Thrust 1 Technical Overview

Jim Szybist (ORNL), Dan Gaspar (PNNL)

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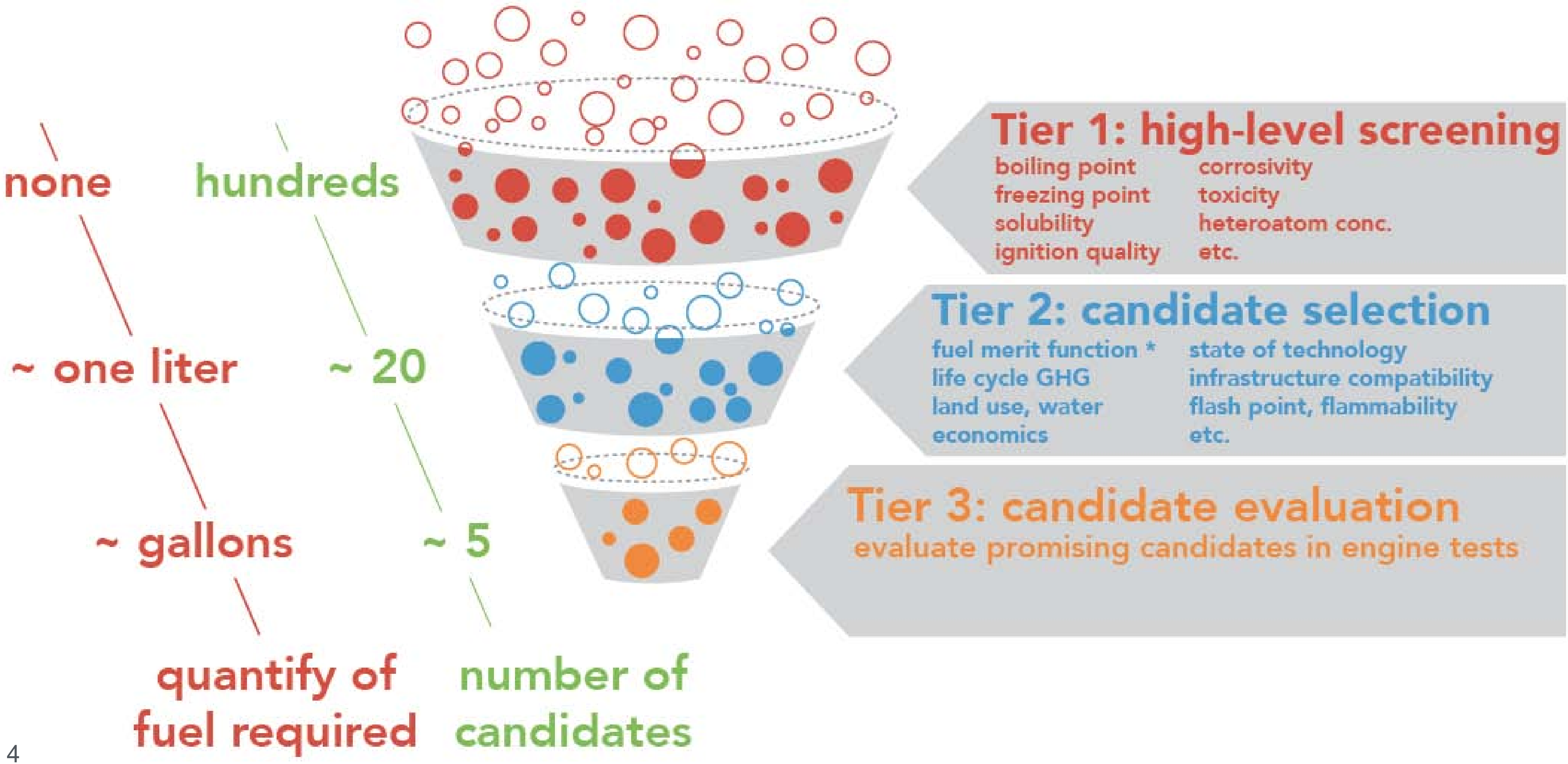
Thrust 1 Approach

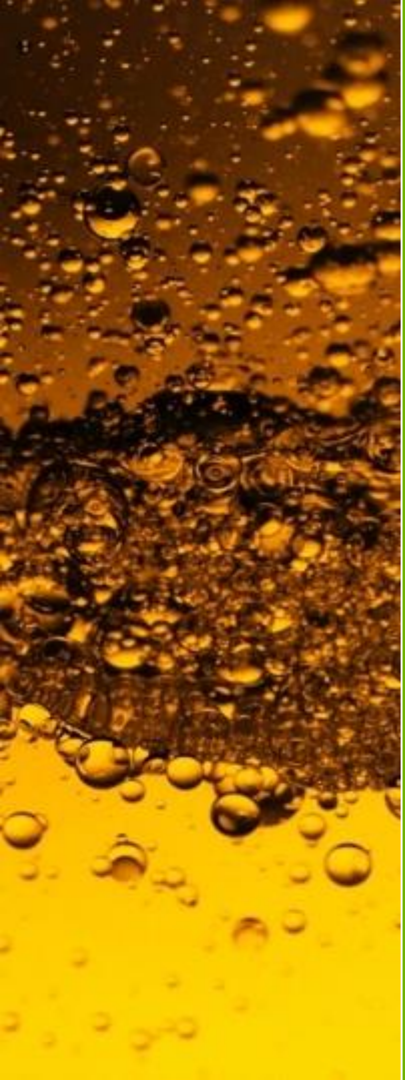
- From biomass to blendstock
- Blendstock properties
- Fuel properties and engine performance
- Advanced spark ignition engine performance

From biomass to blendstocks - spark ignition candidates identified

- Identified 9 molecular classes suitable for further evaluation
  - Paraffins (especially highly branched paraffins), olefins, cycloalkanes, aromatics, alcohols, furans, ketones, ethers, and esters
- Developed list of candidates from these classes based on:
  - Open literature sources
  - Ongoing National Laboratory research
  - Proposed plausible pathways from biomass to spark ignition blendstocks
- Constructed tiered screening process based on fuel merit function, including expected optimal values for properties

Fuel selection “funnel”





- Applied tiered screening process >400 potential candidates in Fuel Property Database to generate ~40 candidates*
- Focused on high octane components (>98 RON) to enable downsized, down-speeded, boosted SI engines
- Other criteria included:
  - Soluble in hydrocarbon
  - Not OSHA known or suspected human carcinogen or reproductive toxin
  - Biodegradation via EPA's BIOWIN (coupled to water solubility)
  - Boiling point <165 ^{o}C and freezing point <10 ^{o}C
  - Low expected corrosivity

Thrust I candidates meeting Tier 1 criteria

Alcohols	Aromatics	Ethers
Ethanol (reference only)	1,3,5-trimethylbenzene (mesitylene)	Methoxybenzene (anisole)
Methanol	Vertifuel (60%+ aromatics)	
n-Propanol	Fractional condensation of sugars plus upgrading	Furans
2-Propanol	Methanol-to-gasoline	2-Methylfuran
1-Butanol	Catalytic fast pyrolysis	2,5-Dimethylfuran
2-Butanol	Catalytric conversion of sugars	40/60 Mixture of 2-methylfuran/2,5-dimethylfuran
2-Methylpropan-1-ol (isobutanol)		
2-Methylbutanol	Esters	Ketones
2-Methyl-3-buten-2-ol	Acetic acid, methyl ester (methyl acetate)	2-Propane (acetone)
2-Pentanol	Butanoic acid, methyl ester (methyl butyrate)	2-Butane (methylethylketone; MEK)
Guerbet alcohols	Pentanoic acid, methyl ester (methyl pentanoate)	2-Pentanone
	2-Methylpropanoic acid, methyl ester	3-Pentanone
Alkanes	2-Methlybutanoic acid, methyl ester	Cyclopentanone
Isooctane	Acetic acid, ethyl ester (ethyl acetate)	3-Hexanone
High-octane gasoline blendstock (triptane rich)	Butanoic acid, ethyl ester (ethyl butanoate)	4-Methyl-2-pentanone (Methylisobutylketone; MIBK)
	2-Methylpropanoic acid, ethyl ester	2,4-Dimethyl-3-pentanone
Alkenes	Acetic acid, 1-methylethyl ester	3-Methyl-2-butanone
Isooctene (2,4,4-trimethyl-1-pentene)	Acetic acid, butyl ester (butyl acetate)	
	Acetic acid, 2-methylpropyl ester	Multifunctional Mixtures
	Acetic acid, 3-methylbutyl ester	Methylated lignocellulosic bio-oil
	Anaerobic acid fermentation plus esterification	

Selected 20 candidates for analysis from Tier 1 list

Selection based on practical considerations:

- Clear production pathway with balance between production approaches
- Cover the chemistry/functional group space
- Series of candidates within alcohols and esters which provide some systematic variation of structure

20 ASSERT Molecules/Mixtures

0	Ethanol (Reference)
1	Methanol
2	1-butanol
3	2-methyl-butanol
4	2-butanol
5	Isobutanol (2-methylpropan-1-ol)
6	Guerbet alcohol mixture
7	2,5-dimethylfuran/2-methylfuran mixture
8	Acetic acid, methyl ester (methyl acetate)
9	Acetic acid, ethyl ester (ethyl acetate)
10	Acetic acid, butyl ester (butyl acetate)

11	Anaerobic acid fermentation and esterification mixture
12	2-pentanone
13	Methylethylketone (2-butanone)
14	2,2,3-trimethyl-butane
15	Isooctene
16	Vertifuel (60%+ aromatics)
17	Fractional condensation of sugars + upgrading
18	Methanol-to-gasoline
19	Catalytic fast pyrolysis
20	Catalytic conversion of sugars

Thank You

Thrust I Engine Research

- Focused in next-generation SI engines
- Taking a fuel-property approach to new fuel candidates

****SI engines accounted for 72% of on-highway energy consumption in the U.S. in 2013. (Energy Transportation Data Book, 2015).***

The Central Fuel Hypothesis

If we identify target values for the critical fuel properties needed to maximize efficiency and emissions performance for a given engine architecture, then fuels with those properties and values will provide comparable performance.

Assumptions Being Evaluated

1. **Fuel properties correctly describe the fuel's performance in modern SI engines.**
2. **Fuel property measurements are valid across a wide range of unconventional fuel chemistries**

Merit Function Allows Individual Fuel Properties to be Valued
Thrust I Research Aims to Refine the Merit Function Terms

Merit = $\sum$

RON

$$\frac{(RON_{mix}-92)}{1.6}$$

Octane Sensitivity

$$-K\frac{(S_{mix}-10)}{1.6}$$

Heat of Vaporization

$$\frac{0.01[ON/kJ/kg](HoV_{mix}-415)[kJ/kg]}{1.6}+\frac{(HoV_{mix}-415)[kJ/kg]}{130}$$

Flame Speed

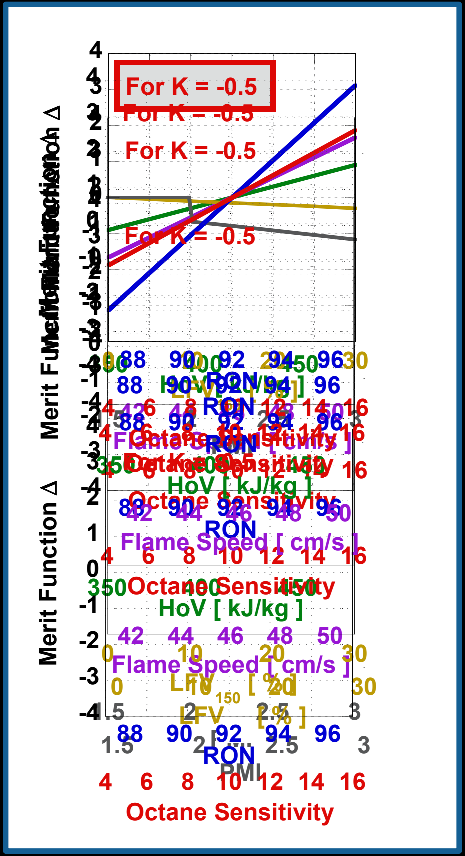
$$\frac{(S_{Lmix}-46\left[\frac{cm}{s}\right])}{3}$$

Distillation

$$-LFV_{150}$$

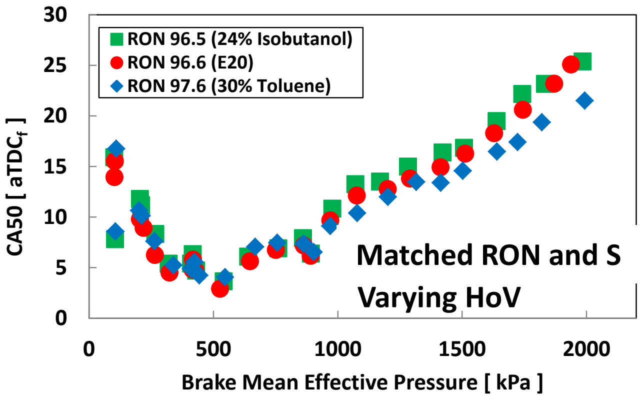
Particulate Emissions

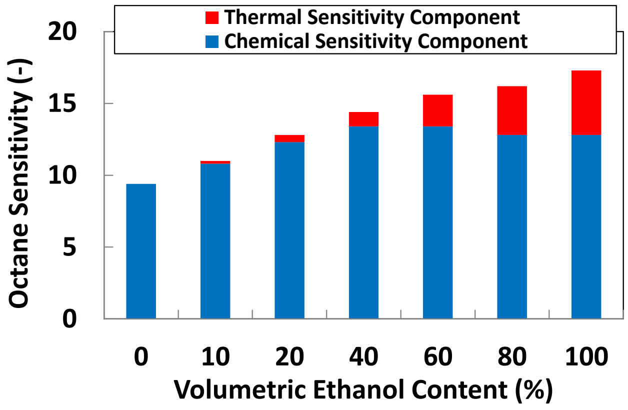
$$-H(PMI-2.0)[0.67+0.5(PMI-2.0)]$$



Example 1: Clarifying the Effects of HoV on Knock Mitigation

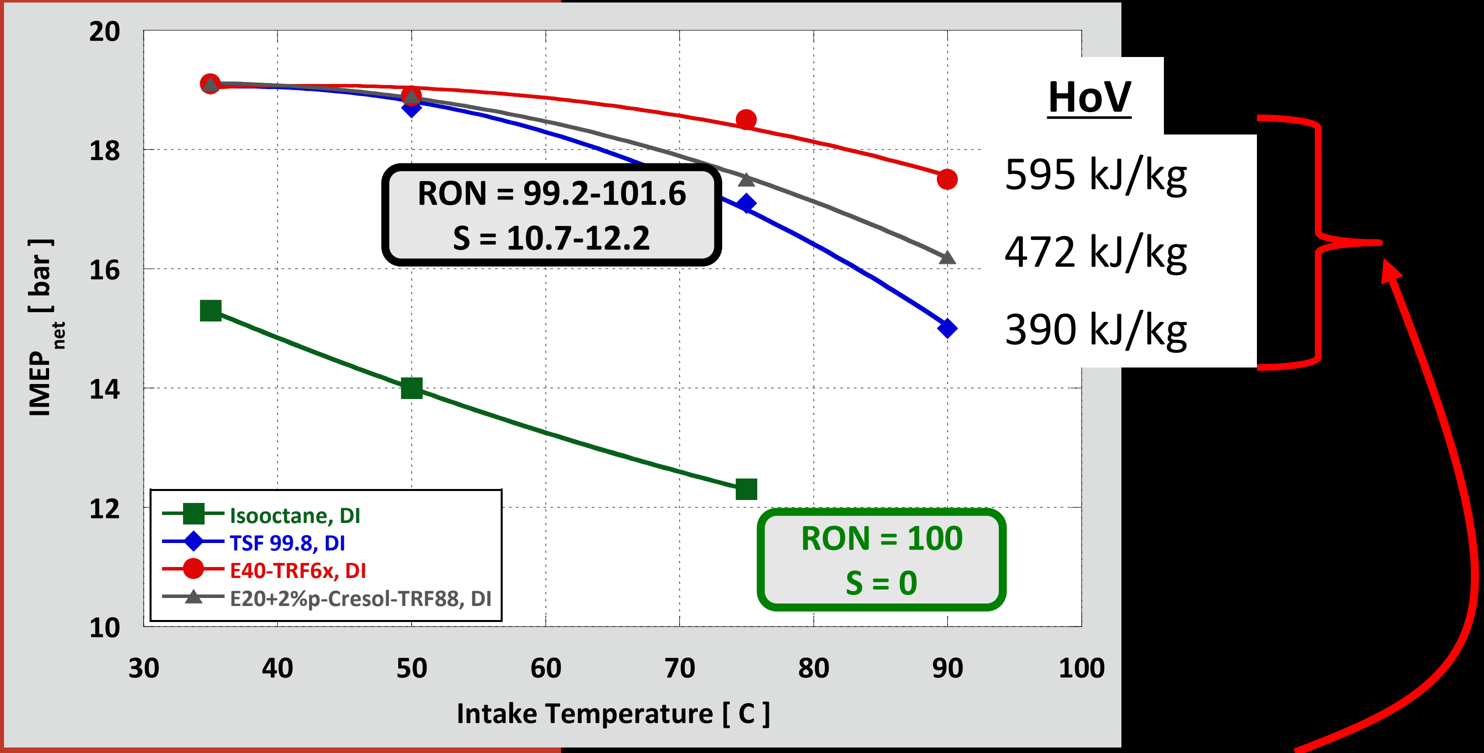
- Inconsistencies in literature of HoV impact on knock propensity
  - HoV effect only been observed when covariant with octane sensitivity
- Expanded with new experimental results from ORNL and NREL
- Main conclusion: HoV is a thermal contributor to octane sensitivity
  - Aligns the findings of seemingly contrary literature findings
  - Consistent with the vaporization effects in the RON and MON tests





Further Research Shows that at Elevated Intake Temperatures, Impact of HoV is Different from that of S

Data represents maximum load at constant combustion phasing



Fuels show fixed RON and S with varying HoV

Example 2. Conditions of RON and MON Tests Raise Applicability Questions

CFR Engine Doesn't Match Modern Engines

Fueling System

Carbureted vs. Direct injection

Air Handling

Naturally Aspirated vs. Boosted

Fixed Cam Position vs. Phasing

Combustion Phasing

Advanced vs. Late Phasing

Additional Mismatches

Intake Temperature

Engine Speed

Equivalence Ratio

Knock Detection

PRFs Aren't Representative Real-World Fuels

PRF's are Paraffin

- Exhibit 2-stage ignition that is unique when compared to most other fuels
- The 2-stage ignition defines the octane number scale

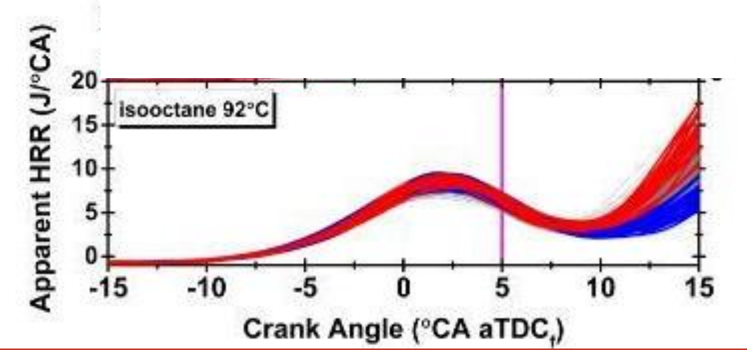
Are RON and MON Still Applicable

- Understanding of the beneficial nature of octane sensitivity is becoming accepted
- With new bio-derived fuels, do RON, MON and octane sensitivity still have the same meaning?

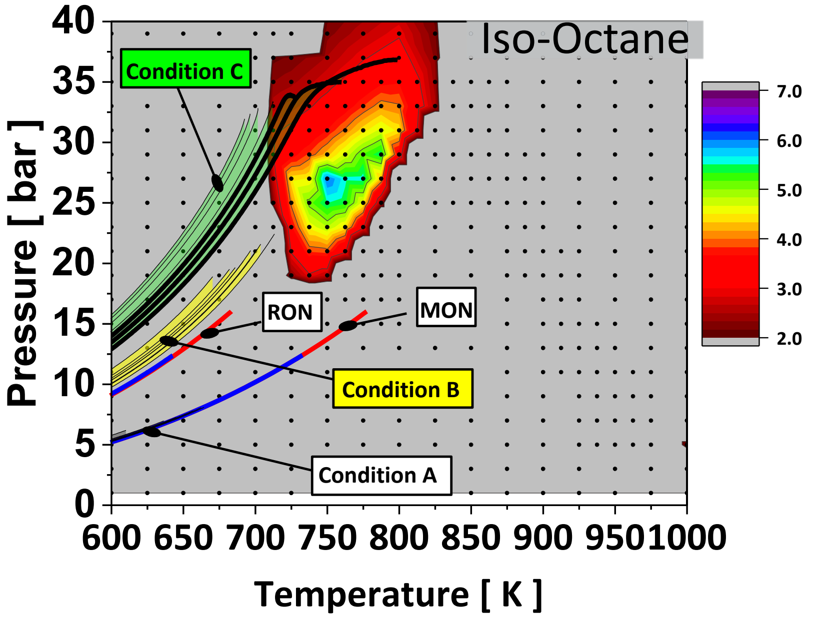
Combination of Experimental Investigations and Kinetic Modeling is Providing Insight into Meaning of RON and MON

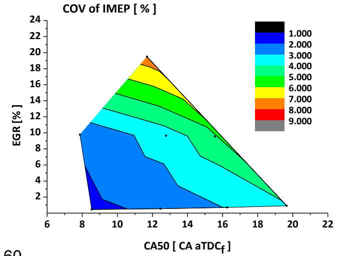
Experiments show some fuels exhibit pre-spark heat release in stoich SI engines

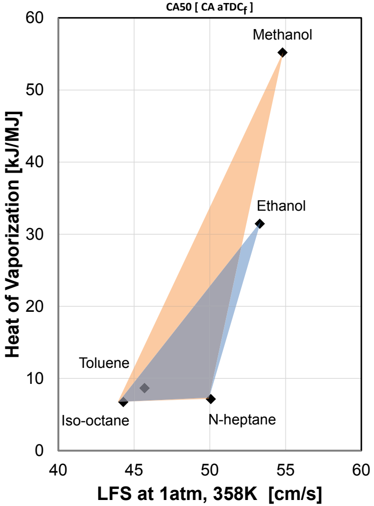
- Boosted operating conditions
- Elevated intake temperatures

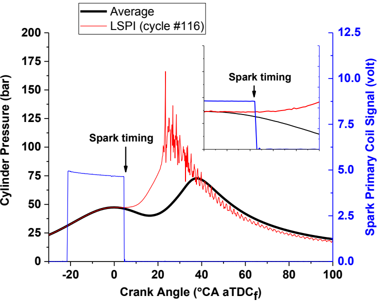


Kinetic modeling is being used to understand the operating conditions in the temperature/pressure space









Additional Thrust I Research Areas Include

- Efficiency benefits of RON and MON
- Improving HoV measurements for mixtures
- Investigating the impact of HoV on engine performance
- Lean and EGR dilution tolerance
- Fuel impacts on particulate emissions
- Fuel impacts on catalyst light-off temperatures
- Fuel impacts on low speed pre-ignition

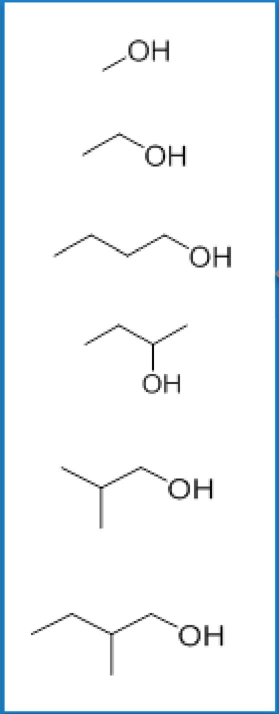
Findings from Thrust I investigations will feedback to test the central fuels hypothesis and to calibrate the merit function

Backup slides

- 12 Single compounds
- 2 Simple mixtures
- 6 Complex mixtures

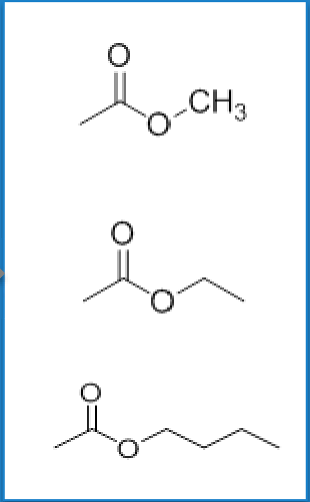
The 20 includes a range of compositions and functional groups:

- 5 alcohols
- 3 esters
- 2 ketones
- 1 paraffin
- 1 olefin
- 1 alcohol mixture
- 1 furan mixture
- 5 hydrocarbon mixtures
- 1 ester mixture
- 2 complex mixtures



Structural series within alcohols…

…and esters



Next steps

- Fill in process gaps as needed for ASSERT analysis
- Examine blending behavior of subset of 20
  - Distillation Properties via ASTM D86 in an RBOB; RVP from other methods
  - Oxidation Stability via ASTM D525 in an RBOB
  - Blending RON and MON in a 4 component surrogate w/ AKI about 88 or 89

Base fuel → Blended fuels @ multiple blending ratios (10, 20, 30 vol%) ← Bio-blendstocks