Long-term Storage and Oxidation Stabilities of Second Generation Biofuels Used as Drop-in Replacement for Marine Diesel

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Navy Alternative Fuel Targets and Strategy

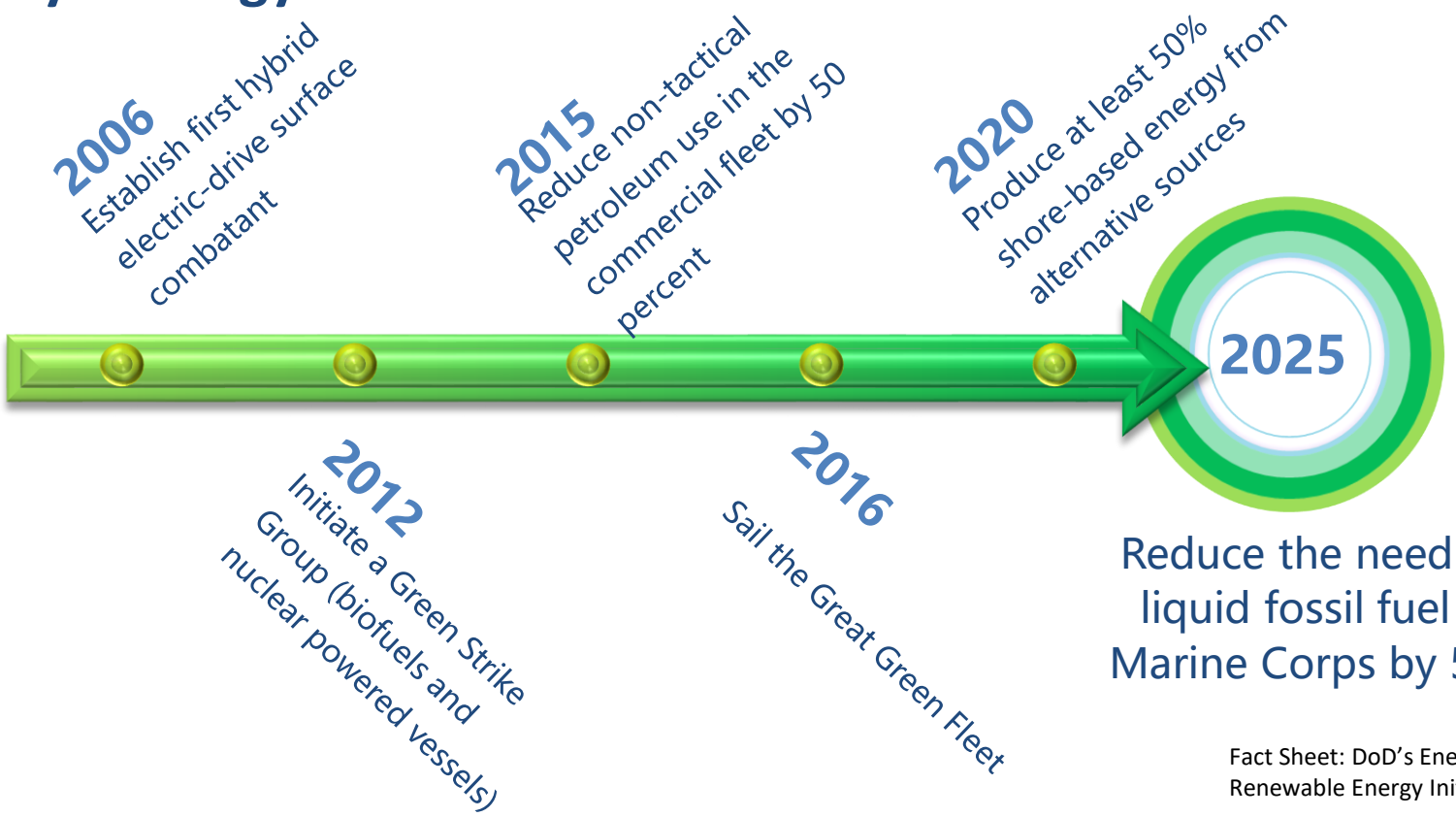
❖ Targets

- Increase alternatives afloat
- Sail the Great Green Fleet
- Increase alternative energy ashore

❖ Strategy

- Meet fuel performance specifications
- Require **NO** change to aircrafts or ships
- Require **NO** change to infrastructures
- Can be mixed with petroleum fuel

❖ Navy's Energy Goal



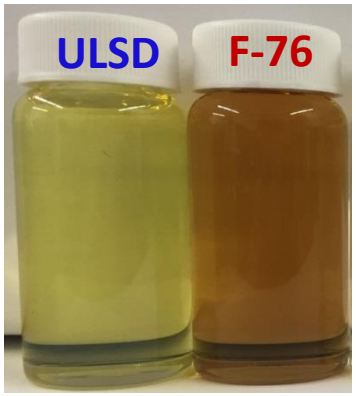
Reduce the need for liquid fossil fuel of Marine Corps by 50%

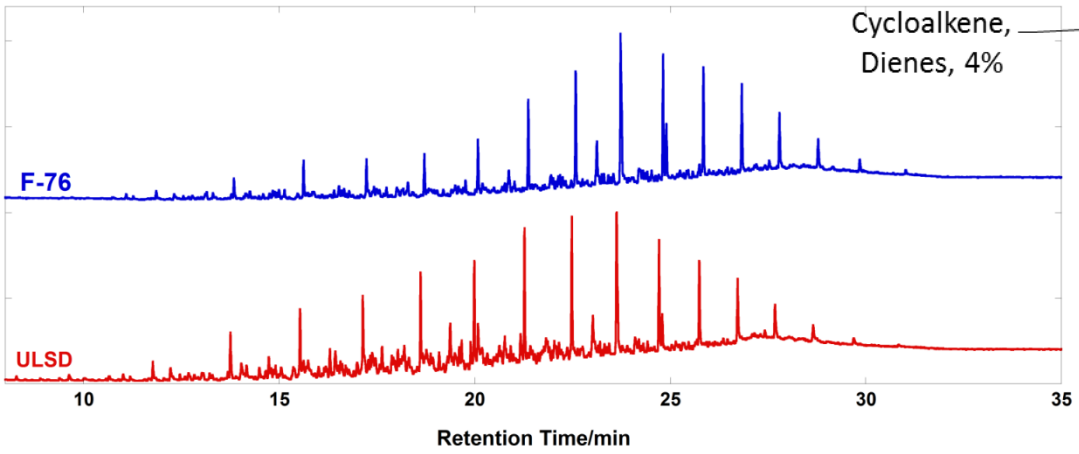
Fact Sheet: DoD's Energy Efficiency and Renewable Energy Initiatives, July 2011

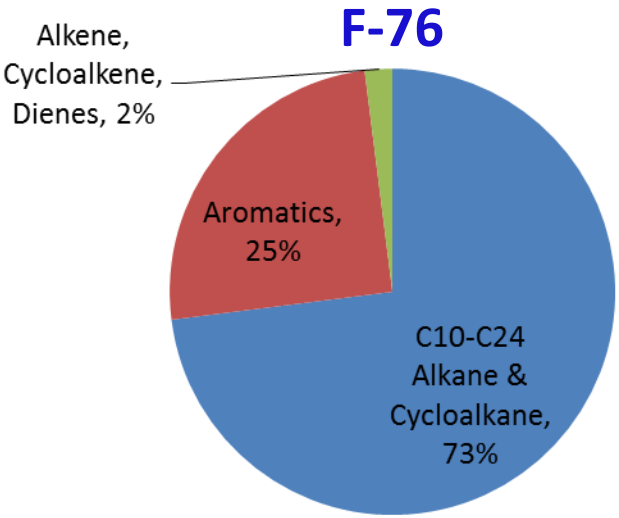
Marine Diesel NATO F-76

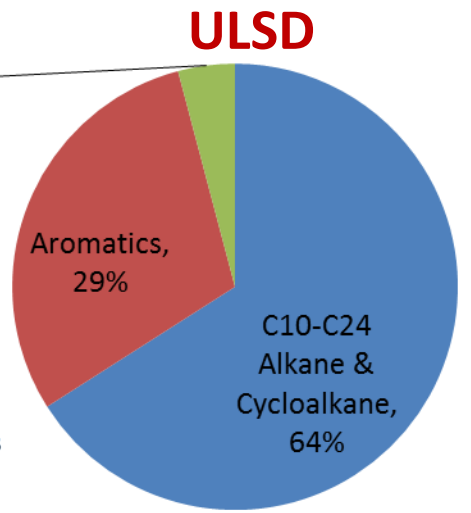
Applications

- Boiler
- Gas Turbine
- Diesel Engine



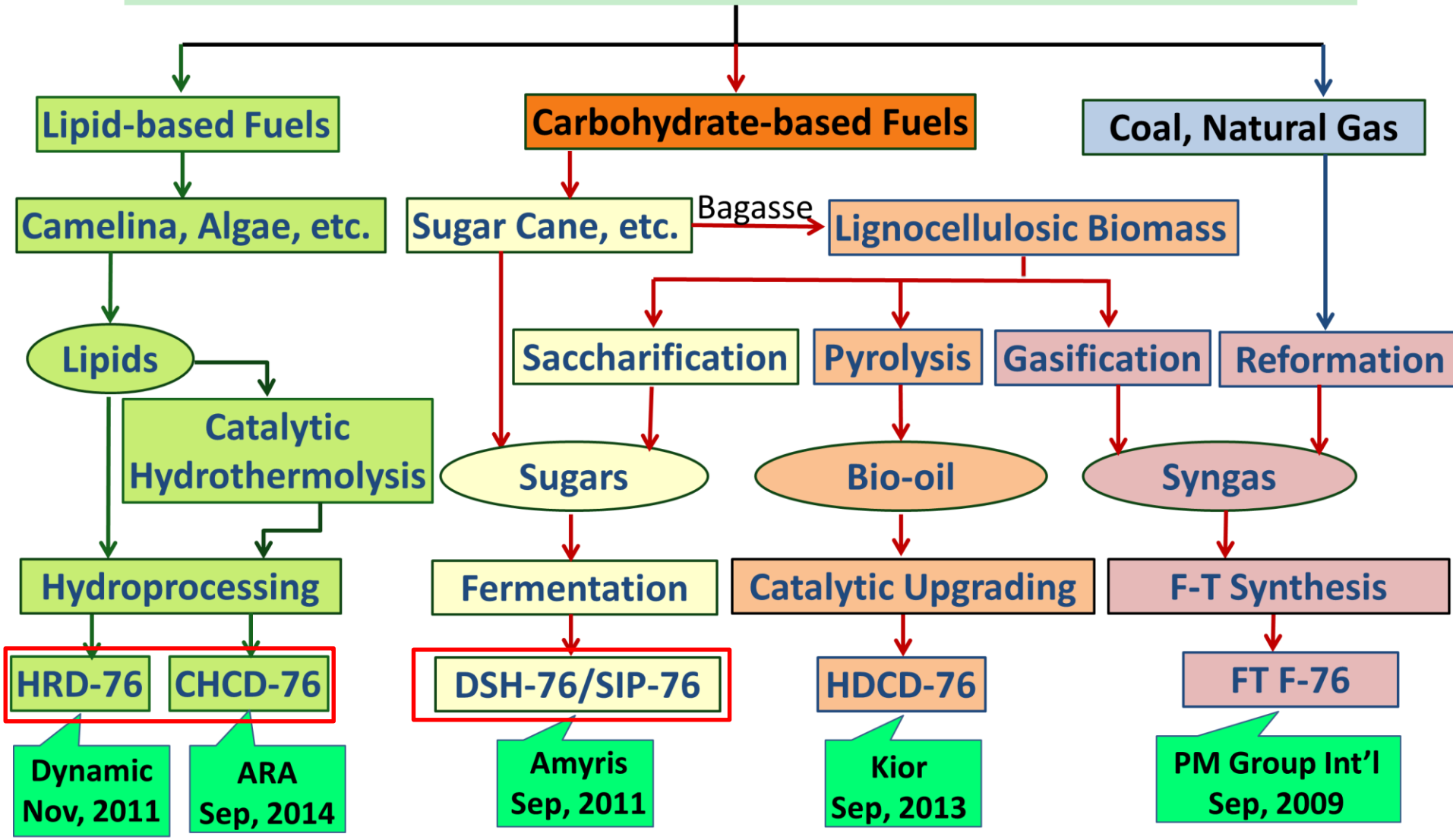






Waynick, J. A.; Giannini, R. M. .International Association for Stability, Handling and Use of Liquid Fuels: 2003
Smagala, T.J.; Christensen, E.. International Association for Stability, Handling and Use of Liquid Fuels: 2013
Kamin, R.; Mcdaniel, A.; et al. International Association for Stability, Handling and Use of Liquid Fuels: 2015

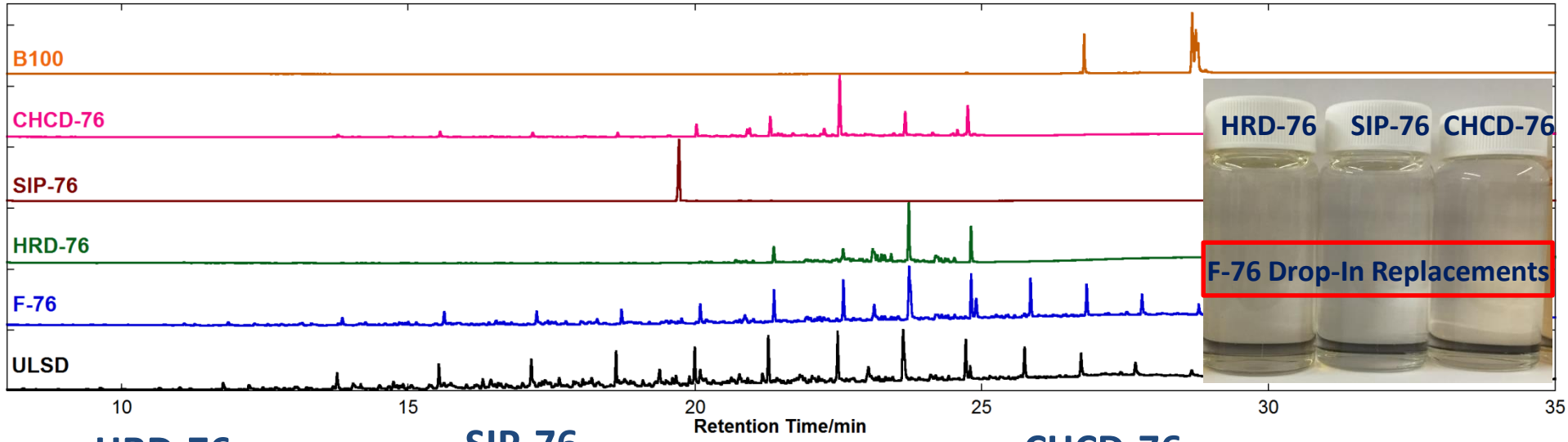
Commercial F-76 Alternative Fuel Pathways



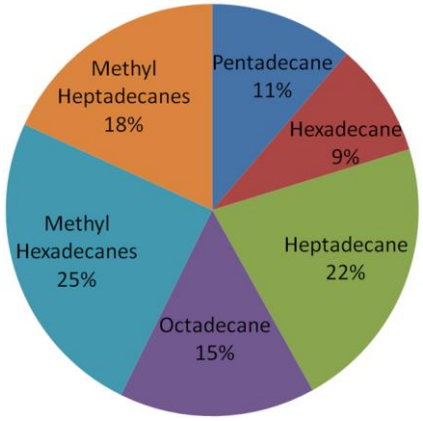
FT F-76: Fischer-Tropsch F-76
SIP: Synthesized Iso-Paraffins
DSH: Direct Sugar to Hydrocarbon

HDCD: Hydrotreated Depolymerized Cellulosic Diesel
CHCD: Catalytic Hydrothermal Conversion Diesel
HRD: Hydroprocessed Renewable Diesel

NATO F-76 Drop–in Replacement Fuels

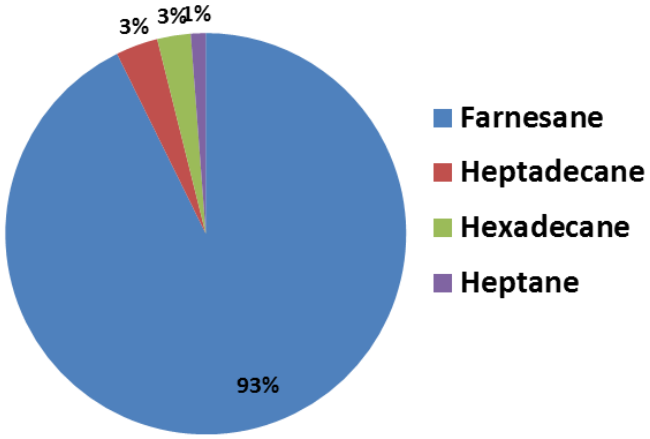


HRD-76

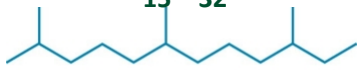


C15-C18 n-alkane & mono-methyl alkane

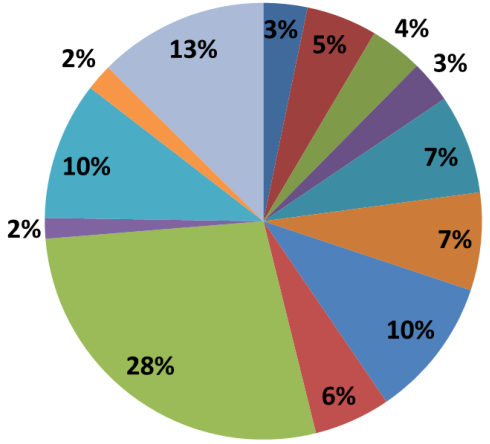
SIP-76



$C_{15}H_{32}$



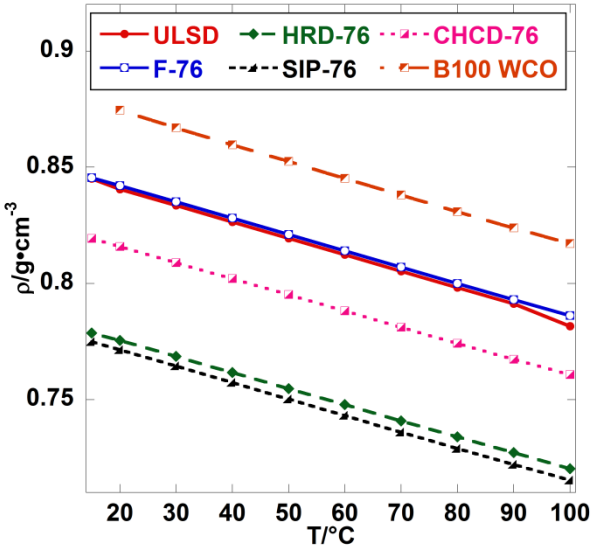
CHCD-76

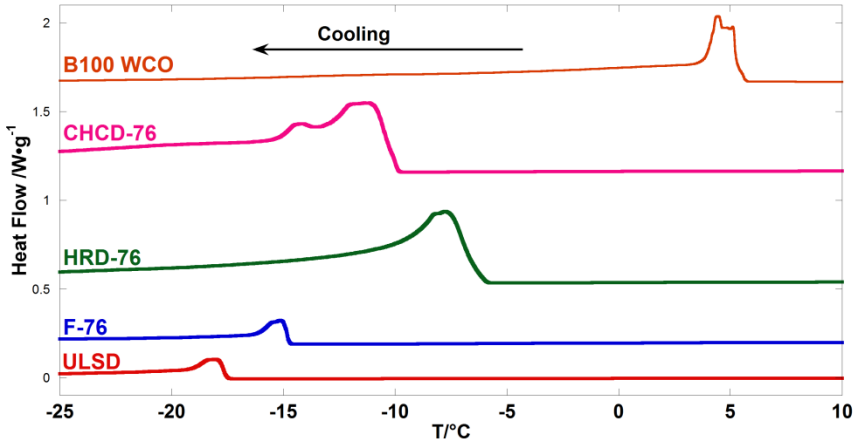


~16% cyclohexanes
~84% Alkanes

Prak, D. L.; Morris, R. E.; Cowart, J. S.; et al., Journal of Chemical and Engineering data, 2013 (58)

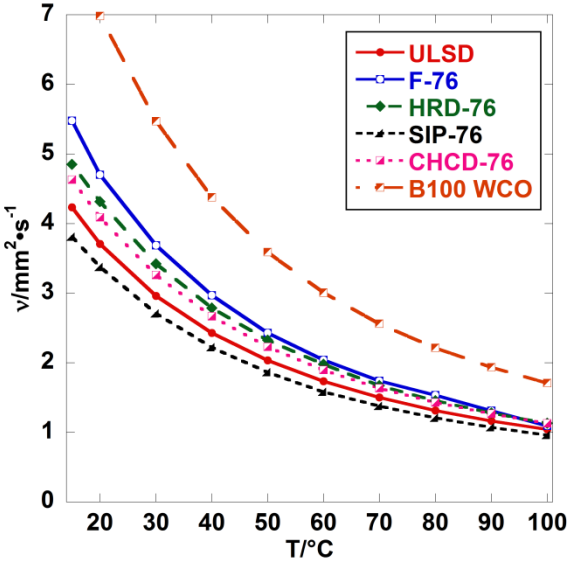
Physicochemical Properties of Fuel





Advantages of Biofuels

- Lower acid number
- Lower peroxide value
- Higher H content
- Higher heating value
- Better lubricity
- Higher Flash Point



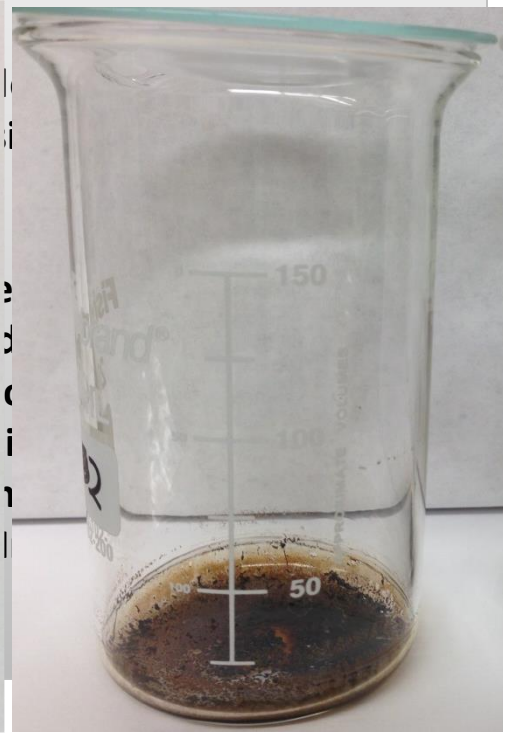
MIL-DTL-16884N specifies:
kinematic viscosity 1.7 - 4.3 $mm^2 s^{-1}$ at 40°C & density 0.800 - 0.876 g cm^{-3} at 15°C
Hydrogen content & Flash Point: minimium 12.5 wt% & 60°C

Fuels	PV (mg kg^{-1})	HHV (MJ kg^{-1})	AN (mg of	H wt%	Flash Point (°C)
SIP-76	0.09 ± 0.01	46.61 ± 0.09	0.01 ± 0.00	15.18 ± 0.08	100 ± 1
CHCD-76	0.05 ± 0.01	45.72 ± 0.11	0.05 ± 0.00	14.31 ± 0.02	95 ± 1
HRD-76	0.13 ± 0.02 [a]	46.41 ± 0.04 [a]	0.00 ± 0.00 [a]	15.29 ± 0.09	81 ± 1
F-76	1.87 ± 0.17 [a]	44.83 ± 0.07 [a]	0.11 ± 0.00 [a]	13.36 ± 0.28	76 ± 1
ULSD	1.33 ± 0.05	44.96 ± 0.18	0.01 ± 0.00	13.32 ± 0.01	61 ± 1
B100	16.59±0.49 [a]	39.17 ± 0.04 [a]	0.23 ± 0.01 [a]	12.49 ± 0.09	165 ± 1

Acid Number(AN), Peroxide Value (PV), & Heat of Combustion (HHV)

Stability Tests

Test Methods	Experiment Conditions	Analysis & Characterization
Standard Storage Stability ASTM D4625	400ml samples in oven T = 43±1°C P= 101.325 kPa 0, 4, 8, 12, 18, 24 we	
O_2 Overpressure Storage Stability ASTM D5304	100ml samples in hot T = 90±1°C P= 800±10 kPa t= 16 h±15 min	
Oxidation Stability ASTM D2274 (16h) MIL-DTL-16884N (40h)	350ml samples in hot T = 95±0.2°C P= 101.325 kPa $Q(O_2)$= 3±0.3 L/h	



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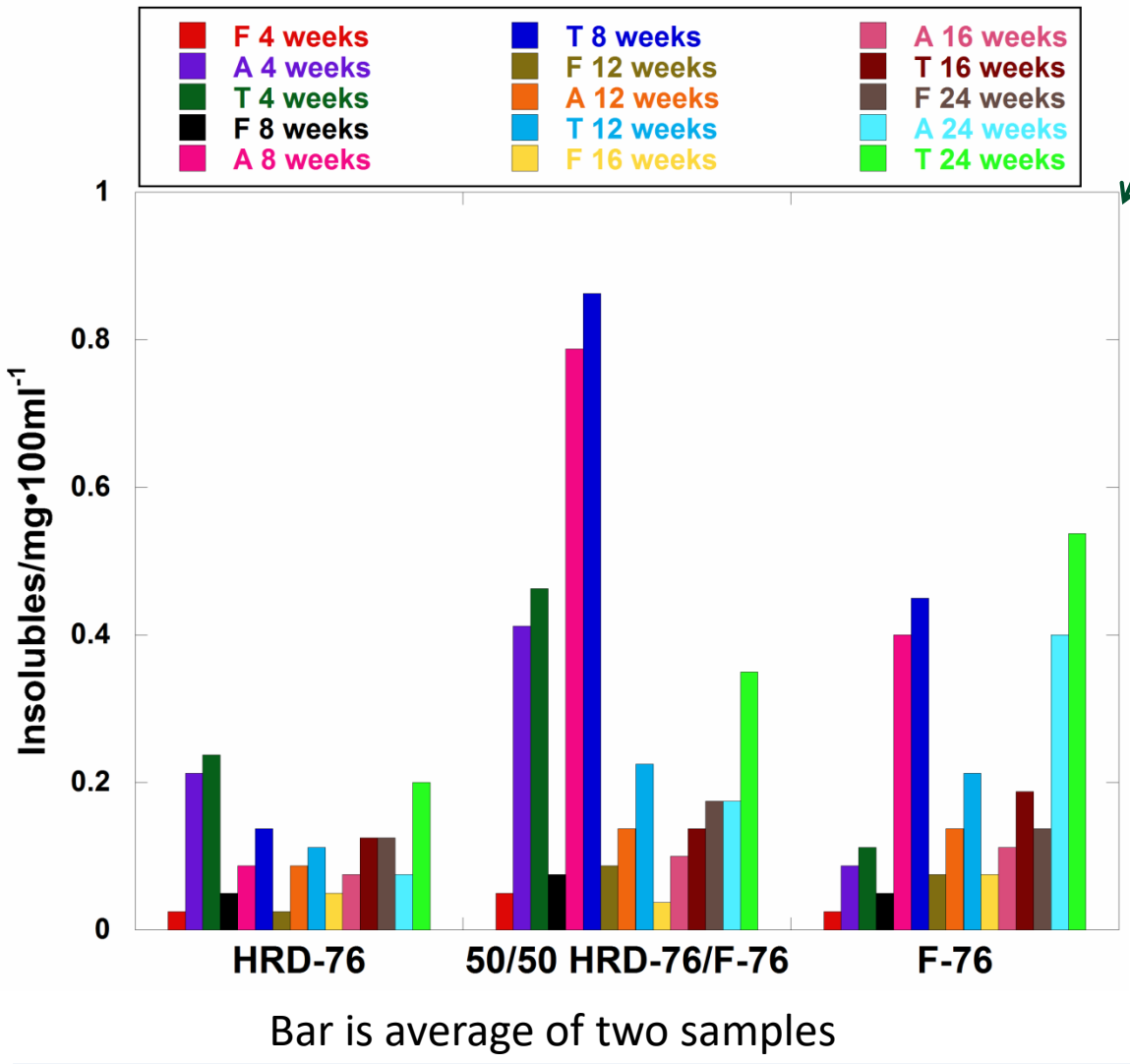
ASTM D4625
Long-Term Storage Testing

HRD-76, F-76 & 50/50 Blend: Insoluble Formation



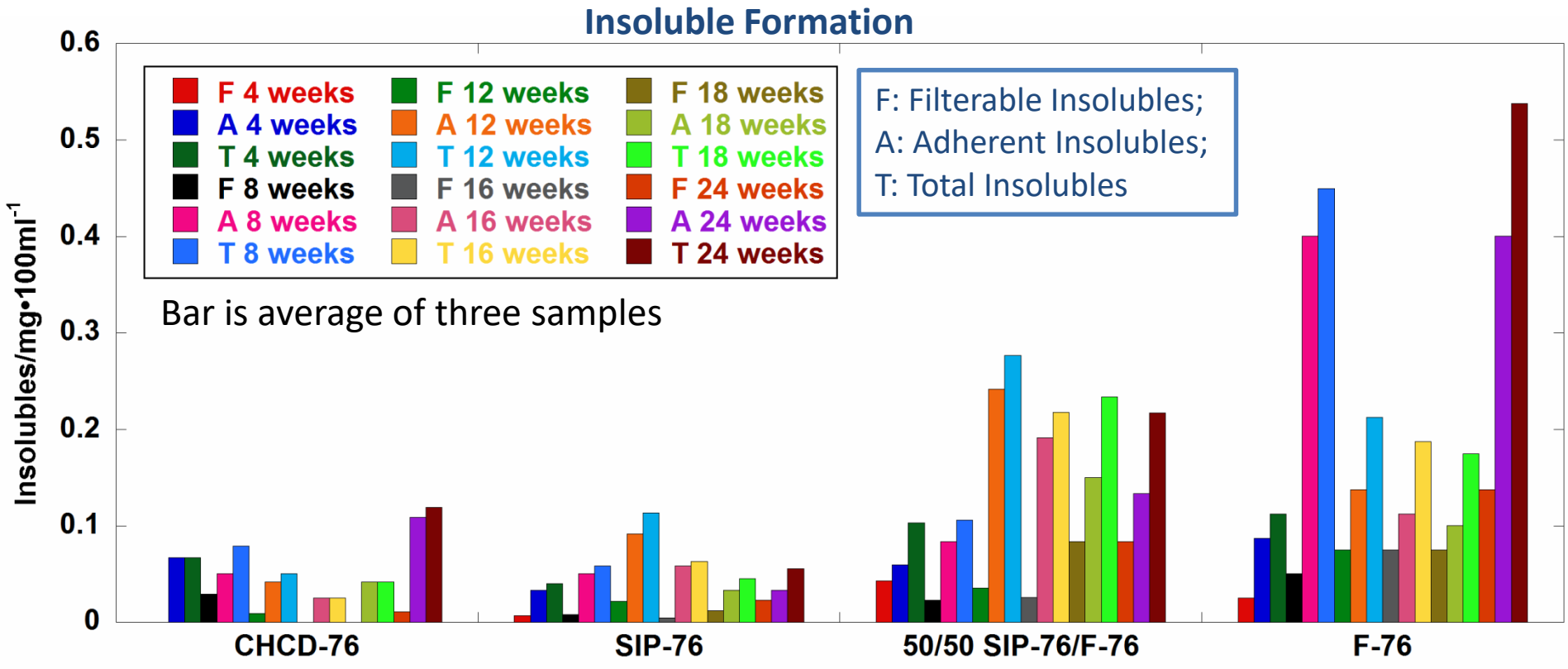
Bar is average of two samples

F: Filterable Insolubles; A: Adherent Insolubles; T: Total Insolubles

MIL-DTL-16884N (2014) specification <3.0mg/100ml for F76

- A week of 43°C storage is roughly equivalent to a month of storage at normal (environmental) ambient temperatures, 21°C.
- The amount of filterable and adherent insolubles formed in HRD-76 samples are almost all lower than those of F-76 samples, demonstrating that HRD-76 is more stable than F-76, and has less unstable precursors.

CHCD-76, SIP-76, and Blends with F-76



- The overall amount of insolubles formed in SIP-76 and CHCD-76 is lower than that of 50/50 blend of SIP-76 and F-76, and neat F-76 sample.
- Biofuels (HRD-76, SIP-76, and CHCD-76) are more stable than F-76.
- Blending biofuels in F-76 improves the storage stability of F-76.
- The 100 % drop-in replacement CHCD-76 is much more stable than F-76.

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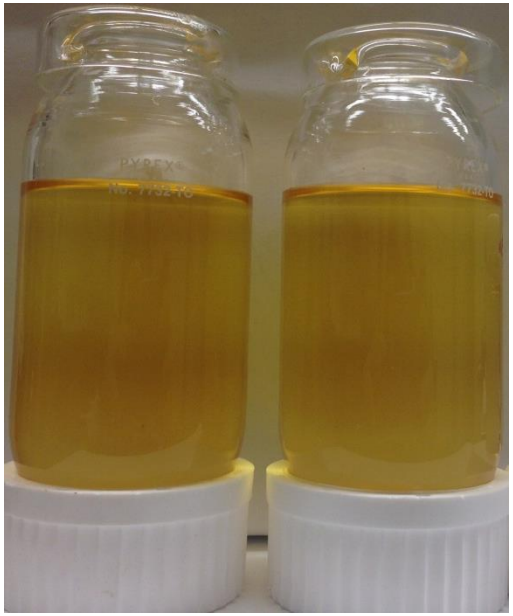
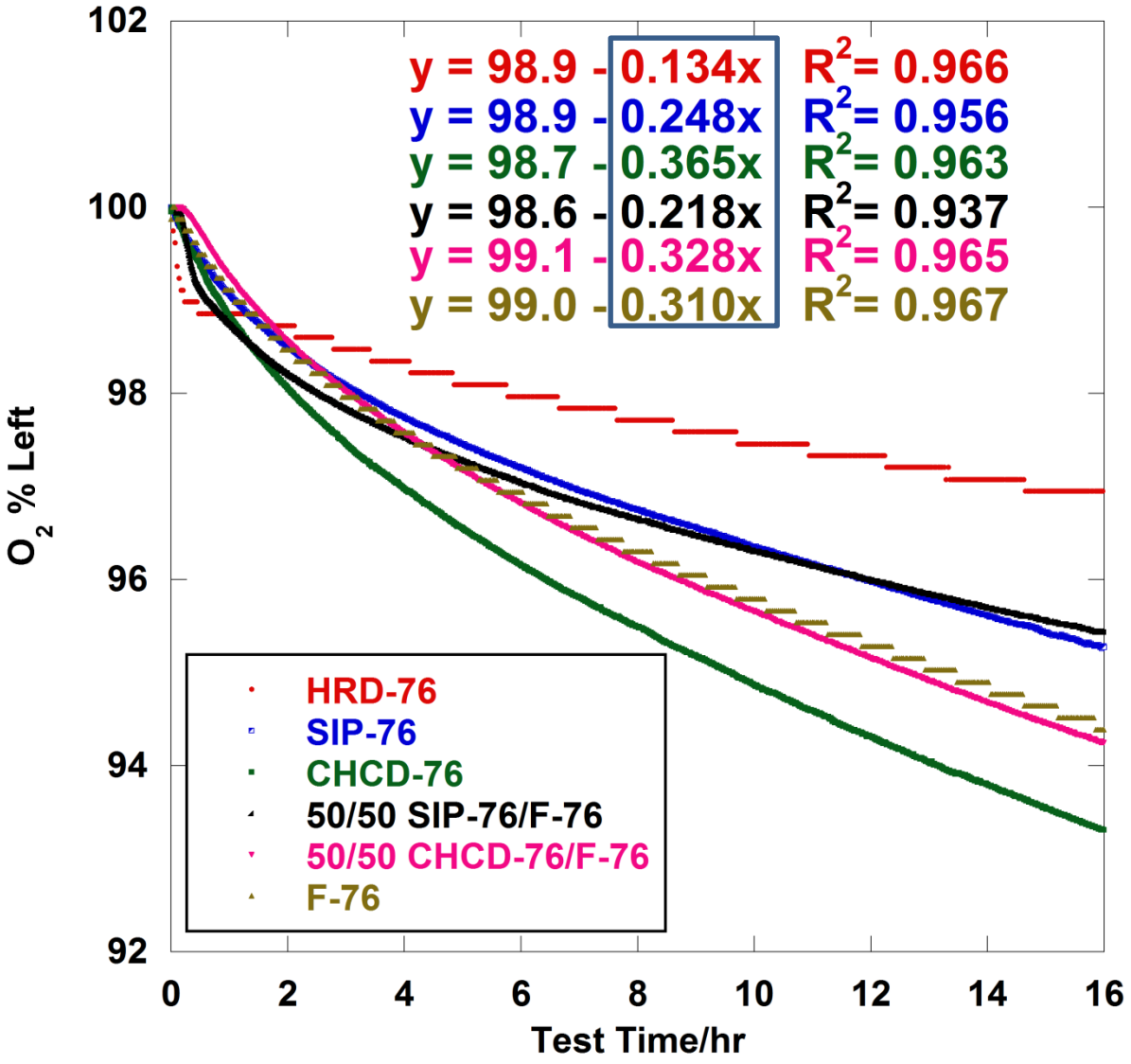
ASTM D5304
Oxygen Overpressure Testing



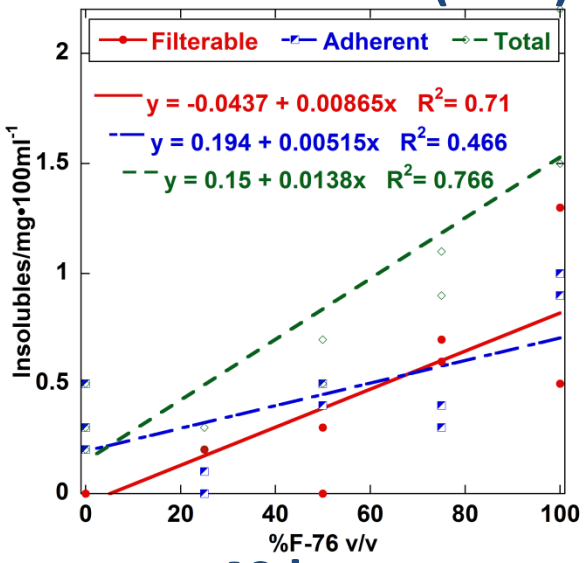
Oxygen Consumption



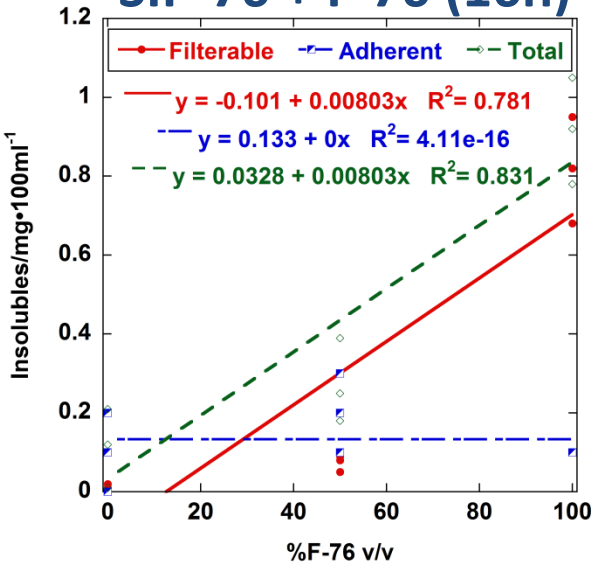
- The pressure of the pressure vessel was continuously recorded during the 16 h testing period.
- The slope of the curve calculated by linear regression reflects the oxygen consumption rate of the fuel sample.
- The oxygen consumption rate of HRD-76 and SIP-76 is much lower than that of F-76.
- The oxygen consumption rate of CHCD is even faster than F-76 probably owing to the existence of cyclohexanes.

Biofuel Blends with F-76: Insolubles Formation

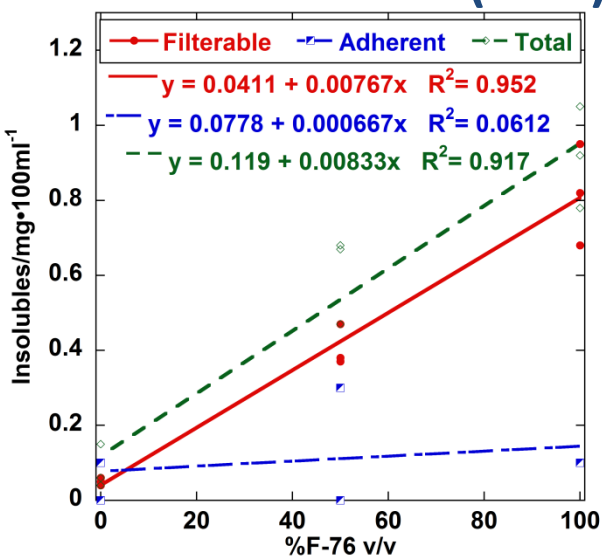
HRD-76 + F-76 (16 h)



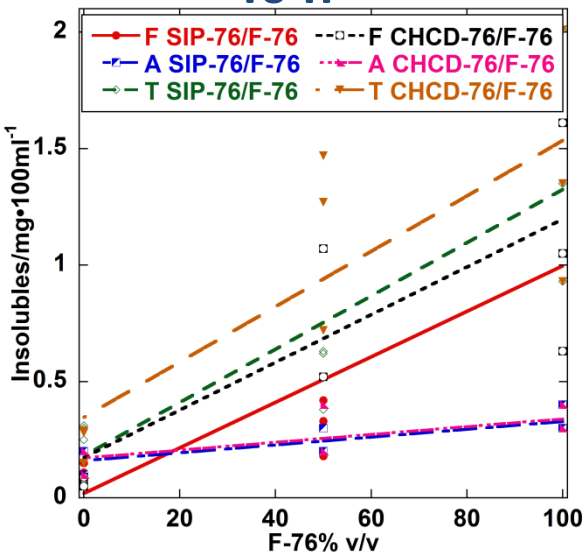
SIP-76 + F-76 (16h)



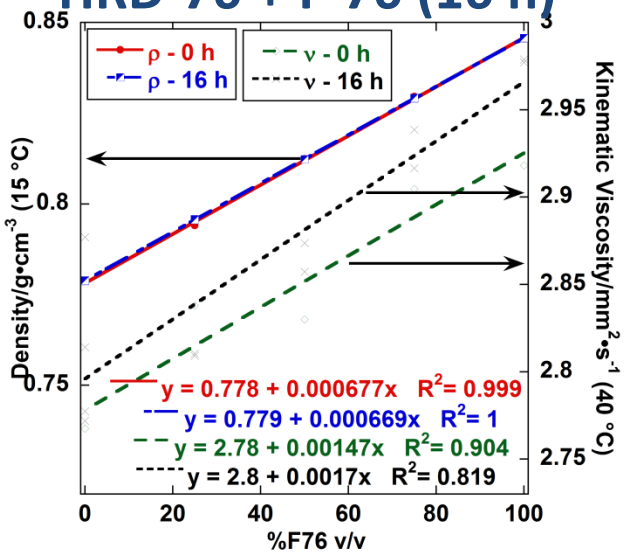
CHCD-76 + F-76 (16 h)



40 h



HRD-76 + F-76 (16 h)



- Biofuels have better storage stability compared to F-76
- The insoluble formation of SIP-76 and CHCD-76 is dominated by the formation of filterable insolubles.
- Longer oxidation time induces more insolubles formation

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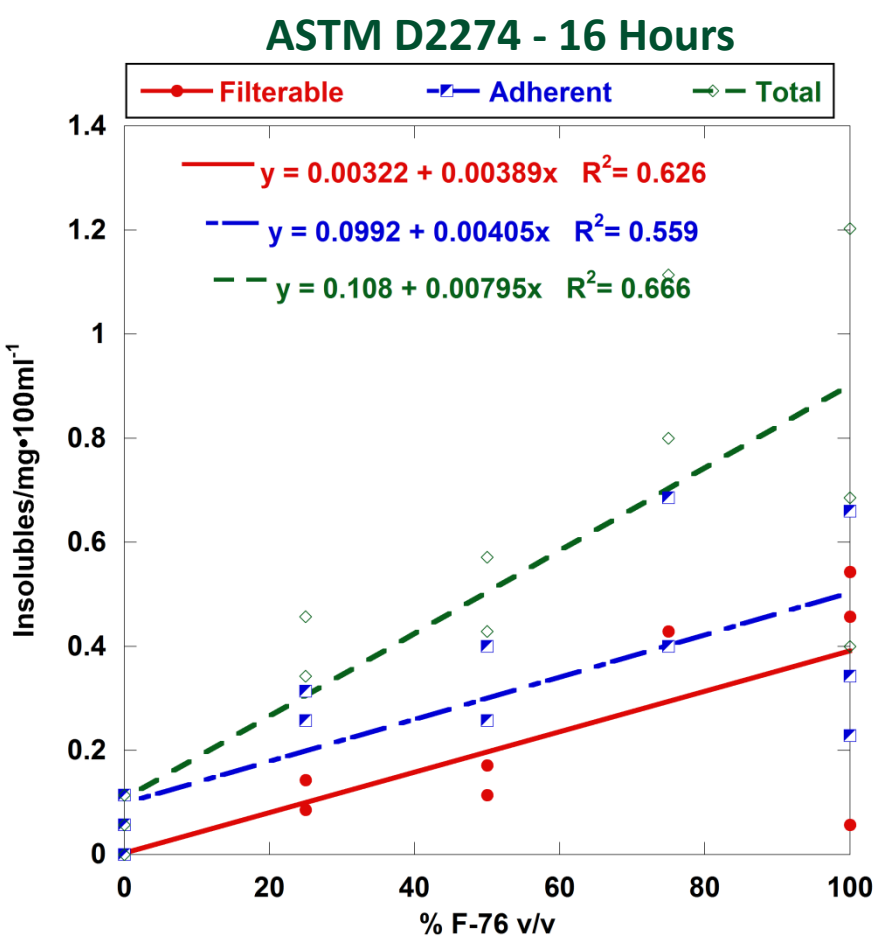
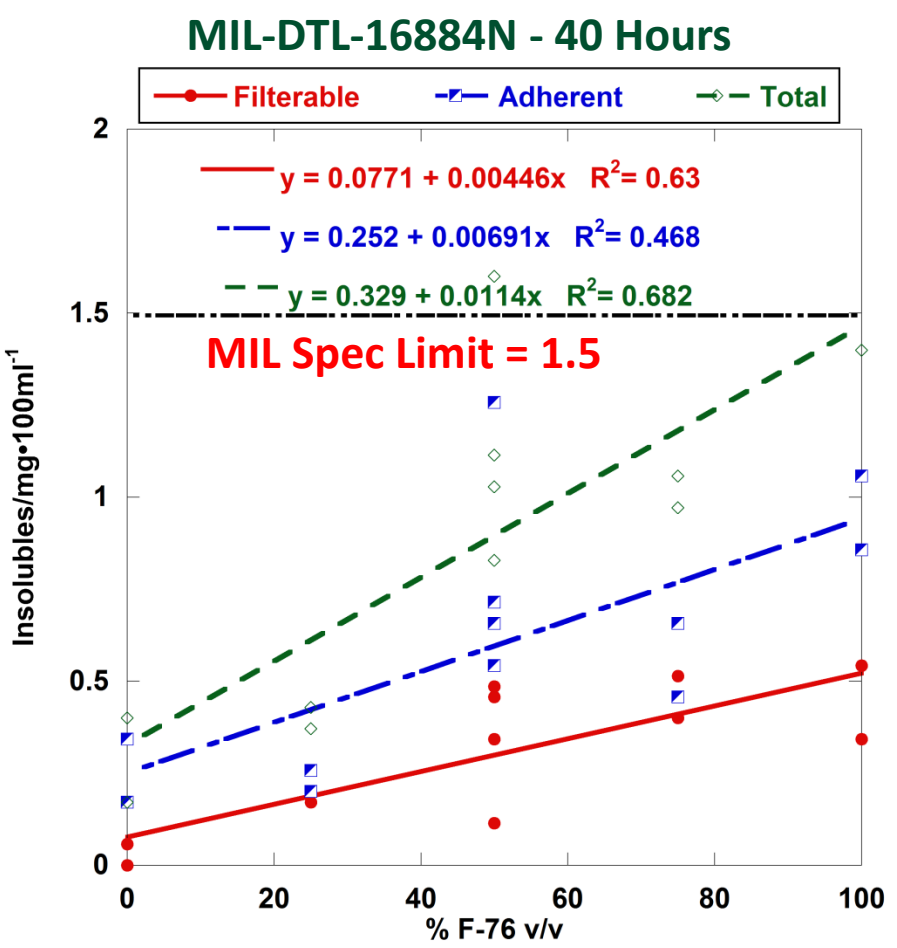
ASTM D2274
Oxidation Stability Testing
Oxygen Bubbling

HRD-76, F-76 & Their Blends: Insolubles Formation

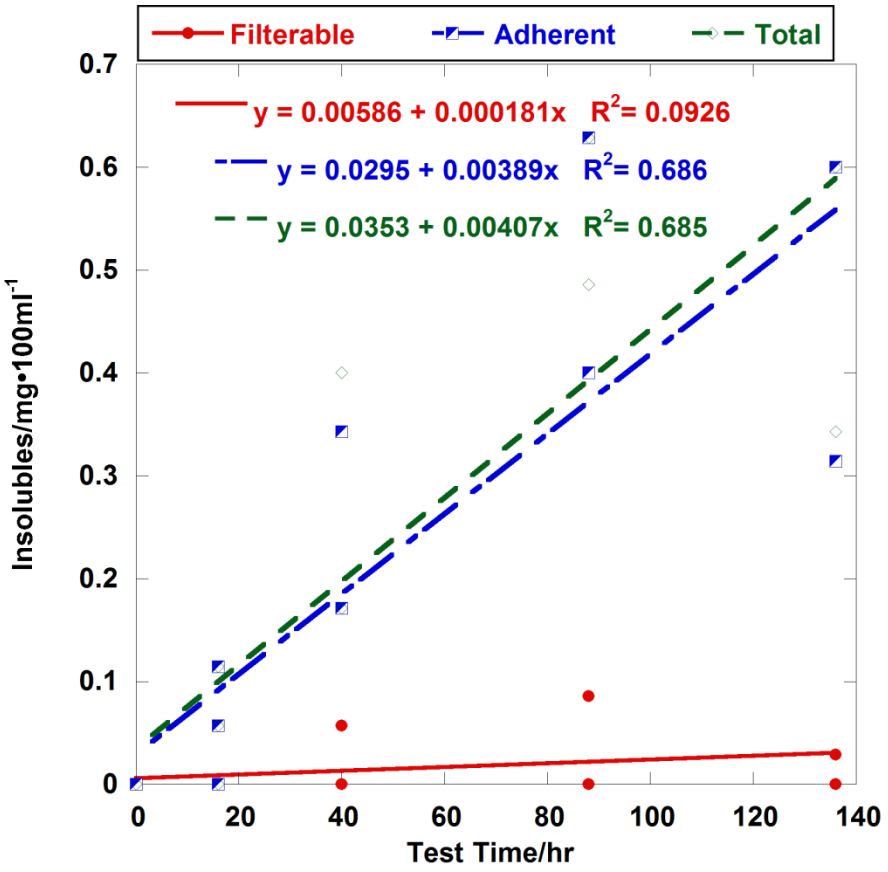


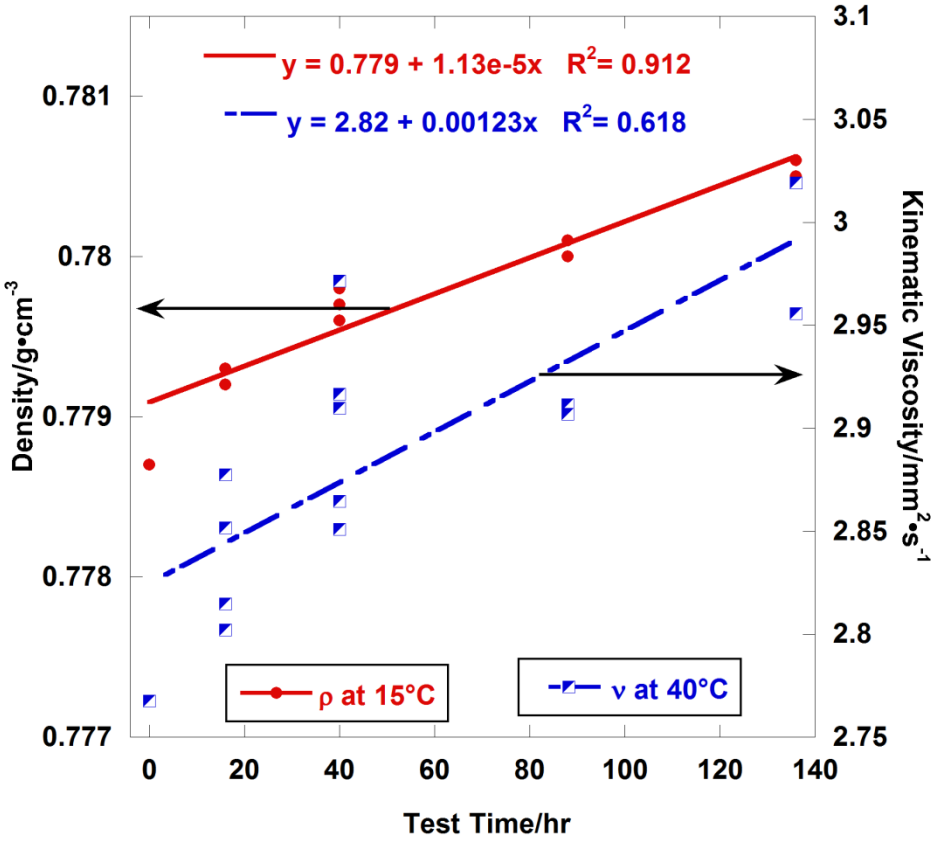


- The longer oxidation times and higher F-76 fractions produced larger amounts of insolubles.
- It is also noted that more adherent insolubles were formed in all fuel samples in the 16 and 40 hours tests compared to the filterable insolubles, differing from the results observed in the ASTM 5304 tests.

HRD-76: Extended Time Testing

ASTM D2274

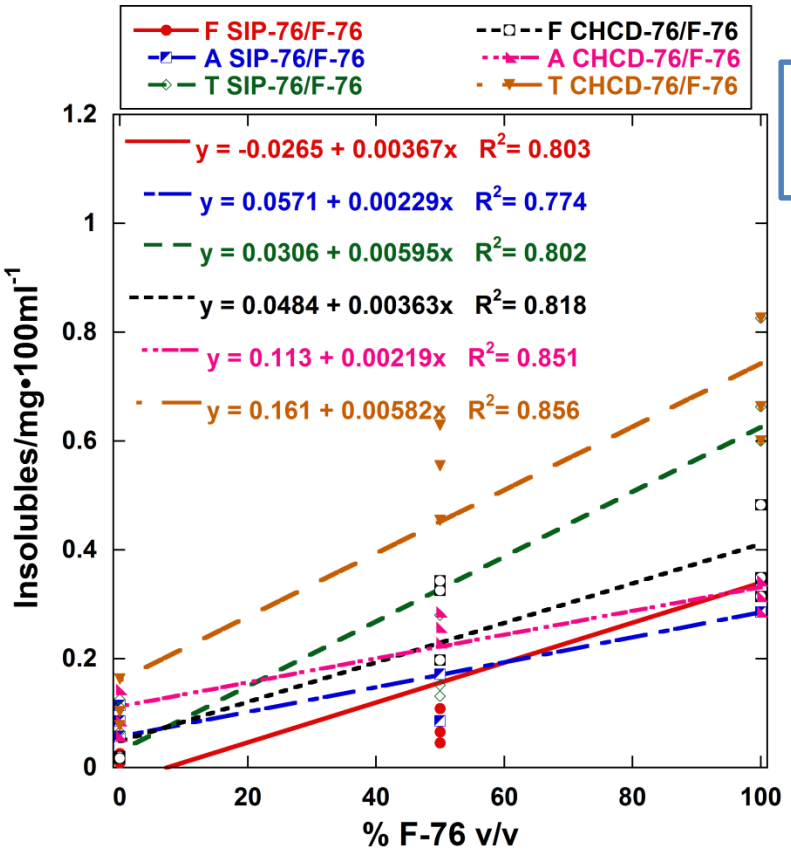




- The insoluble formation in HRD-76 after long-term oxidation is dominated by the formation of adherent insolubles.
- Density and viscosity increases with oxidation time.

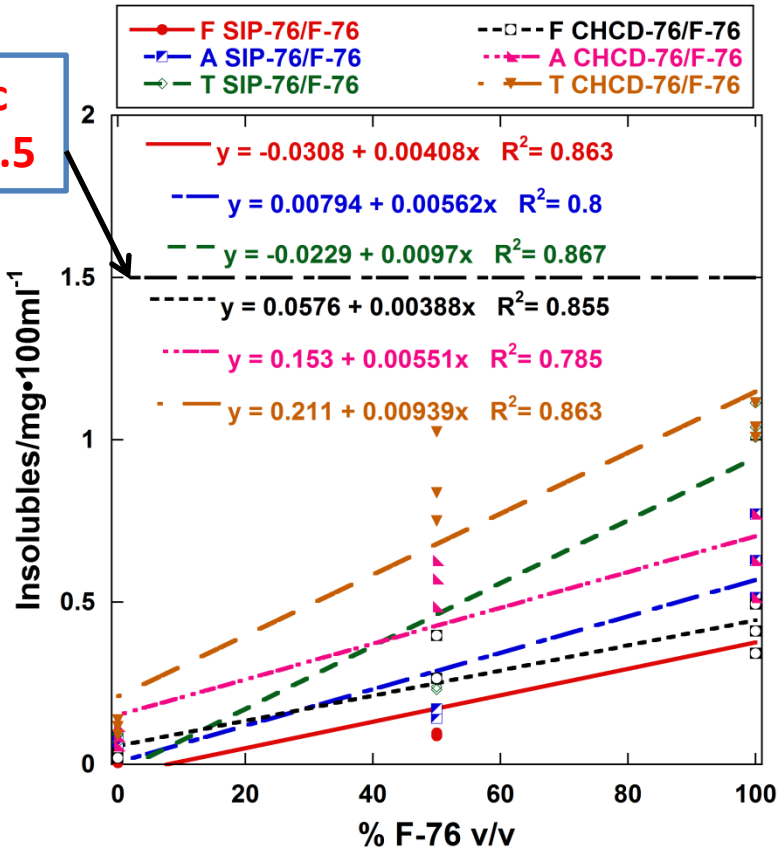
SIP-76, CHCD-76, & F-76: Insolubles Formation

ASTM D2274 - 16 Hours



MIL Spec Limit = 1.5

MIL-DTL-16884N - 40 Hours



- As HRD-76 blends, the longer oxidation times and higher F-76 fractions produced larger amounts of insolubles.
- More insolubles formed in the CHCD-76 blends compared to SIP-76 Blends.

F: Filterable Insolubles; A: Adherent Insolubles; T: Total Insolubles

Summary

- HRD-76, SIP-76 and CHCD-76 all comprise fewer compounds compared to conventional petroleum diesel F-76 and ULSD.
- SIP-76 only includes one single component, i.e. farnesane. The main components of HRD-76 are C15-C18 n-alkanes and branched mono-methyl alkanes, and CHCD-76 is composed primarily of C10-C18 n-alkanes and n-alkylcyclohexanes.
- ASTM D4625, D5304 and D2274 stability test results indicated that the long-term storage and oxidation does not have significant impact on biofuel and biofuel blend properties.
- Oxygen consumption rate of SIP-76 and HRD-76 is lower than that of petroleum fuels F-76, but the rate of CHCD-76 is slightly higher than that of F-76.
- The elevated pressure has different impacts on insolubles formation from elevated temperature. Elevate pressure would accelerate the formation of filterable insolubles, while more adherent insolubles would be formed under elevated temperature condition.
- HRD-76, SIP-76, and CHCD-76 have better storage and oxidation stabilities in comparison with F-76.

Thank You

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