Updating ASTM D8076

Standard Specification for 100 Research Octane Number Test Fuel for Automotive Spark-Ignition Engines

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AAE Meeting

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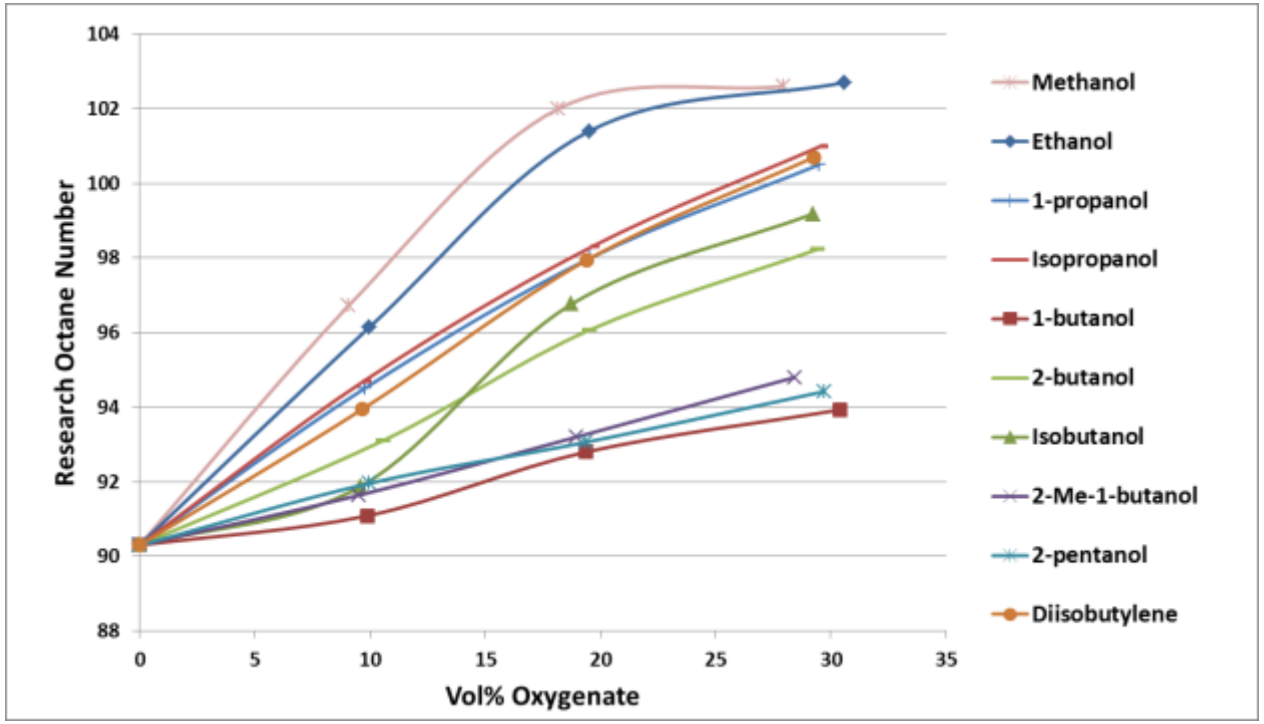
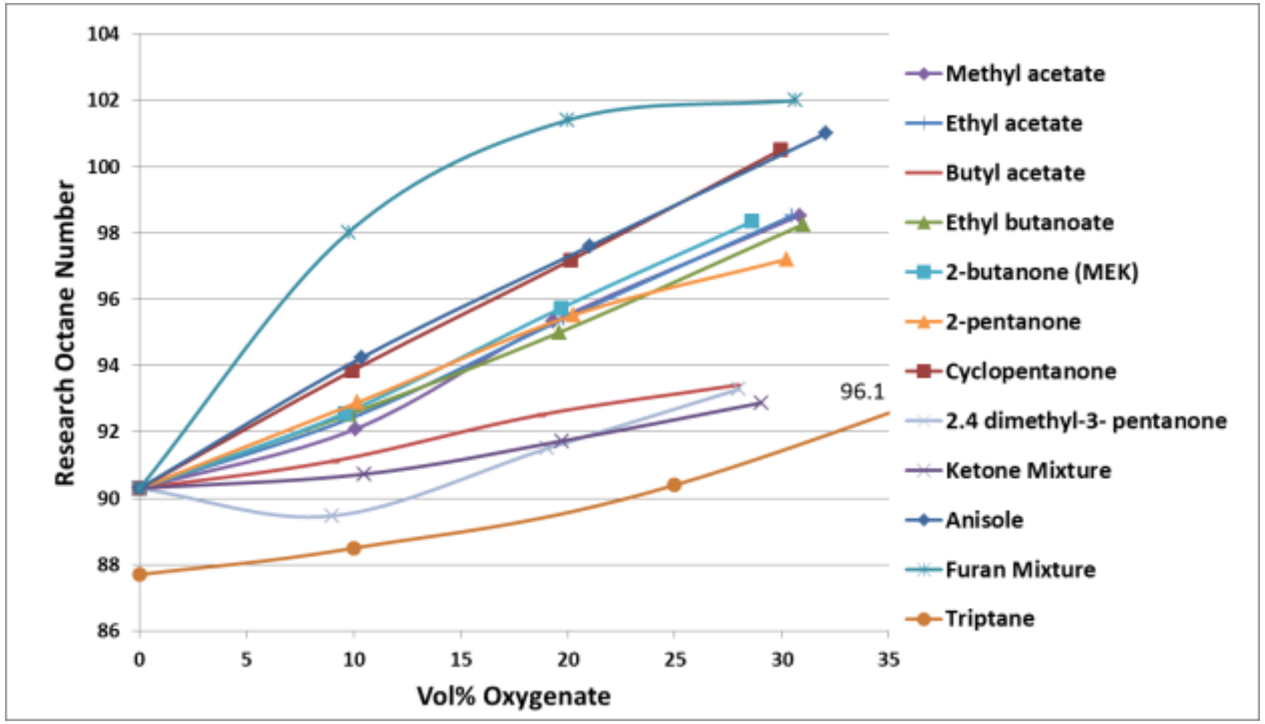
ASTM 100 RON Test Fuel Specification

- The ASTM 100 RON test fuel specification was created to standardize High Octane Low Carbon test fuels
  - This will enable test data from different test labs to be compared
- It is based on the bio-blendstocks identified in the DOE Co-Optima program
- To date we have had the specification approved and published by ASTM
  - Multiple ballots with numerous negatives addressed
  - However, the tightly defined fuels originally envisioned have not as yet been incorporated
- Co-Optima recently further narrowed their list of blendstocks and published octane and volatility data of various blends with both surrogate gasoline and commercial BOBs

Blend Research Octane Numbers – Tier 2 Blendstocks

- Methanol, ethanol and furan mixture have large, non-linear (in volume space) effect on RON
- Isopropanol, 1-propanol, diisobutylene, anisole, and cyclopentanone also achieve > 100 RON
- Isobutanol, 2-butanol, 2-butanone, methyl acetate, ethyl acetate, and ethyl butanoate achieve >98 RON





Blending Octane Numbers

	Vol%
Isooctane	55
n-Heptane	15
Toluene	25
1-Hexene	5

	RON	MON	AKI
Surrogate	90.3	84.7	87.5
Surrogate + 10 vol% EtOH	96.2	88.1	92.2

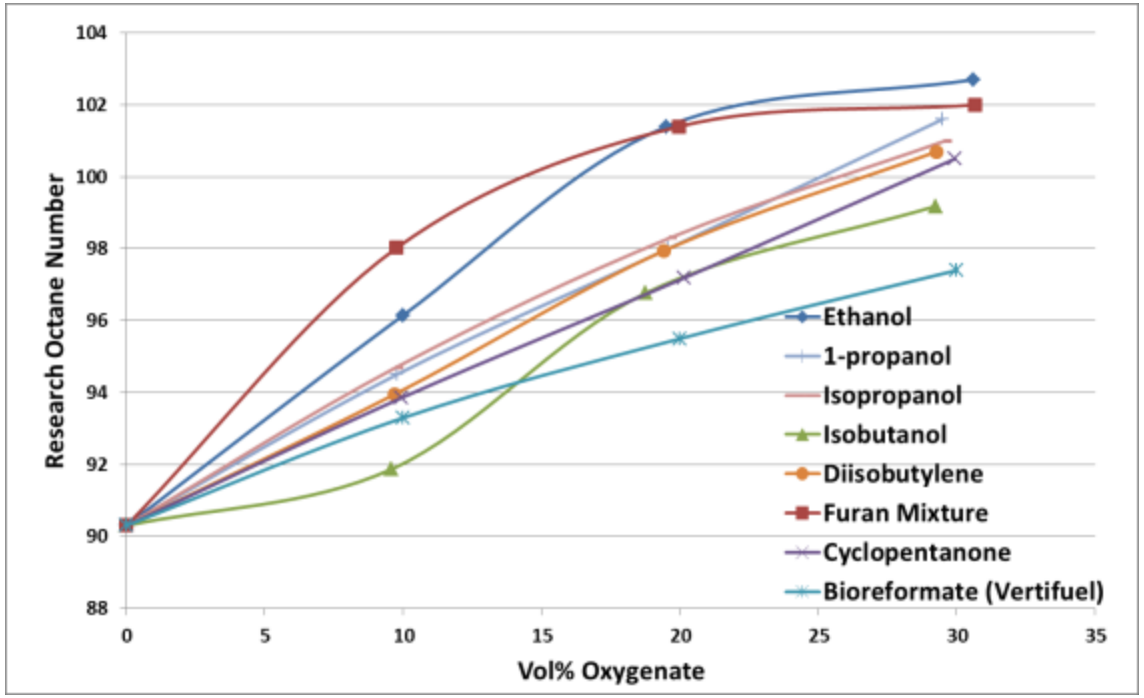
- Knock resistance is well correlated with octane index:

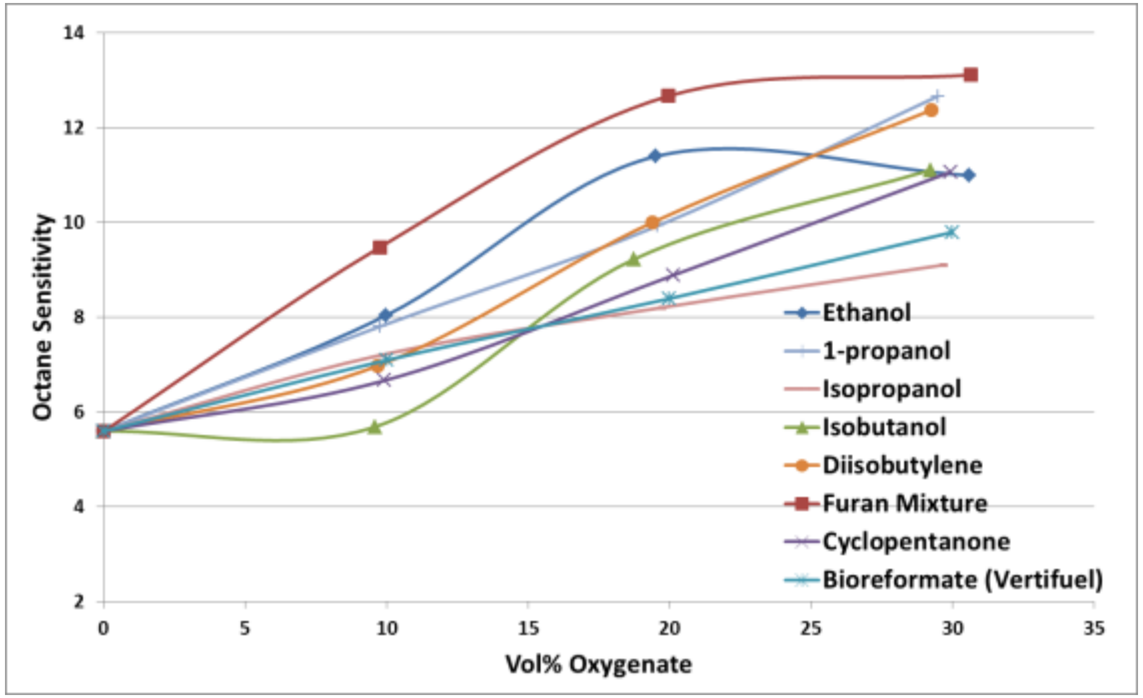
  $OI = RON - K \cdot S$

  where $K < -1$ and $S = RON - MON$
- We seek RON > 98 and S > 8
- 4-component surrogate as hydrocarbon blendstock
- Future chemical kinetic simulation to explain results
- Subset of bioblendstocks on list of “40” at 10, 20, and 30 vol%
- Blend levels verified by GC

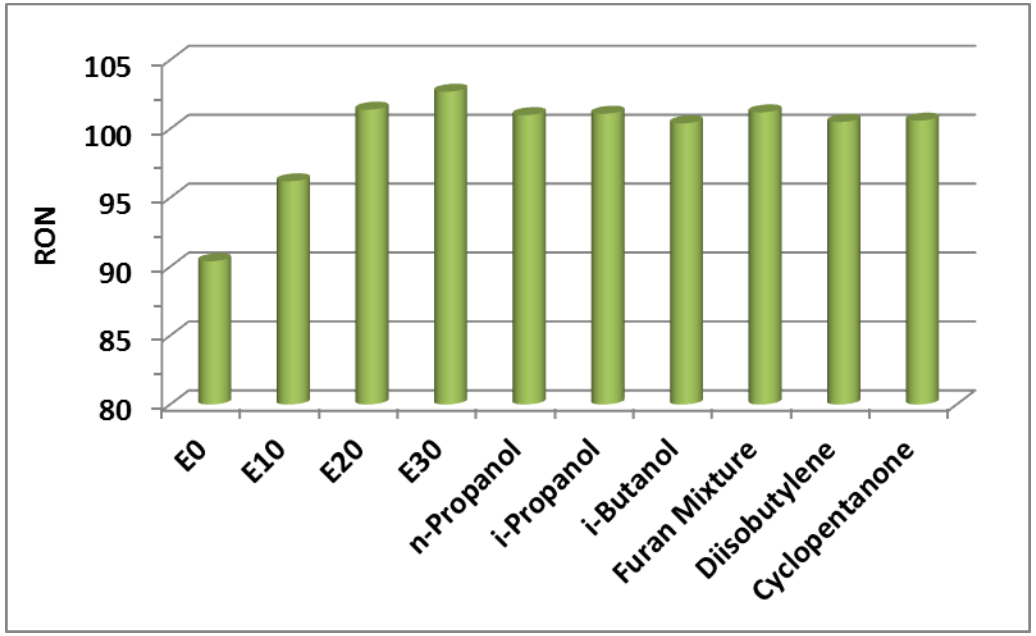
New Octane Blending Results

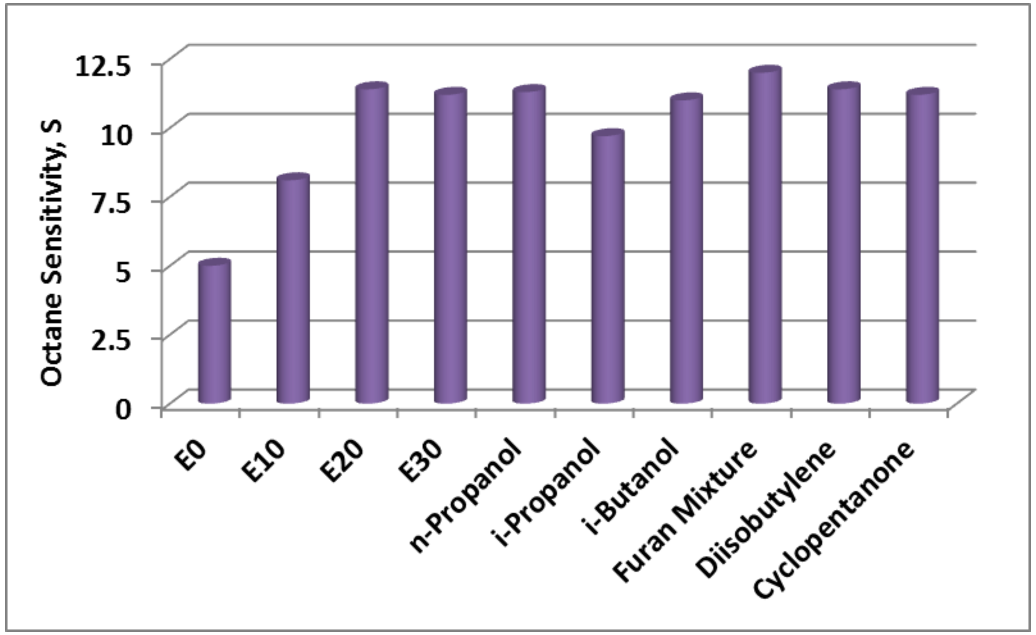
- Tier 3 blendstocks:
  - Blend RON and octane sensitivity (S) on top of E10 – 4 component surrogate
  - Blends in commercial RBOB and CBOB





Blend RON and Sensitivity with E10 – 4 Component Surrogate

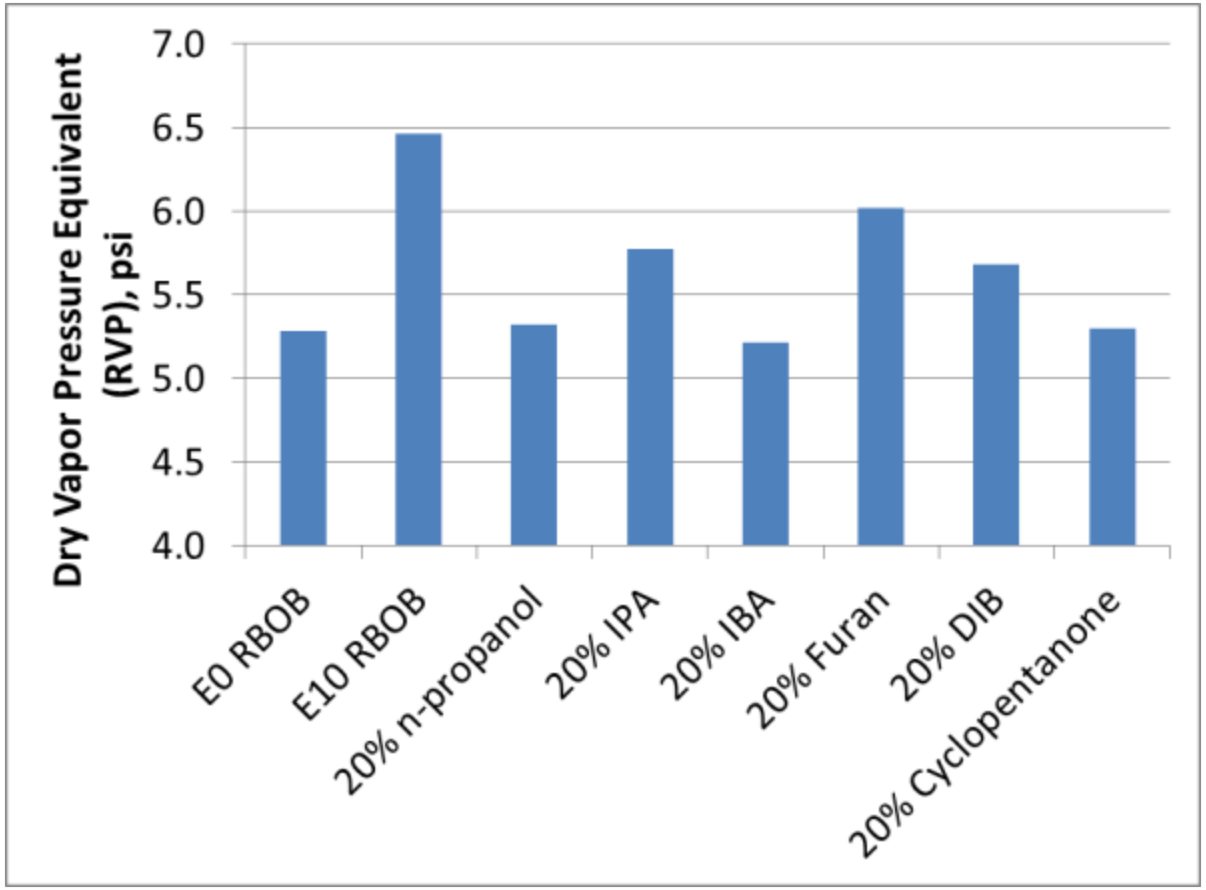




- 20 vol% bioblendstock on top of E10
  - Results for E0 to E30 shown for comparison
- 30% renewable blends are 1.5 to 2.3 octane numbers below E30 level
- Only isopropanol is significantly lower for S than E30

Blending with E10 – Tier 3 Blendstocks – Reid Vapor Pressure

- Blends in commercial RBOB
- Observe well-known increase in RVP for E10
- Blends with n-propanol, i-butanol, and cyclopentanone eliminate E10 RVP increase
- All other blends show reduced RVP but do not eliminate the E10 increase



- Reid Vapor Pressure (RVP) is an outdated term but still widely used
- RVP is the vapor pressure at 37.8°C (100°F)
- Today the Reid method has been replaced by dry vapor pressure equivalent (DVPE)
- Maximum RVP is limited by ASTM to avoid vapor lock, and limited by EPA in summer months to mitigate evaporative emissions - ASTM D5191

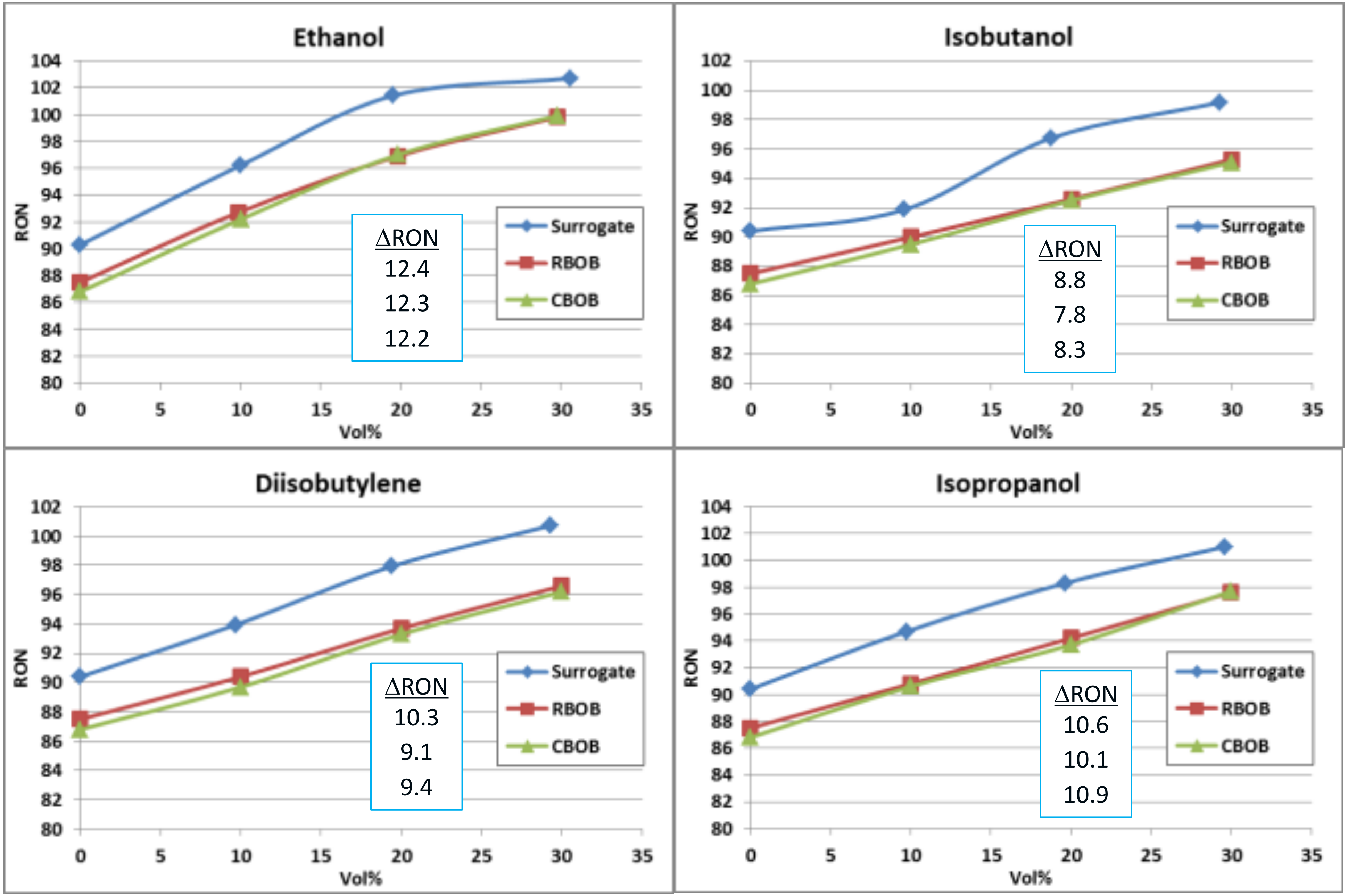
ASTM 100 RON Test Fuel Specification

- The next step is to incorporate a subset of Co-Optima components into gasoline blends that will meet the ASTM specification
- Biopathways are important but not covered in this material
  - These are the 4 molecules that provide best performance with good biopathways
    - Diisobutene
    - Ethanol
    - Isobutanol
    - Isopropanol
- The starting blend is E10
  - Ethanol is already blended with most gasoline
  - Widely available
  - Good octane value

Tier 3 Blendstocks in Commercial BOBs - RON

- Commercial sub-octane BOBs have lower RON than the surrogate – we knew that going in

- ΔRON is for 30% blends (RON at 30% - RON at 0%)
  - May show some small variation with BOB chemistry



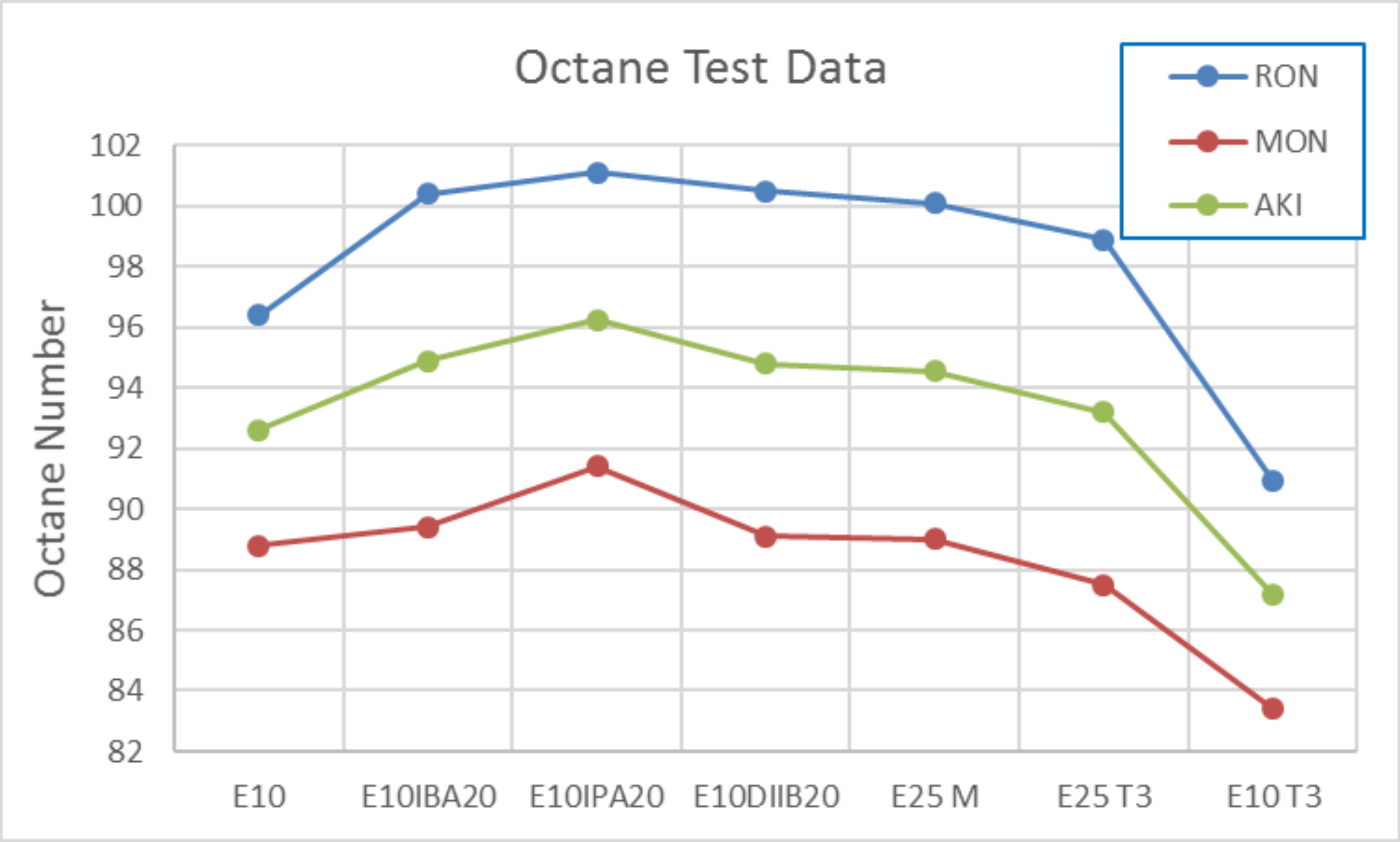
Components for ASTM D8076

- How much Co-Optima blendstock to blend into the fuel?
  - Ethanol
    - E10 is ~3.5% oxygen, E25 is ~8.7% oxygen
    - E25 will reach 100 RON
  - Isopropyl alcohol
    - E10IPA15 is ~7.5% oxygen, E10IPA20 is ~8.8% oxygen
    - Isopropyl alcohol will reach 100 RON at E10IPA20
  - Isobutyl alcohol
    - E10IBA15 is ~6.7% oxygen, E10IBA20 is ~7.8% oxygen
    - Isopropyl alcohol will reach 100 RON at E10IBA20
  - Di-isobutylene
    - E10DIBXX is ~3.5% oxygen
    - Di-isobutylene will reach 100 RON at E10DIB20

Data from E10 blended with 3 Co-Optima molecules at 20%

E25 is modeled using molar blending

E10 Tier 3 certification fuel and E10 T3 + 15% ethanol are also shown



Candidate Standards for the Fuels

- Proposal is to closely specify four Co-Optima Blends using E10 base blend.
  - E25
  - E10DIB20
  - E10IPA20
  - E10IBA20

- Include these four blends in the D8076 standard
  - Blends are based on EPA Tier 3 (E10) certification fuel
    - Fuel is closely specified to ensure reproducible fuel economy and emissions performance
    - Available in regular and premium octane levels
  - Blends are blends of biocomponents, T3 cert fuels, and top up DFE
    - Fuels are easily made and repeatable
  - Allows comparison of test data across labs
  - Addresses concerns that the fuel is underspecified

Four Test Fuels

- Candidate Standards for the Fuels
    - Octane 100 RON or higher

- Closely specified
    - Distillation curve
    - Vapor pressure
    - Aromatics by carbon number
    - Bio-content

			E25		E10IB20		E10DIB20		E10IPA20	
Parameter	Method	Unit	Min	Max	Min	Max	Min	Max	Min	Max
T10	D86	F	120	140	130	150	130	150	130	150
		C	49	60	54	66	54	66	54	66
T50		F	162	168	185	210	190	225	165	175
		C	72	76	85	99	88	107	74	79
T90		F	305	325	310	330	305	325	310	330
		C	152	163	155	166	152	163	155	166
EP		F	370	410	370	410	370	410	370	410
		C	188	210	188	210	188	210	188	210
Recovery		C	Report		Report		Report		Report	
Residue				2		2		2		2
Loss			Report		Report		Report		Report	
Gravity	D4052		Report		Report		Report		Report	
Density	D4052		Report		Report		Report		Report	
Vapor Pressure (EPA)	D5191	psi	8.5	9	7.5	8.5	8.2	9	8.2	9
Vapor Pressure (EPA)	D5191	kPa	59	62	52	59	57	62	57	62
Carbon	D5291		Report		Report		Report		Report	
Hydrogen	D5291		Report		Report		Report		Report	
H/C	D5291		Report		Report		Report		Report	
Oxygen	D4815		Report		Report		Report		Report	
Ethanol	D5501	v/o	24.6	25.0	9.6	10.0	9.6	10.0	9.6	10.0
IsoButanol	D4815	v/o			19.6	20.4				
Di-Isobutylene							19.6	20.4		
Isopropanol	D4815	v/o							19.6	20.4
Total Oxygenates other than Ethanol	D4815	v/o		0.1				0.1		
Total Oxygenates other than Ethanol and isobutanol	D4815	v/o				0.1				
Total Oxygenates other than Ethanol and isopropanol	D4815	v/o								0.1
Sulfur	D5453	mg/kg	7	10		0.1		0.1		0.1
Phosphorus	D3231	g/l		0.0013	6	9	7	10	7	10
Lead	D3237	g/l		0.0026		0.0013		0.0013		0.0013
Aromatics	D5769	v/o	17.5	20.8		0.0026		0.0026		0.0026
C6 Aromatics	D5769	v/o	0.4	0.6	17	20	17	20	17	20
C7 Aromatics	D5769	v/o	4.3	5.3	0.4	0.6	0.4	0.6	0.4	0.6
C8 Aromatics	D5769	v/o	4.3	5.3	4.2	5.1	4.2	5.1	4.2	5.1
C9 Aromatics	D5769	v/o	4.3	5.3	4.2	5.1	4.2	5.1	4.2	5.1
C10+ Aromatics	D5769	v/o	3.7	4.7	4.2	5.1	4.2	5.1	4.2	5.1
Olefins	D6550	v/o	3.3	8.3	3.5	4.5	3.5	4.5	3.5	4.5
Oxidation Stability	D525	Minutes	1000		3.2	8	3.2	8	3.2	8
Copper Corrosion	D130			1	1000		1000		1000	
Existent Gums, Washed	D381	mg/100ml		3		1		1		1
Existent Gums, Washed	D381	mg/100ml	Report			3		3		3
RON	D2699		100		Report		Report		Report	
MON	D2700		86		100		100		100	
(R+M)/2	D2699/D2700		Report		86		86		86	
Sensitivity	D2699/D2700		11		Report		Report		Report	
Net Heat of Combustion	D240	MJ/kg	Report		Report		Report		Report	
					Report		Report		Report	

Path Forward

- Make some candidate blends to confirm specification limits
  - Adjust specs as required
- Reconvene work group to review specs
- Ballot through ASTM
- Address any negatives
- Publish