Washington State DOT Biodiesel Workshop

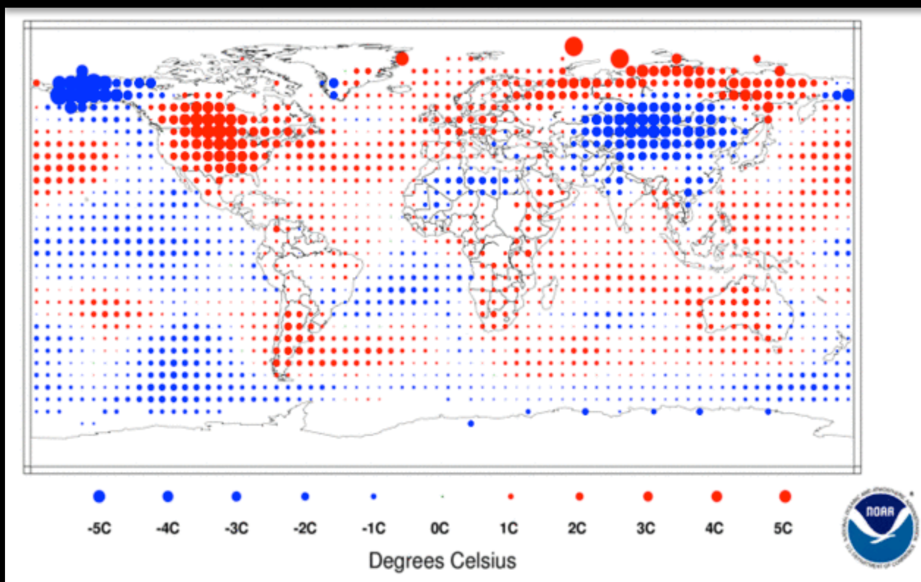
Dr. Andrew McKnight

Innospec Fuel Specialties

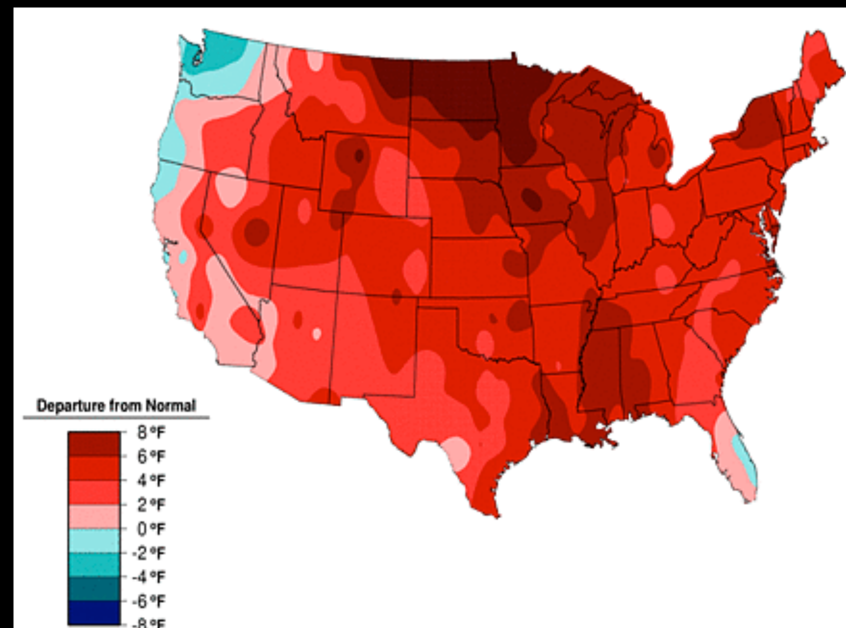
March 22, 2012

It Was a ~~Warm~~ Cold Winter!

Temperature Anomalies -- January 2012*



vs. monthly average for 1971-2000 base period



vs. monthly average for 1981-2010 base period

* source: National Climatic Center/NESDIS/NOAA

Topics

- “The Challenge of ULSD”
- Diesel Fuel Chemistry
- Effect of Fuel Composition on Low Temperature Operability
- Cold Flow Improvers – How do they work?
- The Challenge of Biodiesel
- Washington State Winter 2011-12 Cold Flow Performance

The Challenge of ULSD

The Challenge of ULSD

What happened to the fuel during the conversion?

LOW SULFUR DIESEL

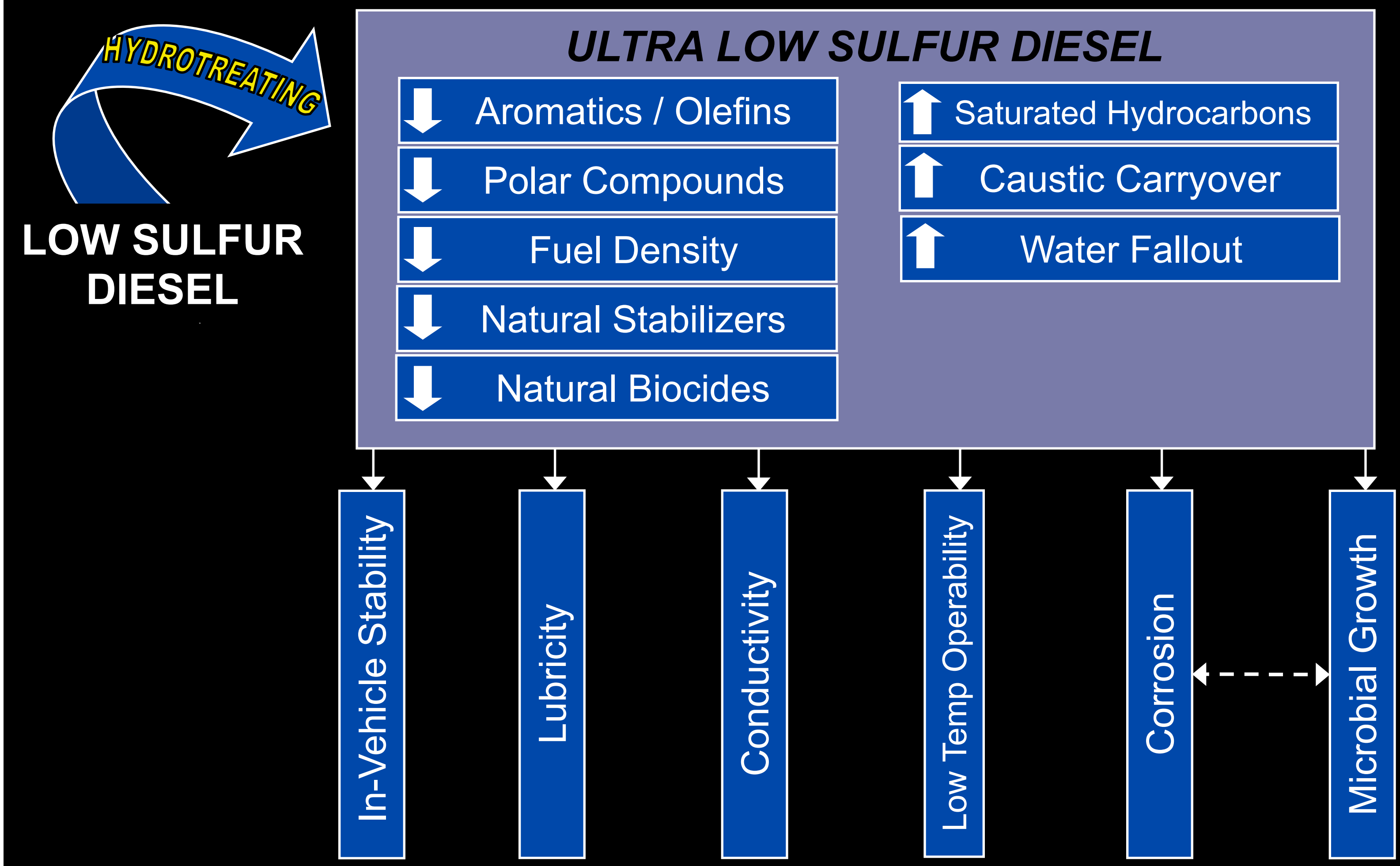
ULTRA LOW SULFUR DIESEL

- ↓ Aromatics / Olefins
- ↓ Polar Compounds
- ↓ Fuel Density
- ↓ Natural Stabilizers
- ↓ Natural Biocides

- ↑ Saturated Hydrocarbons
- ↑ Caustic Carryover
- ↑ Water Fallout

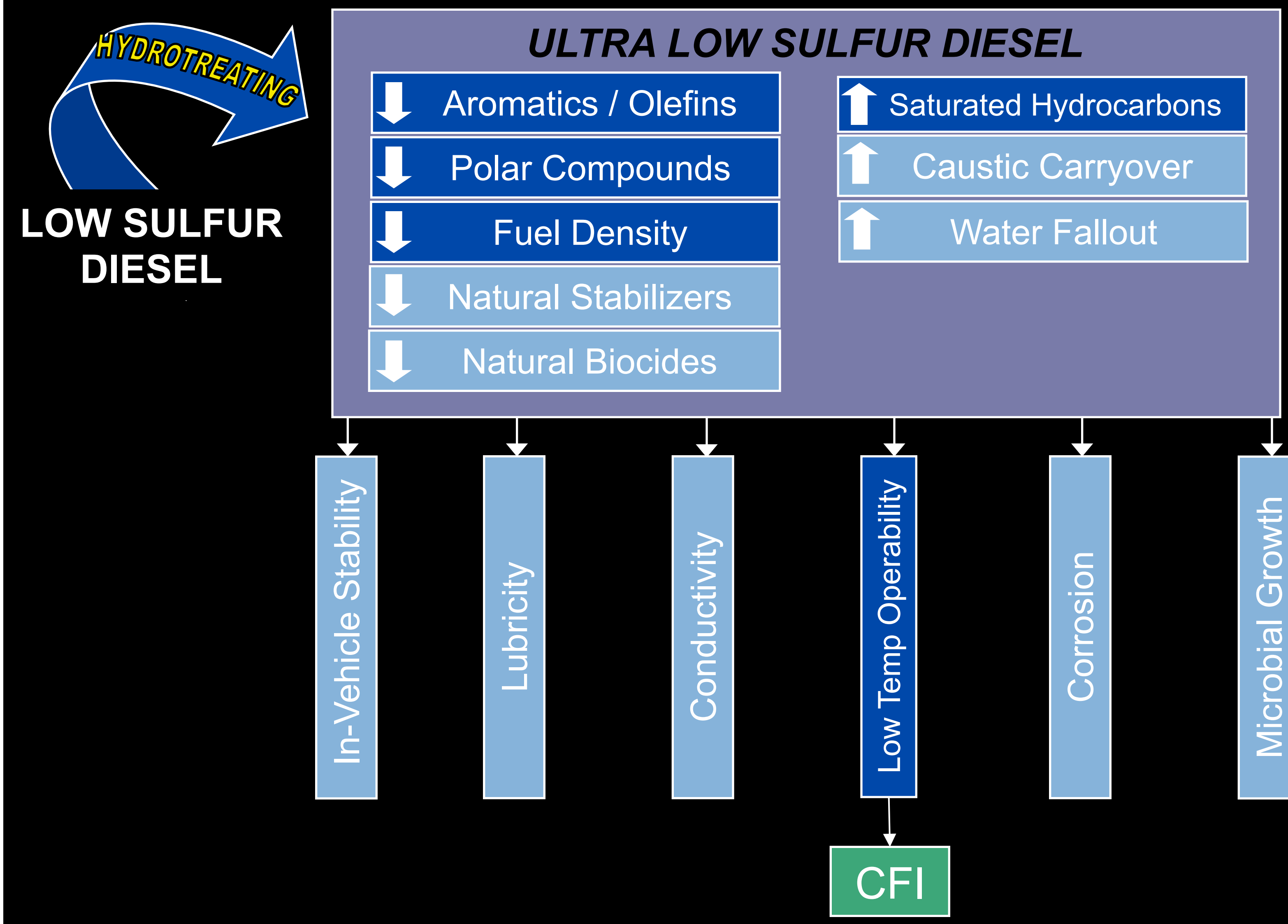
The Challenge of ULSD

What happened to the fuel during the conversion?



The Challenge of ULSD

What happened to the fuel during the conversion?



Diesel Fuel Chemistry

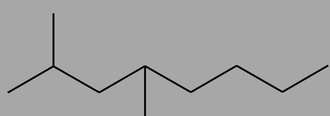
Diesel Fuel...

... Is a Mix of Several Types of Hydrocarbons

Selected Hydrocarbon Types

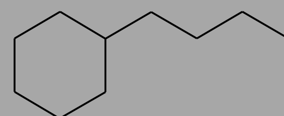
Paraffins

n-Decane

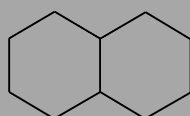


iso-Decane

Naphthenes

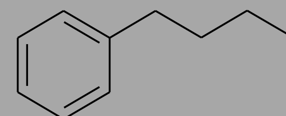


Butylcyclohexane

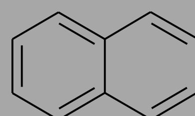


Decalin

Aromatics

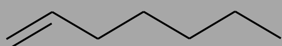


Butylbenzene



Naphthalene

Olefins



Heptene

Diesel Fuel

Straight Chain Paraffins (Wax)

5 Carbons = C_5

12 Carbons = C_{12}

16 Carbons = C_{16}

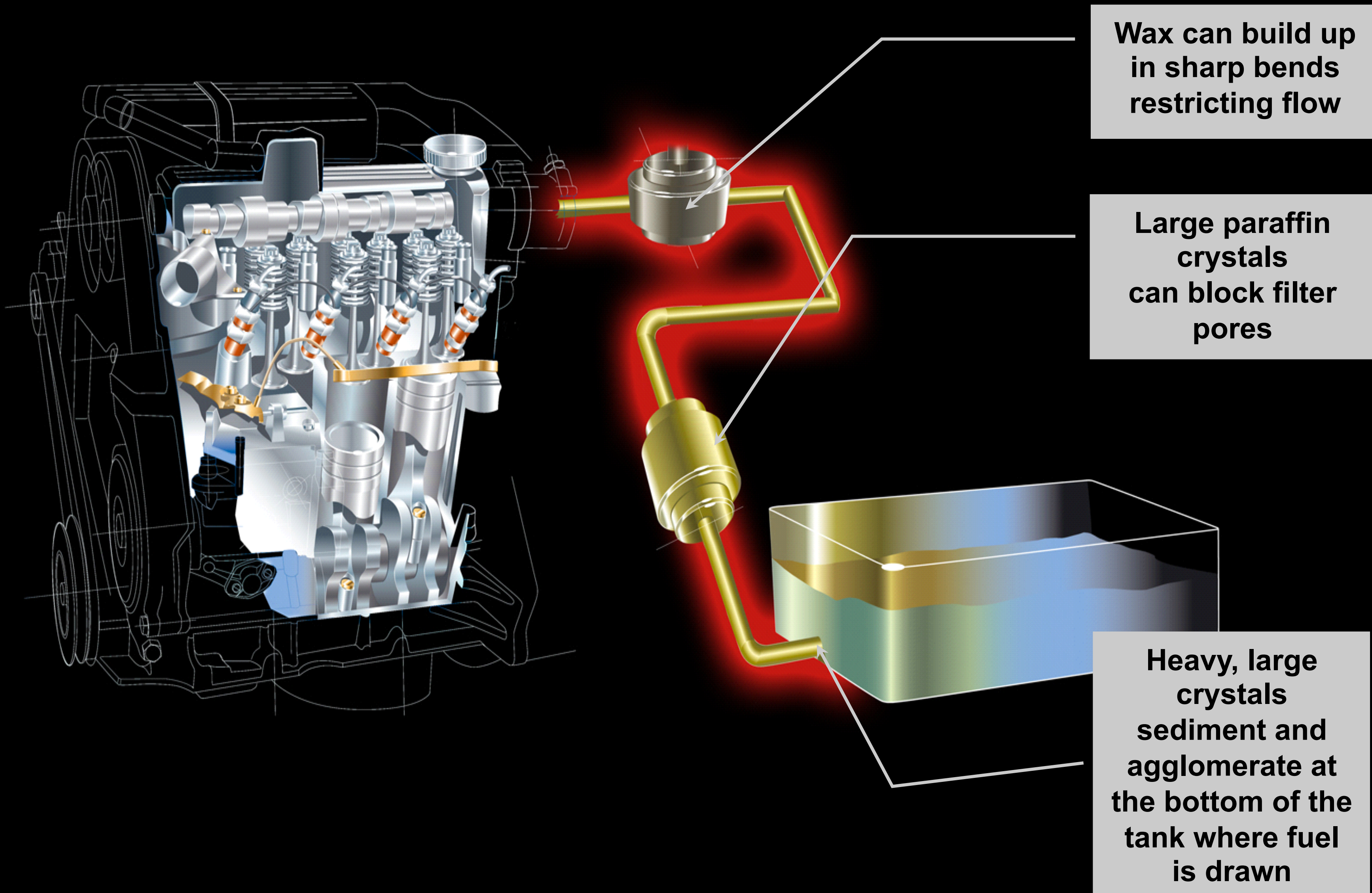
18 Carbons= C_{18}

Diesel Fuel

What Do We See When Paraffins Crystallize?

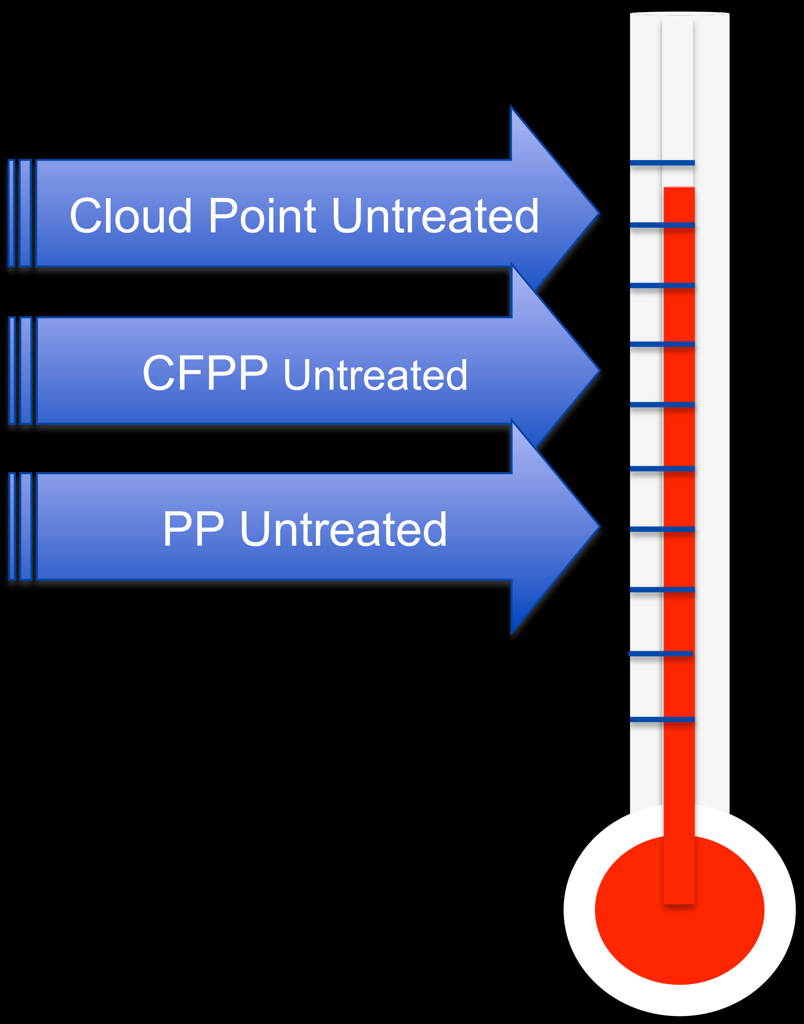
Diesel Fuel

Where Does Crystallization Affect Vehicle Operation?



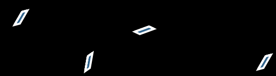
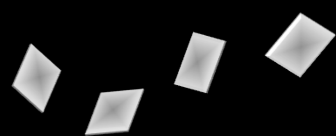
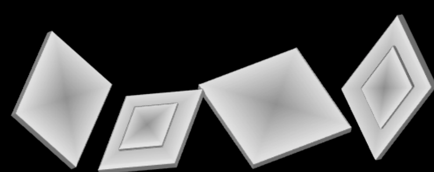
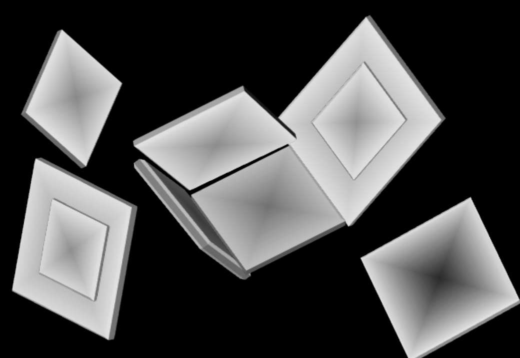
Diesel Fuel

General Low Temperature Operability Terms



Diesel Fuel

What's Really Happening When Paraffins Crystallize?

TEMPERATURE	Morphology	Phenomenon	Observation
13^{o}F		**Super saturation / Nucleation**	No Visible Crystals
10^{o}F		**Crystal growth**	**Cloud Point** Visible Crystals
7^{o}F		**Existing Crystal Grow** **Additional Nucleation Occurs**	**CFPP ?** > 0.4% wax
0^{o}F		**Larger crystals begin to adhere along the edges trapping liquid in "pockets".**	**No Flow Point** **Pour Point** Fuel solid / gelled

Cold Flow Improvers

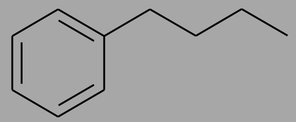
What Affects Their Response?

Fuel Composition

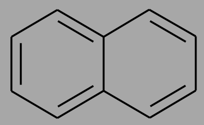
How Does it Affect Wax Crystallization?

- Solvency of the Fuel
  - Primary driver is “aromaticity”
  - Higher aromaticity ~ more wax can be dissolved at a given temperature

Aromatics



Butylbenzene



Naphthalene

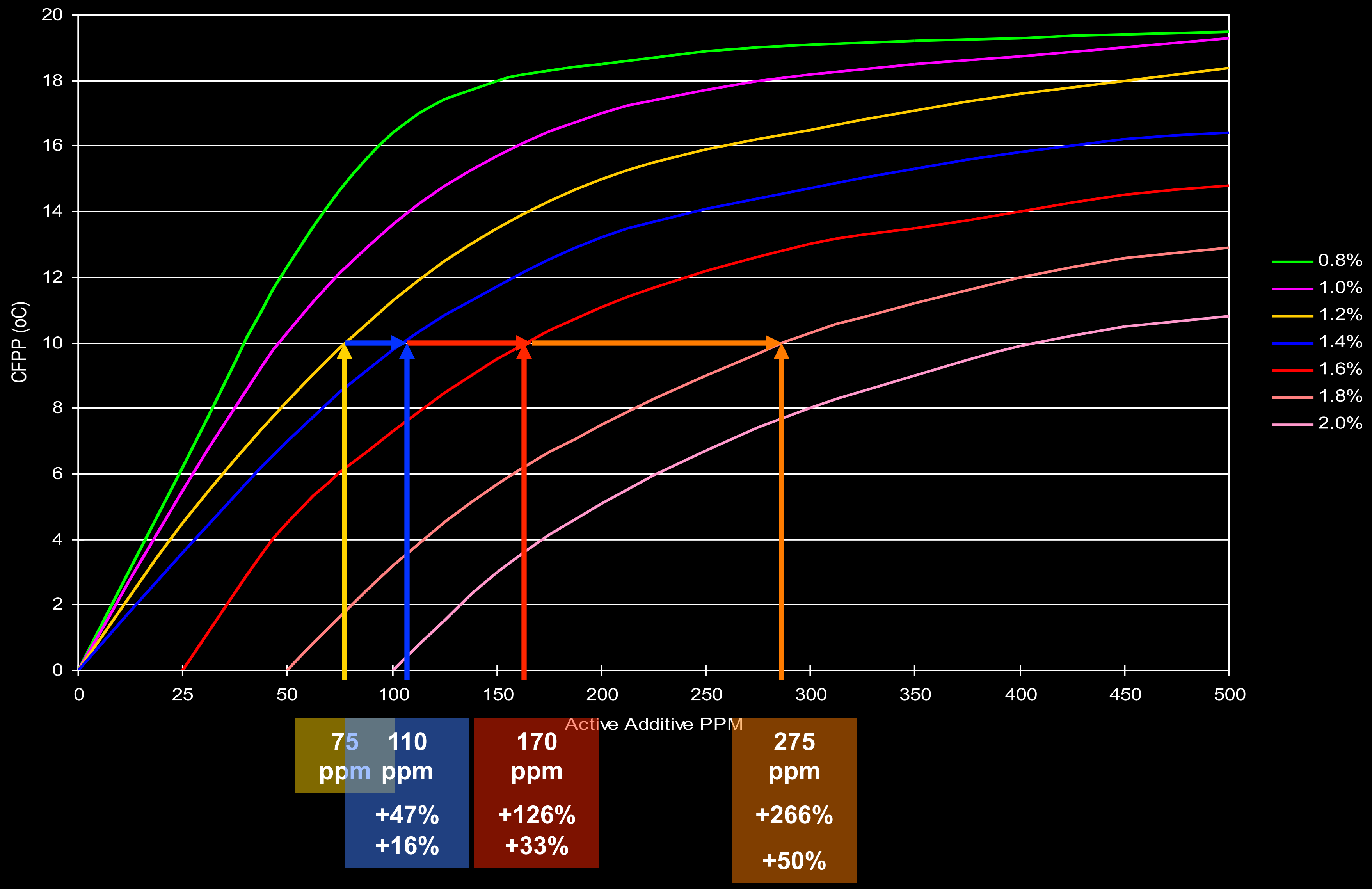
Fuel Composition

How Does it Affect Wax Crystal Growth?

- Solvency of the Fuel
  - How much wax can be dissolved at a given temperature
- Total Wax
  - How much precipitates between the cloud point and a given temperature is a critical factor in Low Temperature Operability (LTO)
  - Higher wax content → more wax near the cloud point

Fuel Composition

Total Wax Content



Fuel Composition

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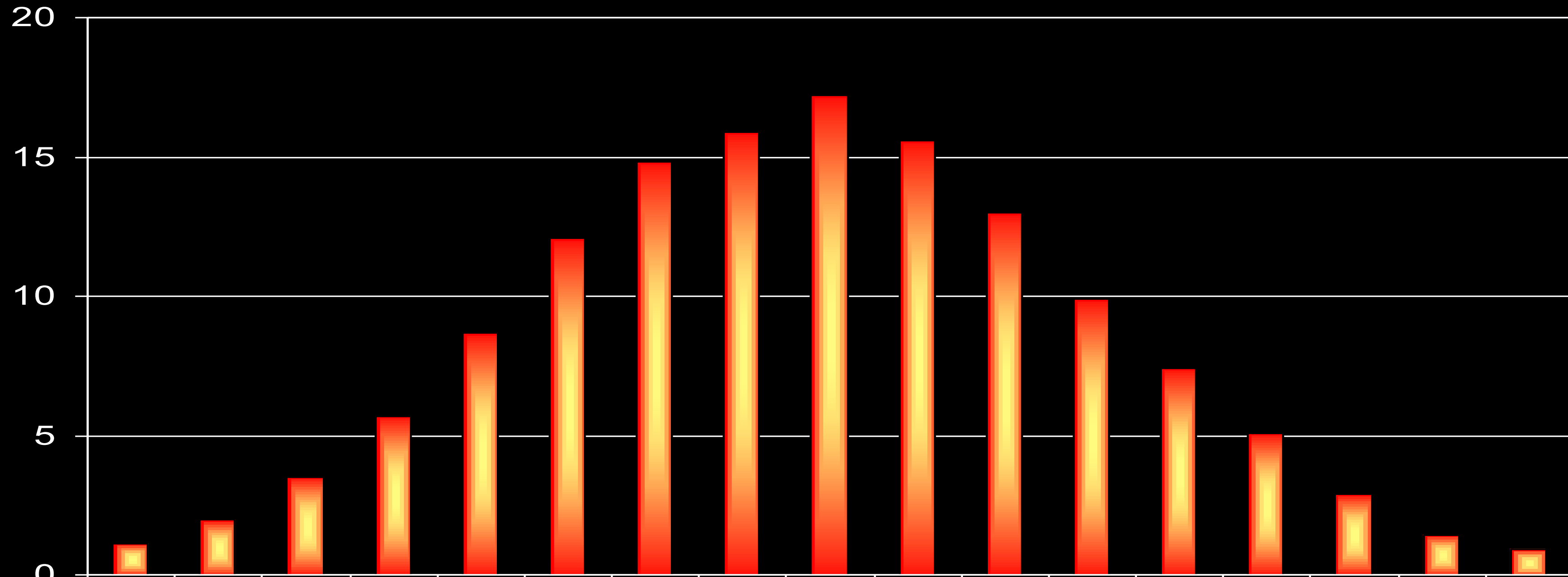
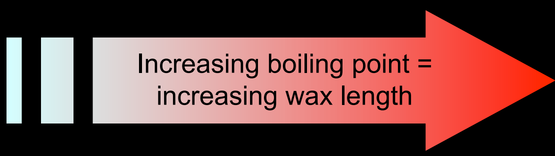
- Total Wax
  - How much precipitates between the cloud point and a given temperature is a critical factor in Low Temperature Operability (LTO)
  - Higher wax content → more wax near the cloud point
- Wax Distribution
  - The amount of each wax chain length relative to the other waxes has a dramatic impact on wax crystal formation, operability at low temperature and ability to treat with CFI

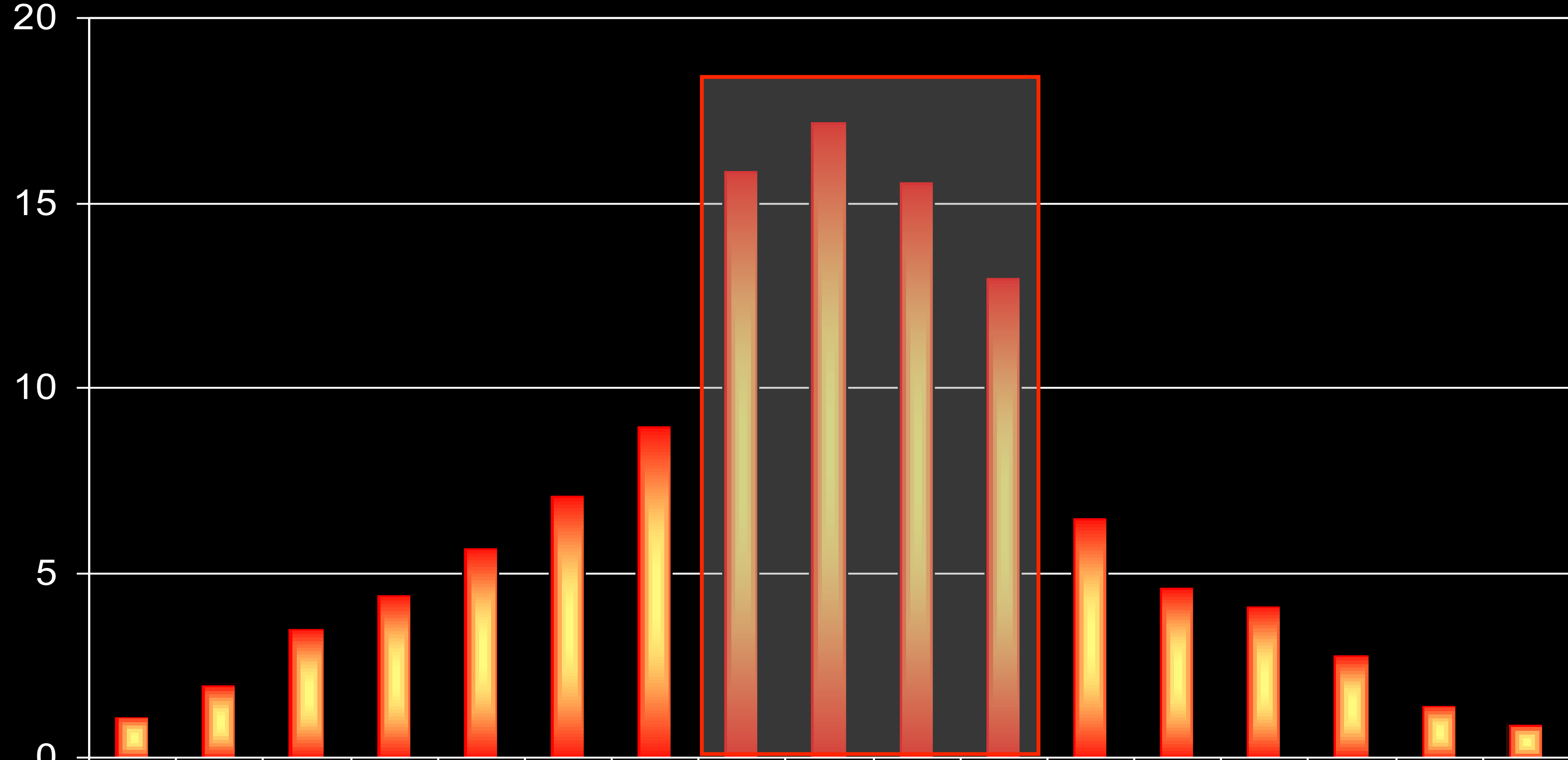
Broad Wax Distribution



	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26
Normal	1.1	2	3.5	5.7	8.7	12.1	14.8	15.9	17.2	15.6	13	9.9	7.4	5.1	2.9	1.4	0.9

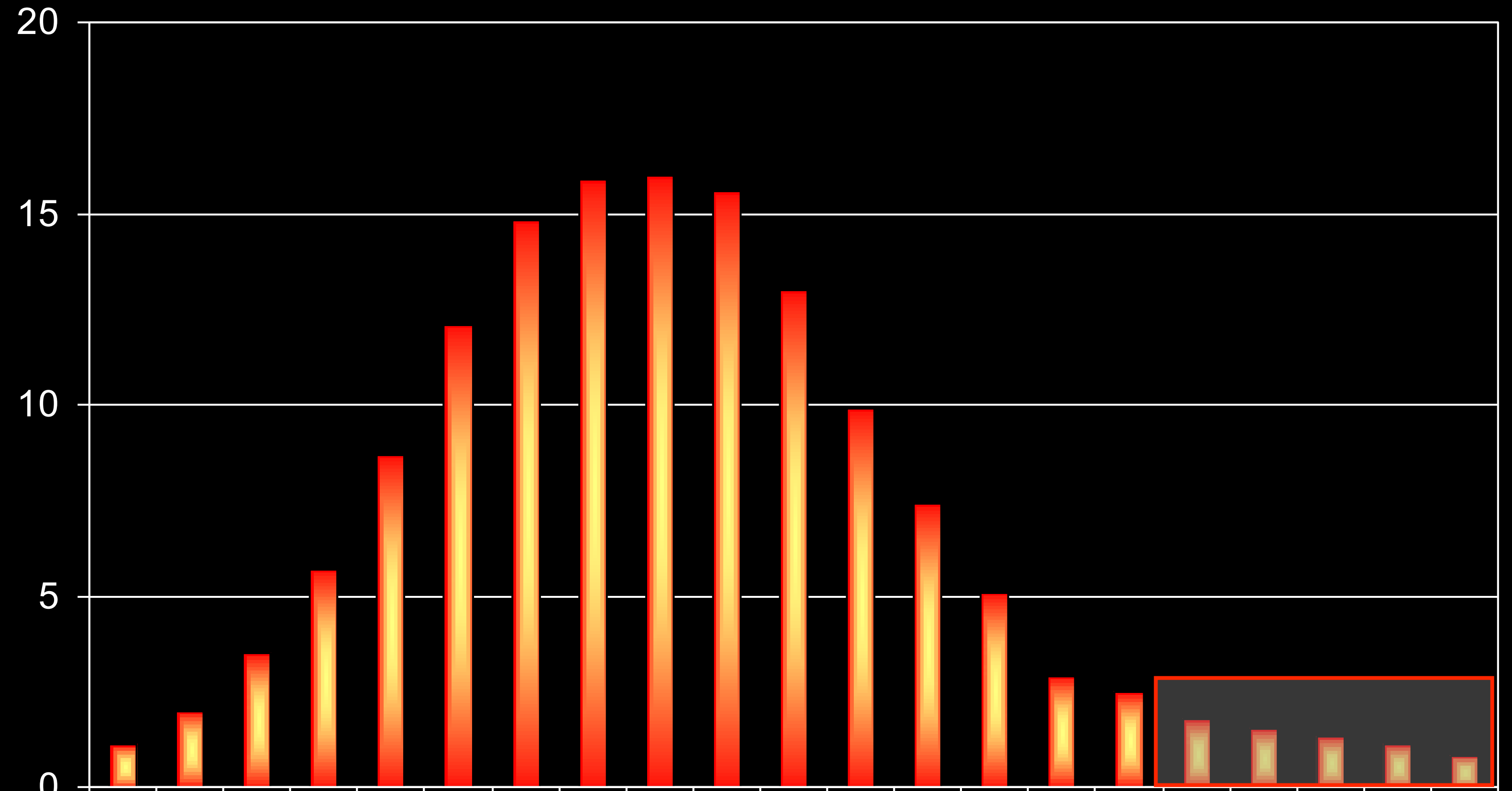


Narrow Wax Distribution



	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26
Normal	1.1	2	3.5	4.4	5.7	7.1	9	15.9	17.2	15.6	13	6.5	4.6	4.1	2.8	1.4	0.9

Heavy End Wax Distribution



	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	26	27	28	29
Normal	1.1	2	3.5	5.7	8.7	12	15	16	16	16	13	9.9	7.4	5.1	2.9	2.5	1.8	1.5	1.3	1.1	0.8

Fuel Composition

Key Points

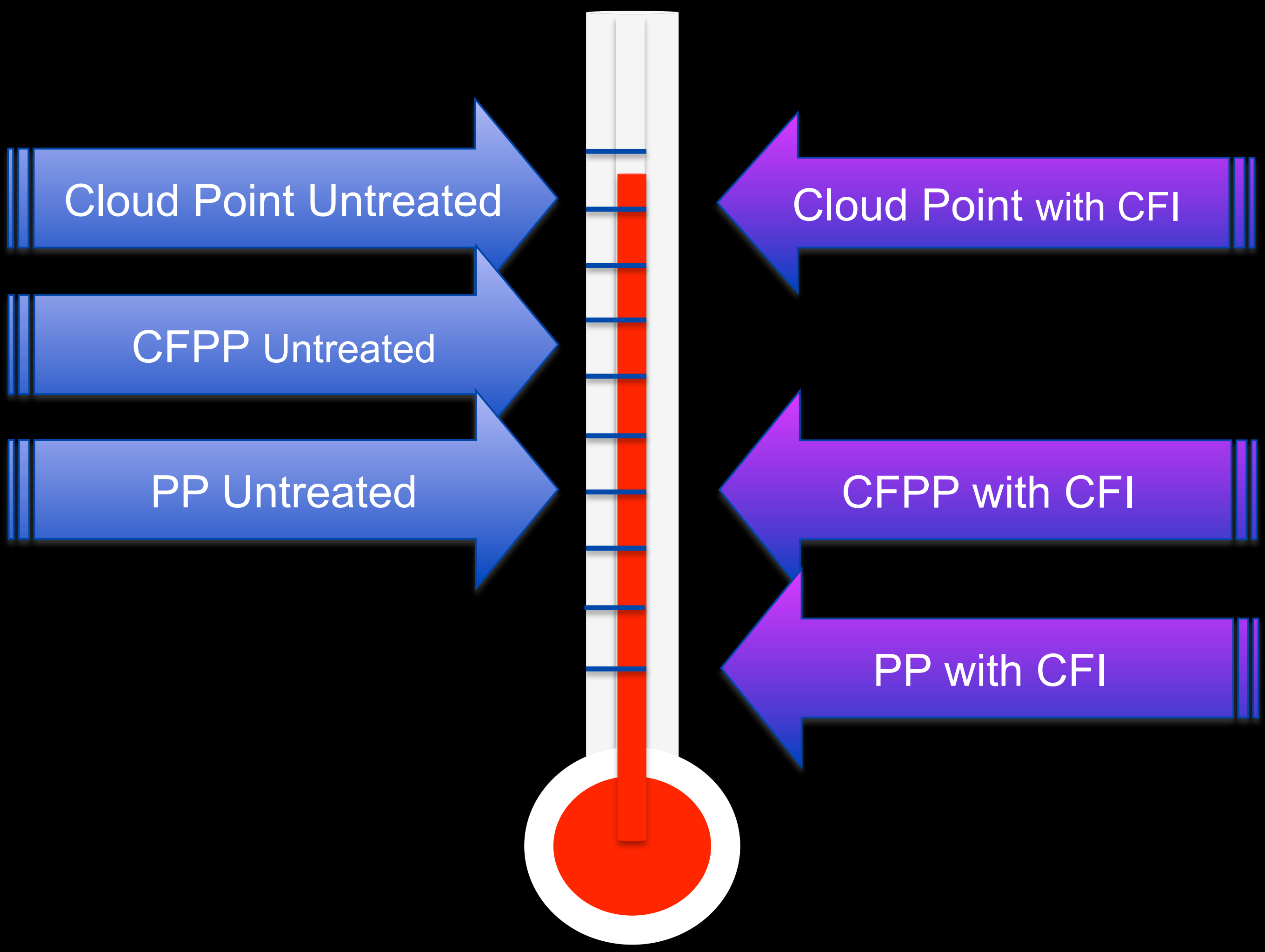
- Solvency of Fuel
- Total Wax
  - More wax requires more CFI
- Wax Distribution
  - No single CFI additive responds well in all diesel fuels.
  - Additive structure and chemistry needs to be "tailored" to the paraffin composition of the fuel to be treated

Cold Flow Improvers

How do they work?

Cold Flow Improver (CFI) Function

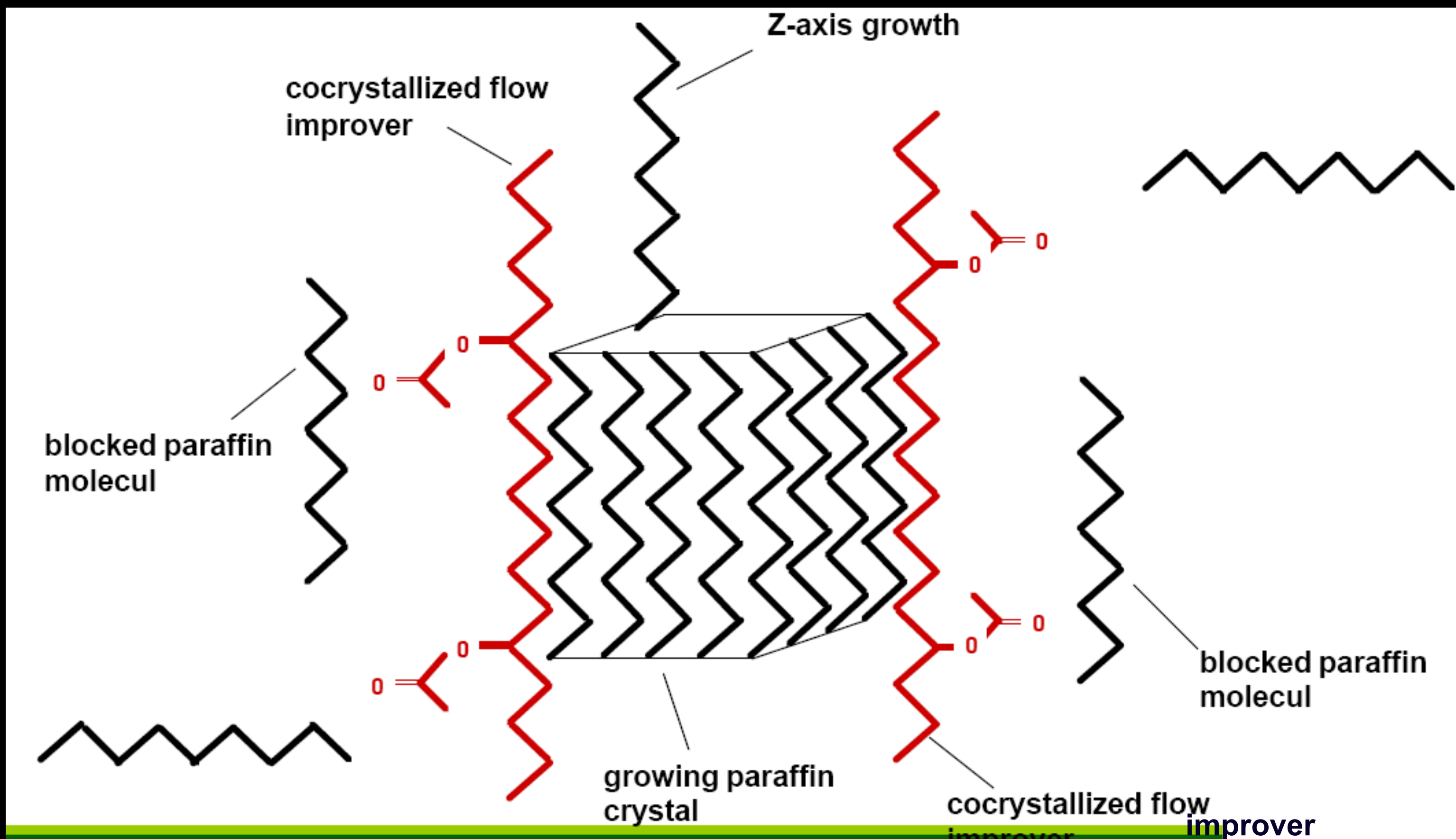
Allows operations lower than that of untreated fuels



Crystal Growth Modification

"Growth Arrest"

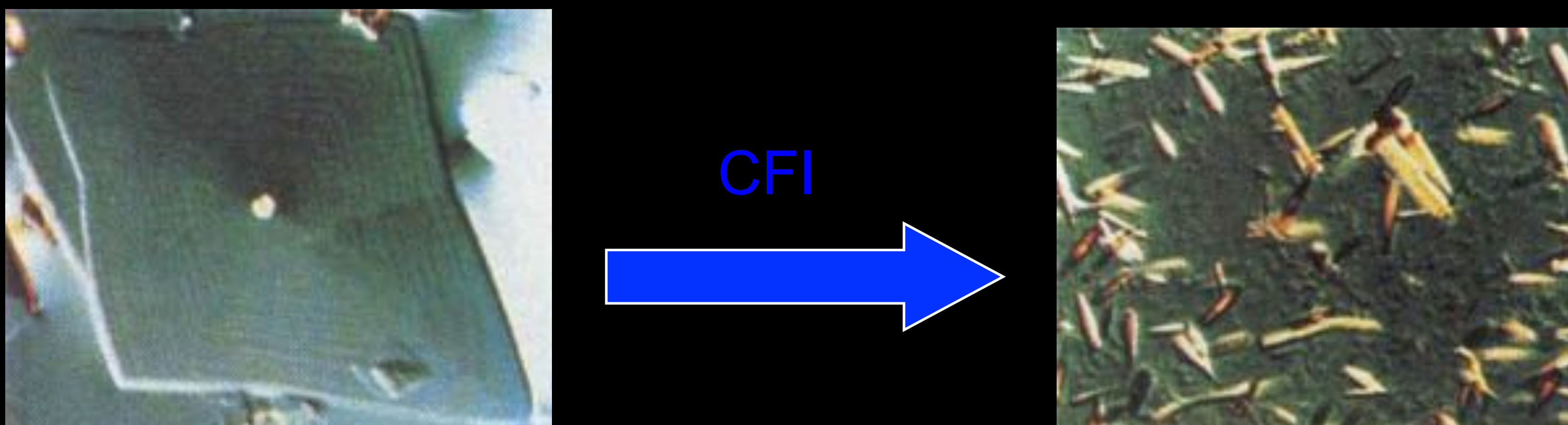
Polymer attaches to growing wax crystal surface and inhibits further wax deposition



Crystal Growth Modification

"Growth Arrest"

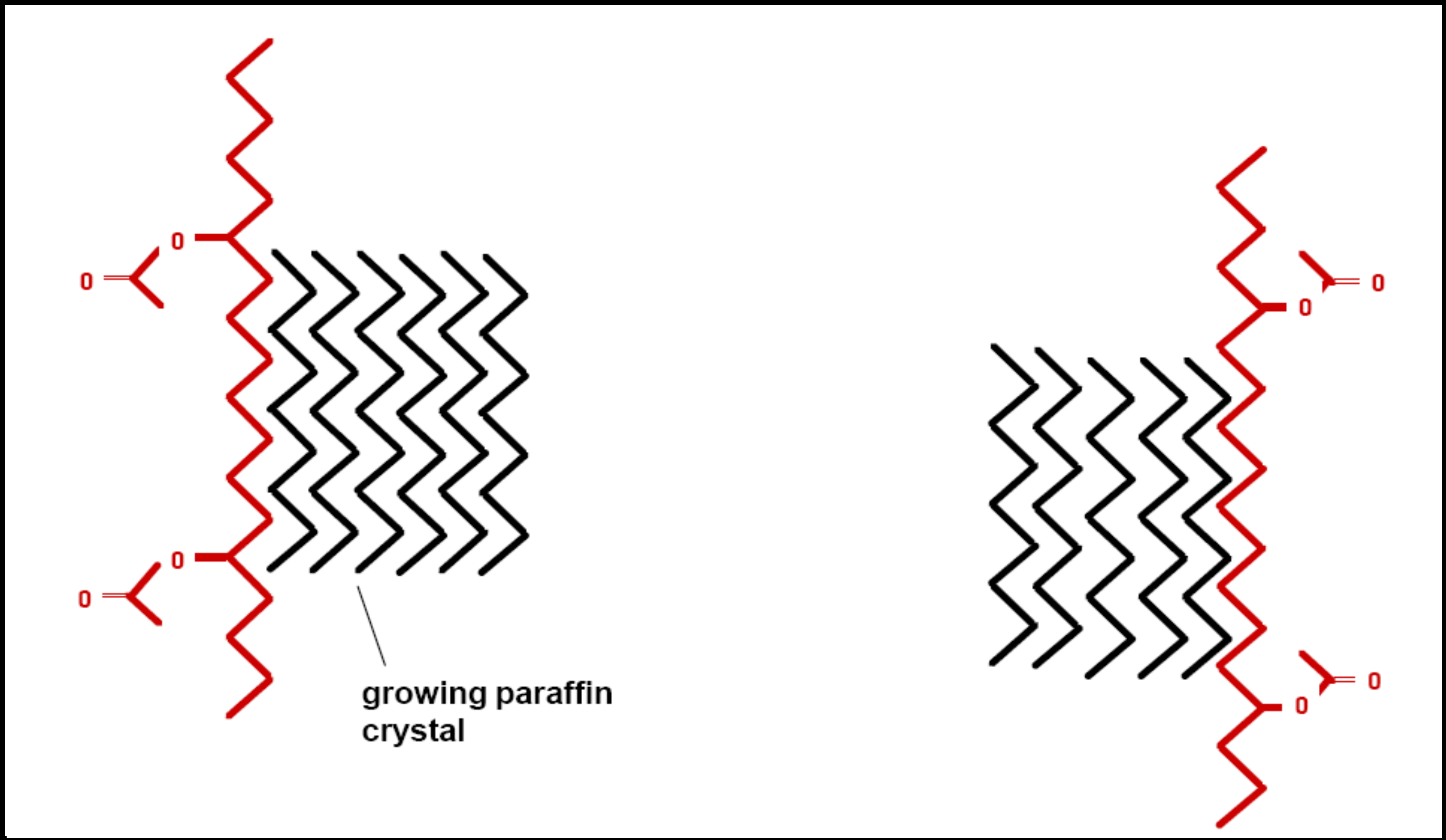
Form and size of n-paraffin crystals are influenced by adding CFI's



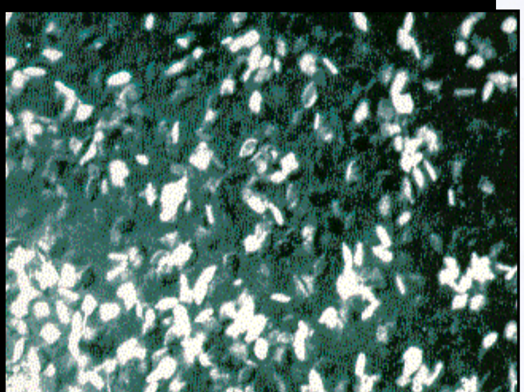
Crystallisation depends on type and amount of waxes as well as on the middle distillate oil matrix, e.g. aromatics, naphthenics

Crystal Growth Modification
"Nucleation"

- Additive precipitates from fuel before *n*-paraffins
- Provides growth / nucleation site for precipitating wax molecules



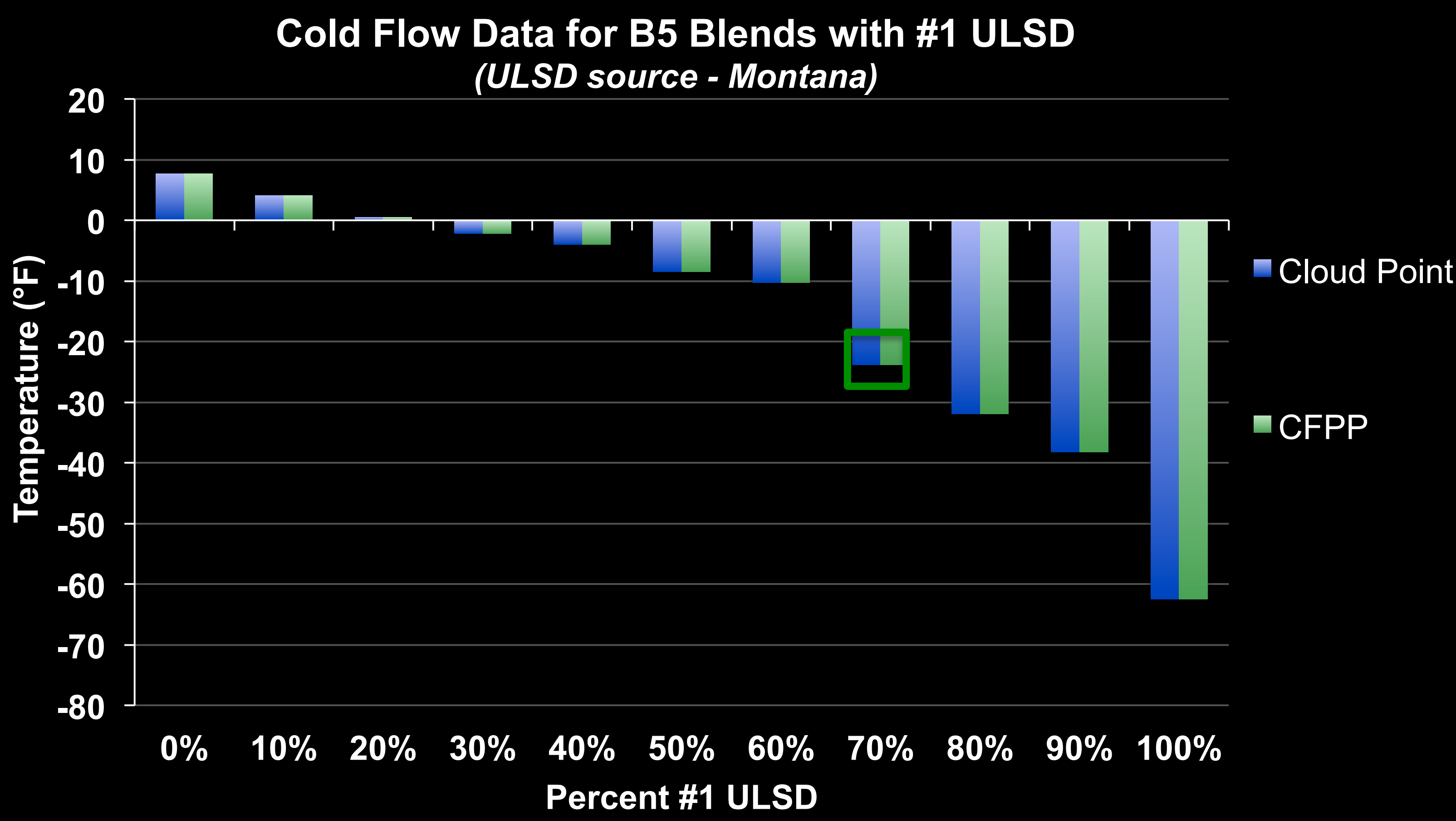
Nucleation and Filter blocking



Treated with MDFI

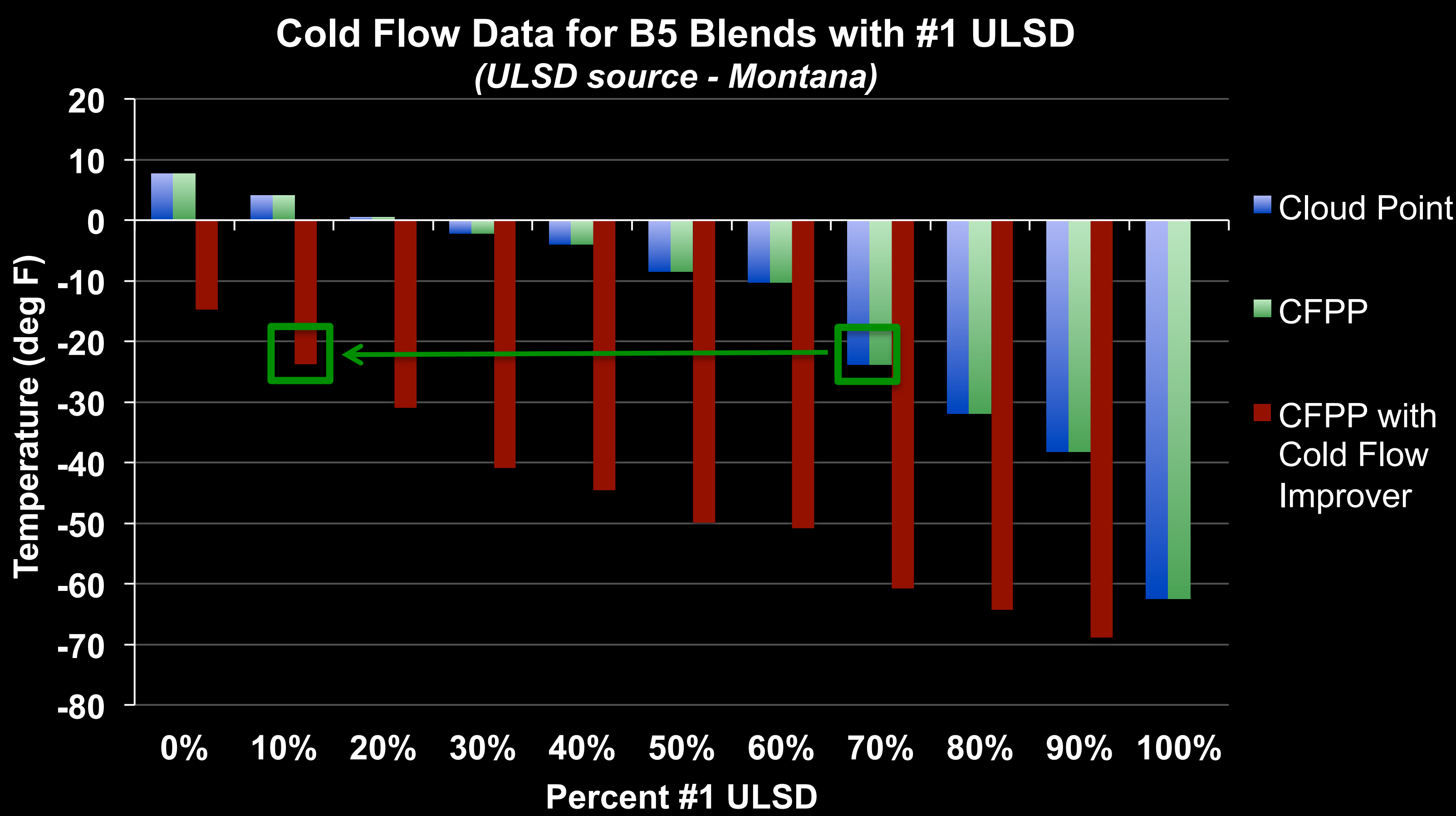
Treated with Typical Anti-Gel/PPD

Effect of Kerosene on B5 CFPP



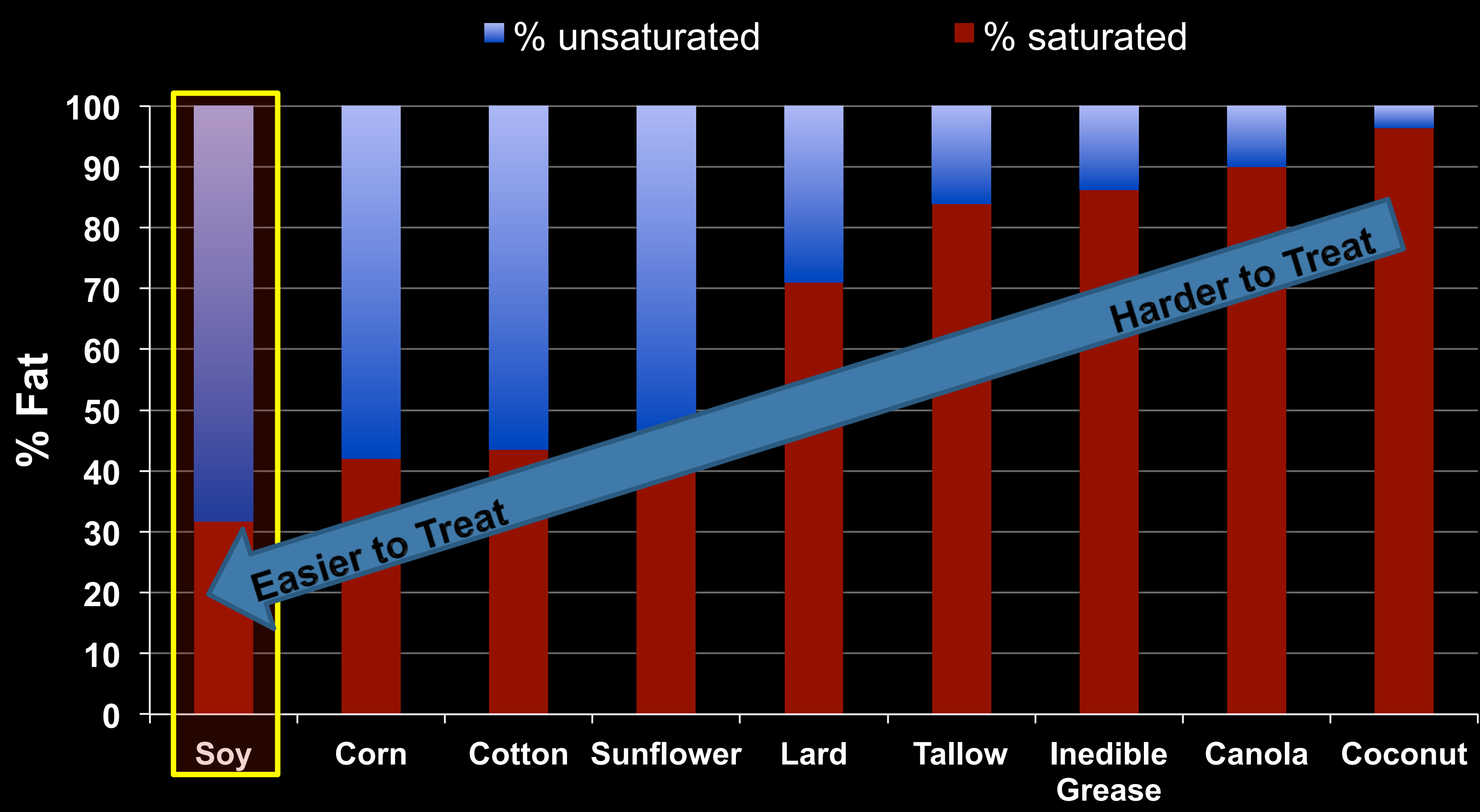
Effect of Kerosene vs Cold Flow Improver on B5 CFPP

CFI much more effective

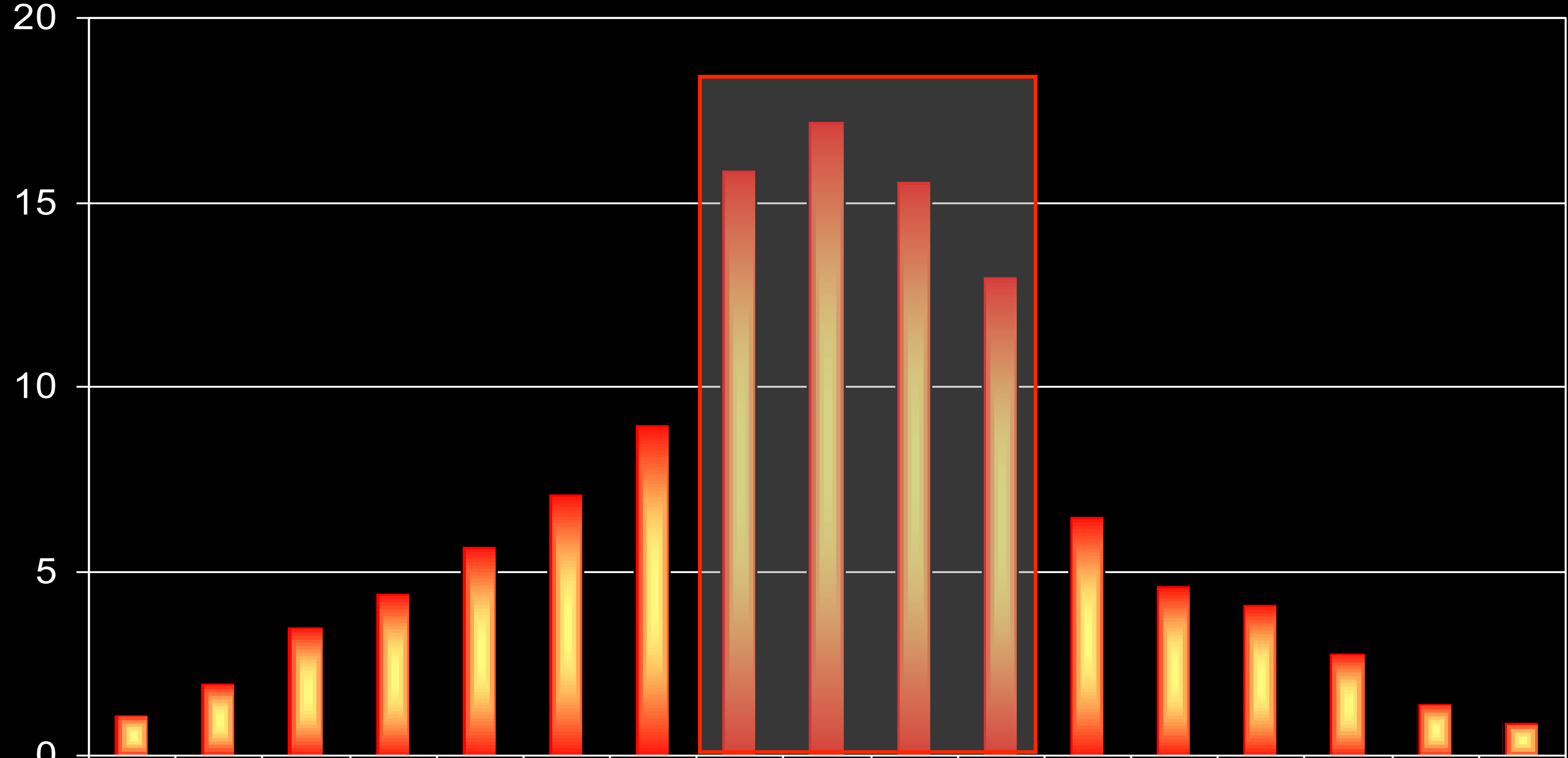


The Challenge of Biodiesel

Biodiesel Saturated Fat Content vs Cold Flow



Remember Narrow Wax Distributions?



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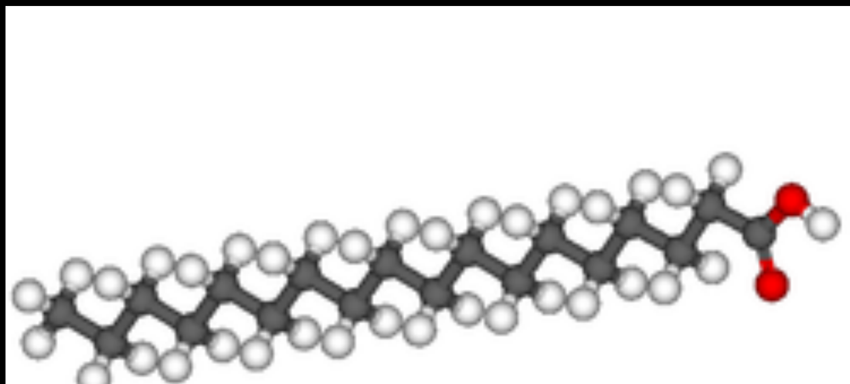
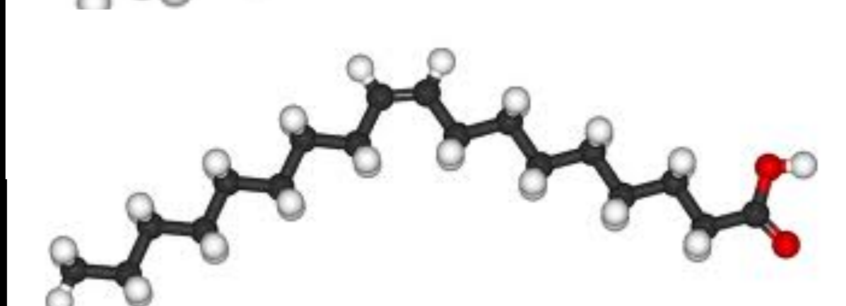
Adding B100 Enriches Diesel in 16 and 18 Carbon Molecules

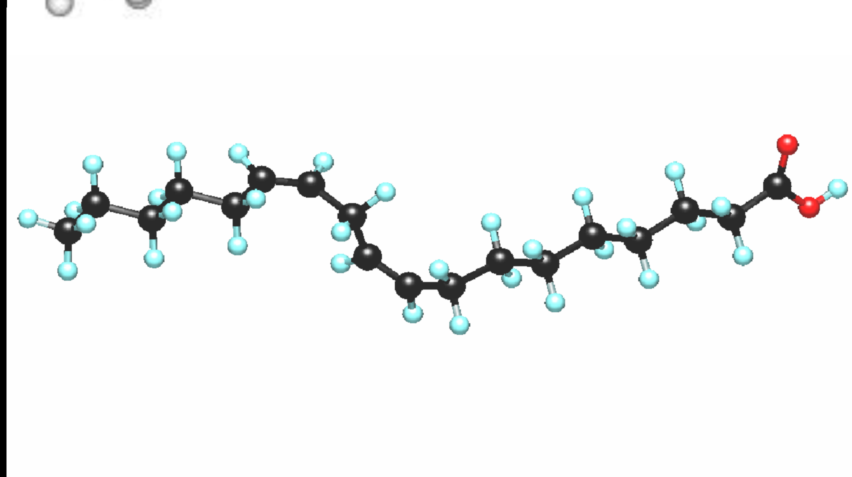
Melting Point of C_{18} Fatty Acids



Stearic Acid MP = 157 °F



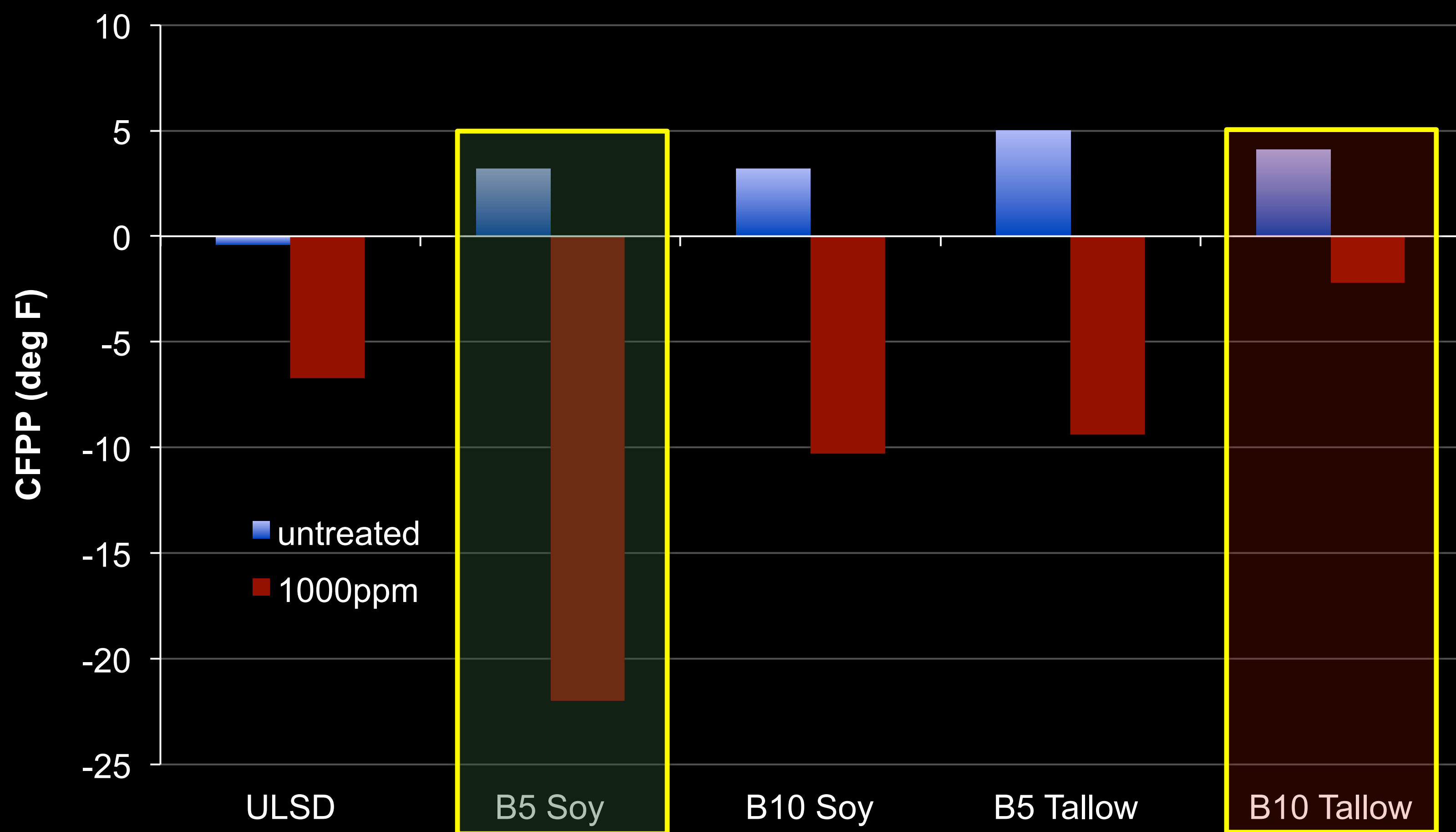
Oleic Acid MP = 55 °F



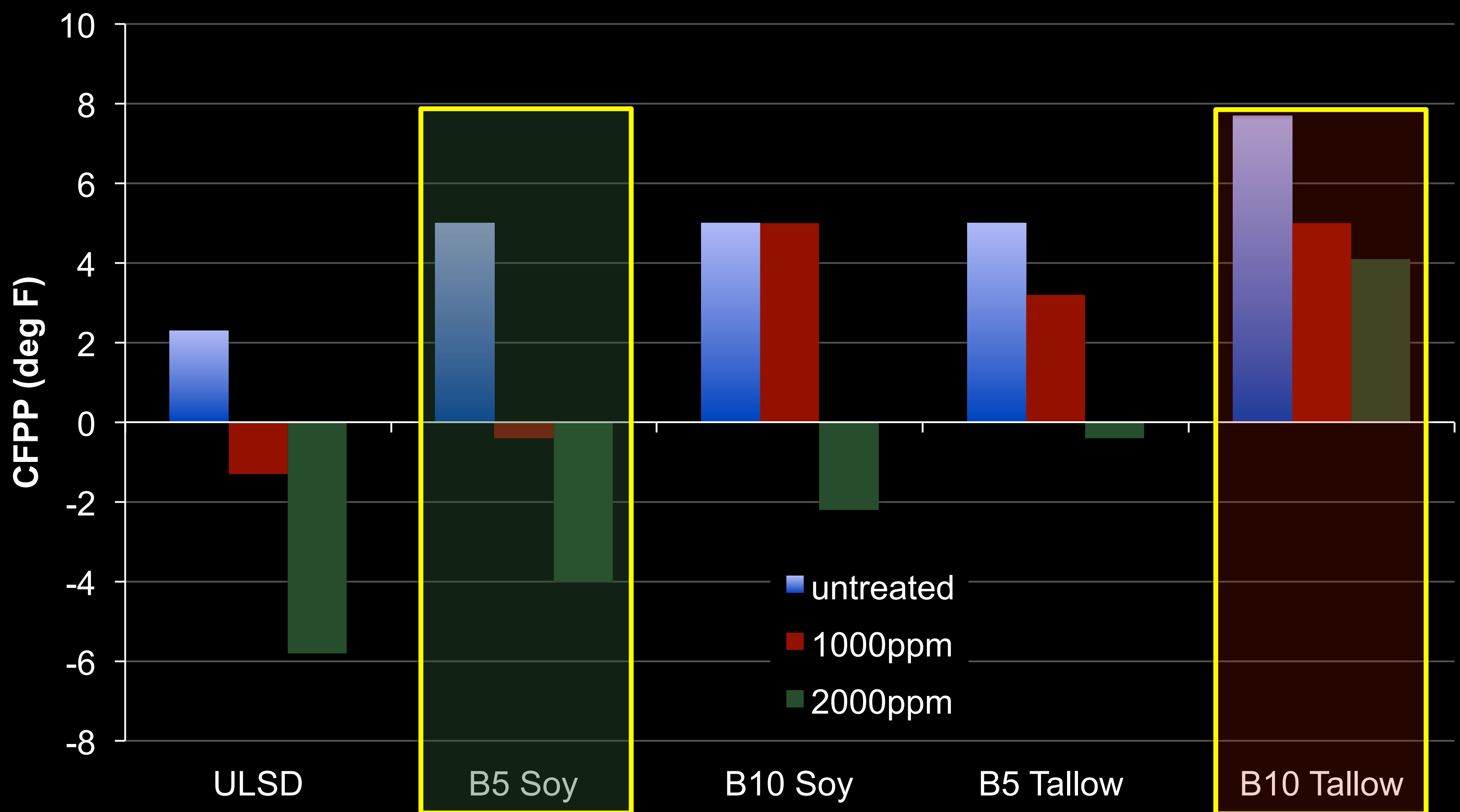
Linoleic Acid MP = 10-23 °F

Soy and Tallow B100 in "easy to treat" N.E. U.S. ULSD

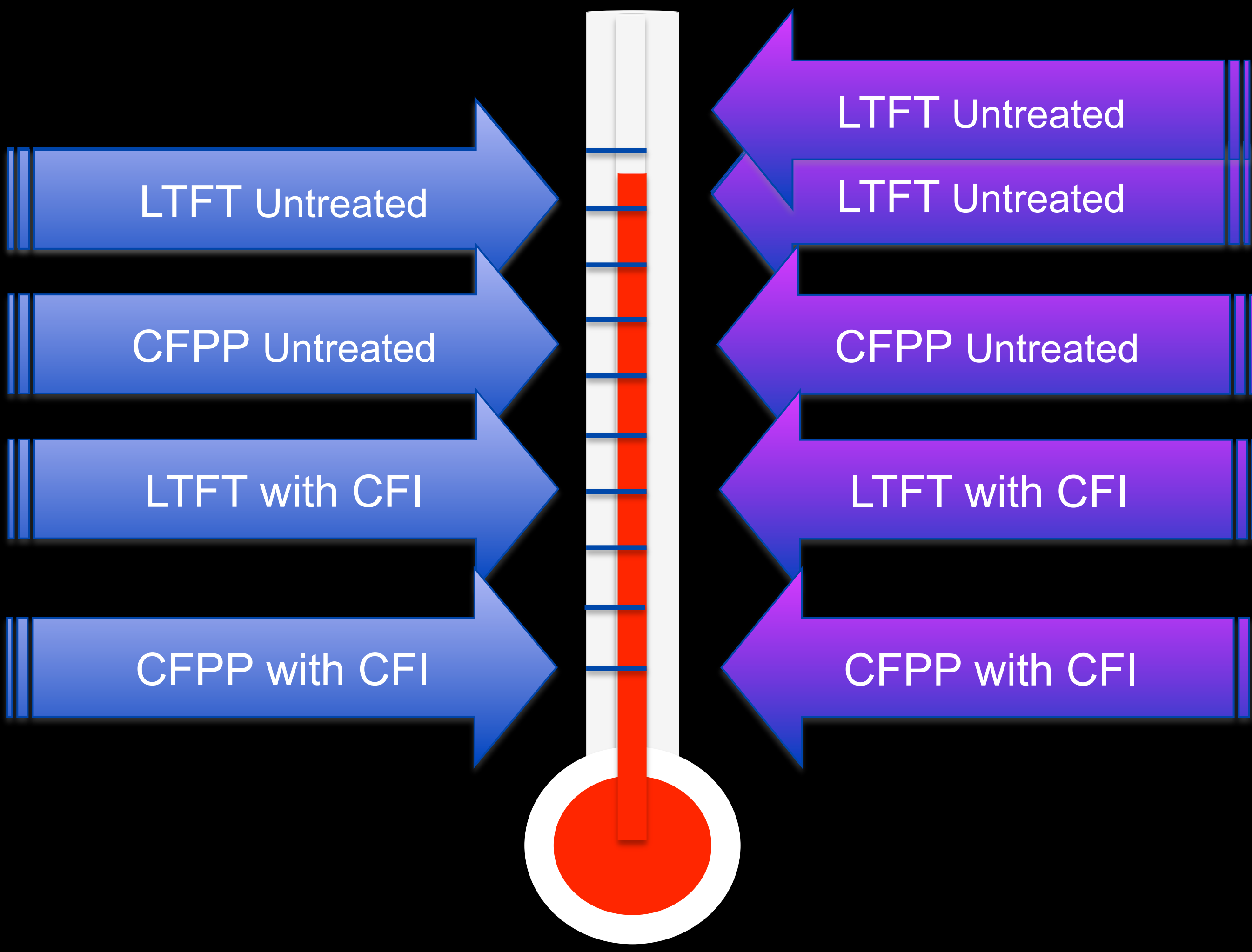
Tallow most problematic, at 10%

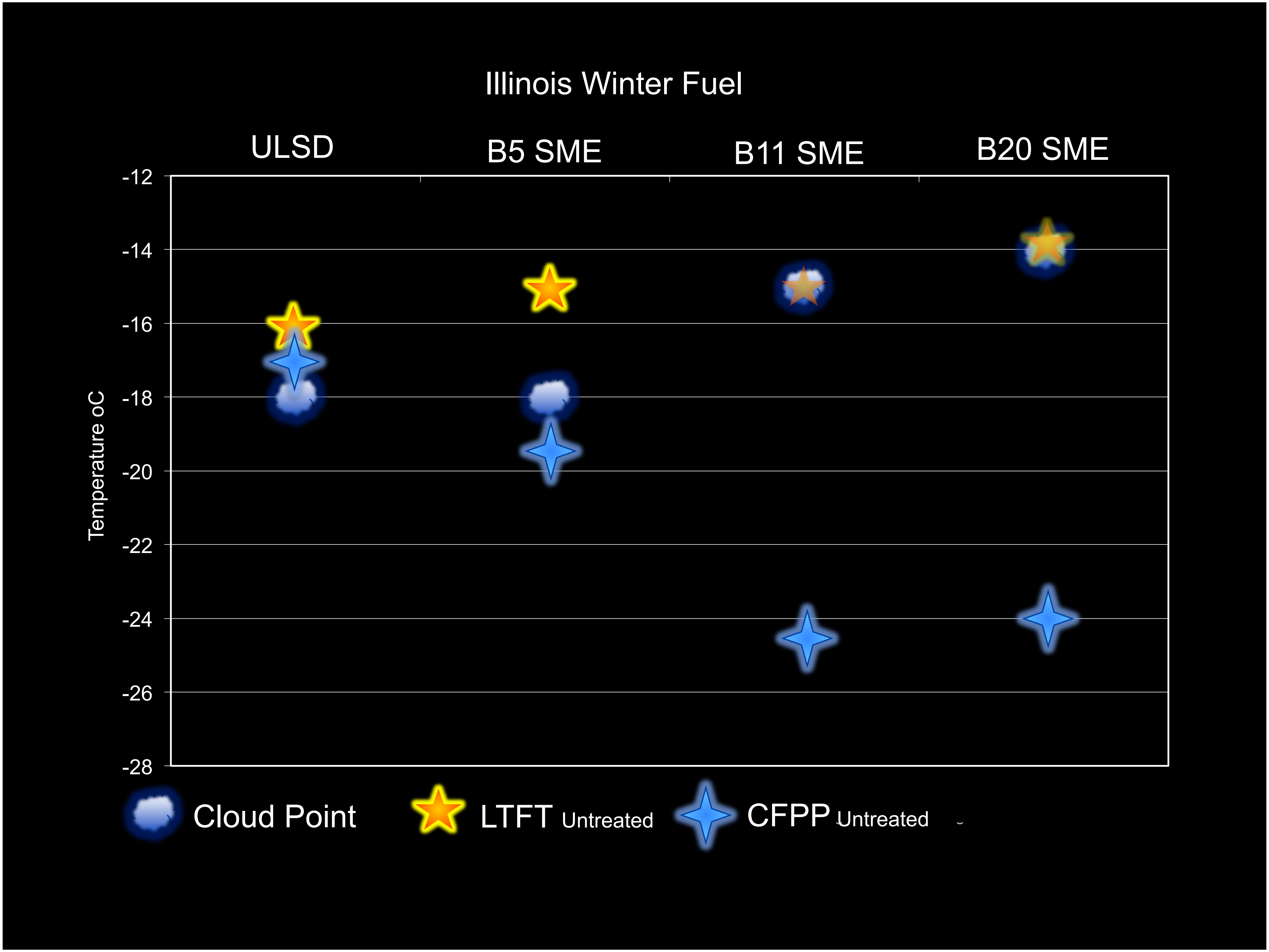


Soy and Tallow B100 in "hard to treat" N.E. U.S. ULSD



Low Temperature Operability of BX Blends



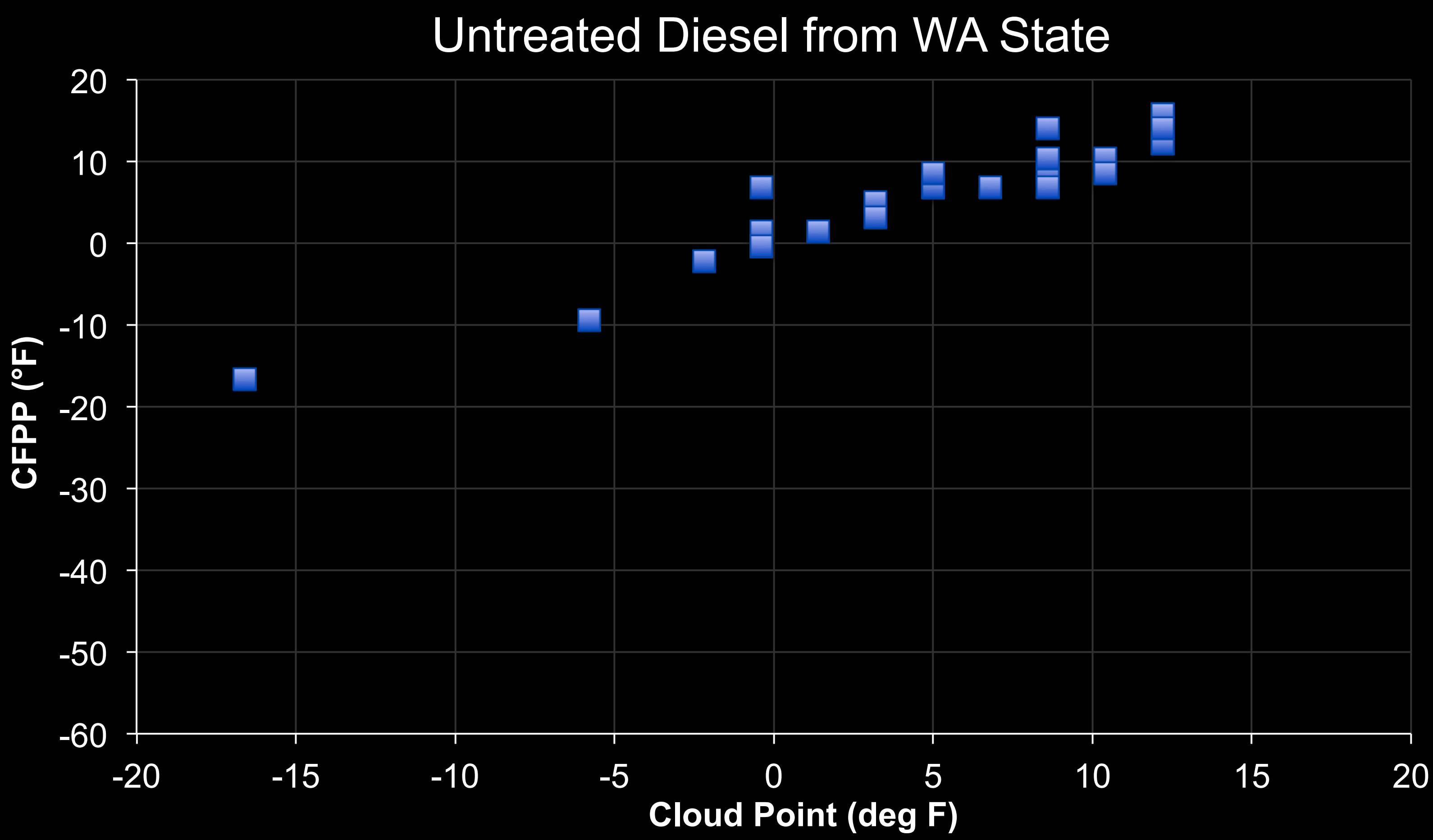


Illinois Winter Fuel
ULSD
B5 SME
B11 SME
B20 SME
-12
-14
-16
-18
-20
-22
-24
-26
-28
Temperature oC
Cloud Point
LTFT Untreated
CFPP Untreated

Washington State Winter 2011-12 Cold Flow Performance

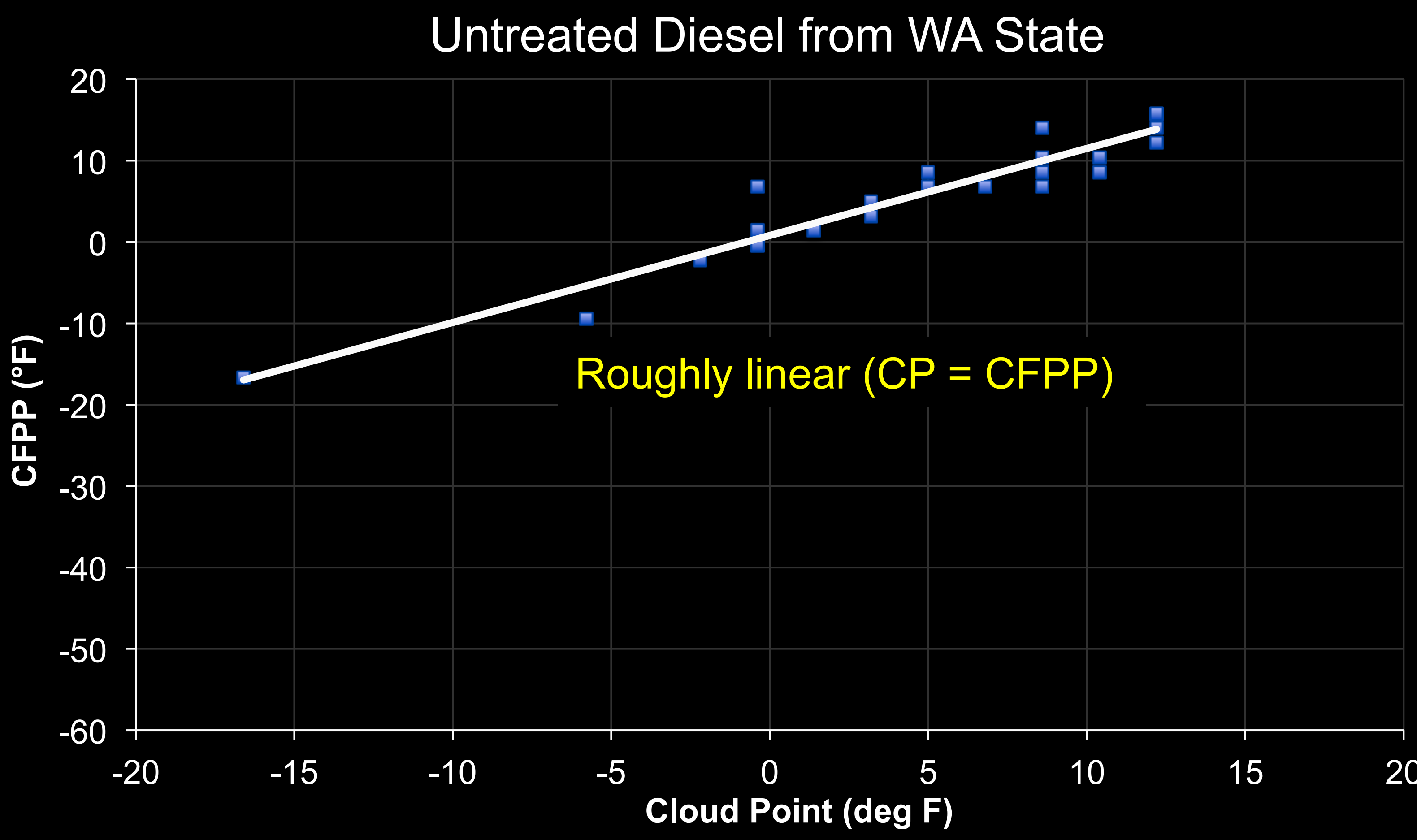
WA State Winter 2011-2012 Field Data

UNTREATED Fuels

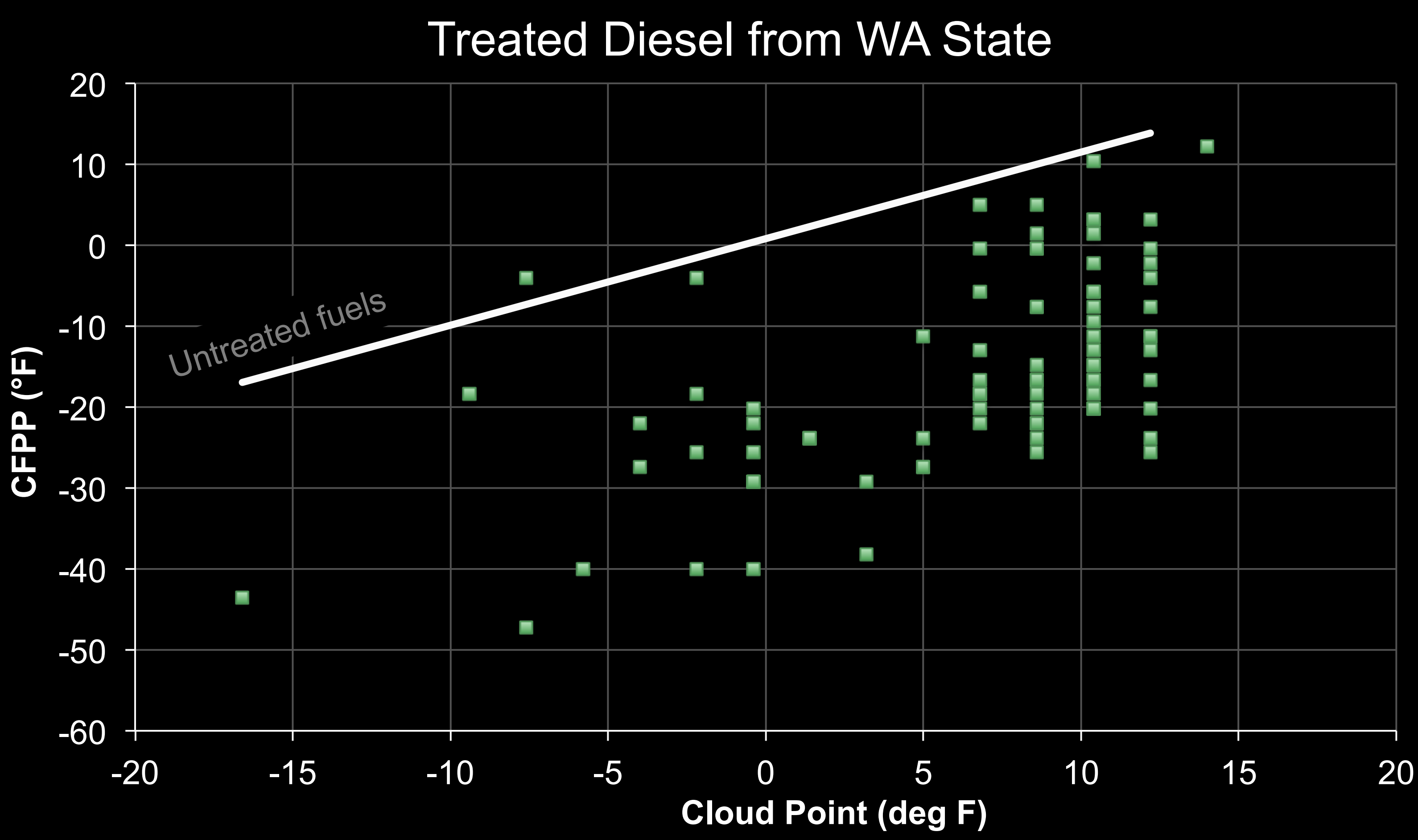


WA State Winter 2011-2012 Field Data

UNTREATED Fuels



WA State Winter 2011-2012 Field Data



WA State Winter 2011-2012 Field Data