Pour Point Depressants

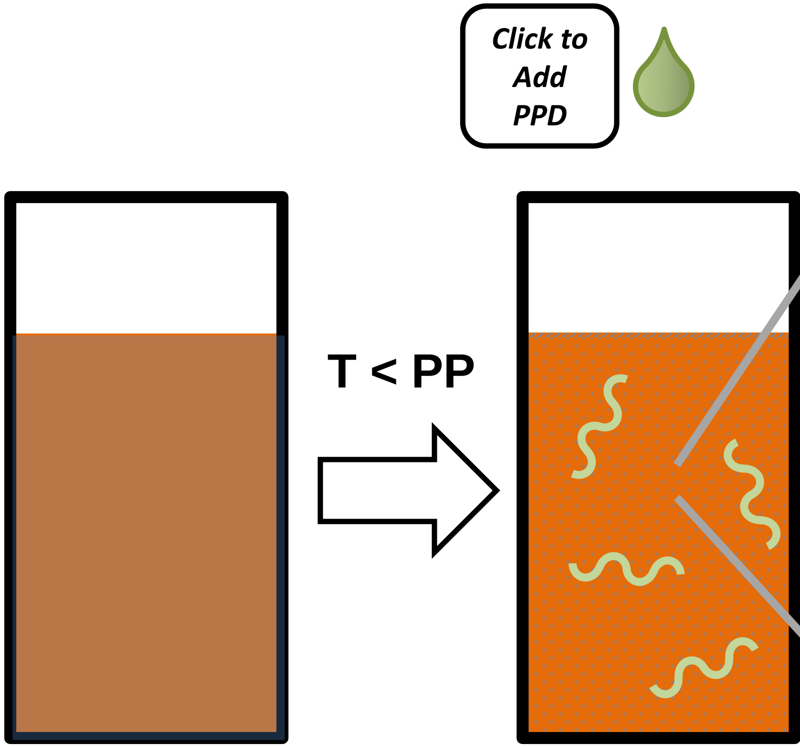
Functional Products Inc.

January 2020

FUNCTIONAL PRODUCTS INC.
Innovative Chemistry for Lubricants

PPDs and Wax

- PPDs modify the surface of wax crystals that bloom from oil at low temp.



Oil with dissolved waxes at room temp.

Oil with small disordered wax crystals

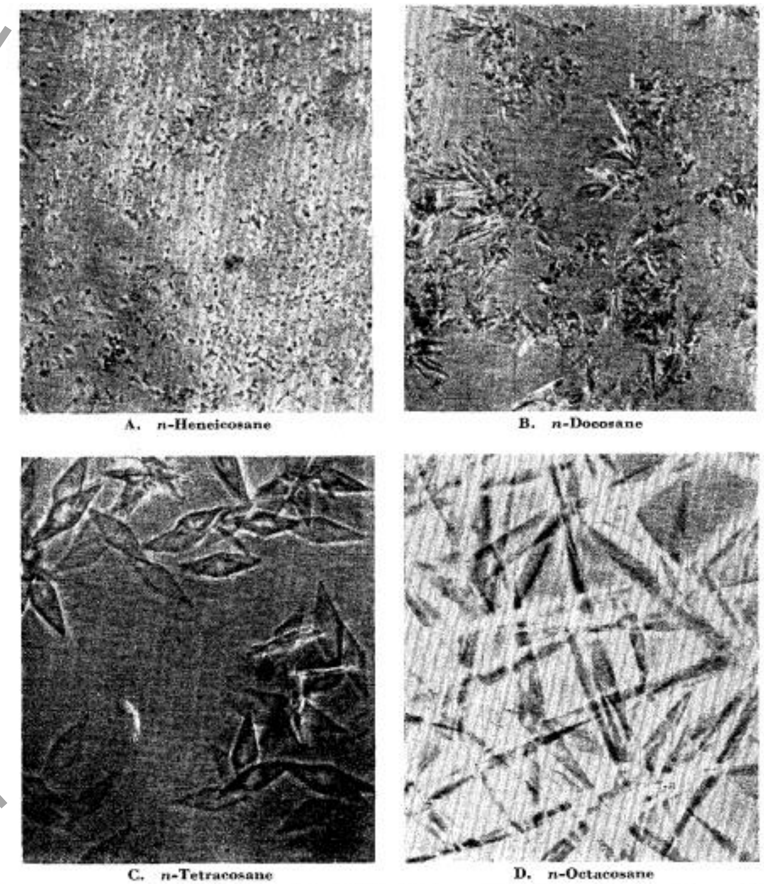
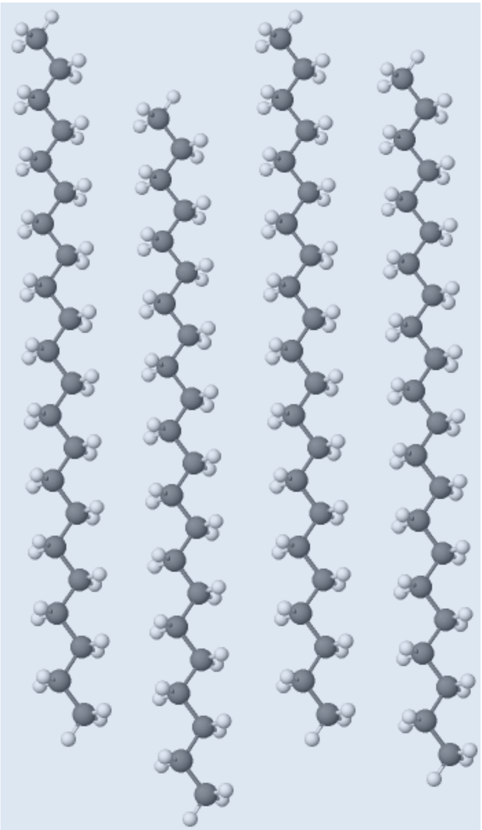


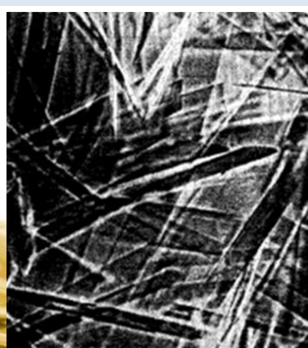
Figure 11. Synthetic n-Paraffins (8 Wt. %) Crystallized from Dewaxed Pennsylvania 150 Neutral Oil Containing 3.5 Wt. % Hexadecyl Polymethacrylate (750×)

Gavlin, G., Swire, E. A. & Jones, S. P. Pour Point Depression of Lubricating Oils. Ind. Eng. Chem. 45, 2327–2335 (1953).
Florea, M., Catrinoiu, D., Luca, P. & Balliu, S. Lubr. Sci. 12, 31–44 (1999).

PPD Effect on Wax

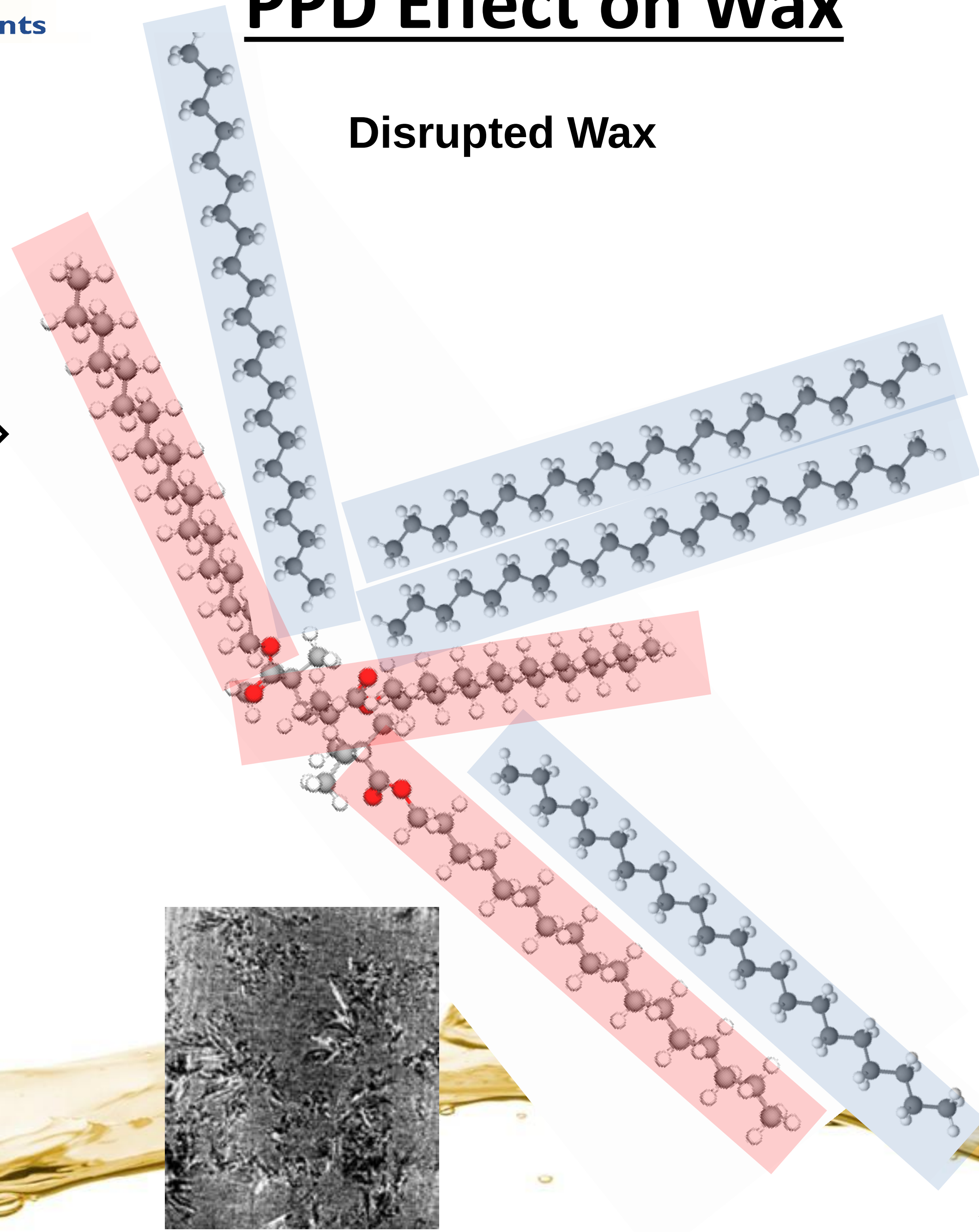
Ordered Wax Crystal





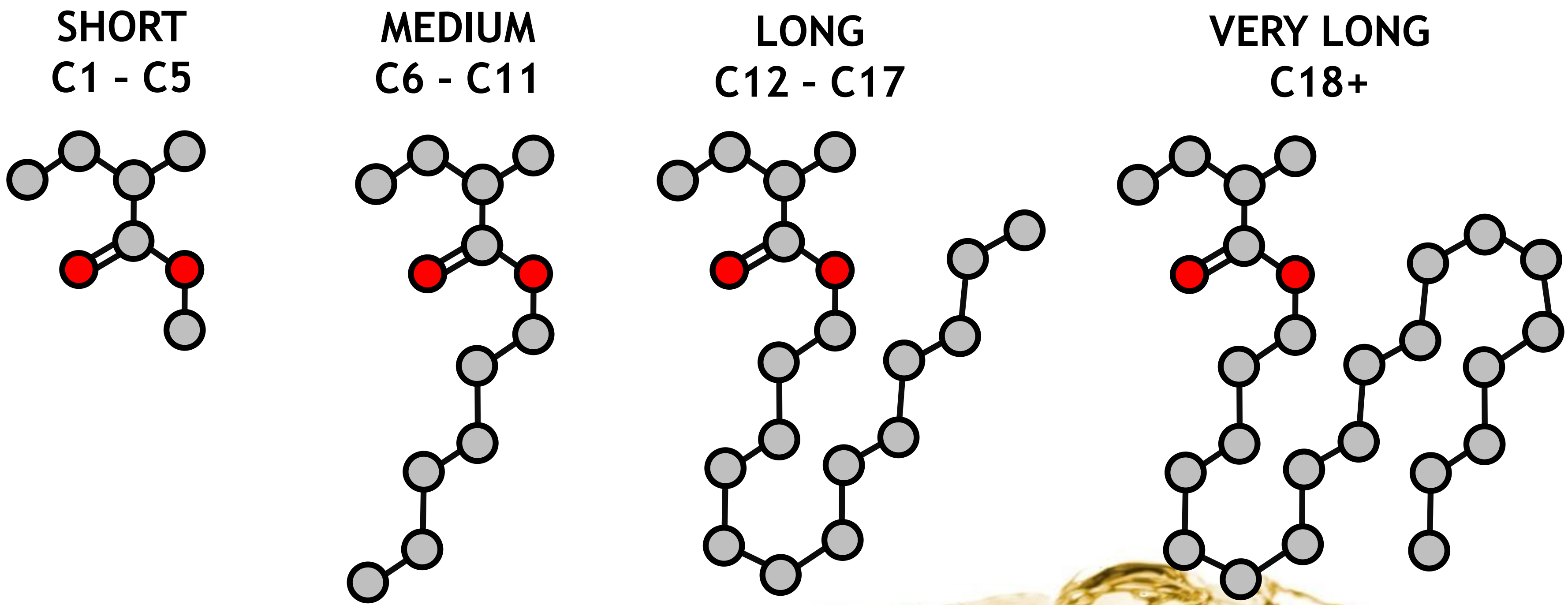
+ PPD

Disrupted Wax



Engineering PMA

- Polymethacrylate PPDs contain a variety of fatty alcohol side groups
- Different lengths and branching control solubility and wax inhibition



Florea, M., Catrinoiu, D., Luca, P. & Balliu, S. Lubr. Sci. 12, 31–44 (1999).

Mineral Oil PPD Selection

- PPDs are engineered to fit specific wax profiles in paraffinic Group I/II/III
  - % wax
  - Size and distribution of wax (carbon number)
  - Crude oil source and refiner's process

- Good vs. great performance of PPD comes down to base oil selection

	Best Performance In… (Lowest pour at lowest wt%)	**Typical Products**
Functional PD-610	High viscosity Gr. I / II (300N – 600N; Bright Stock)	Industrial gear, rock drill, way oils, bar and chain, grease
Functional PD-620	Low viscosity Gr. I / II / III (70N – 220N; 4 cSt)	Engine, automotive gear, HF, high VI industrial gear, ATF
Functional PD-630	High viscosity Gr. III (6 and 8 cSt)	Engine, automotive gear, HF, high VI industrial gear, ATF

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Veg Oil PPD Selection

- Vegetable oil triglycerides contain very high amounts of wax
  - Saturated fatty acids – C16 – C22+
  - Varies by plant species (canola, soy, sunflower, etc.) and harvest

- Treat rate is simpler than with mineral oil – typically 0.5 or 1.0wt%
  - Overtreat or ‘reversion’ is rare

- Ecolabel LuSC status (environmentally acceptable lubricants) on some PPD

	Note	Ecolabel
Functional PD-585	High viscosity, option to use as shear stable thickener (bio HF)	Yes
Functional PD-590	Low viscosity for ease of handling Extra diluent helps PPD work in highly saturated oils (palm, tallow)	Yes
Functional PD-555C	Low viscosity for ease of handling PPD optimized for highly saturated oils	No

Typical Treat of PPD

- Example: PD-610 in ISO 32 (150N) and ISO 150 (600N) Group II:

wt% PPD	PP in ISO 32	PP in ISO 150
0.0%	-18°C	-18°C
0.05%	-33°C	--
0.1%	-39°C	-21°C
0.2%	-42°C	-24°C
0.3%	-48°C	-30°C
0.5%	--	-33°C

- For biobased:

wt%	Pour Point, D97	
PD-585	Canola	Soybean
0.0%	-24C	-12C
0.5%	-33C	-21C
1.0%	-36C	-24C

PPD Screening – Phase 1

- Rough screening with many PPDs in one oil at 0.3wt% to find best fit
  - Drill down to varying treat rate of one PPD to find wt% vs. PP

Base Oil w/ 0.3% PPD	Group	PD-610	PD-620	PD-630
Crystal-Clean HC 150	Group II	-39	-42	-39
Safety Kleen RHT 240	Group II	-36	-42	-39
Neste Nexbase 3043	Group III	-42	-45	-42
Neste Nexbase 3080	Group III	-33	-33	-36
Adnoc Adbase 6	Group III+	-39	-36	-39
Motiva Star 6	Group II	-42	-42	-39
Motiva Star 12	Group II	-33	-30	-30

Base Oil	Group	PPD=	0.10%	0.15%	0.20%	0.25%	0.30%
Crystal-Clean HC 150	Group II	PD-620	-39	-39	-39	-39	-42
Safety Kleen RHT 240	Group II	PD-620	-36	-36	-36	-36	-42
Neste Nexbase 3043	Group III	PD-620	-39	-39	-39	-39	-45
Neste Nexbase 3080	Group III	PD-630	-33	-33	-36	-36	-36
Adnoc Adbase 6	Group III+	PD-630	-33	-33	-33	-36	-39
Motiva Star 6	Group II	PD-610	-36	-39	-42	-42	-42
Motiva Star 12	Group II	PD-610	-33	-33	-33	-33	-33

PPD Screening – Phase 2

- Top treat finished formulas (provided without PPD) with PPD
  - Various components will affect cold temp. performance and the best choice of PPD
    - Base oil blends, friction modifiers (worse PP), PMA VM (better PP)
    - Some additive packages contain a PPD (common with ATF)

Finished Lubricant	PPD=	0.0%	0.1%	0.2%	0.3%	0.5%	0.7%	1.0%	1.5%	2.0%
SAE 30 Transmission Oil	PD-610	-18	-27	-27	-30	-30	-33	-33	-	-
SAE 20W50 Engine Oil	PD-610	-21	-33	-33	-33	-36	-36	-39	-	-
80W90 GL-5 Gear	PD-610	-21	-21	-30	-36	-36	-36	-36	-	-
85W140 Gear	PD-610	-18	-	-	-24	-24	-24	-27	-30	-30

PPD for Brookfield Visc.

- PPD selection can affect many cold temperature tests
- D2983 Brookfield Viscosity (spec for gear oils, tractor, some HF):

Case 1: 80W90	Functional PD-610	Competitor PPD
Pour Point, D97	-36C w/ 0.5wt%	-36C w/ 0.5wt%
-26C BF Visc (D2983)	**49,700 cP**	139,000 cP

Case 2: Tractor HF	Functional PD-610	Competitor PPD
Pour Point, D97	-39C w/ 0.2wt%	-39C w/ 0.2wt%
-35C BF Visc (D2983)	**32,200 cP**	57,000 cP

Brookfield Selectivity

- -40C D2983 Brookfield on Group II and III base stock blends for 75W:

	Gr. II	**Gr. III**	**Gr. III**	**Gr. III+**
Base Stock	Gr.II+BS	Yubase	Motiva HVI	Adbase
wt% PPD	0.5	0.1	0.1	0.1
PPD	**D2983 Brookfield, -40C, cP**			
PD-610	**93100**	**84900**	12100	42900
PD-620	110600	88300	11300	41900
PD-630	256200	89100	**7300**	**14700**
Competitor A	112500	161300	16900	82000
Competitor B	105800	96500	25300	93300
Competitor C	112500	91800	13200	43200

VI Improvers as PPD

- High treat of PMA VI improvers will also provide inherent PP depression
  - MH-2000 in an HF
  - MG-3000 in a 75W gear oil
  - MD-9000 in an ATF
  - Etc.
- At least 1wt% PMA VI improver to see good PPD effect (vs. 0.1-0.5% PPD)
- May require a top treat of 'true PPD' to meet cold performance (75W)

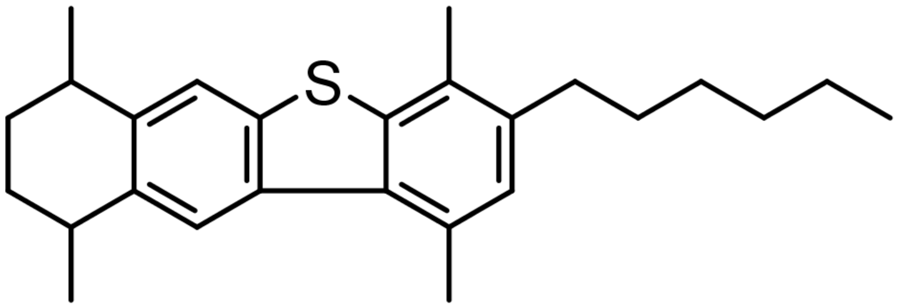
Why Are PPDs Selective to Base Stocks?

(Advanced Look)

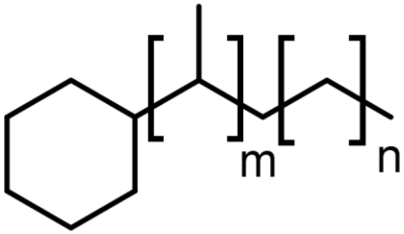
Structure of Group I, II, III

- Carbon-13 NMR identifies types and connectivity of carbon atoms
- GPC and MS identify molecular weights

Solvent Extraction (Group I)

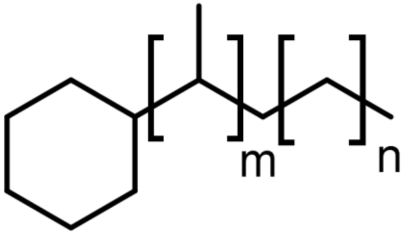


Hydrotreated (Group II)



m < n

Hydrocracked (Group III)

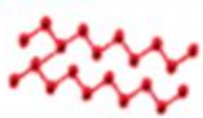


m > n

Espada, J. J. *Energy & Fuels, 23(2), 888–893.*
Abdul Jameel, A.G. “Lube Products: Molecular Characterization of Base Oils.” Encyclopedia of Analytical Chemisty (2018).

Why Different Stocks?

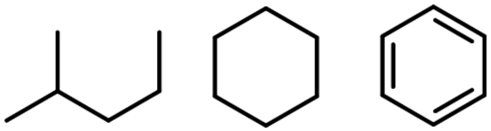
Lubricant Performance of Various Hydrocarbons Found in Crude Oil

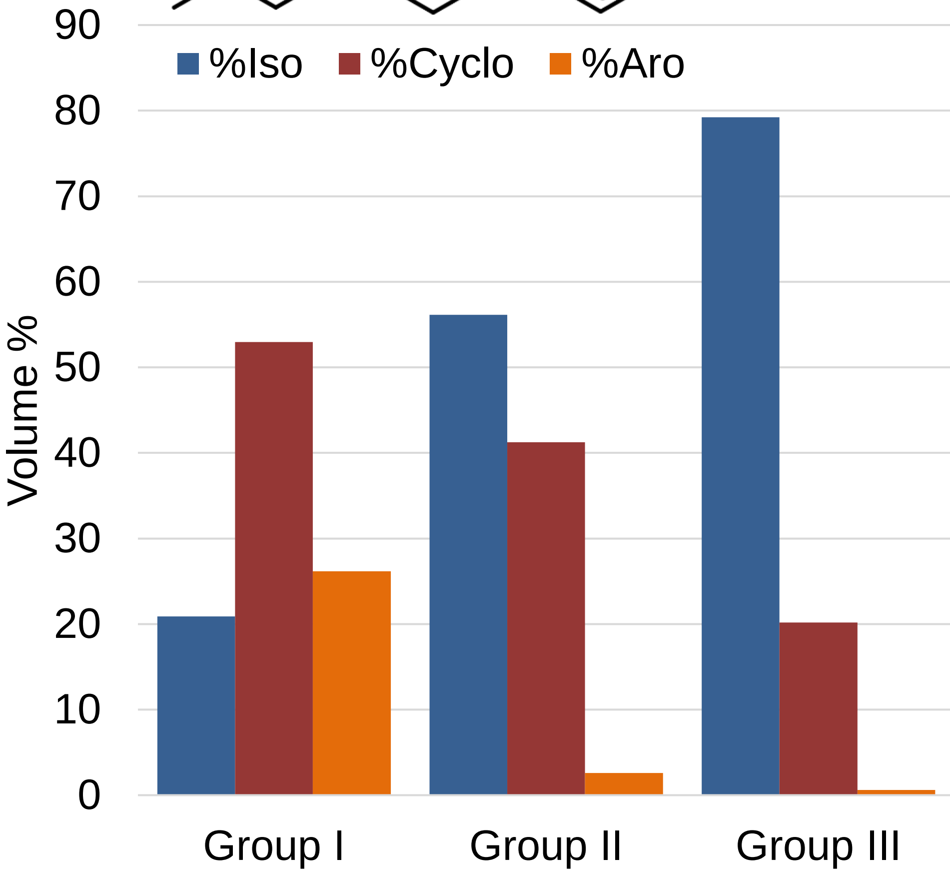
Molecule	Structure	VI	Pour point	Oxidation	Solubility	Toxicity
n-paraffin		Excellent	Poor	Excellent	Poor	Low
Isoparaffin		Good/ excellent	Good	Excellent	Good	Low
Single-ring naphthenic		Good	Good	Good	Good	Low
Multiring naphthenic		Poor	Excellent	Good	Excellent	Low
Alkylbenzene		Good	Excellent	Good	Excellent	Moderate
Polycyclic aromatic		Poor	Poor	Very poor	Good	Very high
Polyalphaolefin		Excellent	Excellent	Excellent	Good/ poor	Low

- Factor in “Cost” and no single base stock can meet every need

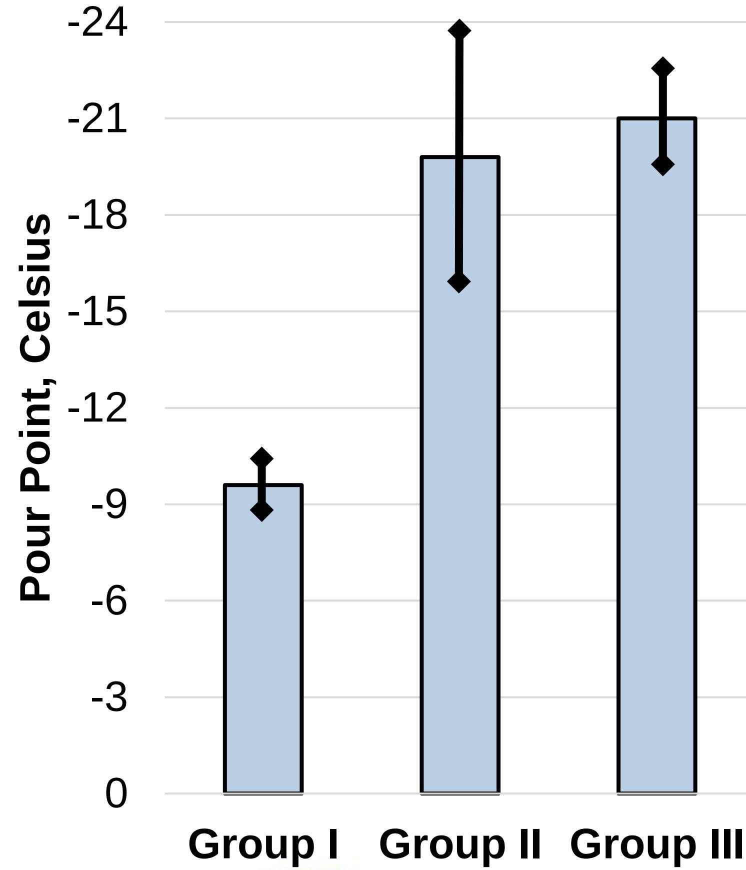
Pirro, D. M., Webster, M. & Daschner, E. *Lubrication Fundamentals, Revised and Expanded*. (CRC Press, 2017), pg 19

Distribution of Groups





Averages for 5 base oils per Group



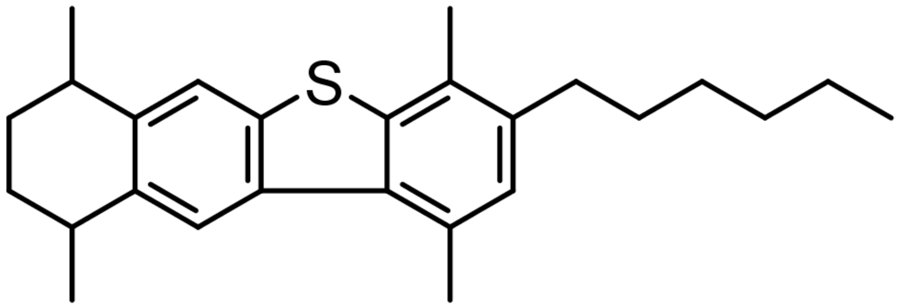
Espada, J. J. *Energy & Fuels, 23(2), 888–893.*
Abdul Jameel, A.G. "Lube Products: Molecular Characterization of Base Oils." Encyclopedia of Analytical Chemisty (2018).

Gr I / II / III PPD Design

- Different structures necessitate different PPDs
- Based on what's been discussed and the properties of Group I / II / III:

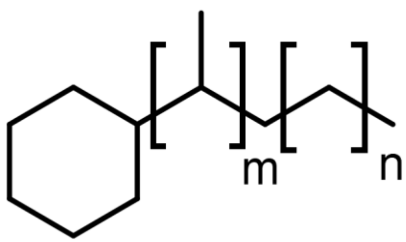
PPD Design

Group I



Mix of short (polar) and long alcohols

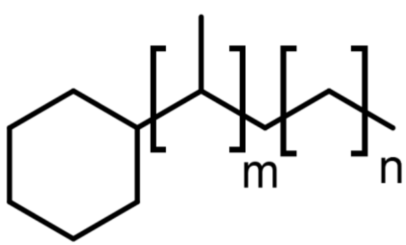
Group II



m < n

Long linear alcohols

Group III



m > n

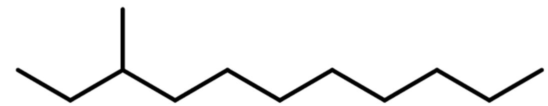
<u>Branched</u> alcohols

Ray, S. S. (2009). "Effect of aromatics and iso-alkanes on the pour point of..." Fuel, 88(9), 1629–1633.
Pillon, L. Z. (2002). "USE OF DSC… HYDROCRACKED BASE STOCKS…" Petro. Sci. and Tech., 20(1-2), 101–111.

Wax and Isomerization

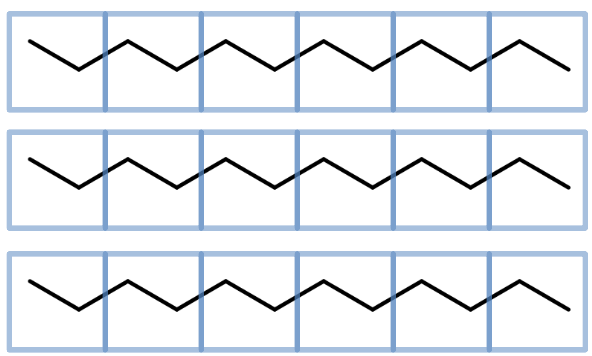
- N-Alkanes (linear, “wax”)

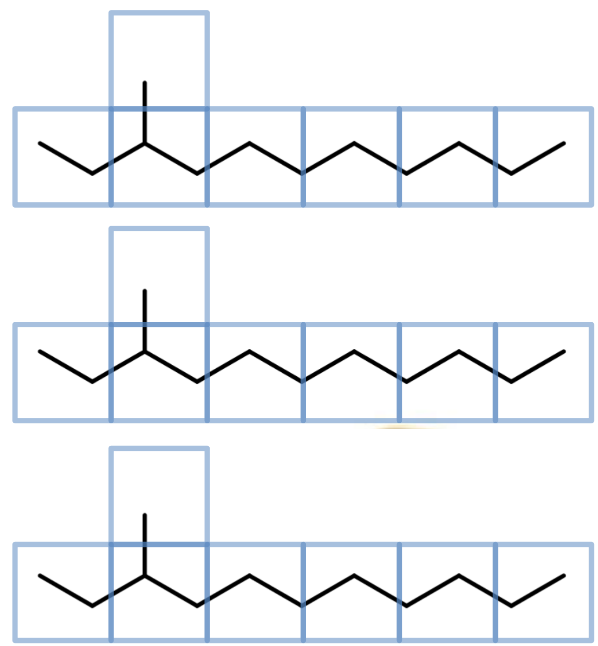
- Iso-Alkanes (branched, isomers)



- N-alkanes generally have higher melting points (waxier) than iso-alkanes
  - A small amount of branch points act as defects in a wax crystal

Crystalline “Waxy”

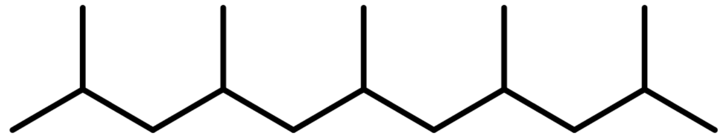




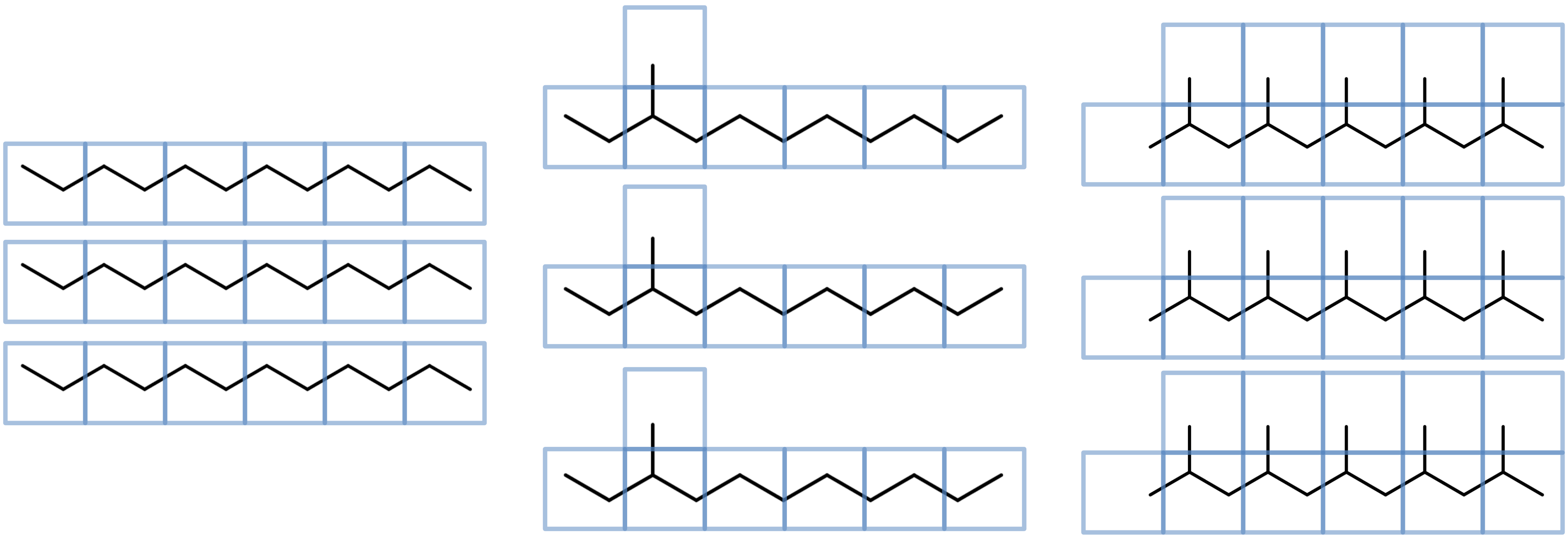
Disordered

Group III PPDs

- Why do highly isomerized oils (Group III / III+) still need PPD?



- *If structure is more branched than not then a branch is no longer a defect!*
  - Order from crystallinity worsens at low temp, inhibits pour point



Ordered “Waxy”

Disordered

Ordered Waxy Again?

Variations Within Group

- **Base oils within the same Group (I / II / III) may respond different to 'optimized' PPDs**

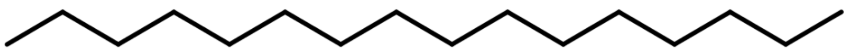
- Base stocks vary by location and type of crude oil feedstock
- New technology and old tricks constantly in flux to make more for less
- New feedstock sources
- Catalyst design and reaction conditions
- Alternative feedstocks:
  - Recycled slack wax or reactor bottoms from petroleum refining
  - Upgrading of less refined oils (I → II → III)
  - Synthetics using polymerized methane (GTL) or olefins (PAO)

- **Improvement to low temp from isomerization and branching will vary heavily (next slides)**

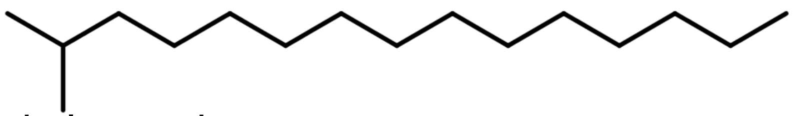
Branch Position Matters

- 30° to 50° depression in melting point for n-C16 vs. iso-C16
  - Still a -10 to -30C pour point; better but not great for most lubricants
  - Increases again as the molecular becomes symmetric

1-methylpentadecane (n-hexadecane)

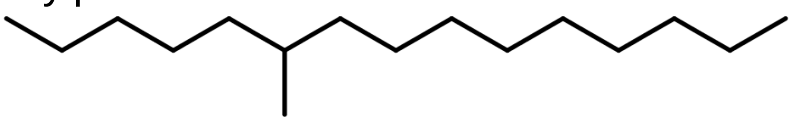


2-methylpentadecane

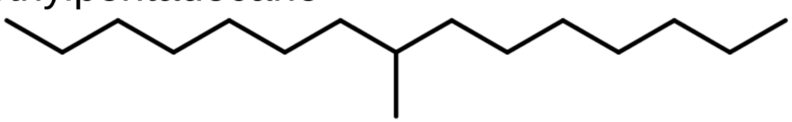


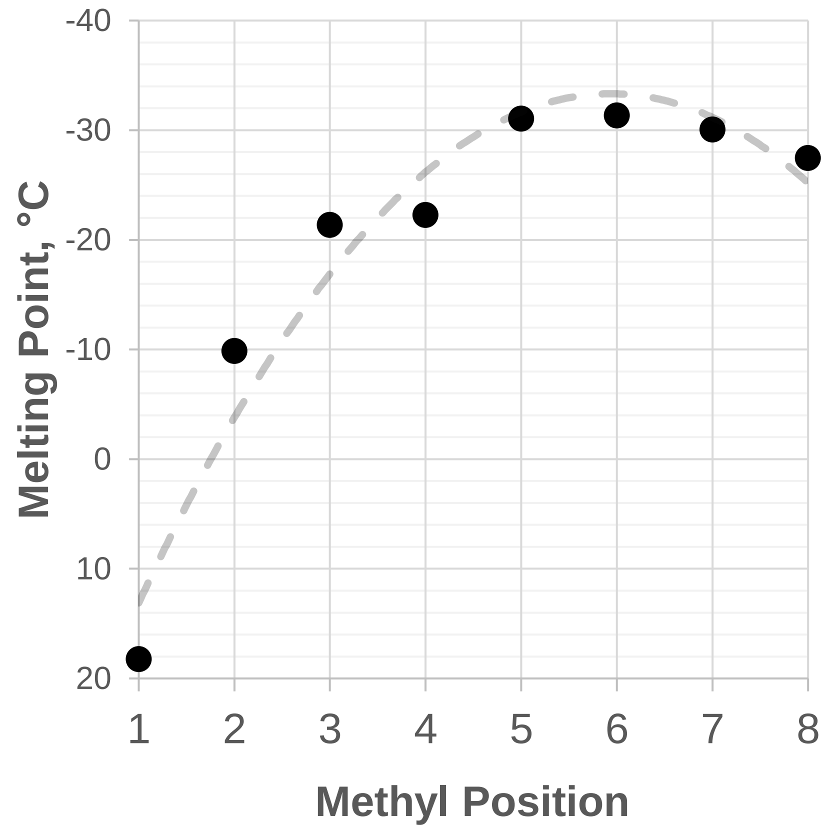
4-methylpentadecane

6-methylpentadecane



8-methylpentadecane

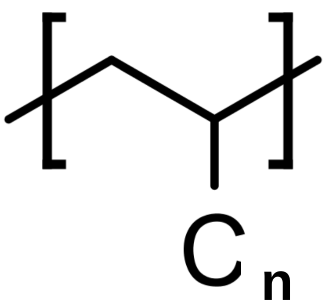


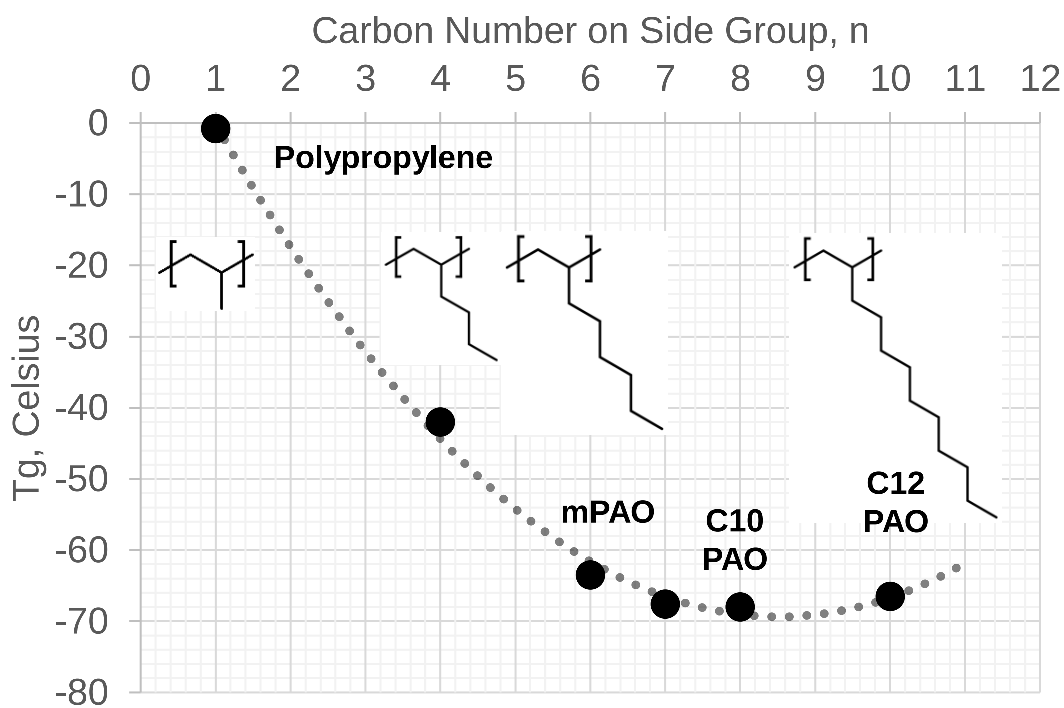


Burch, K. J., & Whitehead, E. G. (2004). "Melting-Point Models of Alkanes." J. Chem. & Eng., 49(4), 858–863.

Branch Length Matters

- Branch length provides internal flexibility and reduces crystallinity (wax)
- Group III iso-alkanes mostly methyl (C1) – still room for improvement
- Look at branch length versus T_g on a series of polymers
  - T_g – glass transition, similar to PP on molecular level for complex fluids

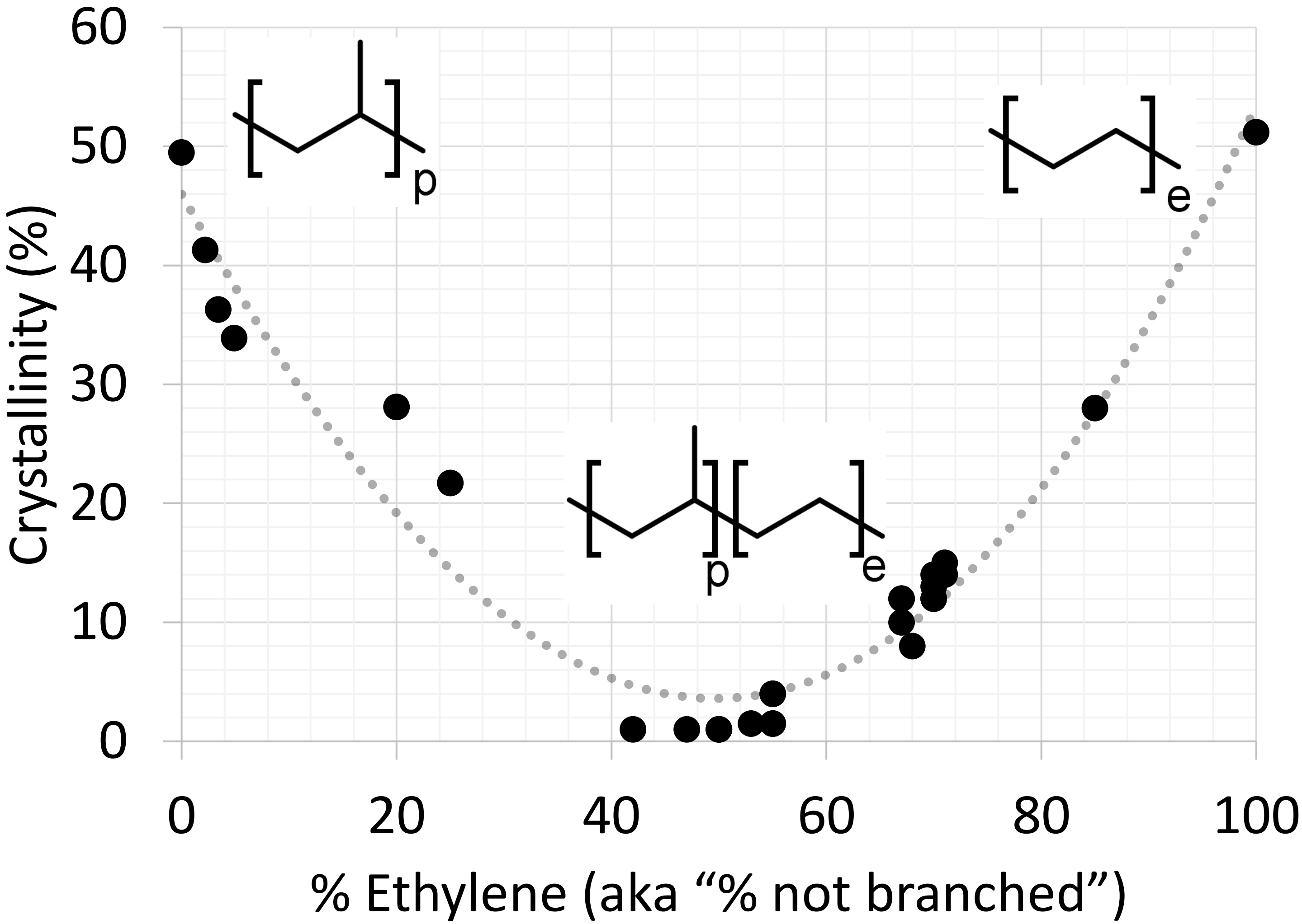




López-Barrón, C. R. (2019). Dynamic Fragility of α-Olefin Molecular Bottlebrushes. J. Poly. Sci. B: Polymer Physics.

Linear vs. Isomerization

- Extreme case – ethylene-propylene copolymers
  - Either too much ethylene OR propylene allow crystalline domains to form



New Base Oil Technologies and Their Demand On Future PPDs

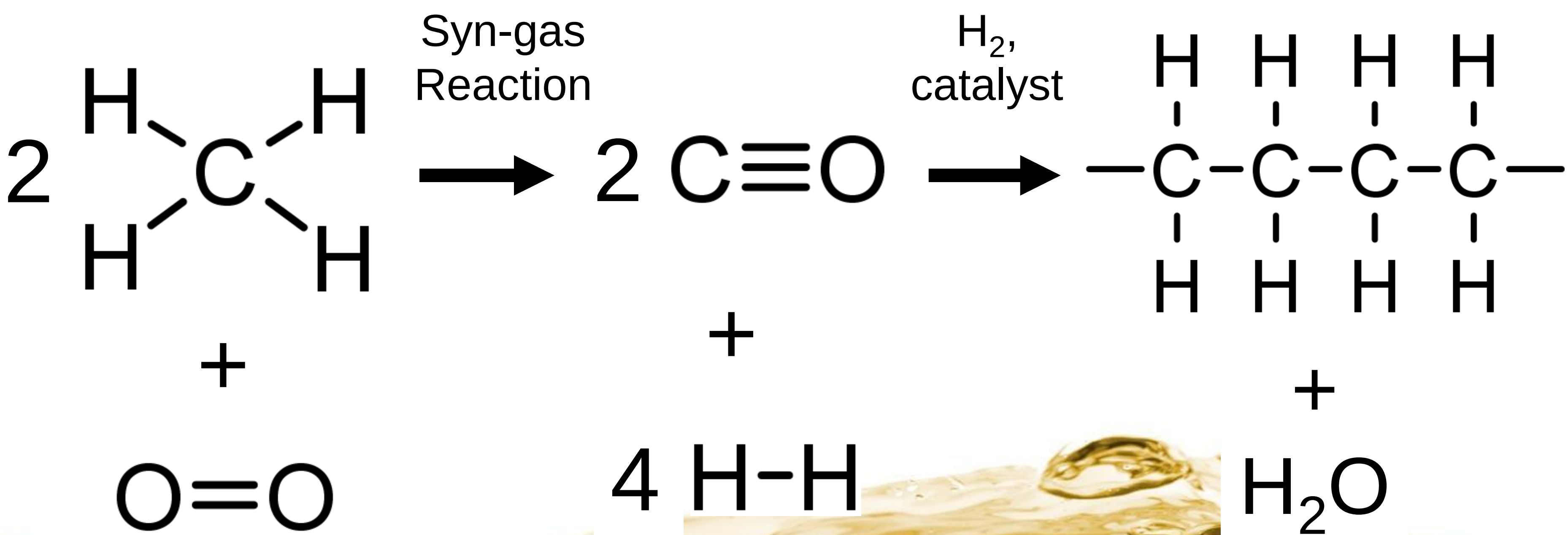
Conventional Processes

- **Vacuum distillation of crude oil**
  - Light ends sent for extraction and reaction to refine into lube oil
- **Solvent extraction (Group I)**
  - Physical separation of polar aromatics, resins, and sulfur by DMSO
- **Hydrotreating (Group II)**
  - Removes reactive impurities like sulfur, nitrogen, unsaturation
- **Hydrocracking (Group III)**
  - Able to break strong carbon-carbon bonds (naphthene rings broken)
- **Dewaxing**
  - Solvent - Physical separation at low temp with MEK and propane
  - Catalytic – Isomerize linear waxes to branched hydrocarbons
- **Hydrofinishing**
  - Additional treatment of color by removing aromatics/S/N with H_2

Kramer, D. C., "The Evolution of Base Oil Technology," Turbine Lubrication in the 21st Century, ASTM STP #1407

GTL Group III Feedstocks

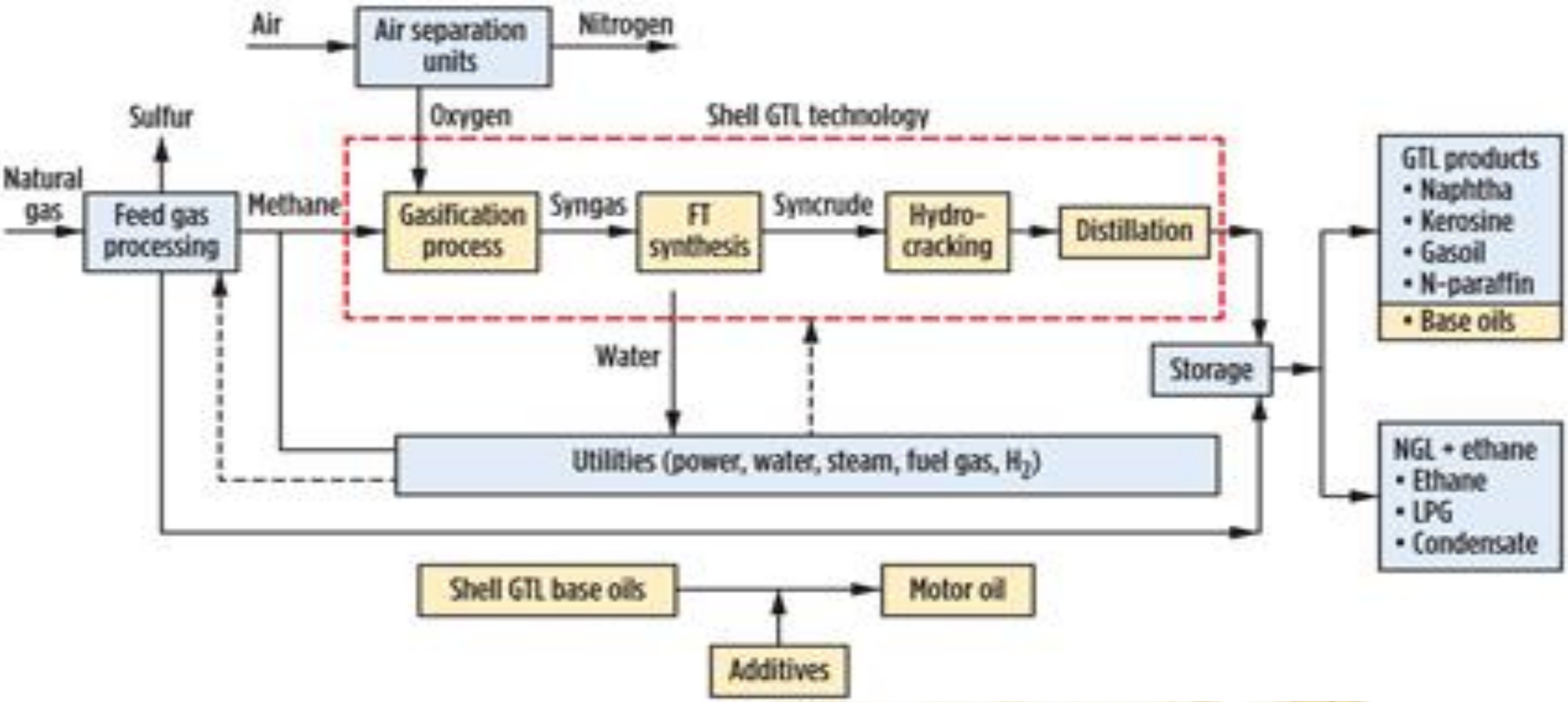
- Natural **gas** converted to **CO** (syn gas)
- **CO** converted to liquid hydrocarbon **polymers** (Fischer-Tropsch)
- **Polymers** (“syncrude”) are hydrocracked and dewaxed into Group III **GTL**



Mahmoudi, H. "A review of Fischer Tropsch synthesis process…” Biofuels Eng. 2017; 2:11-31

Shell GTL Process

- Shell GTL (PurePlus process) in Qatar
  - Economics just right on natural gas pricing



Gullapalli, S. "GTL innovation produces clean base oils from natural gas." Gas Processing News.