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APRIL 9-11
2019
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Screening of Potential Biomass-Derived Streams as Fuel Blendstocks for Mixing Controlled Compression Ignition Combustion

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NREL
Transforming ENERGY

Co-Optimization of
Fuels and Engines

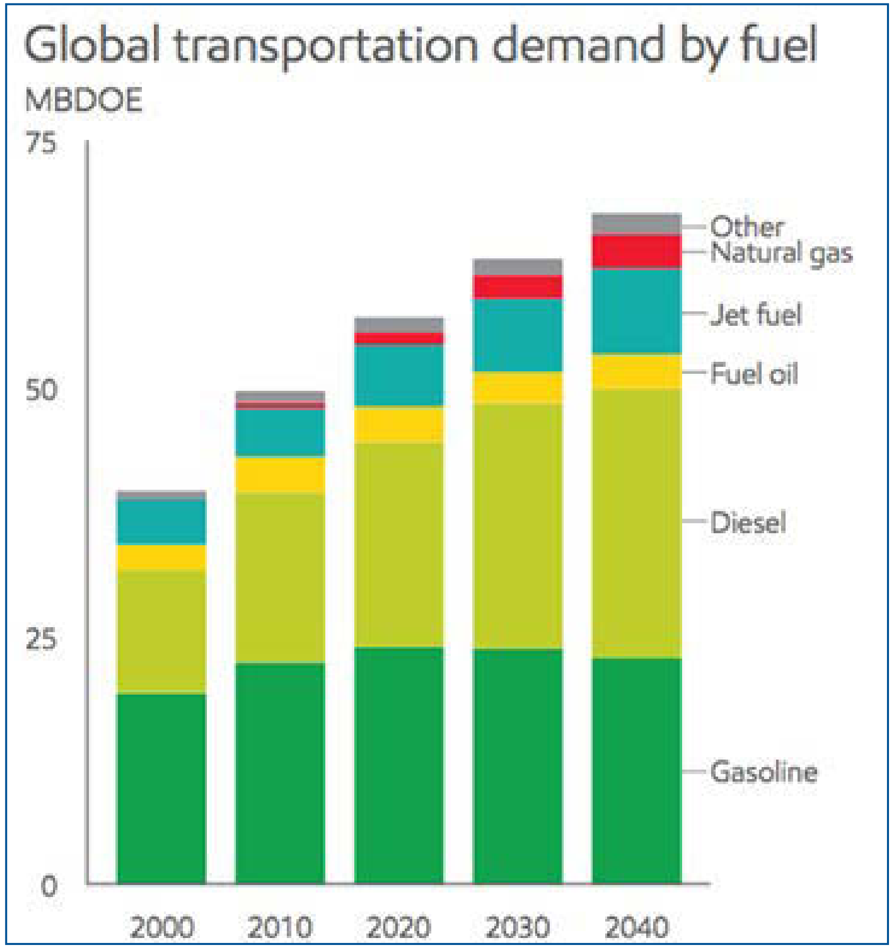
Goal: better fuels and better vehicles **sooner**

Fuel and Engine Co-Optimization

- What fuel properties maximize engine performance?
- How do engine parameters affect efficiency?
- What fuel and engine combinations are sustainable, affordable, and scalable?
- Are there fuel and engine combinations that are optimal – highest life-cycle efficiency?

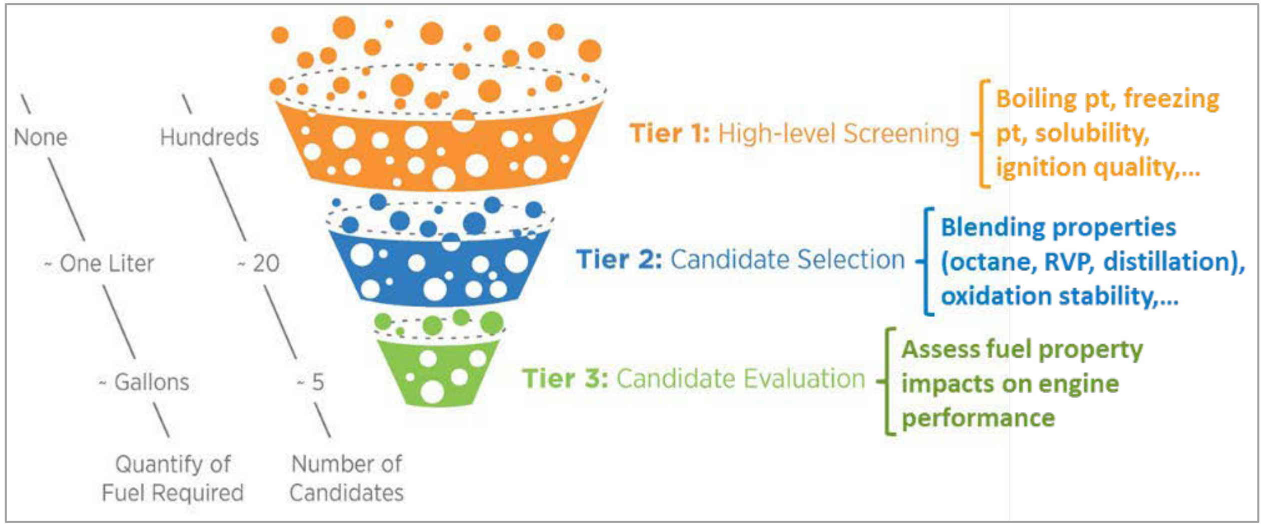
Mixing-Controlled Compression Ignition (MCCI) Engines

- Diesel engines are heavily utilized in freight transport globally.
- They are second only to gasoline in terms of liquid fuel demand.
- Diesel demand is expected to increase.
- Low-net-carbon biofuels have the potential to significantly reduce the carbon footprint of diesel combustion.
- Biofuels could have advantageous properties such as high cetane number and reduced engine-out NO_x and particle emissions.



Approach to Selection and Screening of MCCI Engine Fuels

- Similar to approach utilized for Boosted Spark Ignition (SI) engines: SAE Paper # 2017-01-0868
- Existing publicly available, on-line fuel property database was further expanded with input from multiple labs
- https://fuelsdb.nrel.gov/fmi/webd#FuelEngineCoOptimization



Tiered approach for boosted SI

Tier I Properties for MCCI:

1. Melting point (MP)/cloud point (CP) < 0°C
2. Boiling point/T90 below 340°C (biodiesel allowed)
3. Flashpoint > 52°C
4. Low water solubility
5. Corrosivity equal to or lower than current fuels
6. Toxicity (eliminate category 1 and 2 carcinogens or reproductive toxin)
7. Cetane number (CN) > 40
8. Lower heating value > 25 MJ/kg preferred
9. Sooting tendency – YSI – report

Tier I Answers the Questions: Can it be Fuel? And Can it be Diesel?

- Determine boiling and melting points (diesel range)
- Apply flash point criteria
- Determine fuel handling (diesel distribution system is wet)
- Apply corrosion metric
- Identify known toxicity issues
- Apply ignition metric

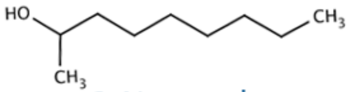
- **400 + molecules and mixtures evaluated.**
- **25 pass into Tier 2.**
- **12 available for further characterization.**

1. Melting point/Cloud point < 0°C
2. Boiling point/T90 below 340°C (biodiesel allowed)
3. Flashpoint > 52°C
4. Low water solubility (< 20g/L)
5. Corrosivity equal to or lower than current fuels
6. Toxicity (eliminate category 1 and 2 carcinogens and reproductive toxins)
7. Cetane number (CN) > 40
8. Lower heating value > 25 MJ/kg preferred
9. Sooting tendency – YSI – report

Christensen, et al. *Energy and Fuels*, **2011**, pp. 4723-4733

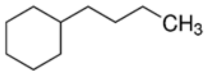
Blendstocks and Mixtures After Tier I Screening

Alcohol



2-Nonanol

Cycloalkane

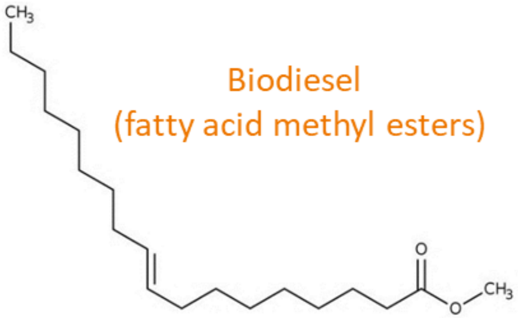


Butylcyclohexane

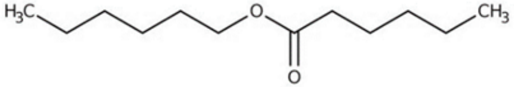
n-Paraffin

n-Undecane

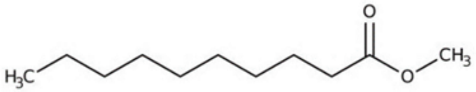
Esters



Biodiesel
(fatty acid methyl esters)



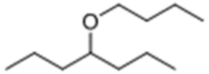
Hexyl Hexanoate



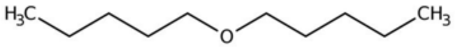
Methyl Decanoate

Ethers

Dibutoxymethane

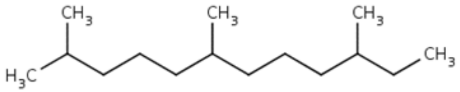


4-Butoxyheptane

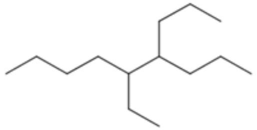


Dipentyl Ether

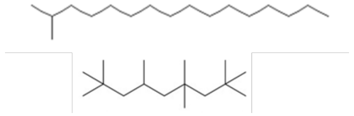
i-Paraffins



2,6,10-Trimethyl Dodecane



5-Ethyl-4-Propylnonane



Renewable Diesel
(mixed isoparaffins)

Multiple functional groups represented

- Developed by predicting what compounds would have desirable properties
- Compounds were synthesized in conjunction with Bioenergy Center within NREL

Selected Functional Group Assessment

Alcohols (1):

- Produced from long-chain fatty acids and triglycerides derived from biomass or via microbial routes
- Can have high MP, high viscosity, and low cetane—limits alcohols that can be used as MCCI blendstocks

Alkanes (5):

- Produced from biological or chemical hybrid routes
- Generally have excellent diesel fuel properties as neat blendstocks
- 5-ethyl-4-propylnonane was developed by predicting what compounds would have desirable MCCI properties and then developing a route to synthesize it

Esters (3):

- Methyl esters are primary components of biodiesel—a commercial biofuel
- Soy biodiesel has slightly higher CP than our screening criteria, but is used as a large scale

Ethers (3):

- Can be produced from fermentation or other routes
- Have high cetane value, but can have low flash point

Tier II Screening: Fuel Blending Properties

Tier II Properties:

1. Effect on distillation curve
2. Conductivity and Lubricity
3. Oxidation stability >1 hr on ASTM D7545 test (based on Top Tier diesel requirement)
4. Viscosity between ~0.5 and 5.0 cSt at 40°C
5. Cloud point
6. Blending DCN (in surrogate)
7. Compatible with commercially available elastomers
8. Density – report
9. Carbon residue – report

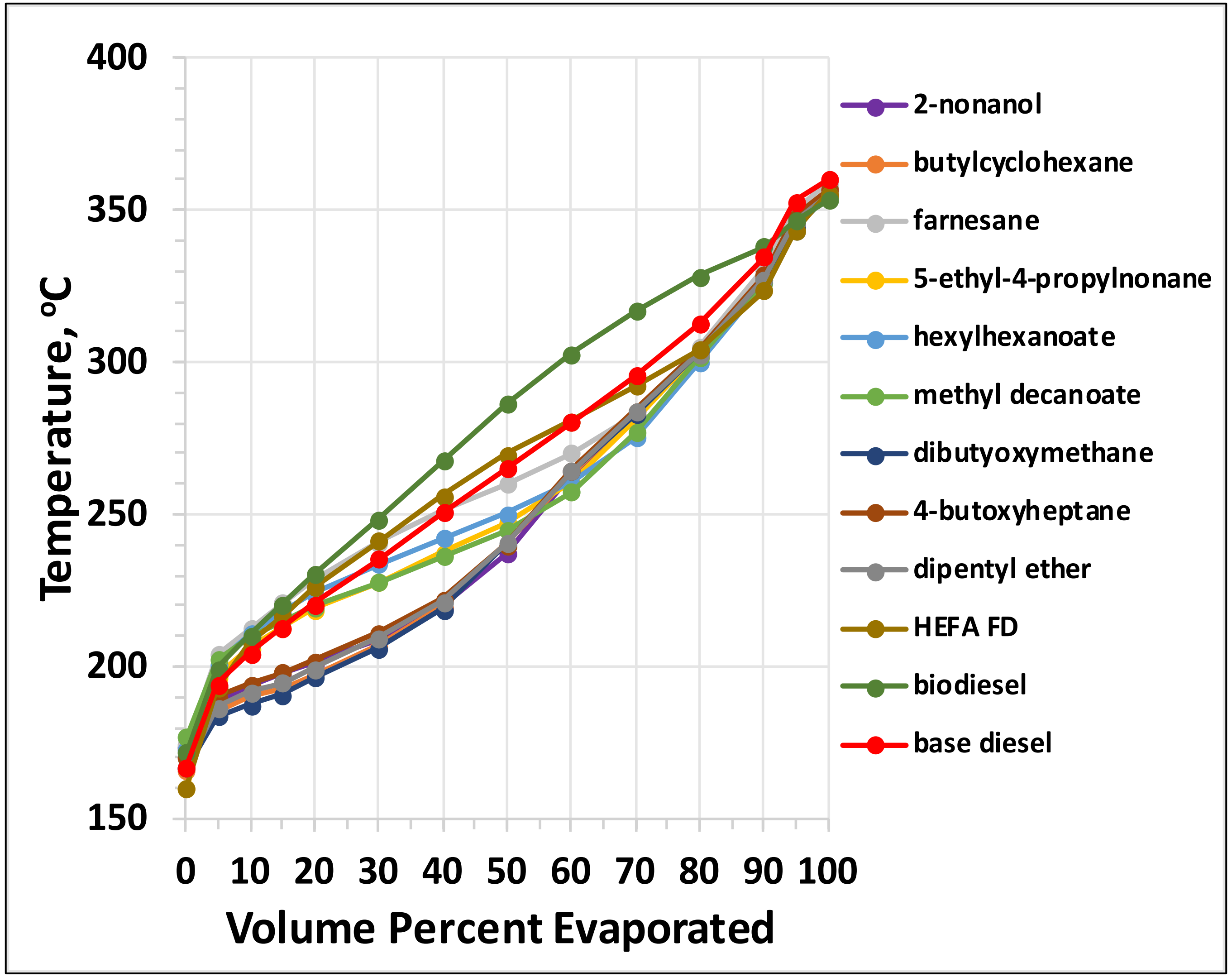
Blended into clay-treated diesel fuel at 20 vol%

Properties of Clay-Treated Diesel and Seven-Component Surrogate

Property	ASTM Method	Units	Value
Flash Point	D93	°C	61
Water and Sediment	D2709	vol.-%	<0.005
Water	D6304	µg/g	37
Viscosity at 40°C	D445	cSt	2.663
Ash	D482	% mass	<0.001
Sulfur	D5453	µg/g	6.2
Copper Strip Corrosion	D130	N/A	1A
Aromatics	D1319	vol.-%	31.6
Cetane Number (ICN)	D8183	N/A	46.8
Distillation T90	D86	°C	330.2
Carbon Residue	D524	% mass	0.09
Lubricity	D6079	micron	520
Conductivity	D4308	pS/m	1
Oxidation Stability	D7545	minutes	68
Total Acid Number	D664	mg KOH/g	0.08
Peroxide Value	AOCS Cd 8b-90	mg/kg	1
Cloud Point	D5773	°C	-9.7

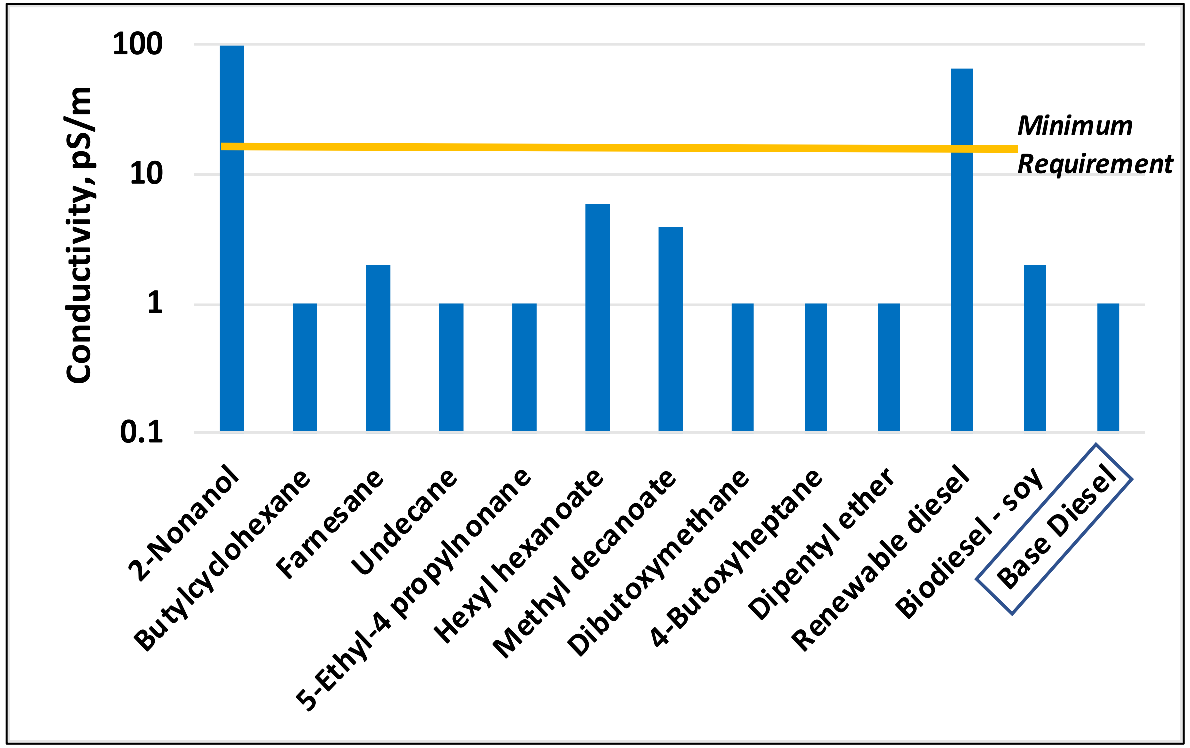
Composition	Molar %	Wt-%	Vol.-%
a-Methylnaphthalene	12.39	9.92	8.12
trans-Decalin	20.08	15.61	14.99
2,2,4,4,6,8,8-Heptamethylnonane	19.00	24.20	26.11
n-Butylcyclohexane	10.50	8.28	8.67
n-Hexadecane	16.61	21.15	22.89
Tetralin	13.78	10.25	8.83
n-Dodecylbenzene	7.64	10.59	10.39
Total	100.0	100.0	100.0
Average Molecular Weight	177.78		
Cetane Number (ICN D8183)	44.5		
Density, g/mL	0.8430		
Cloud point, °C	-10.5		

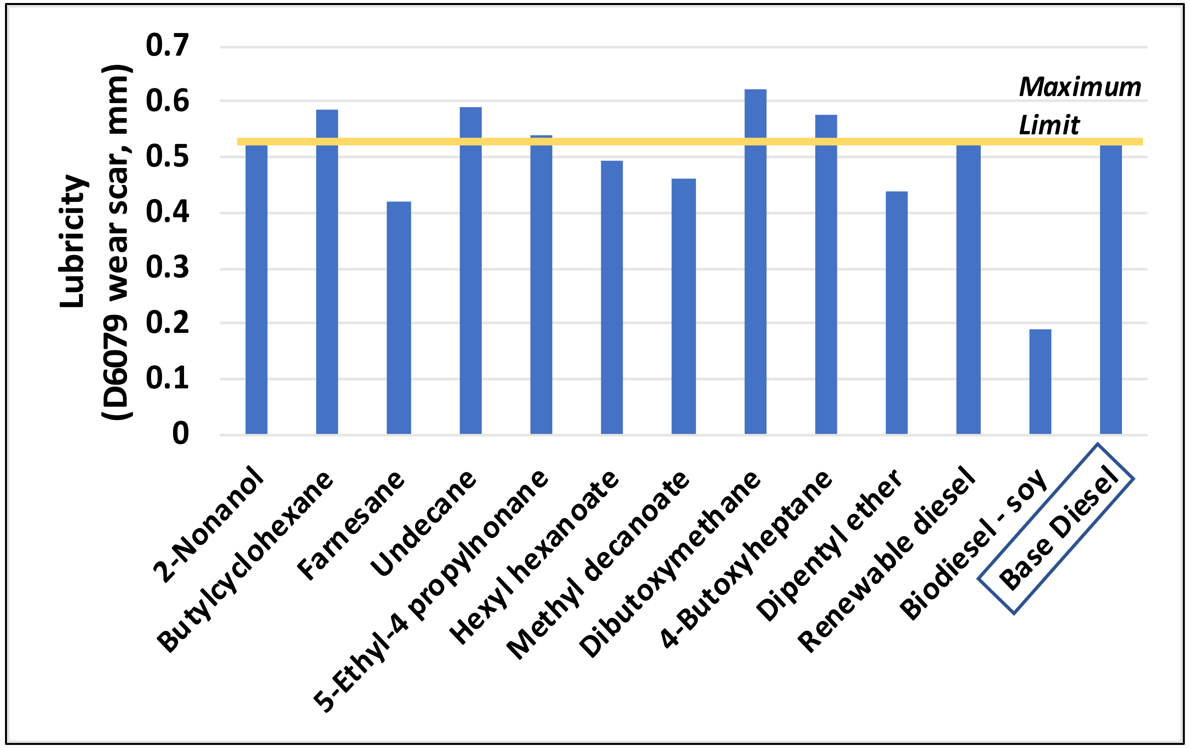
D86 Results: 20% Blends in Clay-Treated Diesel



- 2-Nonanol, butyl cyclohexane, dipentyl ether, 4-butoxy heptane, and dibutoxy methane all show a depression in the D86 curve—especially in the 10%–50% fraction evaporated region.
  - *Could be advantageous for increasing the pre-mixed burn fraction in diesel combustion, which may lead to improved combustion efficiency*
- Methyl decanoate, hexyl hexanoate, 5-ethyl-propyl nonane, and farnesane did not significantly affect the distillation curve.
- Soy biodiesel showed an increase in temperatures across the curve.

Conductivity and Lubricity Results: 20% Blends in Clay-Treated Diesel

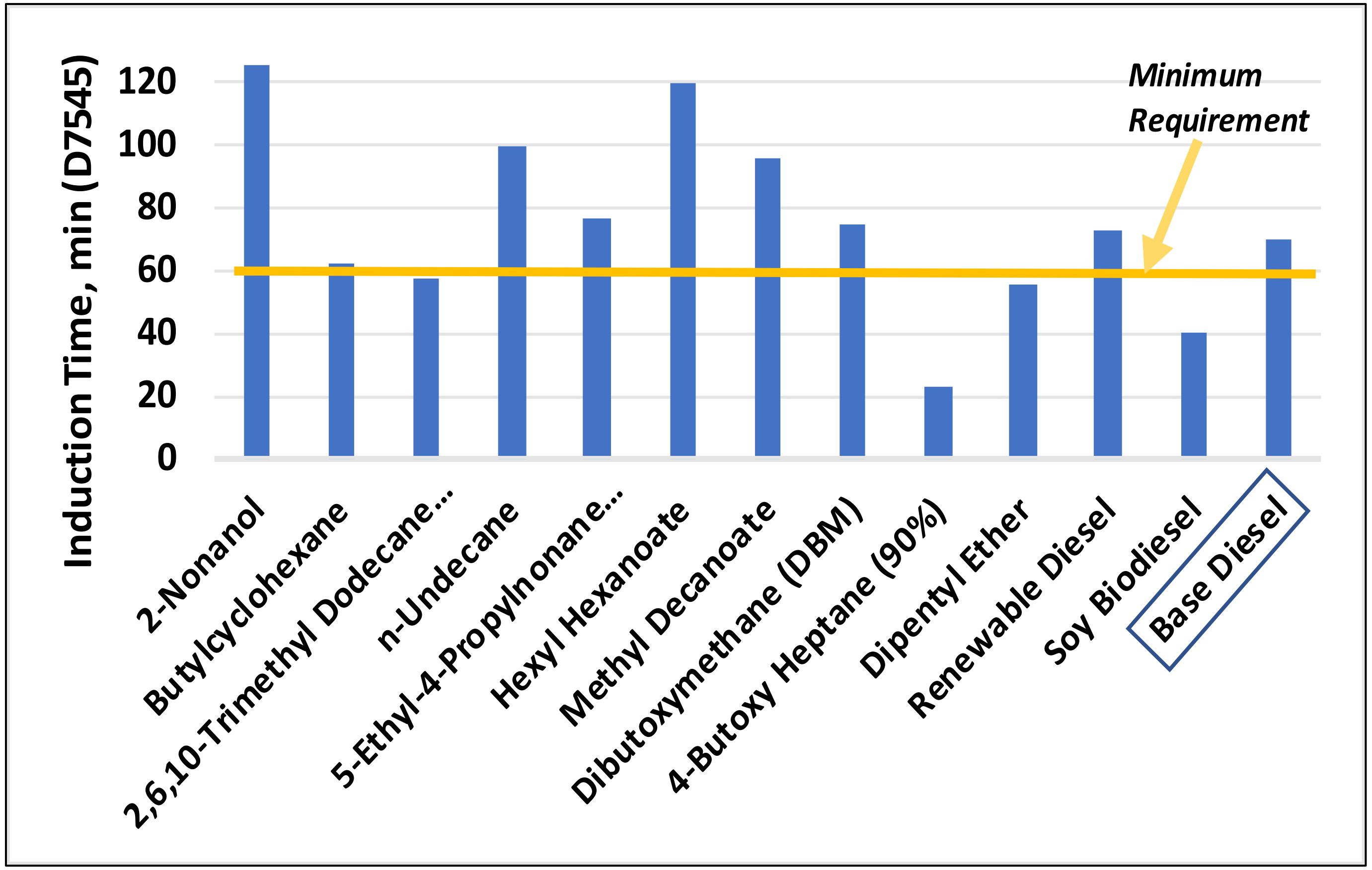




- Renewable diesel and 2-nonanol increase conductivity above the minimum (25 pS/m)
- A conductivity additive could be used to increase the conductivity to an acceptable level for the other blendstocks

- Farnesane and soy biodiesel showed the largest impact on lubricity
- Hexyl hexanoate and methyl decanoate slightly improved lubricity
- Lubricity additives could be used to improve lubricity

Oxidation Stability Results: 20% Blends in Clay-Treated Diesel



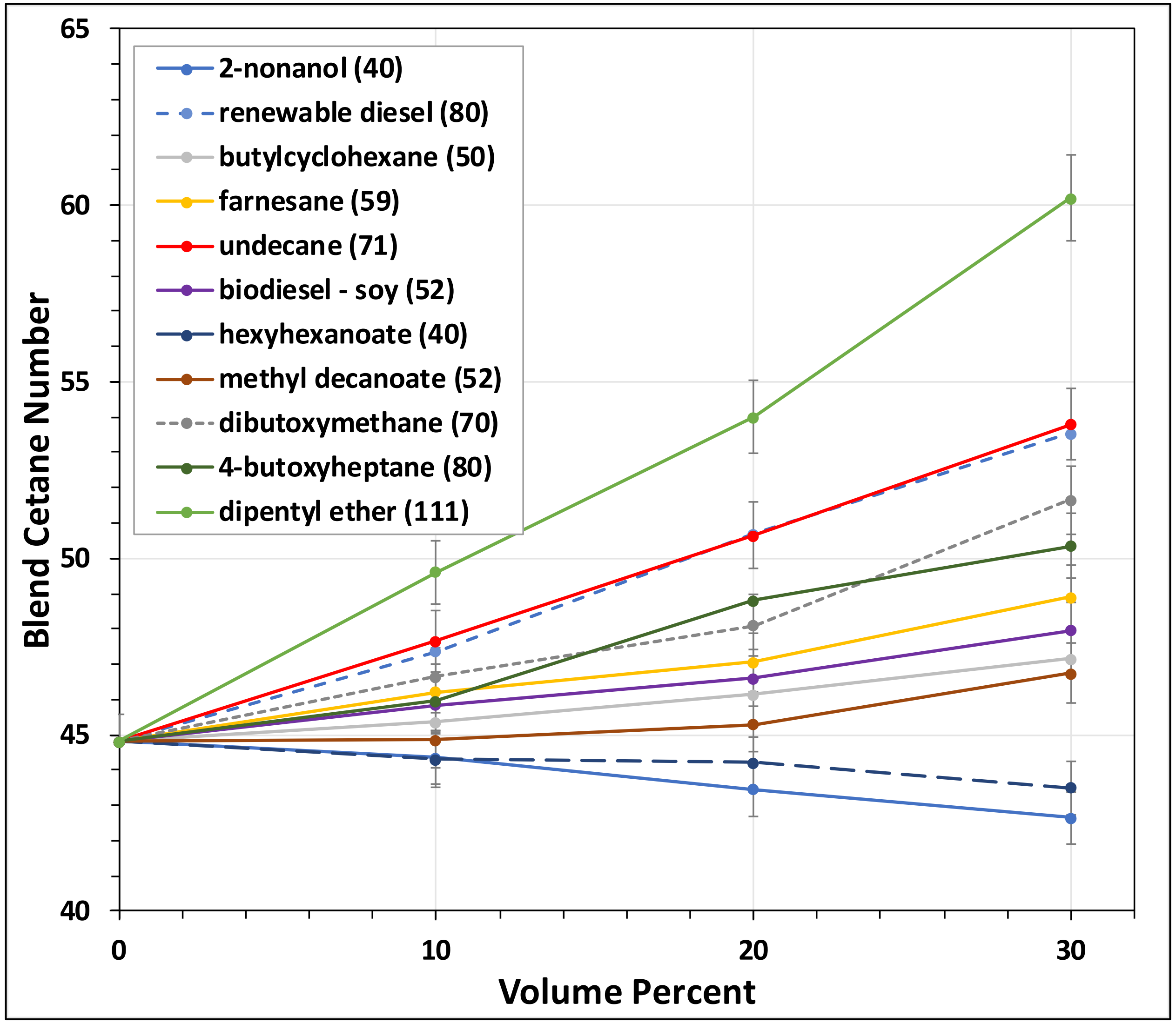
- 2-Nonanol, undecane, hexyl hexanoate, and methyl decanoate significantly increased oxidation stability

- Soy biodiesel and 4-butoxy heptane significantly reduced oxidative stability— an antioxidant additive would be required to meet 60 min minimum– biodiesel is commonly treated with antioxidants to ensure stability in commercial market

- While not shown, treatment of pure 4-butoxy heptane with 100 ppm of the antioxidant butylated hydroxy toluene (BHT) and 20 ppm of a 20% blend in clay-treated diesel was highly effective at preventing oxidation

Oxidation Stability: >1 hr. on ASTM D7545 (based on Top Tier diesel requirement)

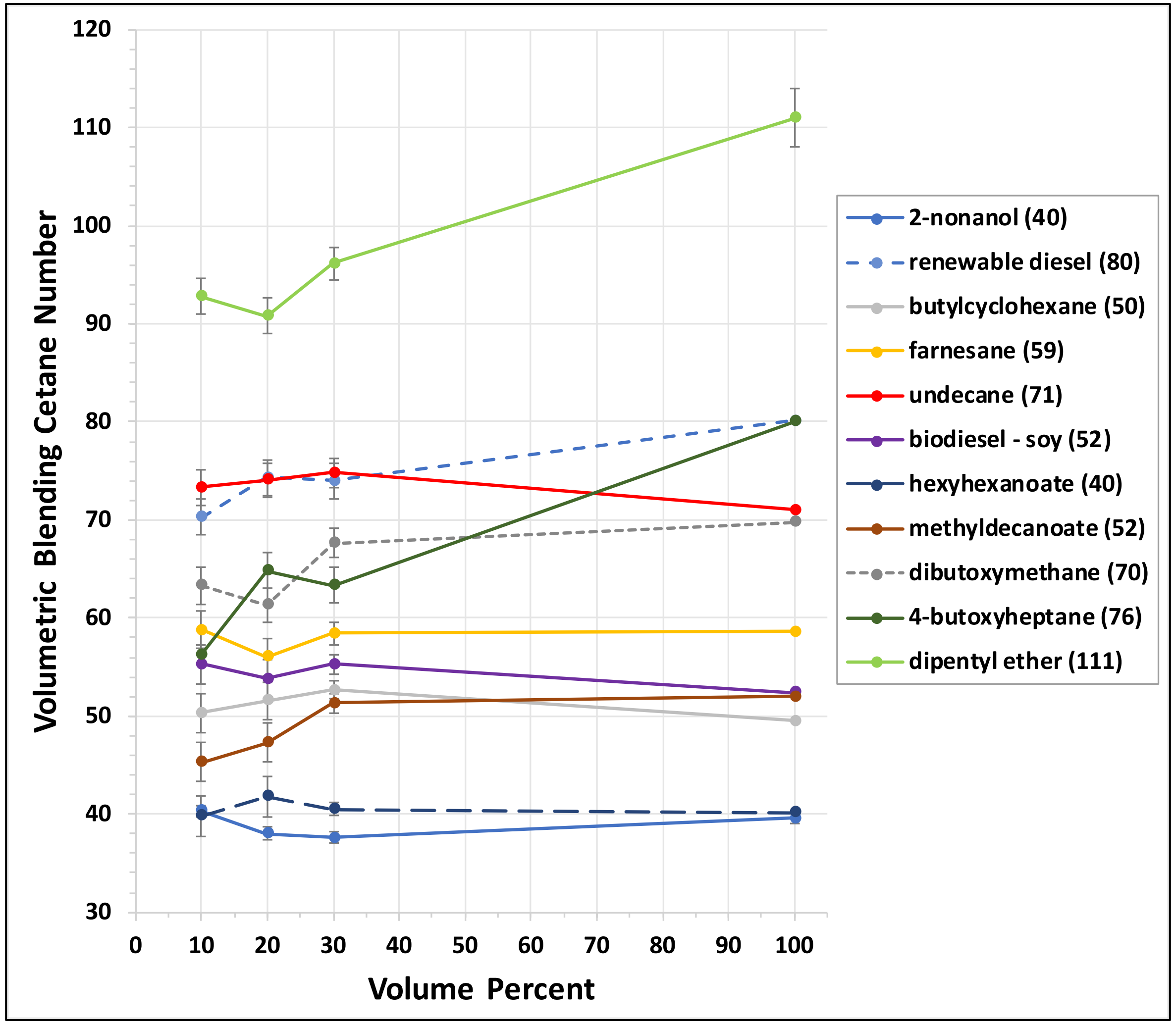
Blending Cetane Results: 10%, 20% and 30% in Seven-Component Surrogate



- Blends were prepared volumetrically in seven-component surrogate
- Values shown in parentheses are neat blendstock cetane
- Cetane was measured using AFIDA
- Blendstocks in general blended linearly

AFIDA: Advanced Fuel Ignition Delay Analyzer

Volumetric Blending Cetane: 10%, 20%, and 30% in 7-Component Surrogate



Volumetric blending cetane was calculated for all blends

bCNv = [Blend CN-Vs*CNs]/Vb

where:

Blend CN = CN of the surrogate+blendstock blends

CNs = CN of surrogate

Vs = volume fraction of surrogate

Vb = volume fraction of blendstock

In a few instances, antagonistic blending—the bCNv is lower than the pure component—was observed

- *Dipentyl Ether*
- *Renewable Diesel*
- *Dibutoxy Methane (10% and 20%)*
- *4-Butoxy Heptane (10% and 20%)*
- *Methyl Decanoate (10% and 20%)*

We speculate that the surrogate interferes with the autoignition of the high-cetane blendstock, acting as a radical scavenger, but more work is needed to fully understand the chemical kinetic interactions

Compatibility with Fuel System and Infrastructure Polymers

Assessed using Hansen Solubility Parameter (HSP) Theory: Done by comparison of the HSPs of pure MCCI blendstocks versus HSPs of polymers and plastics in various applications

Polymer Type	Application
Elastomers	
Fluoroelastomer (Viton™)	Seals, liners, hoses
Fluorosilicone	Seals
Neoprene	Seals and hoses
Epichlorohydrin rubber	Legacy seal material
NBR (HYCAR 1052)	Seals and hoses
NBR (Buna-N)	Seals and hoses
Plastics	
Polytetrafluoroethylene (PTFE) or Teflon™	Liners and seals
Polyvinylidene fluoride (PVDF)	Plastic piping
Nylon 66 (PA 66)	Plastic piping and seals
Nylon 12	Fuel lines and plastic piping material
High-Density Polyethylene (HDPE)	Fuel tanks
Polyoxymethylene (POM) or acetal	Fuel line valves, pump and tank components

- All 11 MCCI candidates evaluated are predicted to be compatible with the elastomers and plastics listed in the table at all blend levels

- Long chain alcohols were the exception: they are likely to be incompatible with neoprene and NBR grades

NBR: nitrile rubber

Summary

- Approach for fuel property-based screening of potential MCCI blendstocks was developed
- Over 400 candidates were assessed, leading to 25 that met the basic Tier I requirements; however, only 12 were readily available
- Several functional groups were represented and include a long-chain alcohol, five alkanes, three esters, and three ethers
- Blends with these 12 candidates were prepared, and Tier II criteria were assessed
- 2-Nonanol, butyl cyclohexane, dipentyl ether, 4-butoxy heptane, and dibutoxy methane all show a depression in the D86 distillation curve—especially in the 10%–50% fraction evaporated region, while the renewable diesel increased the distillation temperatures across the curve
- Most of the blendstocks would likely require the use of lubricity and conductivity improver additives to meet the finished fuel requirements
- Most of the blendstocks exhibited linear blending behavior, except in a few cases were antagonistic blending was observed. Further work to understand the molecular level interactions is needed
- A Hansen solubility analysis indicates that the candidates will likely be compatible with elastomers and polymers; however, the long-chain alcohols may be an issue for NBR and neoprene
- ***Results suggest that the 12 blendstocks have reasonable potential as commercial diesel fuels based on fuel properties***

Acknowledgement

Thank you!!!

This work was authored by the National Renewable Energy Laboratory, operated by Alliance for Sustainable Energy, LLC, for the U.S. Department of Energy (DOE) under Contract No. DE-AC36-08GO28308. This research was conducted as part of the Co-Optimization of Fuels & Engines (Co-Optima) project sponsored by the U.S. Department of Energy (DOE) Office of Energy Efficiency and Renewable Energy (EERE), Bioenergy Technologies and Vehicle Technologies Offices. Co-Optima is a collaborative project of multiple national laboratories and universities initiated to simultaneously accelerate the introduction of affordable, scalable, and sustainable biofuels and high-efficiency, low-emission vehicle engines. The views expressed in the presentation do not necessarily represent the views of the DOE or the U.S. Government. The U.S. Government retains and the publisher, by accepting the article for publication, acknowledges that the U.S. Government retains a nonexclusive, paid-up, irrevocable, worldwide license to publish or reproduce the published form of this work, or allow others to do so, for U.S. Government purposes.

NREL/PR-5400-73569

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