2021 DOE Vehicle Technologies Office
Annual Merit Review

Bioblendstock generation and analysis

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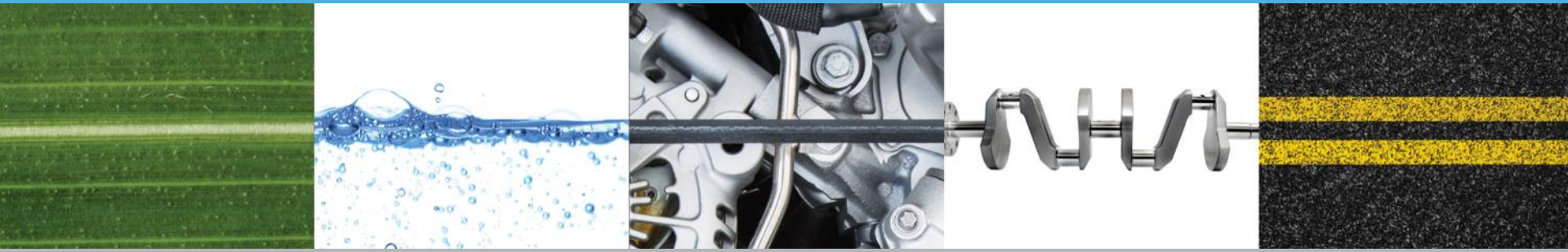
Project ID: ft090
June 24, 2021

CO-OPTIMIZATION OF
FUELS & ENGINES

better fuels | better vehicles | sooner



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Overview | New fuels for light and heavy duty applications

Light-Duty

2030 Goal | 10% fuel economy improvement beyond expected 25% increase from base engine improvements

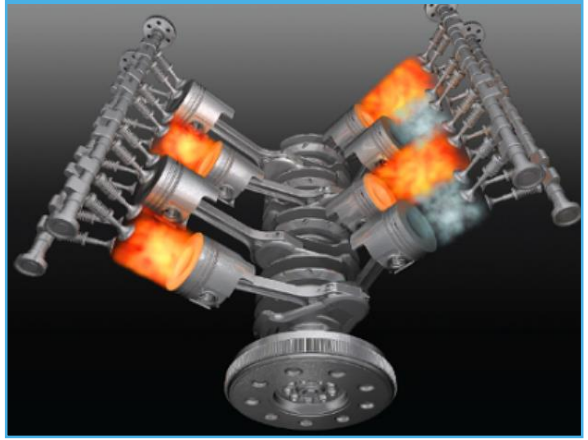
Medium/Heavy-Duty

2030 Goal | 4% fuel economy improvement and lower cost path to meeting criteria emissions regulations

ACI – Advanced Compression Ignition; MCCI – Mixing Controlled Compression Ignition

Overview | BETO's focus is which the best fuel options for the real world?

What fuels do engines *really* want?

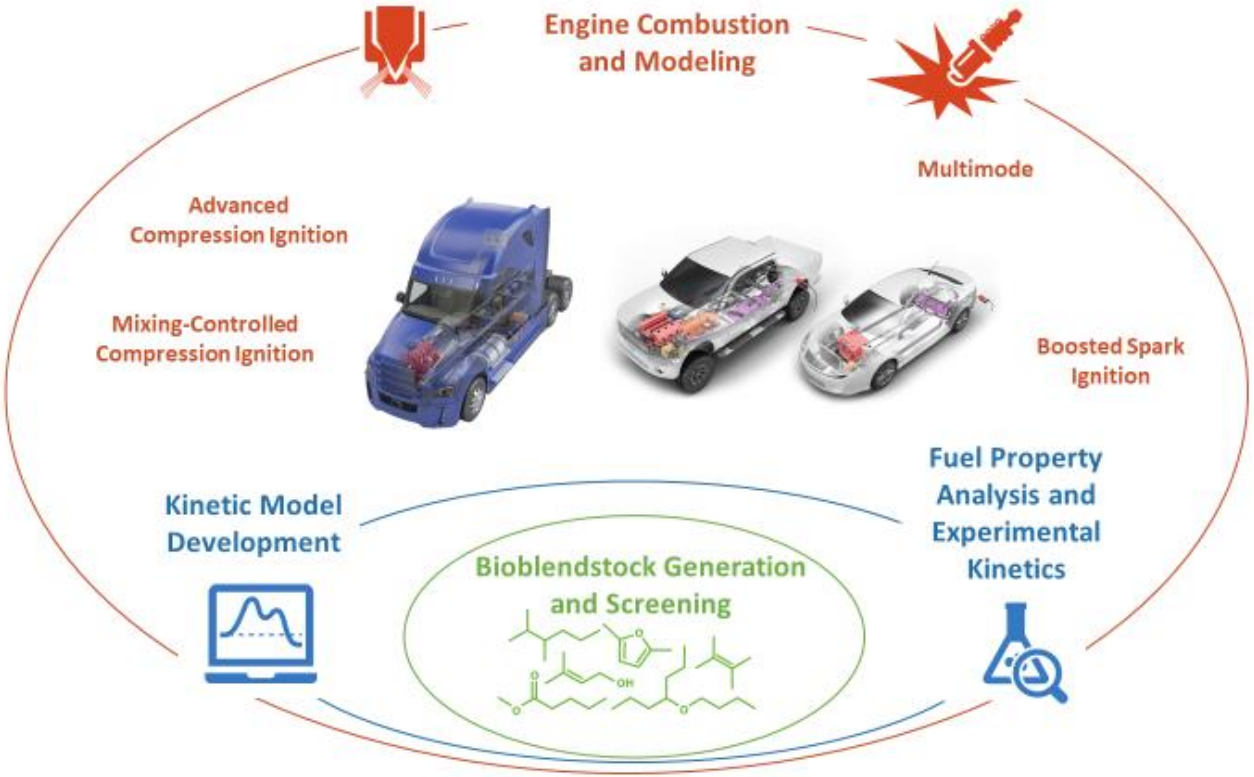


What fuel options work best?

What will work in the real world?

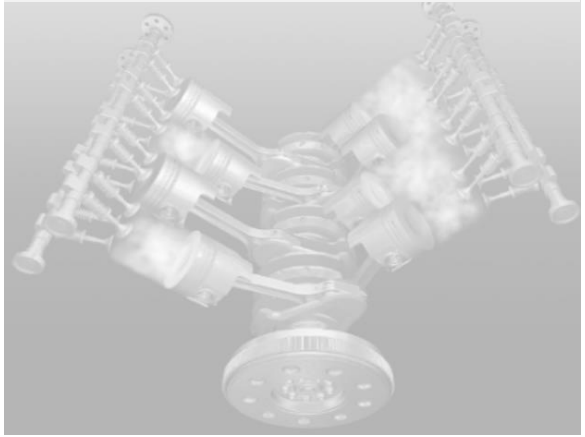
Photos courtesy of iStock

Overview | Questions cannot be answered in isolation



Approach | Focus is to determine the best fuel options for the real world

What fuels do engines *really* want?



What fuel options work best?

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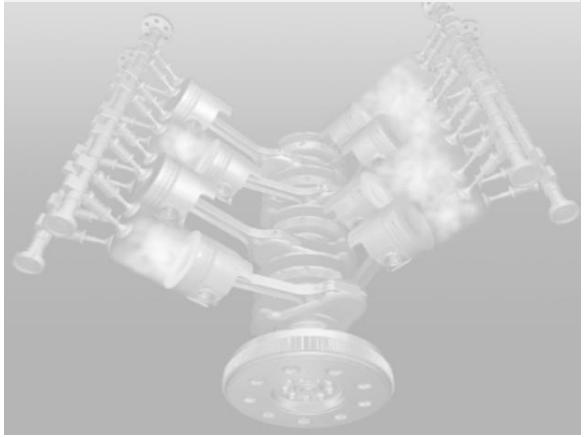
Approach | What fuel options work best?

What fuels do engines *really* want?



What fuel options work best?

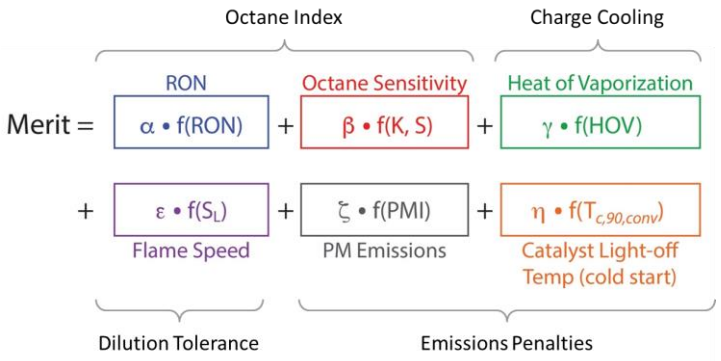
What will work in the real world?

Photos courtesy of iStock

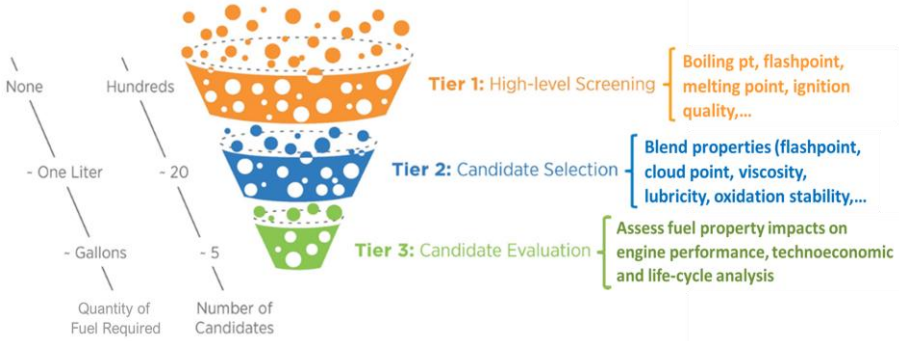
Approach | Important fuel properties defined and molecules screened

- Determine key fuel property metrics to meet co-optima goals
  - Improve efficiency
  - Reduce CO_2 / criteria emissions
  - Achieve cost targets
- Apply screening process
  - Tier 1: High level screening
  - Tier 2: Blend properties
  - Tier 3: Property impacts on engine, LCA/TEA
- Define promising candidate structures

Boosted spark ignition efficiency parameters



MCCI properties & screening process



Approach | Structure-property relationships allow evaluation of many molecular classes

Mapping and predictive identification of accessible, safe, advantaged oxygenates

Pathway validation and testing material generation

Pure and blended blendstock quality evaluation and prediction validation

De-risking oxygenate blendstock use

Process evaluation for economic viability

- More than 12 molecular classes and subclasses
- 1000s molecules and blends evaluated

3 case studies today:

- Iso-alkanes
- Polyoxymethylene ethers
- Iso-olefins

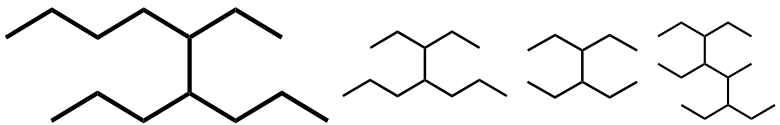
Outcomes | Iso-alkanes provide excellent fuel properties for MCCI engines

Bioblendstock Generation

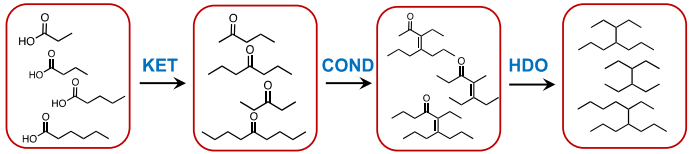
Volatile fatty acids (VFA) derived from food waste converted to mixed isoalkanes with data provided to Analysis for TEA/LCA

Fuel Property Testing

Confirmed food waste-derived mixed iso-alkanes also meet MCCI Tier 1 criteria with high cetane and flash point, despite varying chain lengths, with exceptional freezing point from branching



4-ethly-5-propylnonane *mixed isoalkane analogues*



Waste Derived C3-C6 VFAs **Mixed Ketones** **Enone Dimers** **Mixed Isoalkanes**

MCCI Bioblendstock	DCN	LHV (MJ/kg)	Flash Pt (° C)	YSI	Melting Pt (° C)	Boiling Pt (° C)
Tier 1	**> 40**	**> 25**	**> 52**	**< 200***	**< 0**	**< 338**
4E5PN	45	44.0	74	98	< -80	230
VFA Mix	73	44.4	62	NA	< -53	268

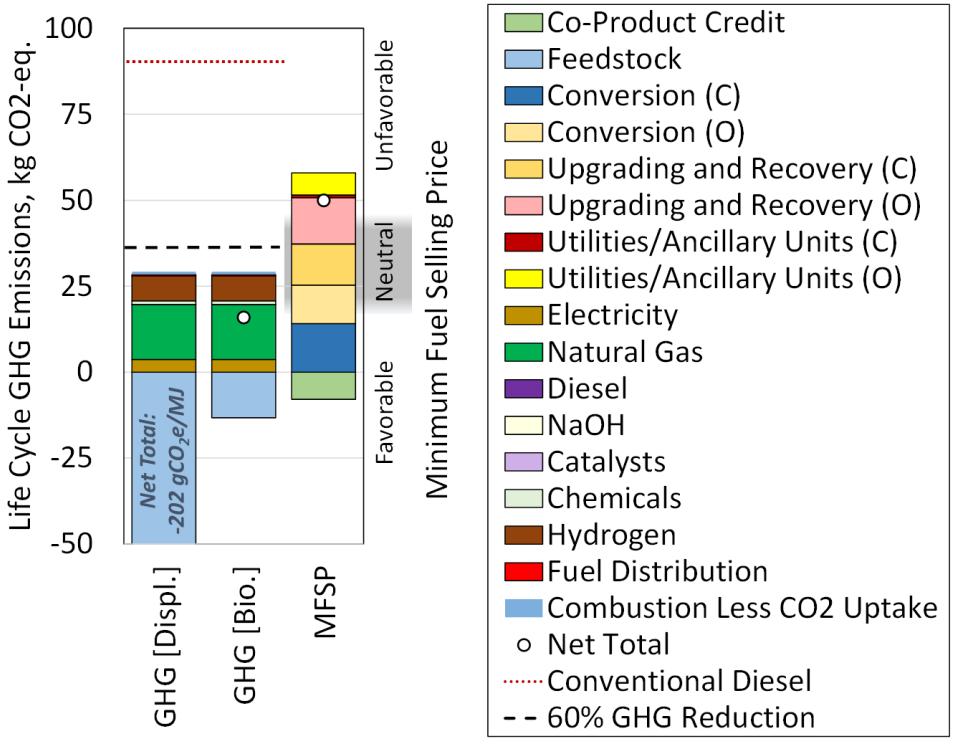
*Measured values. Fossil diesel YSI typically above 200**

Huo et al. (2019) Green Chem. 21, 5813-5827 Huq et al. (2021) PNAS. Accepted. (Ket: Ketonization, COND: condensation, HDO: hydrodeoxygenation

Outcomes | Iso-alkanes have promising economics and low GHG profile

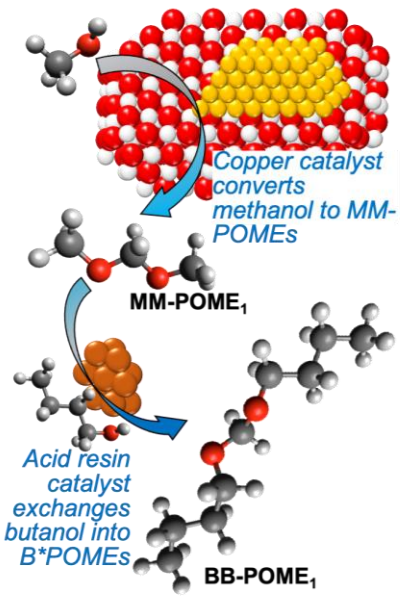
- TEA
  - Projected cost of $3.71/gallon has been offset by use of waste feedstock to produce >C8 iso-paraffins using KET-HDO
  - Analysis may change after larger-scale production generates new data
- LCA
  - Low carbon fuel standard credits could allow for net negative GHG offset

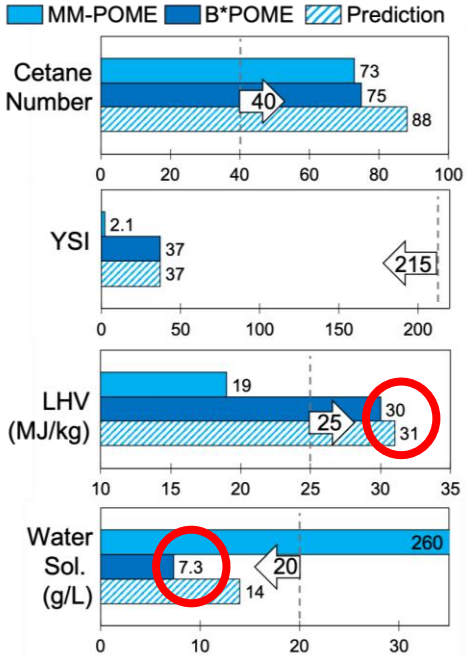
Technoeconomic and life cycle analyses



Slides and report section prepared by Huq, Bartling, Wiatrowski, Vardon, Hawkins and Benavides

Outcomes | End-group exchange for POMEs enables improved properties





*B*POME = butyl-end group exchanged POME*

Polyoxymethylene ether barriers

- Potential for high cetane, low soot
- But low energy density, oxidative stability, water solubility

Bioblendstock Generation

- Developed liter-scale method for butyl end-group exchange at mild conditions with commercial catalysts to enable handoff for testing

Fuel Property Testing

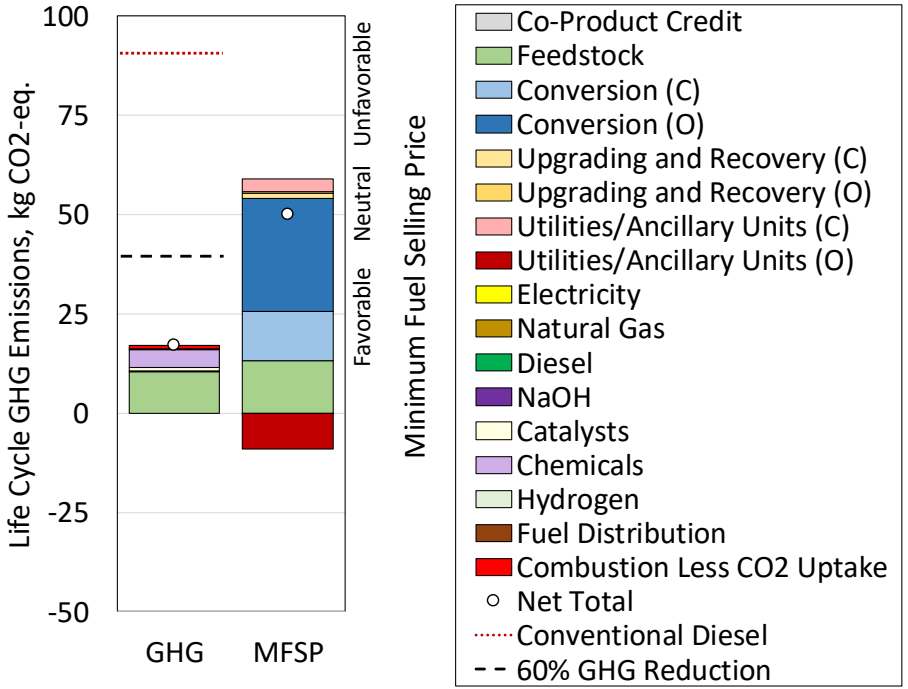
- Confirmed butyl-exchanged POMEs addresses energy density and water solubility limitations, while retaining benefits of high cetane and low yield sooting index (YSI)

Arellano-Trevino et al. (2020) ACS SusChemEng. Submitted. Bartholet et al. (2020) Fuel. Submitted

Outcomes | Further R&D to establish economics but promising GHG emissions

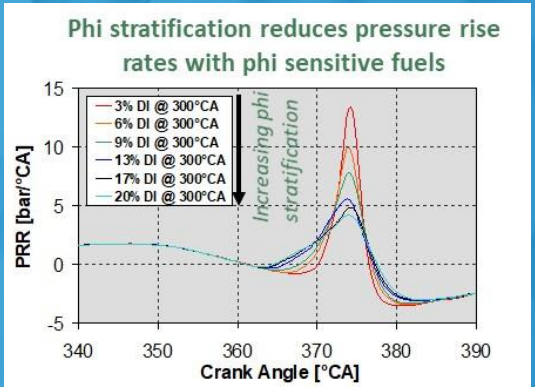
- LCA
  - Fossil energy consumption of the POME pathway is favorable compared to that of petroleum diesel (92 g CO_2-eq/MJ)
  - Modeled pathway achieves ~81% GHG emission reduction
- TEA
  - Target case results show a MFSP between $4.00–4.50/GGE for POMEs produced via oxidative one-step process
  - Novel one-step oxidative process for POME production was entirely based on theoretical thermodynamic equilibrium; further research will be required to confirm assumptions used in process simulation

Technoeconomic and life cycle analyses

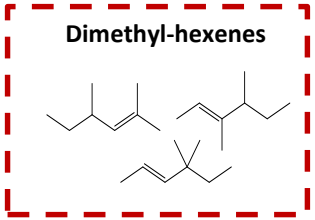


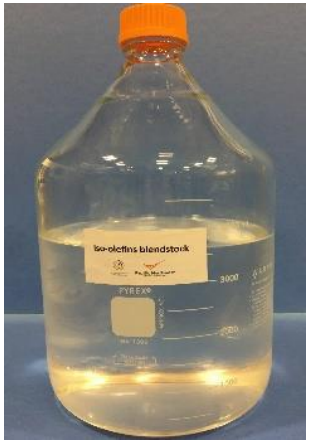
Outcomes | Structure property relationships of iso-olefins lead to ϕ-sensitive fuels

- ϕ-sensitivity has important benefits for the operation and the control of ACI engines, which can enable diesel efficiencies with low NOx / soot
- A fuel is ϕ-sensitive if its autoignition reactivity varies with equivalence ratio for the same thermodynamic conditions



- Iso-olefins show promising fuel properties including high RON & S
- Can we obtain a ϕ-sensitive fuel whilst maintaining other properties?
- Developed conditions and catalysts for bio-butene oligomerization to vary branching in iso-olefin mixture
- Produced gallons to validate predicted autoignition improvements

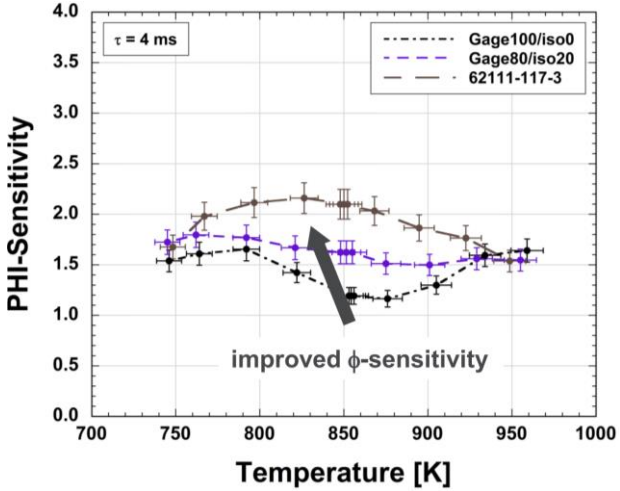




4 liters Dimethyl-hexene-rich olefins

Dagle et al. (2020) Fuel. 277, 118147

Outcomes | Structure property relationships for high ϕ-sensitivity fuels



Sample	Measured RON	Measured MON	S
Base Fuel	86.1	83.1	3.0
100 vol.% dimethyl-hexenes-rich olefins	94.0	80.5	13.5
20 vol% blend	89.5	83.1	6.4

Structure property relationships

- Performed RCM engine testing with neat and 20 vol% blend of iso-olefin to confirm synergistic autoignition improvements in RON MON
- Found a measurable increase in ϕ-sensitivity of the petro-derived gasoline when blended with the iso-olefin mixture

Leads: Dagle and Kolodziej

Outcomes| What will work in the real world?

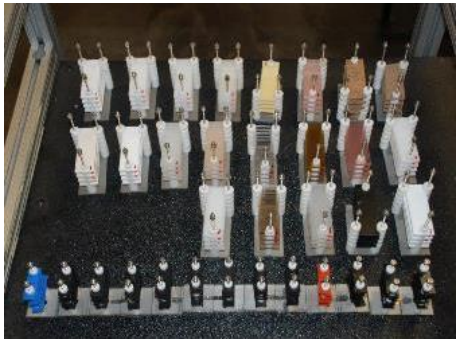
What fuels do engines *really* want?

What fuel options work best?

What will work in the real world?

Photos courtesy of iStock

Outcomes | Polymer compatibility necessary for real-world applicability

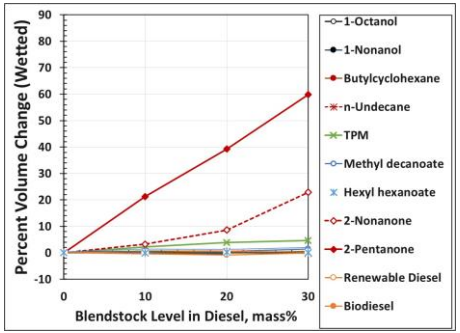


- Volume swell is proportional to solubility, which depends heavily on polarity.
- Many elastomers are polar.
- Highly polar blendstocks produce more swell in the elastomer materials.

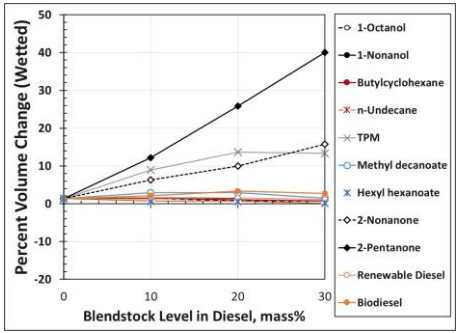
Compatibility Testing

- Validated material compatibility fuel properties including infrastructure elastomers and plastics, which are used as seals and hoses.
- Elastomers exposed to fuel immersion for 4 weeks/plastics exposed for 16 weeks.
- Key properties include volume/mass change and point change in hardness.

Viton (seal material)



Nitrile rubber (hose material)



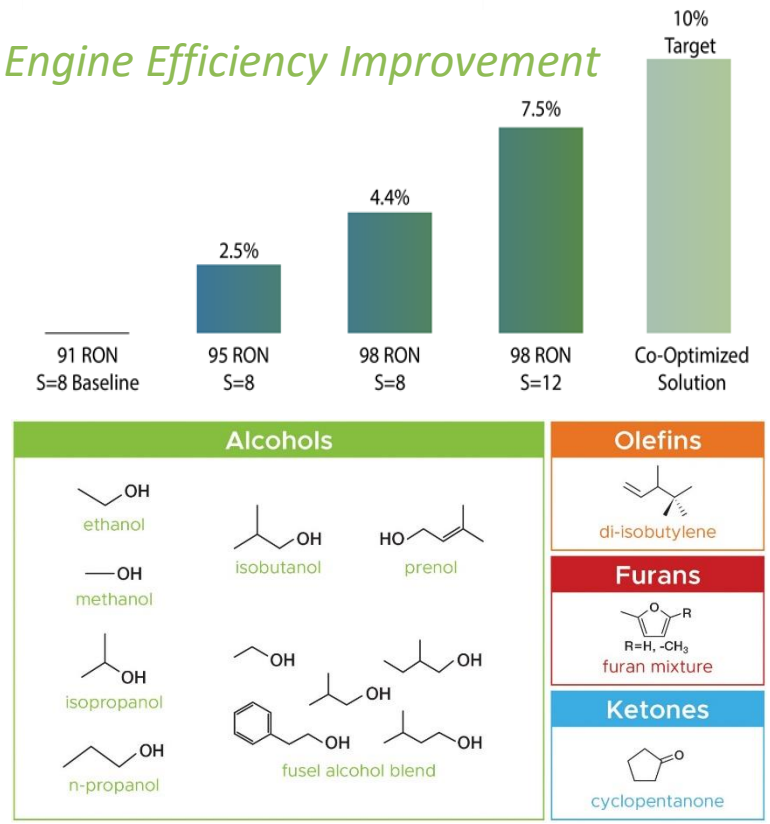
Key Findings

- Alkanes, esters, and alcohols were suitable with many of the elastomers. For some materials (e.g. neoprene), these blendstocks improved the compatibility compared to diesel.
- In contrast, the ketones and TPM produced unsuitable volume expansion in many elastomers
- Analysis of the results showed that the swelling behavior is predominantly due to high polarity matchup between the elastomer and test fuels.

Lead: Vardon, NREL Huq et al. (2019) PNAS. 52, 26421-26430 Kass et al. Energy Fuels 2021, 35, 4979–4996

Outcomes | Several options for achieving 10% efficiency gains in LD engines

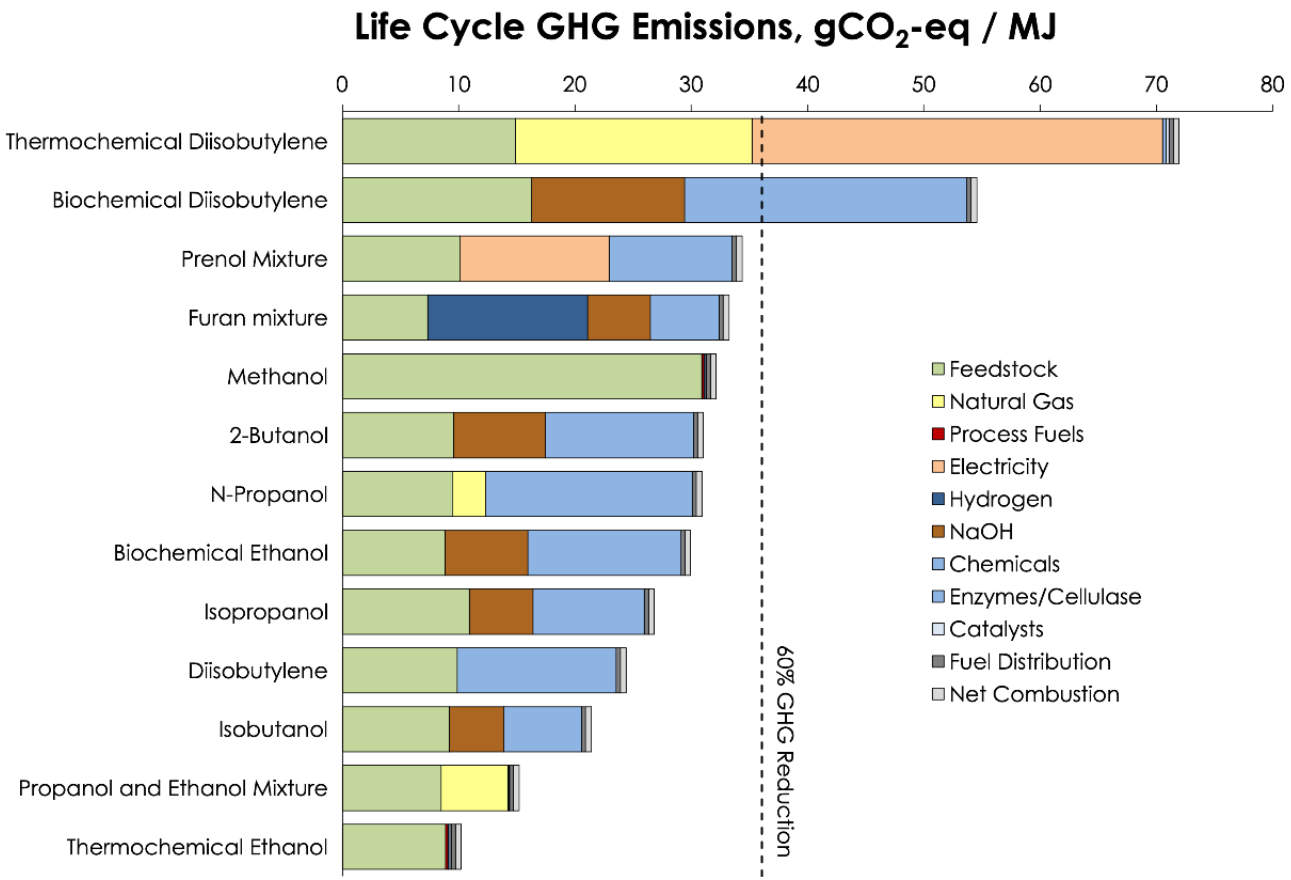
- Demonstrated properties to achieve 10% efficiency gain
- Identified 10 blendstocks
  - High RON and S
  - Meet gasoline property requirements
- Chemical structure-fuel properties-engine performance relationships enable identification of more efficient fuel-engine combinations



S = sensitivity = RON - MON; Engine efficiencies calculated for conditions appropriate for boosted downsized engines (K = -1.25)

Source: Miles, Paul. "Efficiency Merit Function for Spark Ignition Engines: Revisions and Improvements Based on FY16–17 Research." Technical Report. U.S. Department of Energy, Washington, DC. 2018. DOE/GO-102018-5041.

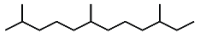
Outcomes |… and well-to-wheel CO_2 emissions reductions



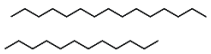
Outcomes | Thirteen MCCI blendstocks with potential to reduce GHG by 60%+ and criteria emissions

- Potential to reduce criteria emissions vs. market diesel
- Potential for production at larger scale
- CN > 40 (most > 48), LHV > 28 MJ/kg, acceptable flashpoint and cloud point
- Blendstock GHG emissions reduced by 50% or >60% in many cases
- Potential to be produced at $5.50/gge or better

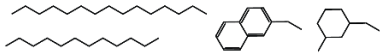
Hydrocarbons



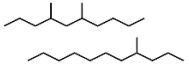
farnesane



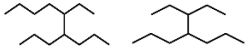
Fischer-Tropsch diesel



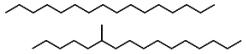
hydrothermal liquefaction oil from wet waste, algae, and algae-wood blends



isoalkanes made from ethanol

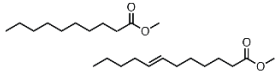


isoalkanes via volatile fatty acids from food waste

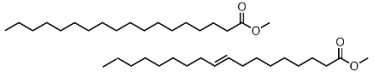


hydroprocessed esters and fatty acids (renewable diesel)

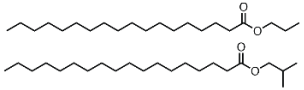
Esters



short chain esters from oilseed crops

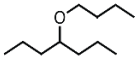


fatty acid methyl esters/biodiesel

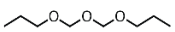


fatty acid fusel esters

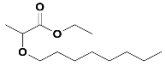
Ethers



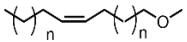
4-butoxyheptane



polyoxymethylene ethers (POMEs)

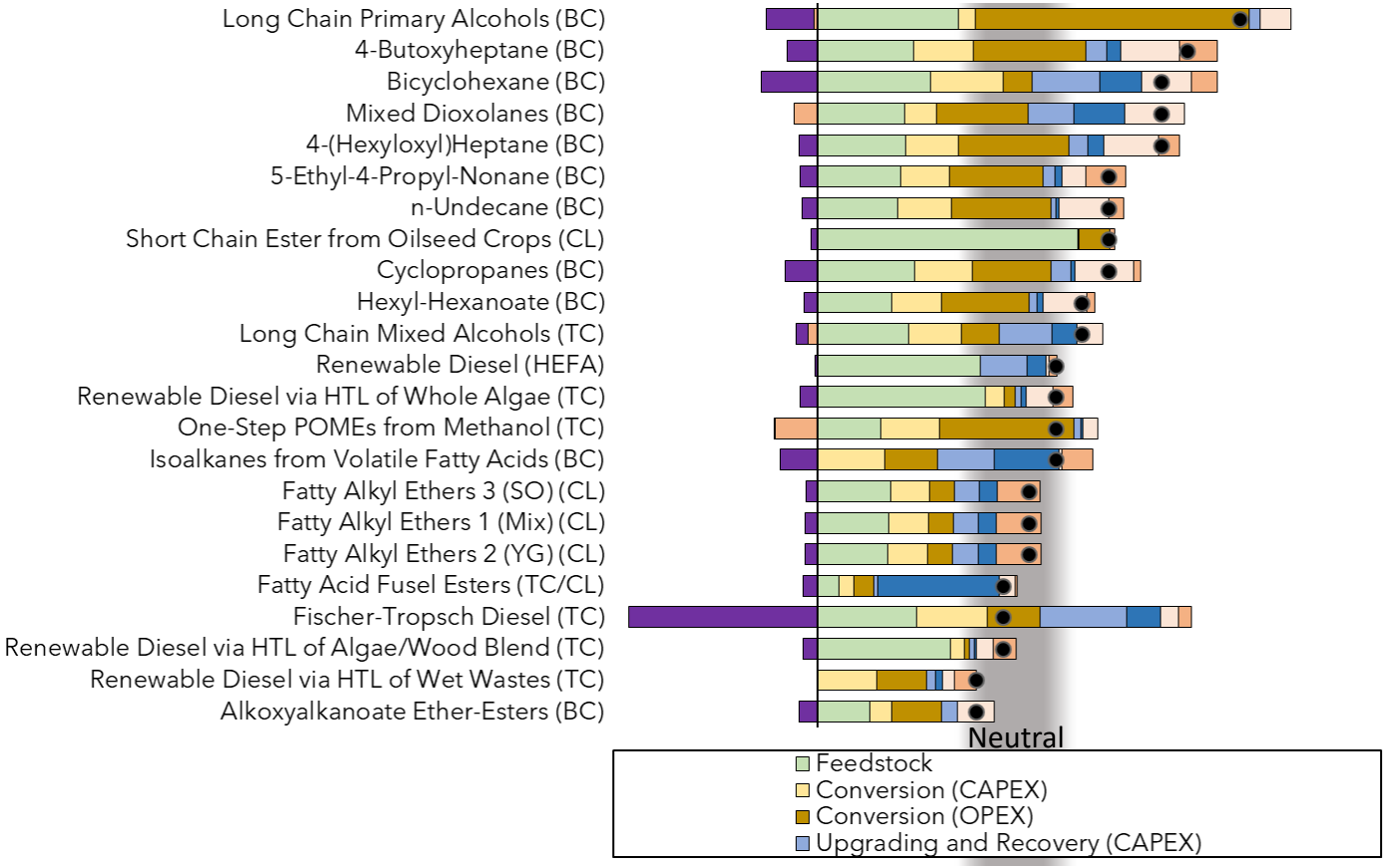


alkoxyalkanoates

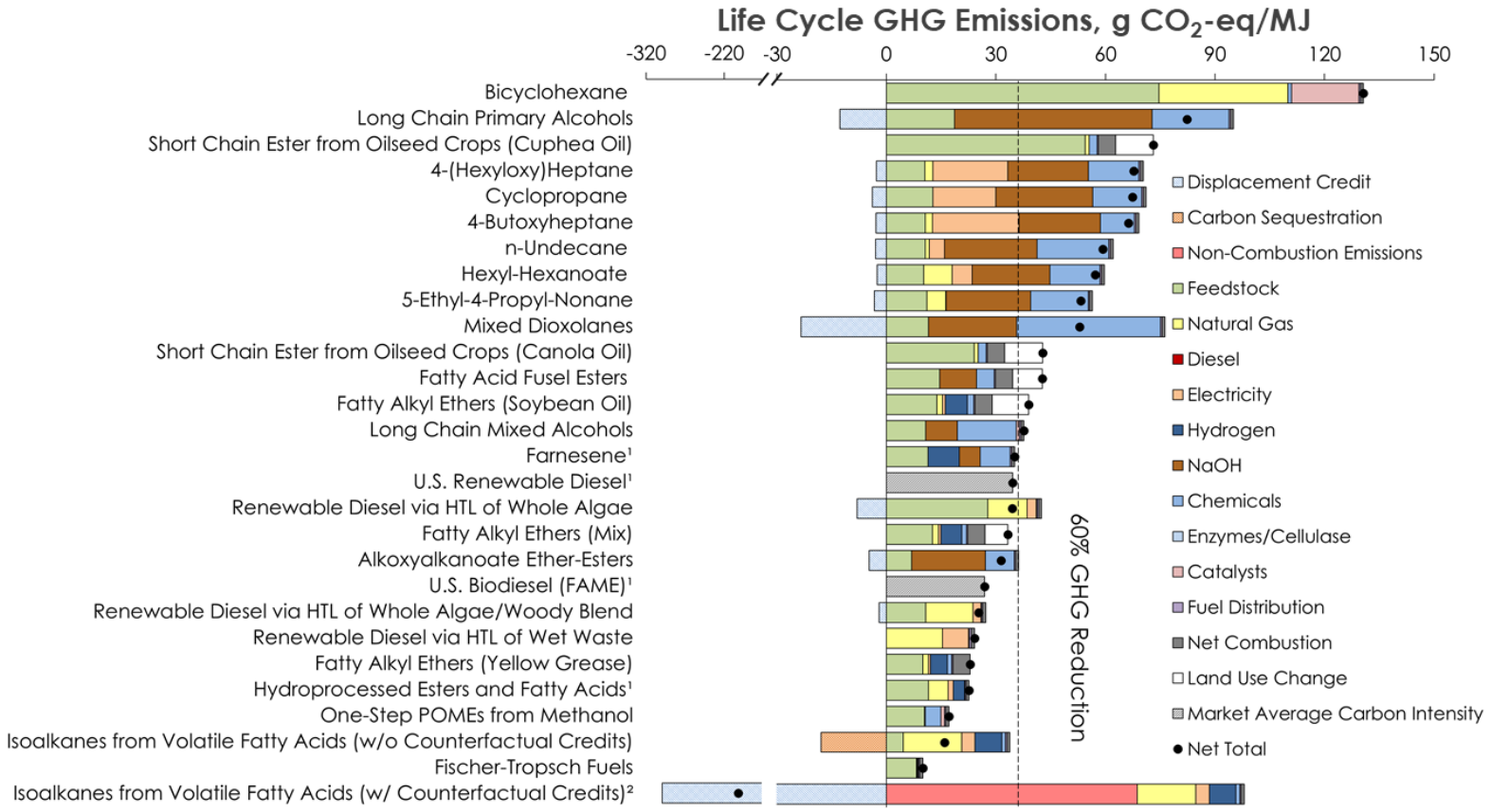


fatty alkyl ethers

Outcomes | Bringing down cost is a key challenge for emissions-reducing bioblendstocks



Outcomes | Significant gains can be made in lifecycle GHG emissions



¹ *GHG emissions of these pathways are from either an earlier study or average of market fuels.*
² *The negative GHG emissions from the "Isoalkanes from Volatile Fatty Acids" pathway is because of the credits of avoided emissions from landfill of the food waste feedstock.*

Conclusions and Future Directions | Realizing the potential

- Systematically identified best fuel options for different engines
- Identified cost effective pathways to produce low-carbon, performance advantaged biofuels from diverse feedstocks
- Provided comparable, transparent, and reproducible TEA and LCA for bioblendstock production pathways
- Designed production pathways with potential for 70-90% GHG reductions

The world has changed since 2016

- Initial Co-optima targets:
  - Displace fossil fuels with 30% sustainable fuel
  - Reduce GHG emissions by 20%

Need aggressive deployment for net-zero

- Diversify resource base
- Provide economic options to fuel providers to accommodate changing demands and drivers
- Increase market opportunities for biofuels

Acknowledgements

U.S. DEPARTMENT OF ENERGY | Office of ENERGY EFFICIENCY & RENEWABLE ENERGY

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Alicia Lindauer
Technology Manager, BETO Bioenergy Analysis & Sustainability

David Howell
Acting Director, Vehicle Technologies Office (VTO)

Gurpreet Singh
Program Manager, VTO Advanced Engine and Fuel Technologies

Kevin Stork and Michael Weismiller
Technology Managers, VTO Advanced Engine and Fuel Technologies

Publications and Patents | Peer-reviewed publications

- Y. Kim, A.E. Thomas, D.J. Robichaud, K. lisa, P.C. St. John, B.D. Etz, G.M. Fioroni, A. Dutta, R.L. McCormick, C. Mukarakate, S. Kim. (2020). A Perspective on Biomass-Derived Biofuels: From Catalyst Design Principles to Fuel Properties. Journal of Hazardous Materials. 400, 123198
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