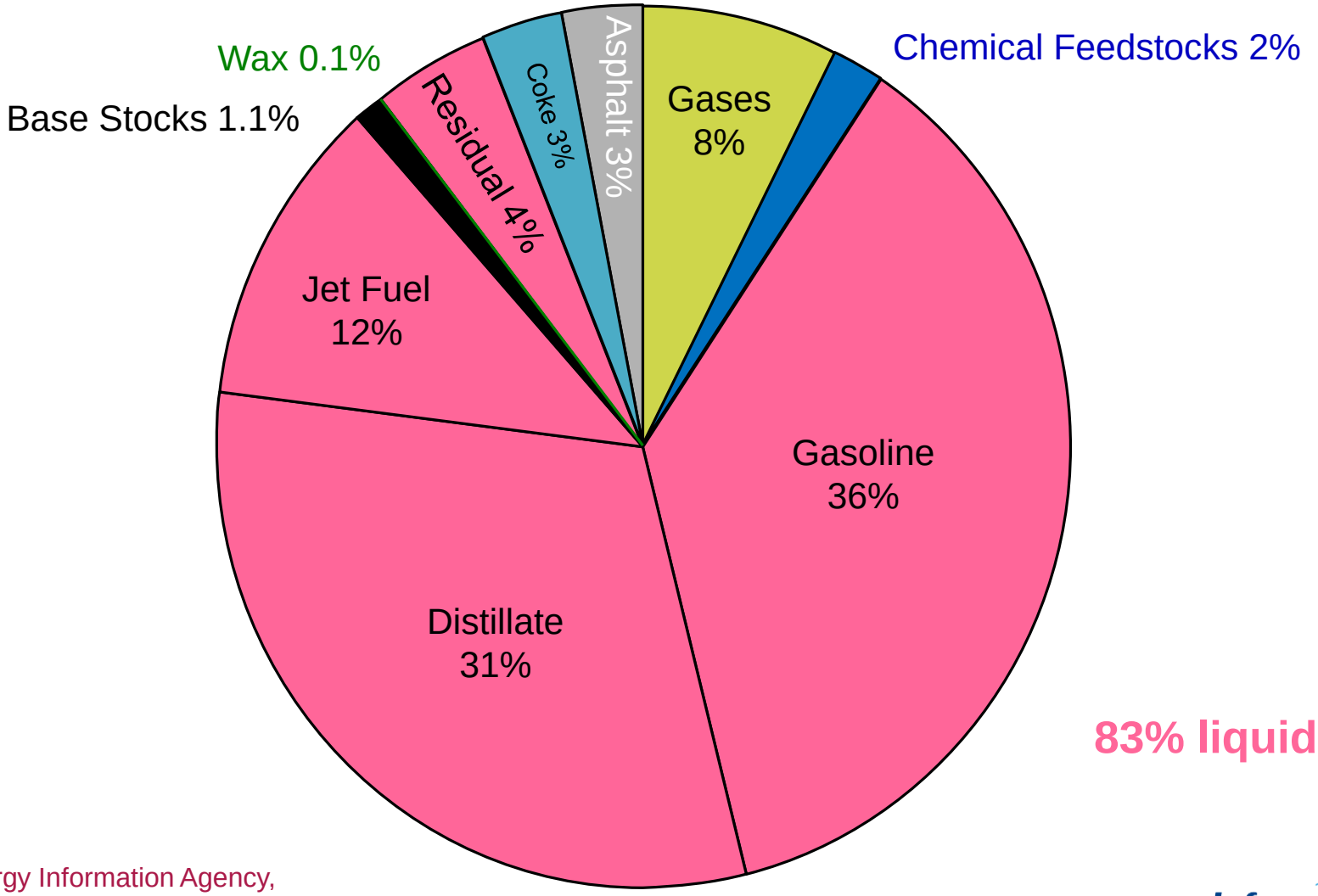
Major base stock refinery processes – 1

- Distillation
  - Separates lighter from heavier fractions
  - Selects viscosity 'cut' →
  - Controls volatility (evaporation) →





U.S. refinery yields



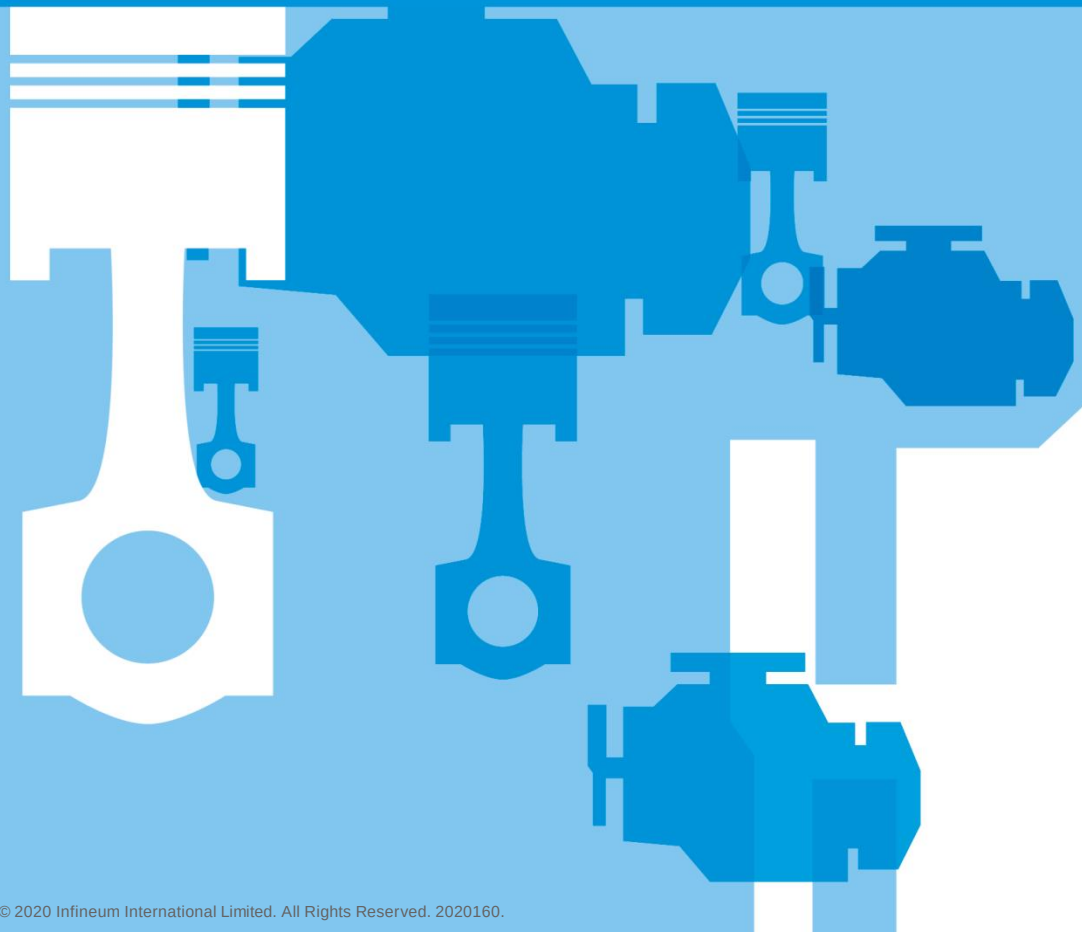
83% liquid fuels

Energy Information Agency,
U.S. Department of Energy

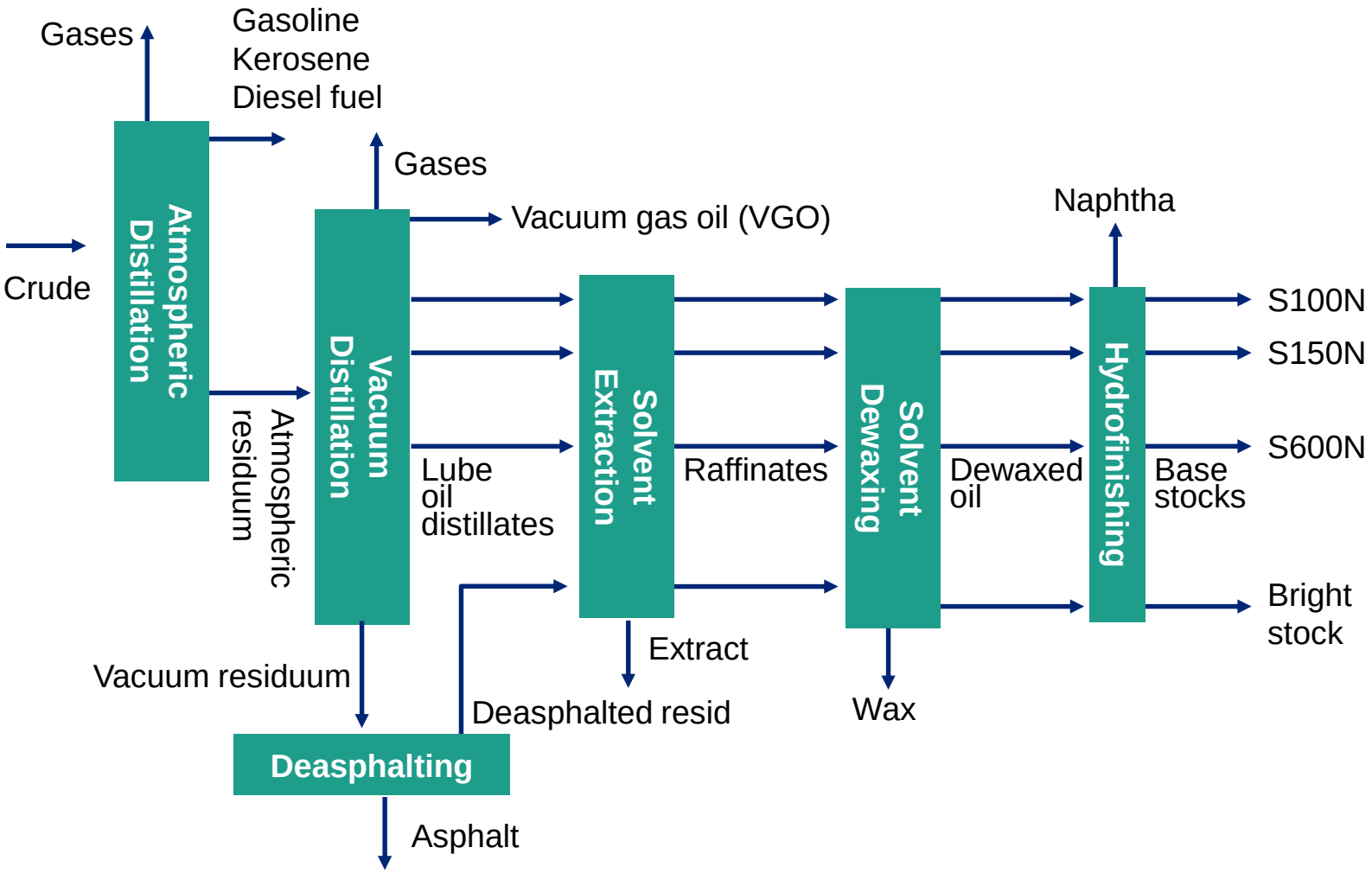
Major base stock refinery processes – 2

- Solvent Extraction (Group I)
  - Separation technology
  - Polar solvent removes aromatics leaving good saturated molecules
  - Removes sulfur, which is predominantly in aromatic molecules
- Hydrocracking (Group II & III)
  - Conversion technology
  - Breaks chemical bonds and adds hydrogen
  - Increases saturates by adding hydrogen
  - Removes sulfur, converting to volatile H_2S
  - Group II *vs* III is a function of feedstock and hydrocracker severity
- Synthesis (Group III, IV, & V)
  - GTL – Gas to Liquid – combine methane (natural gas) into large hydrocarbons
  - PAO – PolyAlphaOlefin – combine small double-bond molecules
  - Esters – Build up specific molecules using various starting molecules

Solvent Extraction



Solvent extraction refinery process



Solvent extraction

- Separation based on solubility
  - "Good" molecules are less polar
    - Straight and branched chain paraffins
    - Naphthenes
  - "Bad" molecules are more polar
    - Aromatics
- Use a polar solvent
  - "Bad" polar molecules end up in polar solvent
  - "Good" non-polar molecules stay in oil
- Must chose crudes with significant "good" molecules

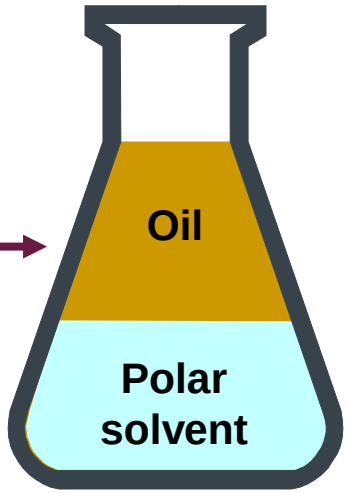
More "like oil"

More "like water"

Phenol
Furfural
N-methyl pyrrolidone

Less polar 'good' molecules end up here

More polar 'bad' molecules end up here



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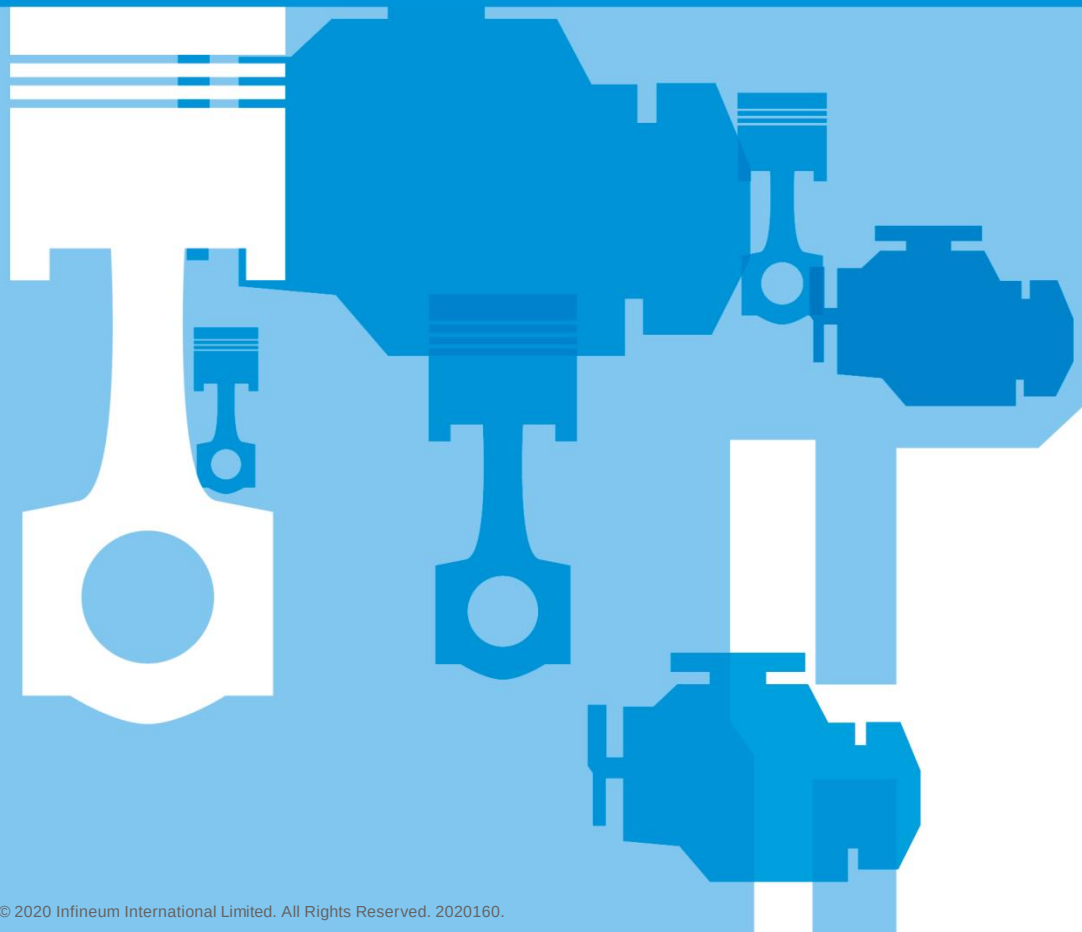
Hydrocracking



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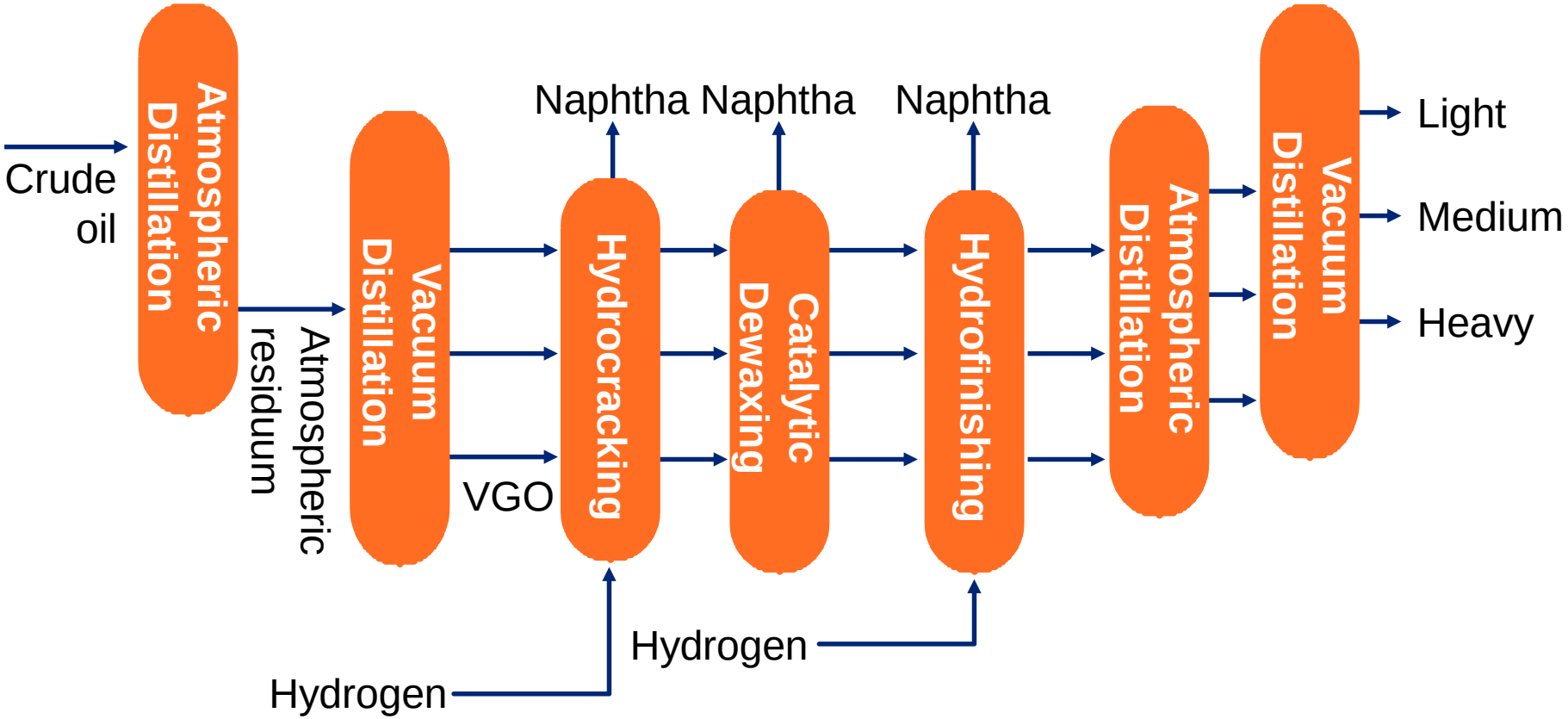
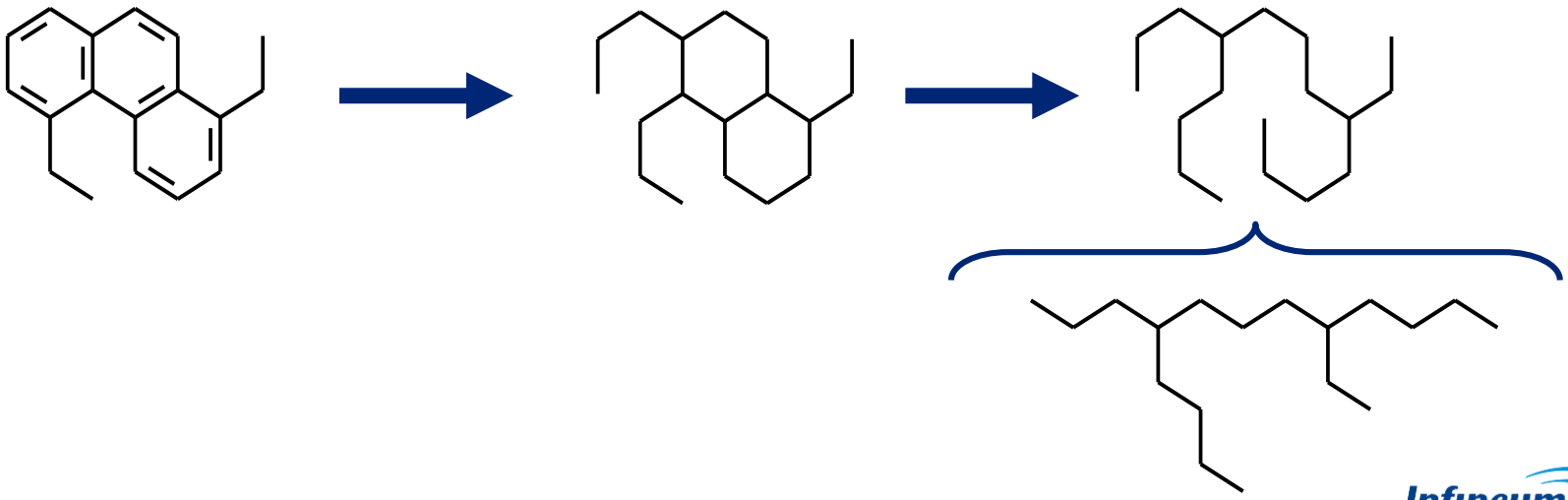
Hydrocracking refinery process



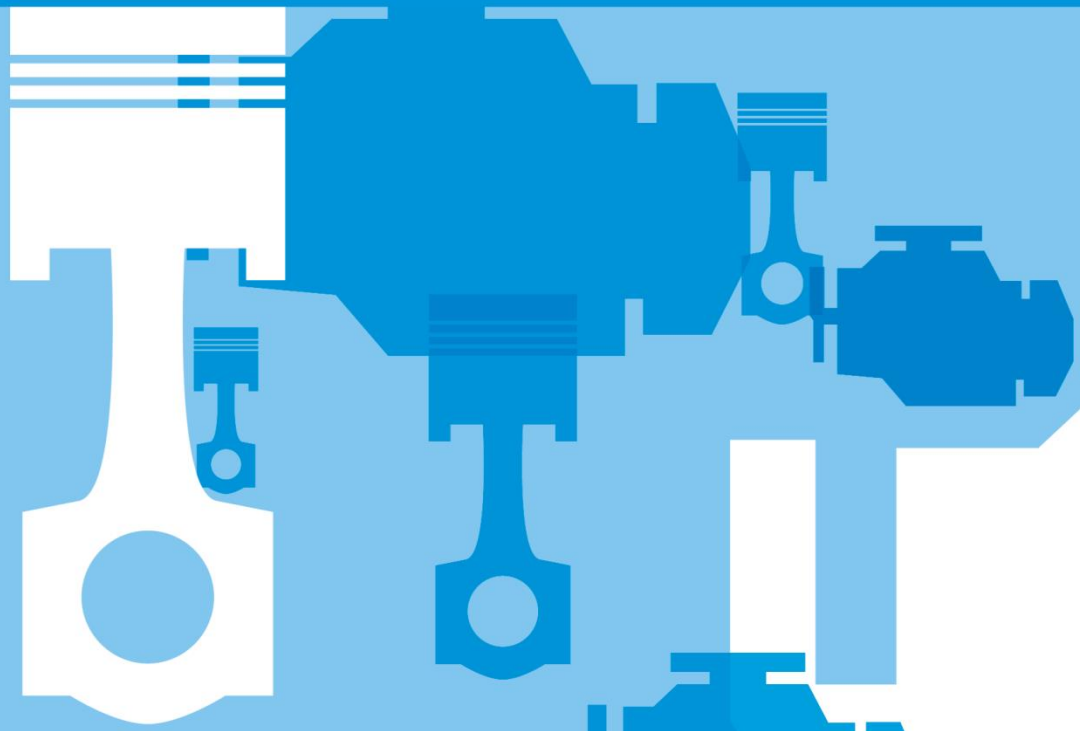
Hydrocracking

- Conversion of “bad” molecules into “good” molecules
  - “Cracking” means breaking apart
  - “Hydro” means adding hydrogen
  - “Hydrocracking” is breaking bonds and adding hydrogen
    - Hydrocracking usually implies high severity
    - Hydrofinishing usually implies low severity
    - Hydrotreatment can mean either



Performance you can rely on.

Synthetics



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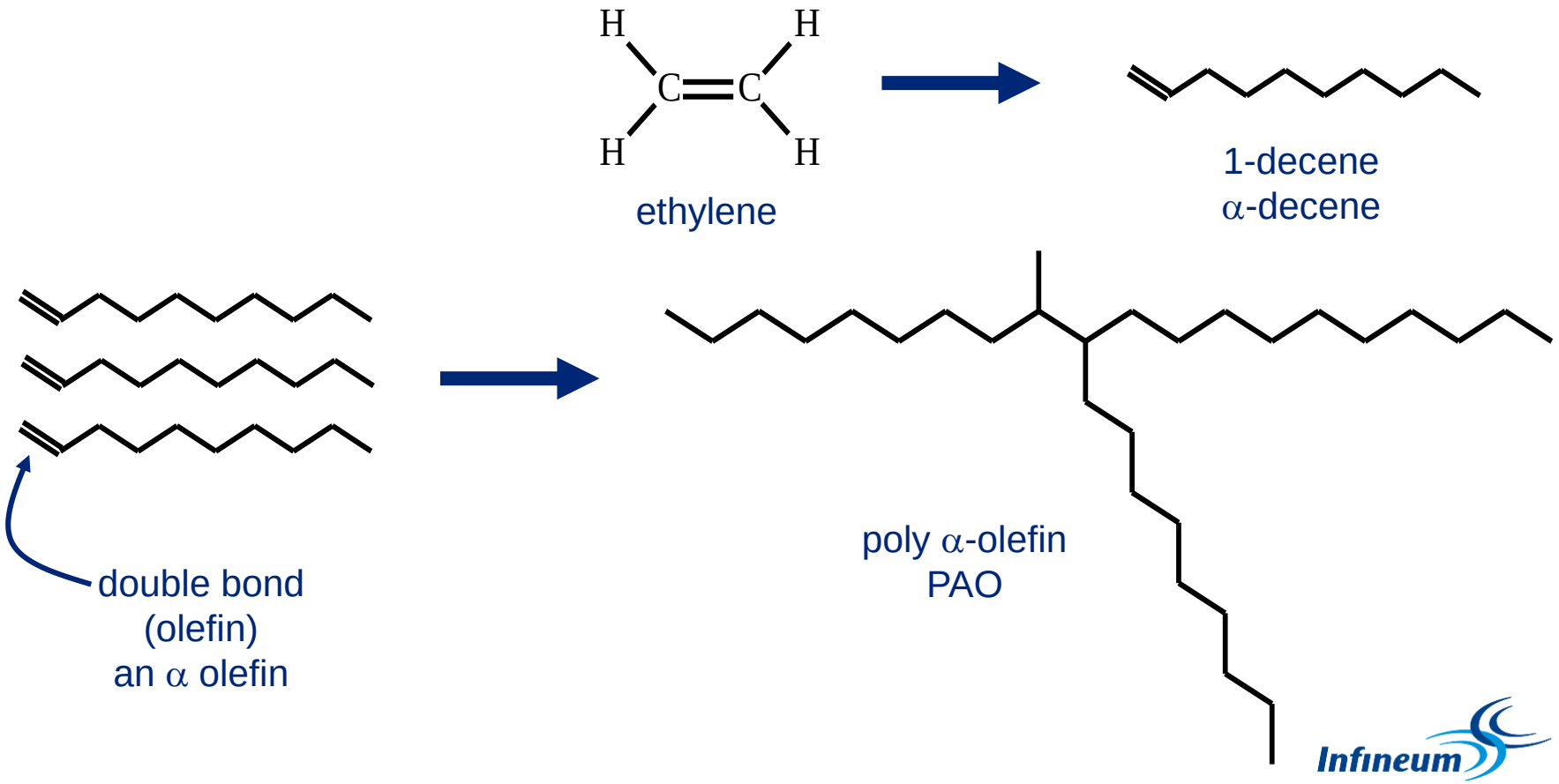
Synthetic process – PAO

- Select small molecules from other refinery streams
- Build up good molecules from the small ones



Synthetic process – GTL*

- GTL = Gas-to-Liquids
  - Process of turning natural gas into liquid hydrocarbons
  - Primary focus is liquid fuel production, but base stocks can also be made
- Steam-Methane Reforming (SMR) to make "syngas" ← Also other ways to make syngas

$$CH_4 + H_2O \rightarrow CO + 3H_2$$
$$CO + H_2O \rightarrow CO_2 + H_2$$
$$CH_4 + CO_2 \rightarrow 2CO + 2H_2$$

Net Reaction:

$$CH_4 + H_2O \rightarrow 2CO + 3H_2$$

"Syngas"

- Followed by Fischer-Tropsch synthesis

$$nCO + (2n+1)H_2 \rightarrow C_nH_{(2n+2)} + nH_2O$$

- GTL base stocks have:
  - Very high saturates and Viscosity Index
  - Essentially no sulfur, nitrogen, aromatics, or olefins
- GTL's meet the chemical and physical definition of API Group III
- A few GTL plants started supplying
  - A large fuels plant could become largest source of base stock

*"Chemistry and Technology of Lubricants," 3ed., Mortier, Fox, and Orszulik (Eds.), Springer, 2010

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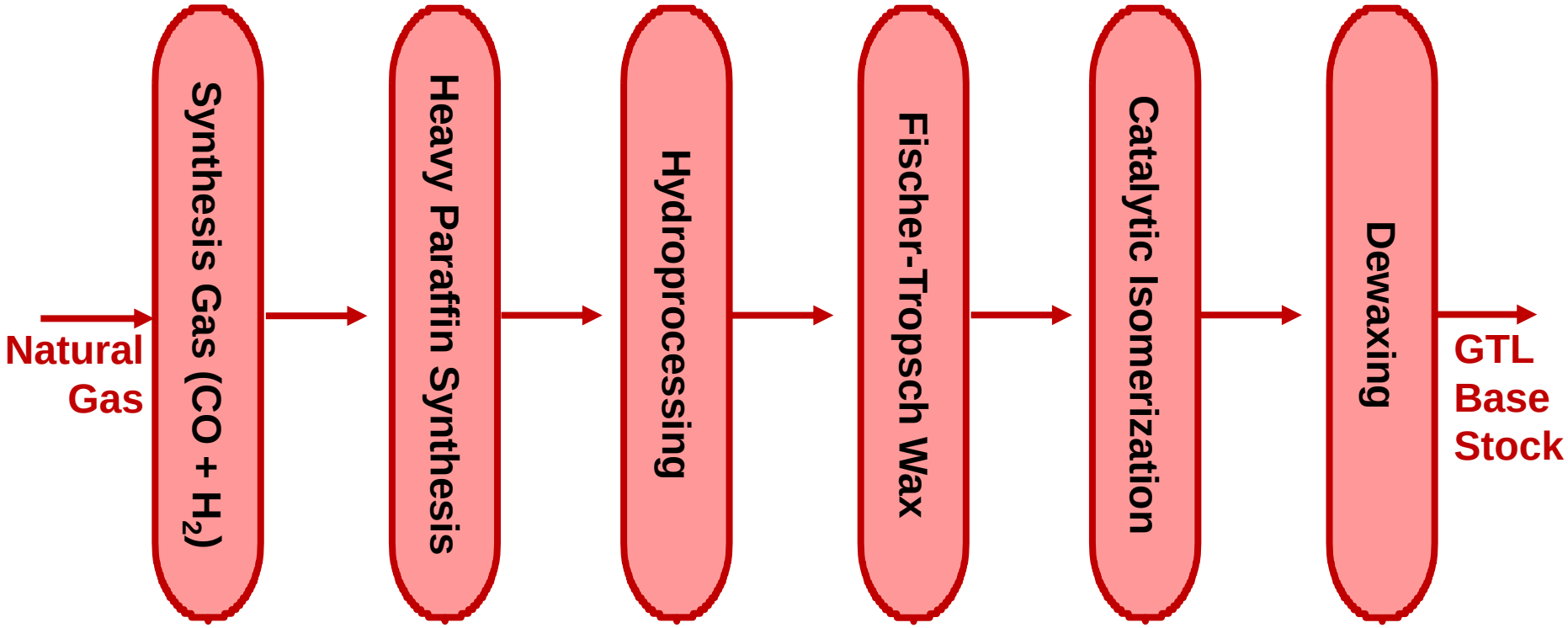
Gas-to-liquids



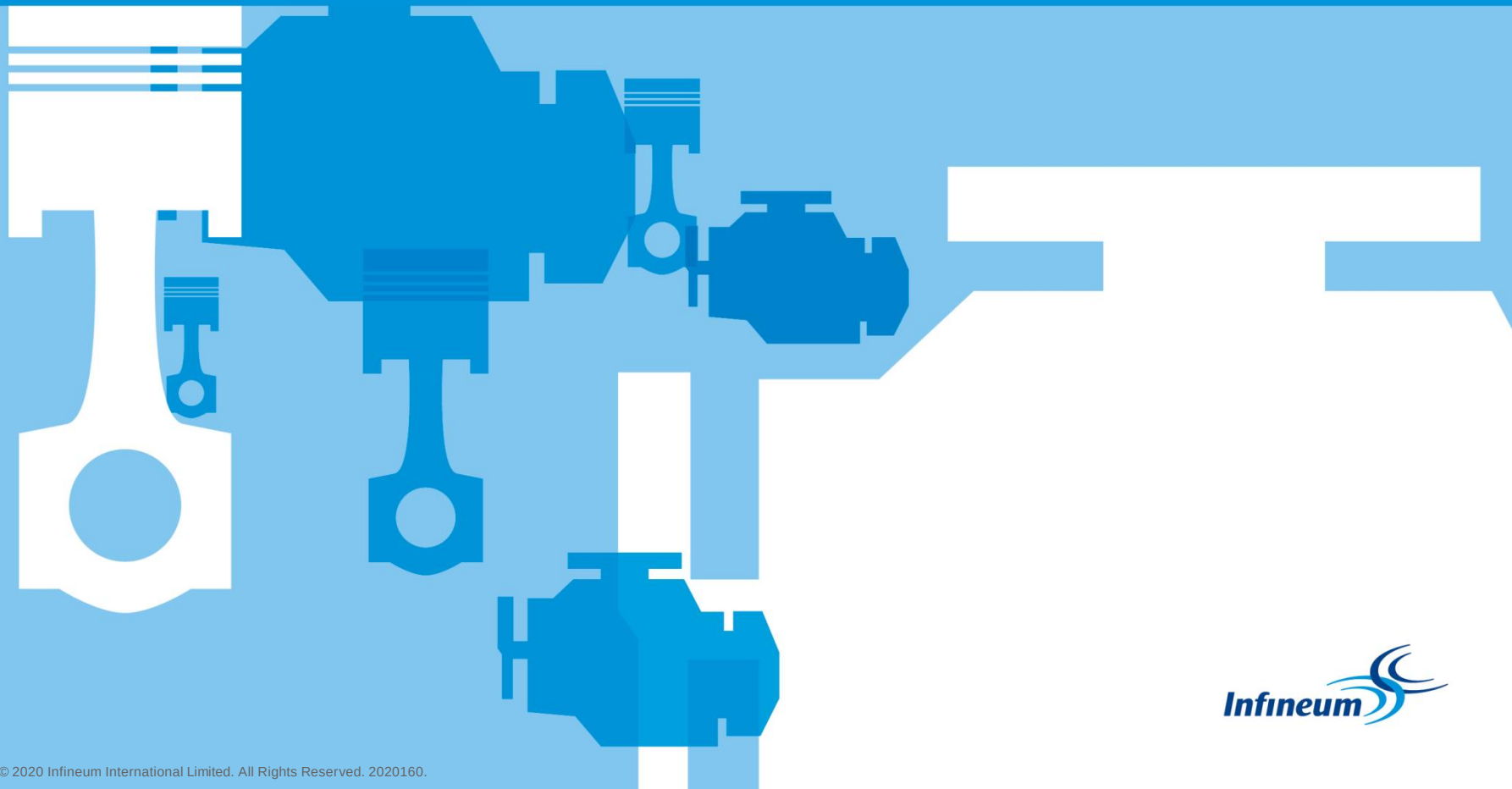
Source: RPS Energy, Lubes 'n' Greases, May 2014

Other base stock types (reference)

- Esters
  - Diesters
  - Polyol esters
  - Phosphate esters
- PolyAlkylene Glycol (PAG)
- Alkylated naphthene (AN)
- Polyphenyl ether
- Silicones
- Bio-based
  - Natural oils
  - Chemically-functionalized vegetable oils
  - Biotechnology renewable oils (*e.g.*, from plant sugars *via* algae)
- Many others

Ref: "Synthetics, Mineral Oils, and Bio-Based Lubricants, Chemistry and Technology"
L. R. Rudnick (ed.), CRC Taylor and Francis, 2006

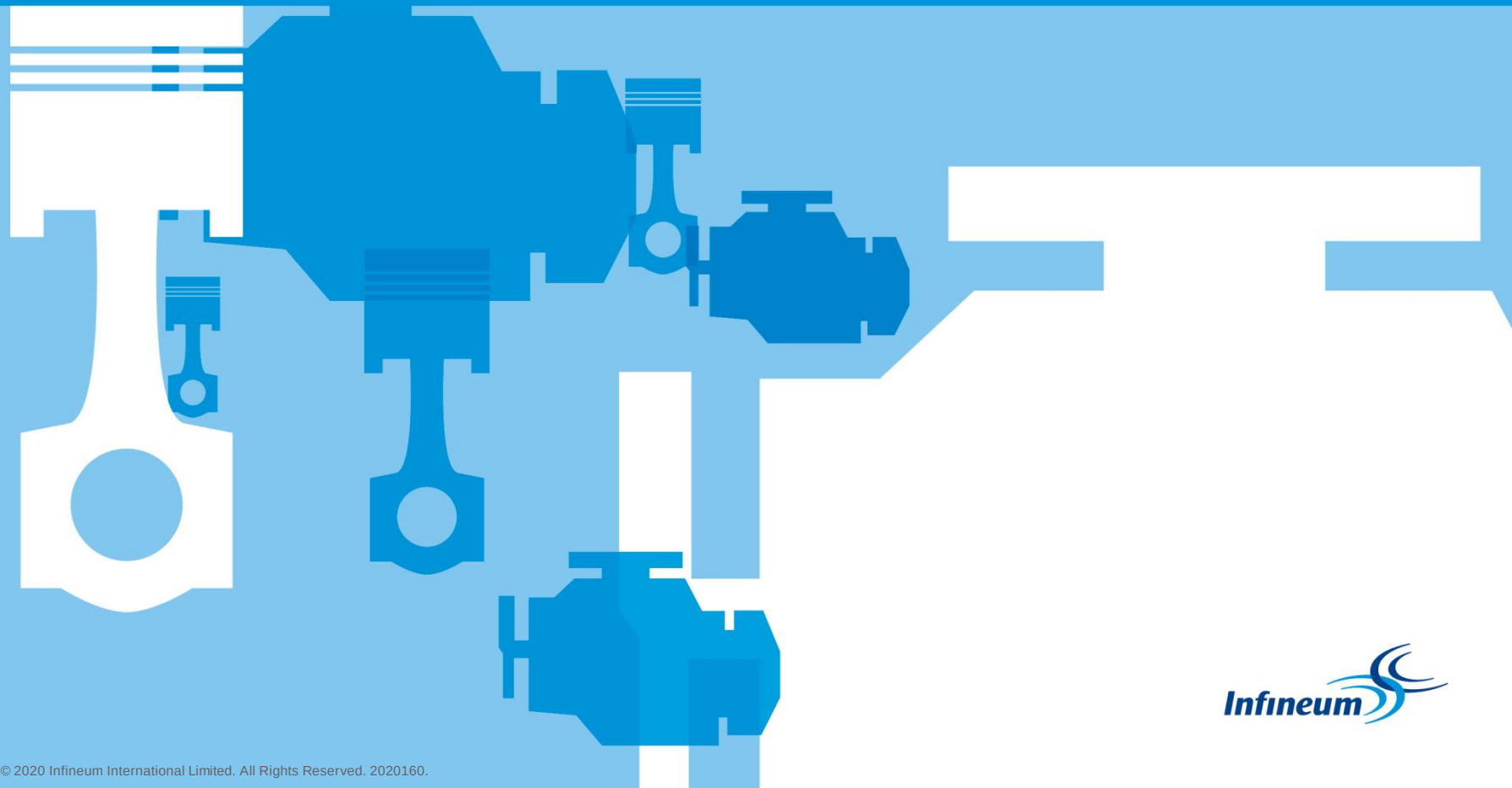
Base stock key inspections



Key base stock properties – overview

- Viscosity (D445)
  - Sometimes kinematic viscosity at 100°C
    - Examples: HC4, HC6, HC12
  - Sometimes "Neutral Number" – approx. 4.6 times kinematic viscosity at 40°C
    - Examples: S100N, S150N, S600N
  - ISO Grade for Industrial Oils – related to kinematic viscosity (mm^2/s) at 40°C
- Viscosity Index (D2270)
  - Rate of change of viscosity with temperature
- Low temperature properties
  - CCS (D5293), MRV (D4684), SBV (D5133), or Pour point (D97)
- Saturates (D2007)
  - Measure of "stable" vs. "reactive" molecules
  - Intended as an approximation of oxidative stability – Not perfect
- Sulfur (D4294)
  - Corrosive and poison to exhaust catalysts
- Volatility (D5800)
  - Evaporation
- Chemical properties are also very important

API base oil classification



Base oil classification

- American Petroleum Institute (API)
  - Trade association of oil companies
- Wanted a way to classify base oils
  - Base oil is a mixture of (one or more) base stocks
- Intended for Base Oil Interchange Guidelines (BOIG)
  - To approve an additive package previously approved in another base oil
    - Using Read-Across
    - More detail in the Specifications and Passenger Car sections
- Now used for marketing, lobbying, and other commercial activities

API base oil classification

Group	Vis. Index	Saturates		Sulfur	Other Properties
I	80≤ x <120	<90%	and / or	>0.03%	
II	80≤ x <120	≥90%	and	≤0.03%	
III	≥120	≥90%	and	≤0.03%	
IV					PAO (Poly Alpha Olefins)
V					Everything Else

- Companies started using their own (unofficial) marketing phrases
  - "Group II Plus" and "Group III Plus"
  - Now used generally to mean "towards the high end of the group"
- Note: The word "Synthetic" is not part of the API Classification
  - "Synthetic" is a marketing term, not a technical term
  - "Group III" can legally be labeled 'synthetic'

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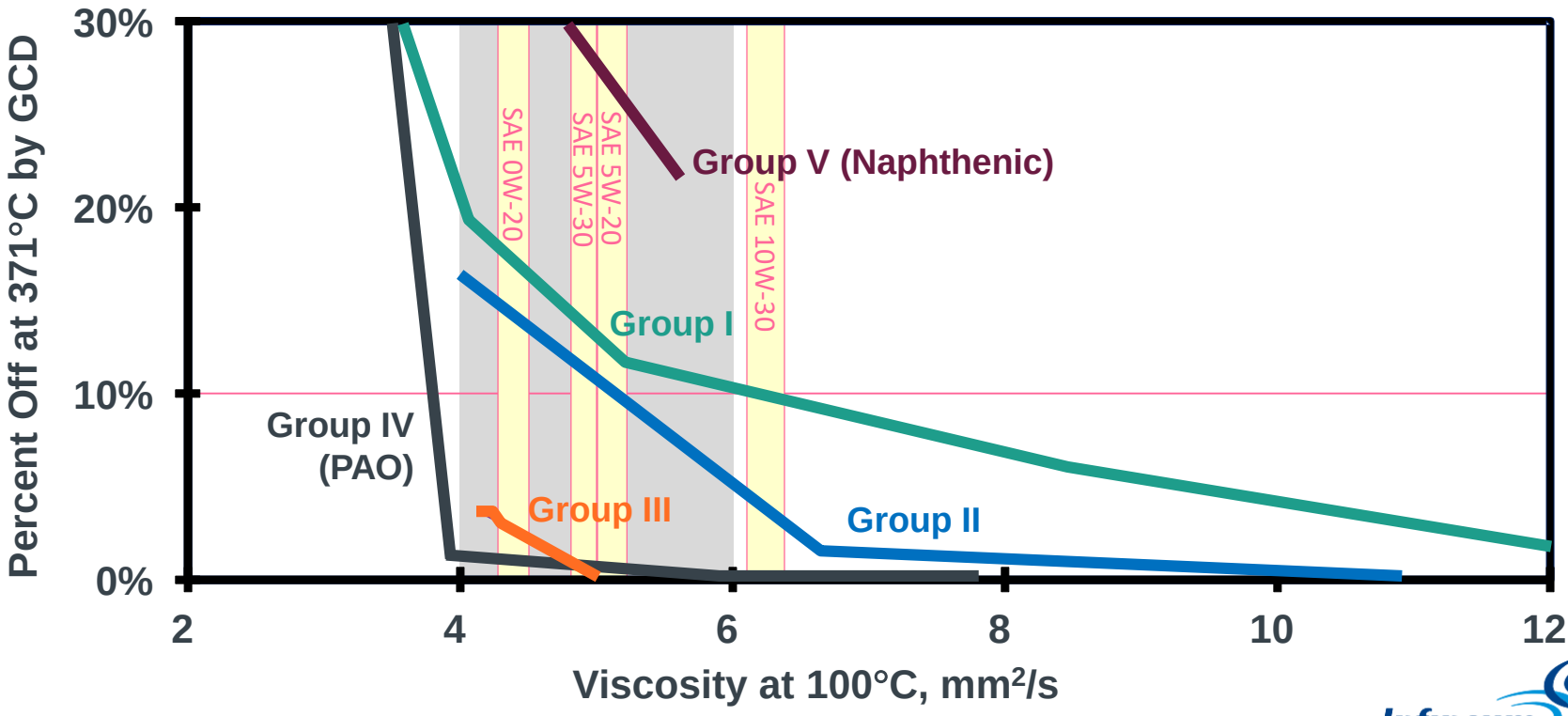
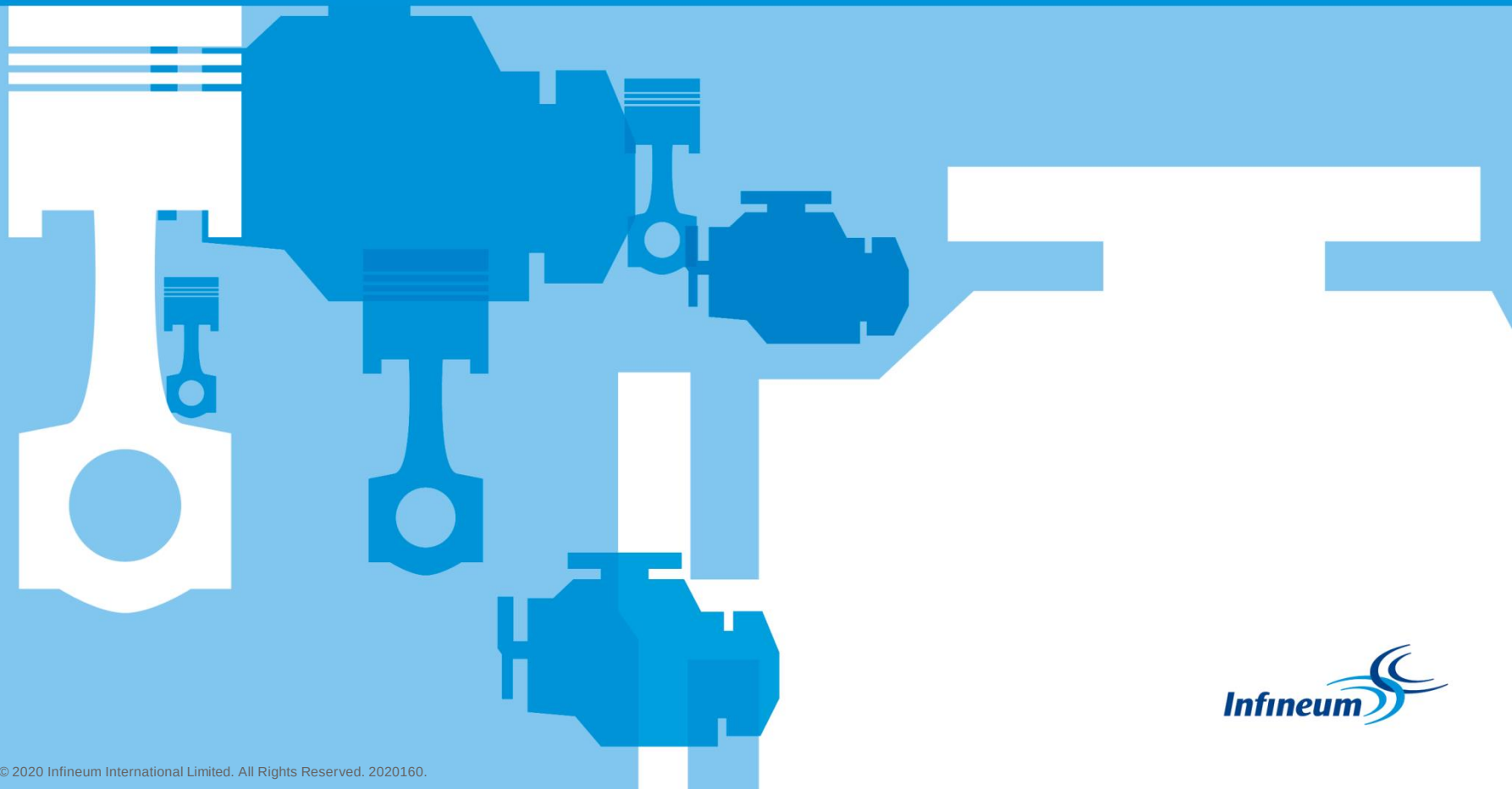
Volatility

- Volatility depends on viscosity and molecular structure
  - Advantages for Group III and Group IV at low viscosity



Base stock names



Base stock viscosity

- Absolute viscosity
  - Measure of resistance to flow
  - Viscosity = (Shear Stress/Shear Rate)
    - (How hard you push it)/(How fast it moves)
  - Preferred unit = milliPascal-second (mPa-s)
- Kinematic viscosity
  - Viscosity/Density
    - Measure of flow under the force of gravity
  - Preferred unit = millimeter squared per second (mm2/s)
    - Common unit = centiStoke (cSt = mm2/s)
    - Common unit = Saybolt Universal Seconds (SUS)
      - SUS ≈ 4.6*(mm2/s)
- Viscosity varies strongly with temperature

Base stock names – API Group I

- Base stock names are brand names
  - Specific to each producing company
  - These are typical naming conventions:
- Solvent xxx Neutral (SxxxN, or SNxxx, or xxxSN, *etc*.)
  - Solvent from “Solvent Extracted”
  - xxx = viscosity
    - Saybolt Universal Seconds at 100°F
    - Approximately 4.6 times mm^2/s at 210°F (~100°C)
  - Neutral from “Neutralization after Acid Washing”
    - First base stock refining technique
- HVI
  - Redwood Number 1 Seconds at 140°F (European)
- Bright Stock
  - Heaviest grade of base stock (~ S2500N ≈ 650 Redwood)
  - xxx Bright Stock = SUS viscosity at 210°F (*e.g.*, 150 Bright Stock)
    - Approximately 4.6 times mm^2/s at 100°F (~40°C)
    - “Bright” because heavy aromatics often fluorescent

Base stock names – API Groups II, III, IV, & V

- Base stock names are brand names
  - Specific to each producing company
  - These are typical naming conventions:
- HC xxx
  - HydroCracked xxx
    - xxx viscosity usually mm^2/s at 100°C
      - HC4
    - Sometimes equivalent “Neutral Number”
      - HC100
- MVI, HVI, VHVI and XHVI

– Medium Viscosity Index	Naphthenic	(Group V)
– High Viscosity Index	Paraffinic	(Group I)
– Very High Viscosity Index	Hydrocracked	(Group II)
– eXtra High Viscosity Index	Hydrocracked	(Group III)

- PAO x = usually some number related to mm^2/s at 100°C
  - PAO 4 Usually 4 mm^2/s at 100°C
  - PAO 45 Could be 4.5 or 45 mm^2/s at 100°C
  - PAO 954 Could be 4 or 54 or 95.4 mm^2/s at 100°C

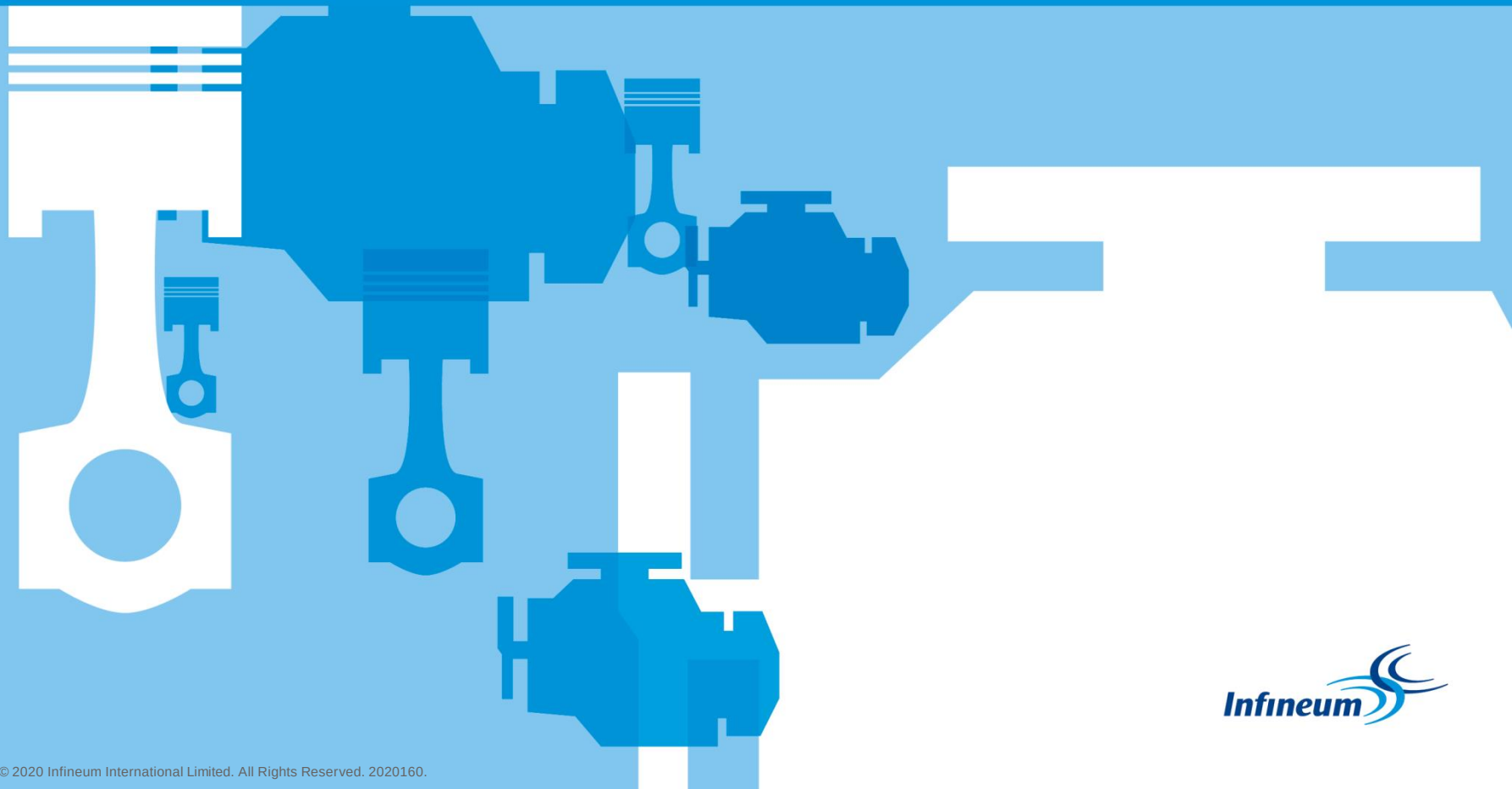
Base stock grade equivalents

Grade	SUS* at 100°F	Redwood# at 140°F	mm^2/s at 100°C	mm^2/s at 40°C
S 75N	75	-	3.1	13
S100N	105	-	4.1	20
S150N	155	-	5.1	30
S325N	330	-	8.5	65
S600N	590	160	12.1	115
150 Bright Stock	2500	650	31.5	5000

150 SUS at 210°F

*SUS = Saybolt Universal Seconds
#Approximate

Base stock typical properties



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Typical lube base stock properties (solvent neutrals – API Group I)*

	Light (S100N)	Medium (S150N)	Heavy (S600N)	Bright Stock (S2500N)
Viscosity at 100°C, mm^2/s	4	5	12	32
Viscosity at 40C, mm^2/s	20	30	110	490
Viscosity Index	95	95	95	95
Pour Point, °C	-18	-18	-9	-18
Volatility, GCD % off at 371°C	20	15	0	0
Volatility, NOACK	24	18	2	1
Flash Point, °C	200	210	250	280
Saturates, mass percent	75	75	70	60
Sulfur, mass percent	0.3	0.3	0.4	0.7

*Nominal, and not representative of any particular manufacturer

Typical lube base stock properties (hydrocracked – API Group II)*

	Light (100N)	Medium (200N)	Heavy (600N)
Viscosity at 100°C, mm^2/s	4	6	12
Viscosity at 40C, mm^2/s	20	40	110
Viscosity Index	100	100	100
Pour Point, °C	-18	-18	-18
Volatility, GCD % off at 371°C	16	2	0
Volatility, NOACK	23	11	2
Flash Point, °C	200	220	250
Saturates, mass percent	95	95	95
Sulfur, mass percent	0.01	0.01	0.01

*Nominal, and not representative of any particular manufacturer

Typical lube base stock properties (hydrocracked – API Group III)*

	Light (100N)	Medium (150N)	Heavy (250N)
Viscosity at 100°C, mm^2/s	4	6	8
Viscosity at 40C, mm^2/s	17	33	50
Viscosity Index	130	130	130
Pour Point, °C	-18	-18	-12
Volatility, GCD % off at 371°C			
Volatility, NOACK	13	6	4
Flash Point, °C	240	250	260
Saturates, mass percent	97	97	97
Sulfur, mass percent	0	0	0

*Nominal, and not representative of any particular manufacturer

Typical lube base stock properties (GTL – API Group III)*

	Very Light (GTL 3)	Light (GTL 4)	Medium (GTL 6)	Heavy (GTL 8)
Viscosity at 100°C, mm^2/s	3	4	6	8
Viscosity at 40C, mm^2/s	11	17	32	46
Viscosity Index	120	130	135	145
Pour Point, °C	-42	-33		-24
Volatility, GCD % off at 371°C		3	0.6	0
Volatility, NOACK	34	9	3	1
Flash Point, °C	200	230	240	270
Saturates, mass percent	98	97	97	96
Sulfur, mass percent	0	0	0	0

*Nominal, and not representative of any particular manufacturer

Typical lube base stock properties (PAO – API Group IV)*

	Light (PAO 4)	Medium (PAO 6)	Heavy (PAO 10)	Very Heavy (PAO 100)
Viscosity at 100°C, mm^2/s	4	6	10	100
Viscosity at 40C, mm^2/s	18	30	65	1300
Viscosity Index	130	135	130	160
Pour Point, °C	-63	-63	-51	-30
Volatility, GCD % off at 371°C	1	0	0	0
Volatility, NOACK	12	2	1	1
Flash Point, °C	200	240	270	290
Saturates, mass percent	96	96	96	94
Sulfur, mass percent	0	0	0	0

*Nominal, and not representative of any particular manufacturer

Base stock recent trends

- Transition from API Group I to Group II continuing
  - Demand for higher quality (oxidation, dispersancy, *etc*.)
  - Specifications with sulfur restrictions
  - Demand for lower volatility in lower viscosity grades
- API Group I base stocks still have uses
  - Higher viscosity: Marine, railroad, gear oils
  - Lower viscosity: Transformer oils, process oils, spray oils
- Demand for API Group III (and Group III Plus) will increase
  - Growth of SAE 0W-xx and 5W-xx grades
- Supply-Demand imbalance in many regions
- PAO capacity expected to increase
- Green base stocks are niche for now
  - Re-refined (derived from used oil re-cycling)
  - Bio-lubricants (derived from sugarcane, algae, *etc*.)

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Base stock summary

- Base stocks are the main component in lubricants
  - Have a significant effect on performance
- Base stocks are complex mixtures of molecules
  - Derived from crude oil by refinery processes
- Chemical composition determines performance
  - Saturates and sulfur usually most important, but not the whole story
- Physical properties are also important
  - Viscosity, Viscosity Index, pour point, volatility
- Performance testing of products still required
  - Compositional effects not well enough known
  - Additives are a major factor in finished products
  - API BOIG's are used to read-across testing
- Base stock research continuing
  - Develop better analytical test methods
  - Improve performance predictions
  - Demand for higher quality expected to continue

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