Design of Simple Drop-in Gasoline Biofuels

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Outline

✕ Matching Gasoline Volatility

✕ Application of Volatility Models

✕ Volatility Testing Results

✕ Engine Testing Results

✕ Conclusions

Matching Gasoline Volatility: Volatility Requirements

- Gasoline needs correct volatility properties to work in current engines
  - Distillation curve
  - Reid vapor pressure (RVP)
  - Temperature of vapor/liquid ratio of 20 ($T_{V/L=20}$)
  - Drivability
- Driveability index calculated from empirical correlation:
- DI=1.5 * T_{10} + 3.0 * T_{50} + 1.0 * T_{90} +1.33 * Ethanol Volume % [4]
- Recent results indicate that matching distillation curve is sufficient to match other volatility properties
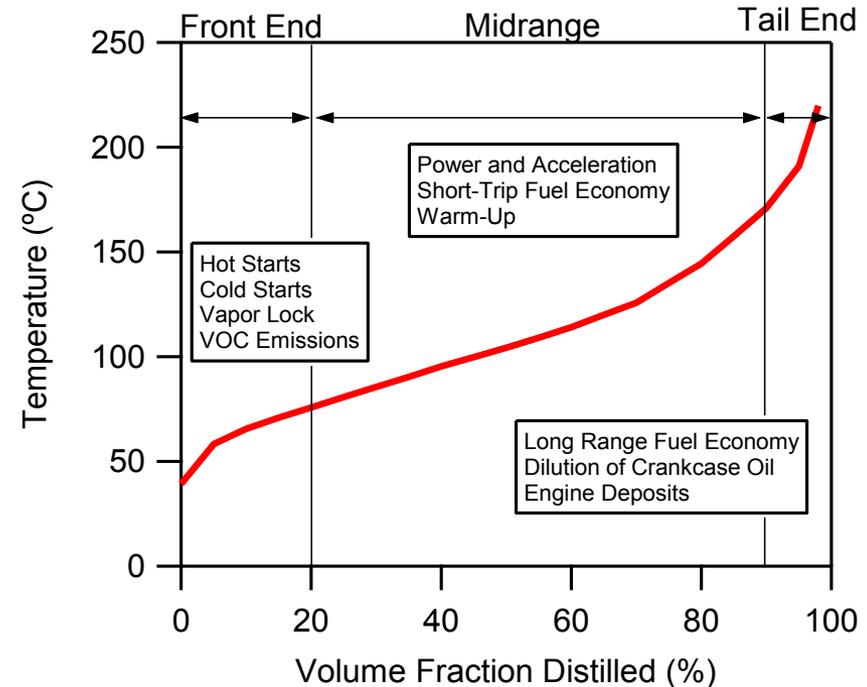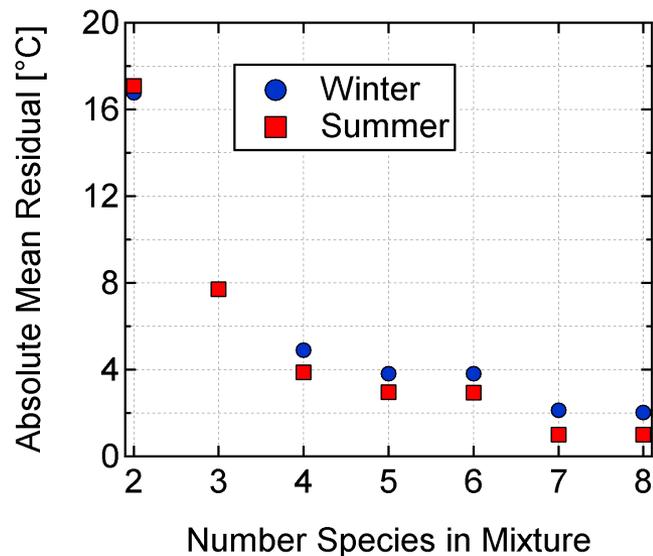

Distillation curve impact on overall performance of gasoline. Adapted from Chevron gasoline technical review [2].
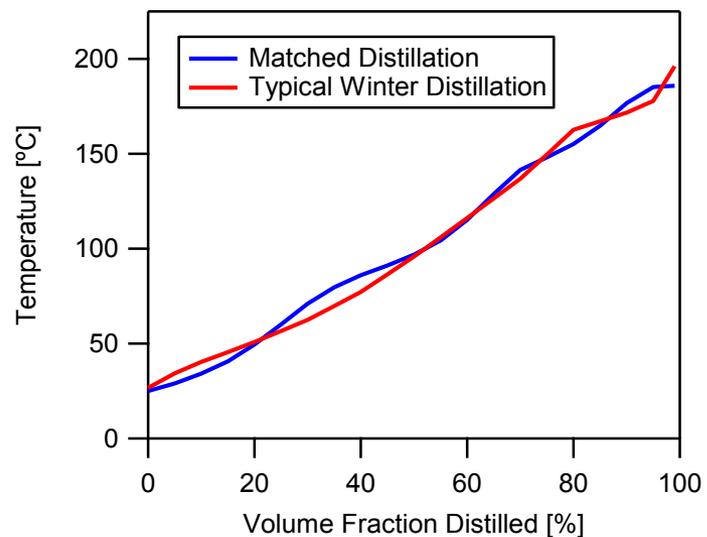
[2]   Chevron, *Motor Gasolines Technical Review,* 2004.
[4]   ASTM Standard D4814-09b, "Standard Specification for Automotive Spark-Ignition Engine Fuel". 2009

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Matching Gasoline Volatility:
Minimum Number of Components

Average difference between best fit distillation and target distillation curve vs. # of chemical species in the mixture

Distillation curves for typical Winter gasoline and a matched mixture containing butene, hexene, methyl pentanoate, and pentanoic acid.

✖ Four component mixtures were found to be adequate for matching distillation → Other volatility properties also matched

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Application of Volatility Models:
Chemical Palette

Alkanes	Alkenes	Aromatics	Alcohols	Esters
n-butane	n-butene	toluene	ethanol	methyl pentanoate
isobutane	n-hexene	p-xylene	propanol	ethyl pentanoate
2,3 dimethylbutane	2,5 dimethyl-2-hexene	ethylbenzene	butanol	butyl pentanoate
2,2,4 trimethylpentane	2,2,5,5 tetramethyl-3-hexene	**Cycloalkanes**	isobutanol	ethyl levulinate
2,2,5 trimethylhexane	**Acids/Other**	cyclohexane	pentanol	
2,2,3,3 tetramethylhexane	pentanoic acid	methylcyclohexane	5-nonanol	
2,3,5,6 tetramethylheptane	levulinic acid	**Ketones**		
2,3,4,7, tetramethyloctane	γ-valerolactone	5-nonanone		

✗ Developed and implemented models to estimate values of each volatility parameter: distillation curve, RVP, $T_{V/L=20}$, drivability

✗ Applied these to design simple (4-species) mixtures that meet gasoline volatility requirements

✗ Chemical Palette Selection
- Boiling point
- Availability and cost
- Components that can be produced through biological and catalytic processing of biomass.
- Components representative of gasoline for comparison purposes

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Application of Volatility Models:
Biofuel Mixture Compositions Selected

✖ Optimization was used to match distillation properties of mixtures to a target gasoline distillation

✖ Two biofuel mixtures chosen for further testing

  ▪ Mixtures chosen because components could be produced through lignocellulosic biomass conversion processes

Properties of biofuel mixture 1
*Assumes ideal solution. **For liquids at 20 ˚C or for gases at the boiling point of the liquified gas.

Components	Liquid mole fraction xi	MW (kg/kmol)	*Volume fraction	**Density (kg/L)
n-butene	0.111	56.106	0.083	0.595
n-hexene	0.477	84.160	0.483	0.673
methyl pentanoate	0.328	116.158	0.366	0.8947
γ-valerolactone	0.084	100.116	0.067	1.0794

Properties of biofuel mixture 2
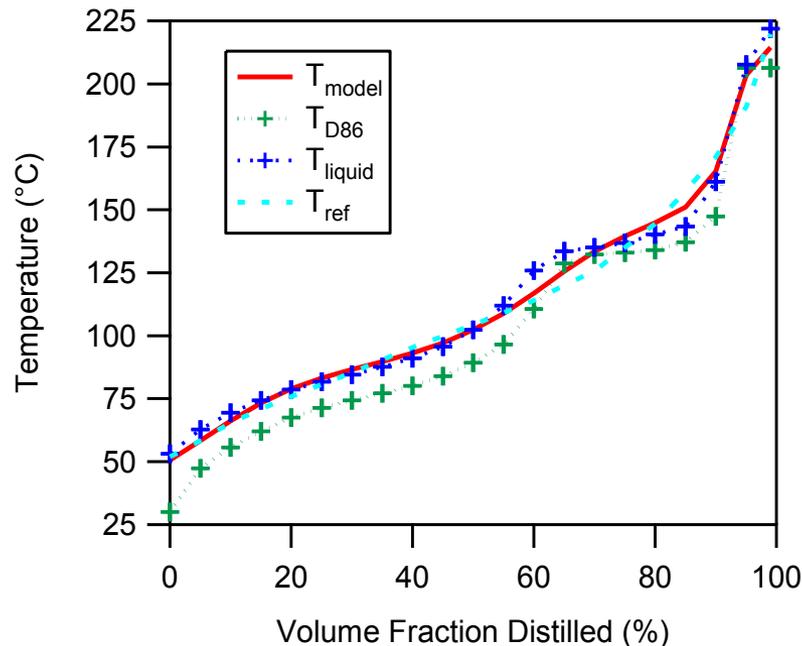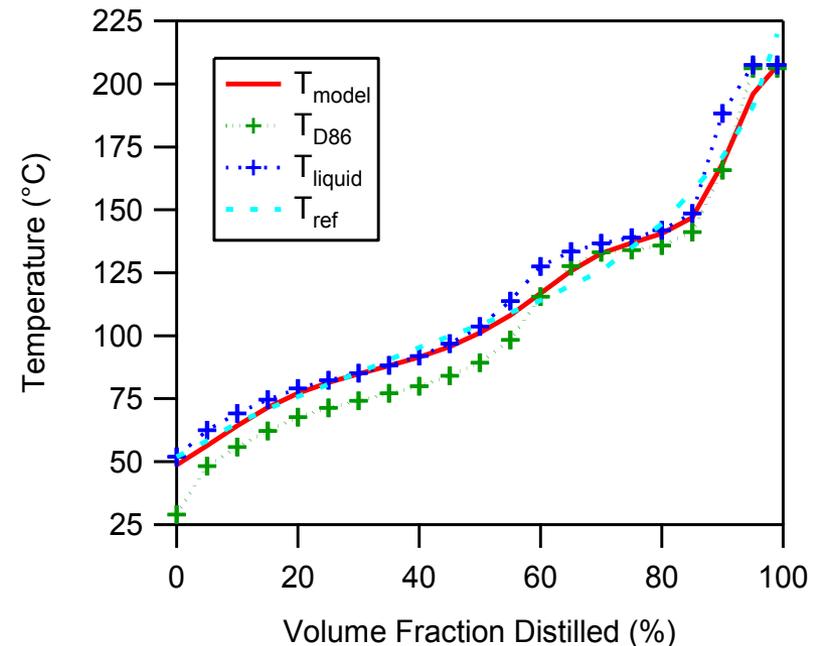***Assumes ideal solution. **For liquids at 20 ˚C or for gases at the boiling point of the liquified gas.**

Components	Liquid mole fraction xi	MW (kg/kmol)	*Volume fraction	**Density (kg/L)
n-butene	0.113	56.106	0.086	0.595
n-hexene	0.475	84.160	0.477	0.673
methyl pentanoate	0.338	116.158	0.352	0.8947
ethyl levulinate	0.074	144.168	0.085	1.0111

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Volatility Testing Results:
Distillation of Biofuel Mixtures

Distillation results of biofuel mixture 1

Distillation results of biofuel mixture 2

- ✗ Distillations match target distillation well for both mixtures
  - Biofuel mixture 1 absolute average residual = 4.4 ℃ average deviation
  - Biofuel mixture absolute average residual = 6.4 ℃ average deviation
- ✗ Results validate distillation model

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Laboratory Volatility Testing Results:
RVP and $T_{V/L=20}$

✘ Experimental results validate volatility models

Matching distillation to petroleum derived gasoline results in gasoline-like volatility!

RVP results

	Biofuel Mixture 1	Biofuel Mixture 2
RVP Experimental (kPa)	65.0 ± 3.0	75.8 ± 3.0
RVP Model (kPa)	66.0 ± 1.0	69.6 ± 0.7

$T_{V/L=20}$ results

	Biofuel Mixture 1	Biofuel Mixture 2
$T_{V/L=20}$ Experimental (°C)	59.5 ± 0.3	57.2 ± 0.3
$T_{V/L=20}$ Model (°C)	59.7 ± 0.5	57.8 ± 0.4

Laboratory results for measuring biofuel mixture 1 and biofuel mixture 2

Biofuel Mixture	RVP (kPa)	T_{10} (°C)	T_{50} (°C)	T_{90} (°C)	T_{end} (°C)	$T_{V/L=20}$ (°C)	Distillation and Vapor Lock Class
1	65.0	55.6	89.3	147.4	206.3	59.5	B-1
2	75.7	55.8	89.3	165.7	206.2	57.4	C-1

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BUT WILL THEY BURN?

Engine Testing:
Experimental Setup
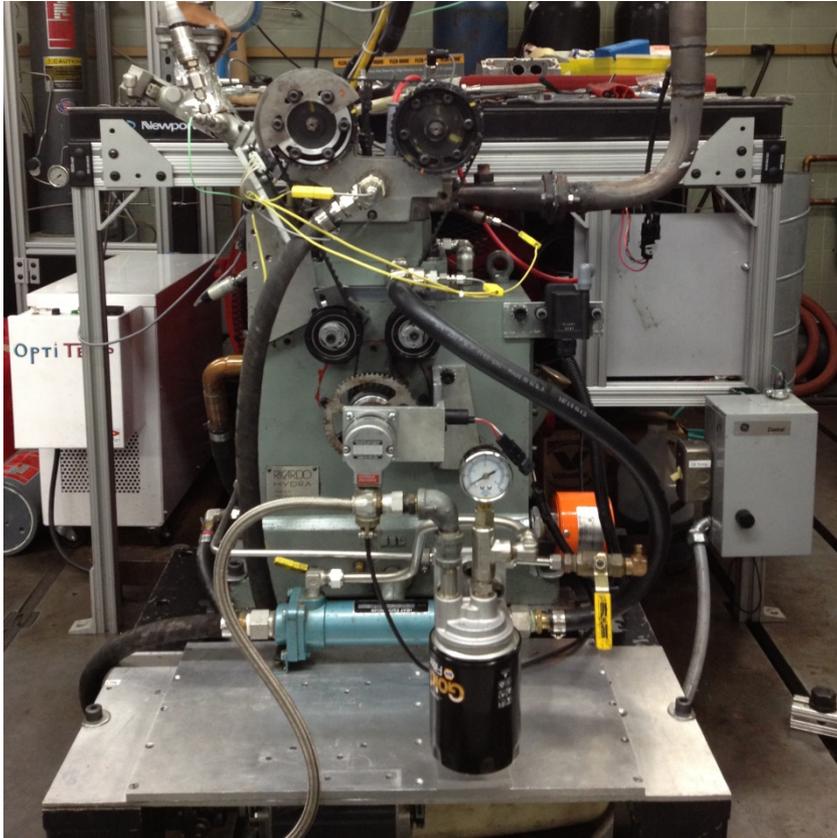
Single-cylinder spark-ignition direct-injection engine

Engine Specifications	
Engine Type	Ricardo Hydra base 4-Stroke, 4-Valve, SI
Combustion Chamber Geometry	Pentroof
Displacement (cm^3)	696
Compression Ratio	12:1
Bore (mm)	90.20
Stroke (mm)	108.89
Connecting rod length (mm)	161.72
Clearance Volume (cm^3)	64.3
Squish Height (mm)	1.01
IVC (CAD ATDC)	-133
EVO (CAD ATDC)	153

Engine Testing:
Matched DISI and Homogeneous SI Conditions
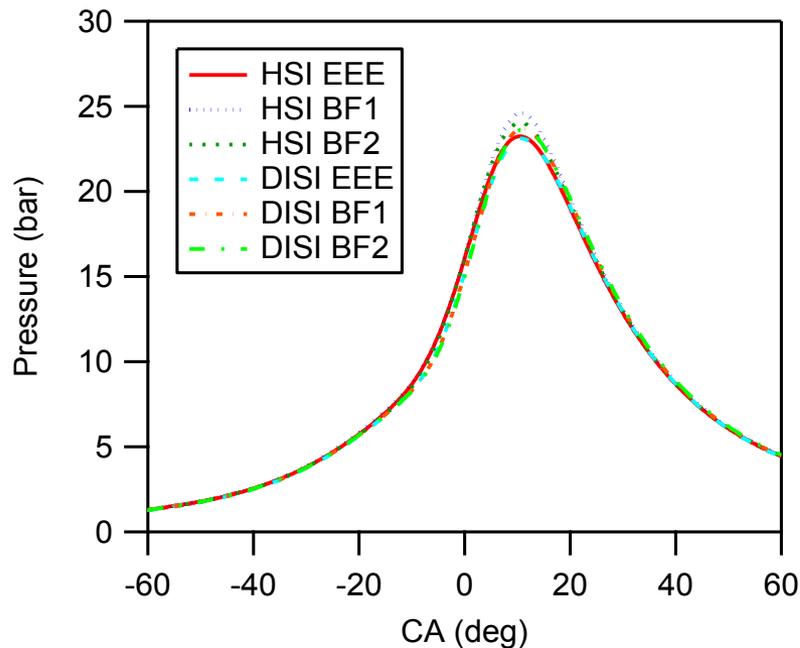
Cylinder pressure vs crank angle. Conditions: 40 kPa IMAP 100 °C intake air temperature
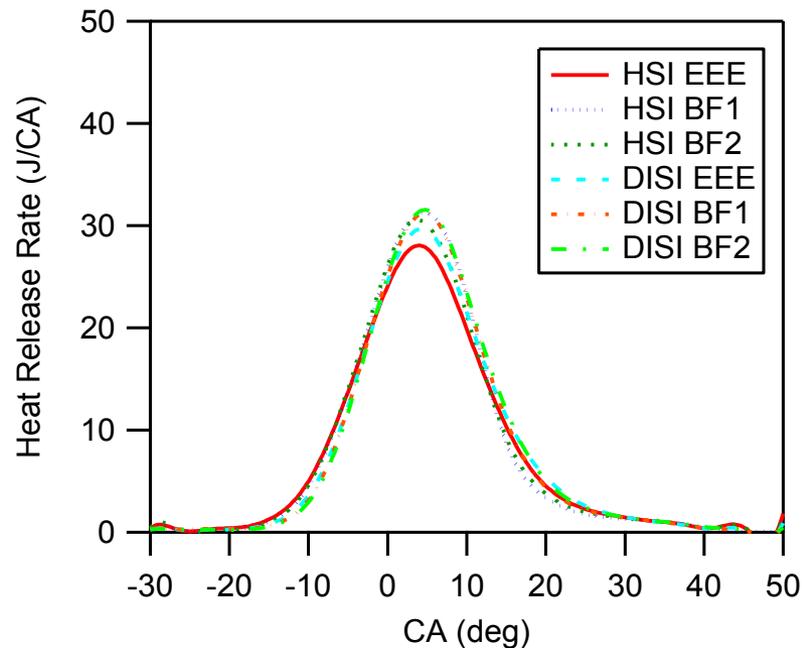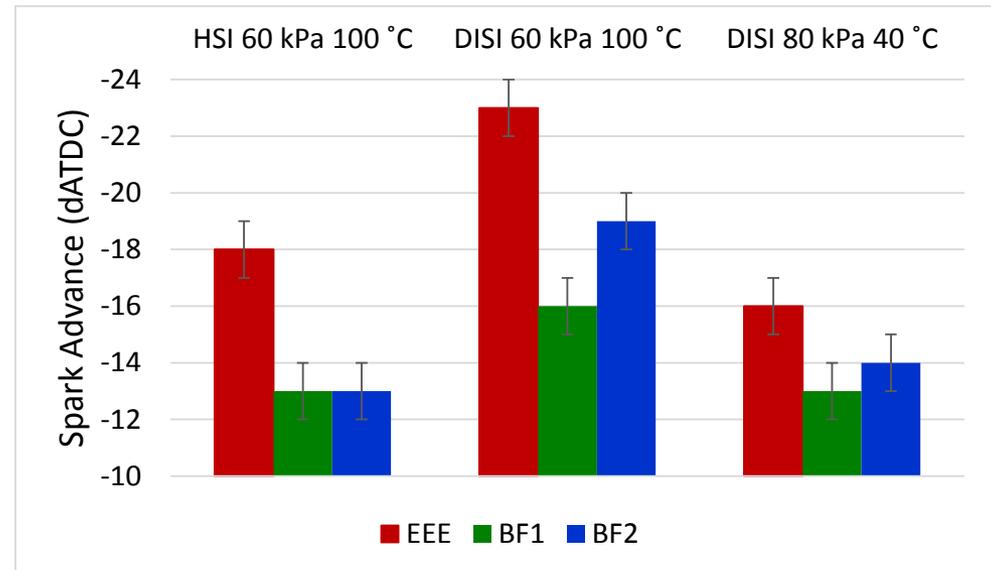

Heat release rate. Conditions: 40 kPa IMAP 100 °C intake air temperature

- ✕ In-cylinder pressure and heat release are similar for all fuels
- ✕ Combustion process is closely matched between gasoline (EEE) and biofuels

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Engine Testing:
Knock Limited Spark Advance Results

- KLSA compared for knocking cases for all fuels

- Changed spark timings for biofuel mixtures to match location of CA_{50} of gasoline

- 80 kPa IMAP 40 °C intake cases closest to RON test
  - Every degree in spark advance corresponds to 0.5 to 1.0 increase in RON [12]
  - Expect RON on the order of 93 to 95 for these biofuel mixtures

[12] Leppard, SAE 820074, 1982

KLSA for three operating conditions where knocking was experienced. Both biofuel mixtures and EEE compared. Spark timings changed for biofuel mixtures to have equivalent location of CA_{50} for EEE.

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Engine Testing:
Emissions Results

✖ Emissions were compared for the non-knocking operating conditions

✖ Emissions show no obvious trends for all operating condition

Indicated specific emissions
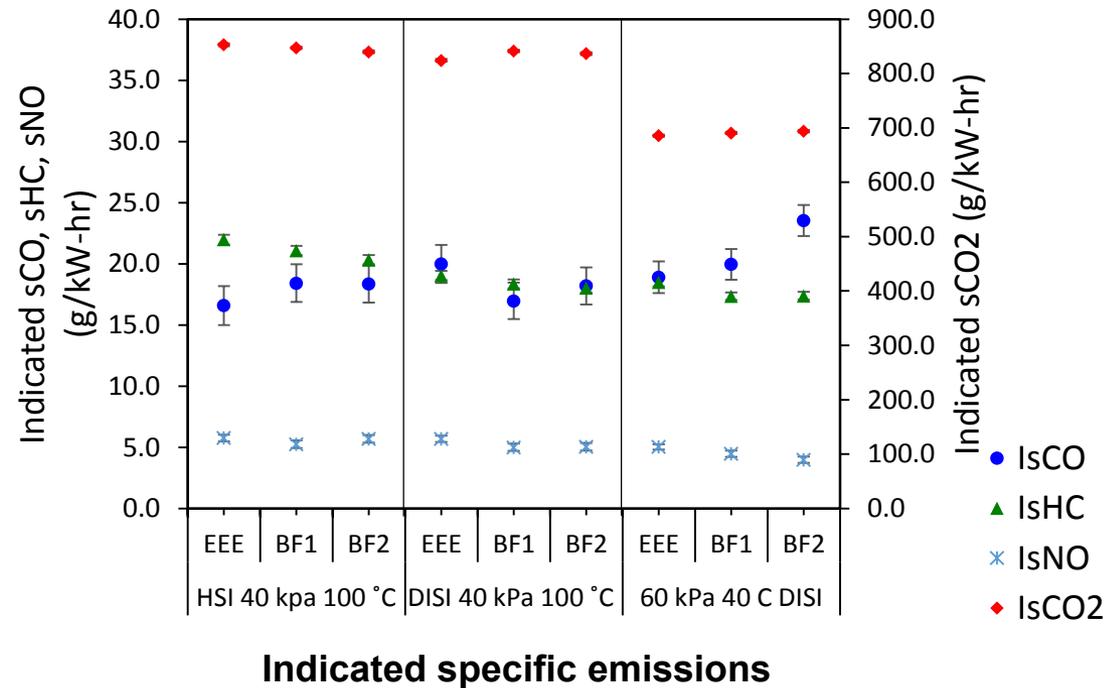
Engine out emissions of standard pollutants not significantly different for biofuels compared to gasoline

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Conclusions

✗ Distillation was found to be an effective criterion for matching gasoline volatility

✗ Four component mixtures were found to be the minimum required to meet ASTM D4814 requirements for SI engine fuel

✗ Engine testing showed faster flame development time, and slightly faster flame speeds for the biofuel blends

✗ Average corrected KLSA for biofuel 1 was 5 CAD less than EEE and for biofuel 1 was 4 CAD less than EEE

✗ Biofuels likely have sufficient ON for 87 AKI fuel

Volatility and combustion properties of biofuel mixtures developed replicate gasoline performance

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Acknowledgements

✕ Graduate students: Jacob Backhaus, Alison Ferris

✕ Funding: GLBRC, DOE

Background

✗ Petroleum derived gasoline is comprised of hundreds of different hydrocarbons containing different boiling points [1,2]

✗ This diversity presents desirable volatility characteristics for spark-ignition engine fuels [1,2]

✗ Improvements in the conversion of lignocellulosic biomass give opportunity to engineer biofuels that meet gasoline specifications and are made from 100 % biomass

✗ Catalytic and biological conversion processes result in chemical species that are not nearly as diverse as petroleum gasoline [3]

✗ Intermediate oxygenates may also be of interest, however, volatility for these species must be calculated from fundamental principles because empirical ASTM correlations are not sufficient

[1]   R. G. Montemayor, in: ASTM International: pp 77-84.
[2]   Chevron, *Motor Gasolines Technical Review,* 2004.
[3]   D. M. Alonso, Green Chemistry, 2010

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Objective

✖ Lower complexity fuels (less than 10 chemical species) align better with biological and catalytic conversion processes

 ▪ Potential lowered cost due to less processing

✖ How complex does a bio-derived gasoline need to be to be considered a drop-in replacement for petroleum derived gasoline?

✖ Once minimum is found

 ▪ Methodology for finding component mixtures that can meet all of the specifications found within ASTM D4814 must be developed

 ▪ Laboratory testing procedure for validating the developed methodology must be developed and performed

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Approach

- ✕ Choose chemical palette that is appropriate for modeling drop-in gasoline fuels
  - ▪ Representative of different biofuel conversion processes
  - ▪ Include species that are typical of petroleum derived gasoline
- ✕ Find minimum number of species needed to meet specifications for petroleum derived gasoline
- ✕ Use ASTM D4814 standard as a baseline
- ✕ Develop thermodynamic sub-models to model volatility properties from fundamental principles
- ✕ Automate the process for finding mixtures that meet volatility requirements
  - ▪ Match distillation
  - ▪ Calculate remaining volatility parameters
- ✕ Laboratory volatility testing to validate the volatility model and engine testing to characterize combustion parameters and evaluate emissions

Volatility Standards

✕ Gasoline volatility standards from ASTM D4814

ASTM specifications for vapor pressure, distillation, and driveability for each distillation class. Adapted from ASTM D4814 [4].

| Distillation Class	Vapor Pressure Max (kPa)	10 % Volume max	Distillation Temperature (°C)		90 % Volume max	End Point max	Driveability Index (°C) max
			50 % Volume min	50 % Volume max			
AA	54	70	77	121	190	225	597
A	62	70	77	121	190	225	597
B	69	65	77	118	190	225	591
C	79	60	77	116	185	225	586
D	93	55	77	113	185	225	580
E	103	50	77	110	185	225	569

ASTM specifications for vapor lock protection. Adapted from ASTM D4814 [4].

Vapor Lock Protection Class	Minimum $T_{V/L=20}$ (°C)	Minimum $T_{V/L=20}$ (°C) (Special Requirements)
1	54	60
2	50	56
3	47	51
4	47	47
5	41	41
6	35	35

[4]   ASTM Standard D4814-09b, "Standard Specification for Automotive Spark-Ignition Engine Fuel", 2009

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Volatility Standards

- Distillation affects many performance aspects of gasoline fuels

- Driveability index defined from empirical correlation from ASTM D86 distillation curve

  - $DI = 1.5 * T_{10} + 3.0 * T_{50} + 1.0 * T_{90} + 1.33 *$ Ethanol Volume %   [4]
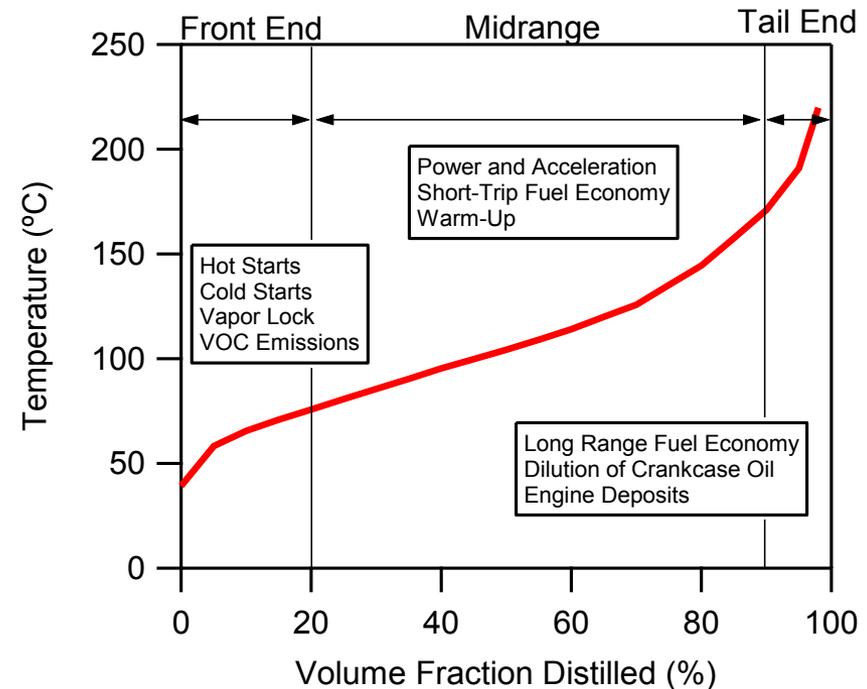
Distillation curve impact on overall performance of gasoline. Adapted from Chevron gasoline technical review [2].

[2]   Chevron, *Motor Gasolines Technical Review,* 2004.
[4]   ASTM Standard D4814-09b, "Standard Specification for Automotive Spark-Ignition Engine Fuel" 2009

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# Thermodynamic Sub-models:
Distillation, RVP, $T_{V/L=20}$

- ASTM D86 performed using laboratory batch distillation [5]
  - Open batch distillation is basis for distillation model
  - ASTM D86 and an open batch distillation are not interchangeable because of the location of where the temperature is measured in ASTM D86 (more detail later)
  - Equations governing equilibrium batch distillation implemented into model
- $T_{V/L=20}$ and RVP modeled with vapor liquid equilibrium of closed system
  - $T_{V/L=20}$ - temperature when vapor-to-liquid ratio is equal to 20, p=101.3 [kPa] [4]
  - RVP – Pressure for a vapor-to-liquid ratio of 4, T=100 °F [4] Vapor pressure regulated by Reid vapor pressure
- Models validated using experimental data

[4]   ASTM Standard D4814-09b, "Standard Specification for Automotive Spark-Ignition Engine Fuel", 2009
[5]   ASTM Standard D86-10, "Standard Test Method for Distillation of Petroleum Products at Atmospheric Pressure,"

Thermodynamic Sub-models:
Driveability Index

✗ Driveability index empirically derived from ASTM D86 distillation curve.

✗ Need to model process occurring for cold start driveability to properly model to define driveability.

✗ Standard enthalpy requirement used for describing driveability [7]

- Energy required to heat liquid fuel and air mixture with metered A/F ratio of 11 from a temperature of 0 ℃ to the temperature where the lean misfire limit is reached
- A metered equivalence ratio of 1.3 was also explored because it was thought to be more characteristic of modern vehicles with an ECU
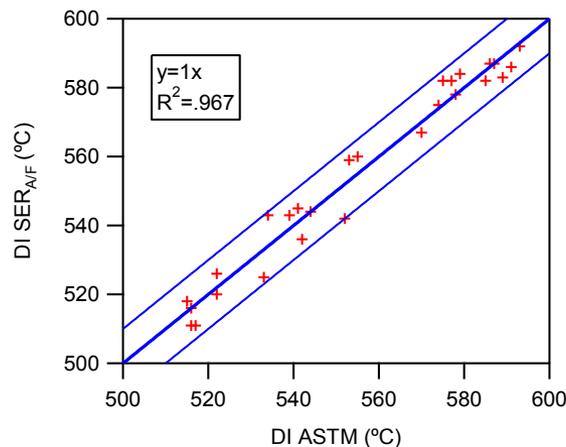
DI results metered A/F ratio
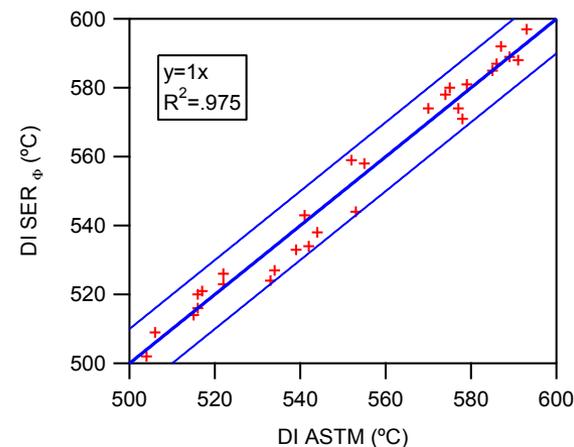
DI results metered equivalence ratio

[7]   Harrison, SAE 881670, 1988

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Application of the Volatility Model:
## Chemical Palette

✕ Chemical Palette

- ▪ Boiling point

- ▪ Availability and cost

- ▪ Components that can be produced through biological and catalytic processing of biomass.

- ▪ Components representative of gasoline for comparison purposes

**Chemical Palette for volatility study**

Alkanes	Alkenes	Aromatics	Alcohols	Esters
n-butane	n-butene	toluene	ethanol	methyl pentanoate
isobutane	n-hexene	p-xylene	propanol	ethyl pentanoate
2,3 dimethylbutane	2,5 dimethyl-2-hexene	ethylbenzene	butanol	butyl pentanoate
2,2,4 trimethylpentane	2,2,5,5 tetramethyl-3-hexene	**Cycloalkanes**	isobutanol	ethyl levulinate
2,2,5 trimethylhexane	**Acids/Other**	cyclohexane	pentanol	
2,2,3,3 tetramethylhexane	pentanoic acid	methylcyclohexane	5-nonanol	
2,3,5,6 tetramethylheptane	levulinic acid	**Ketones**		
2,3,4,7, tetramethyloctane	γ-valerolactone	5-nonanone		

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Minimum number of components for drop-in gasoline

✦ Four component mixtures were found to be adequate for matching distillation
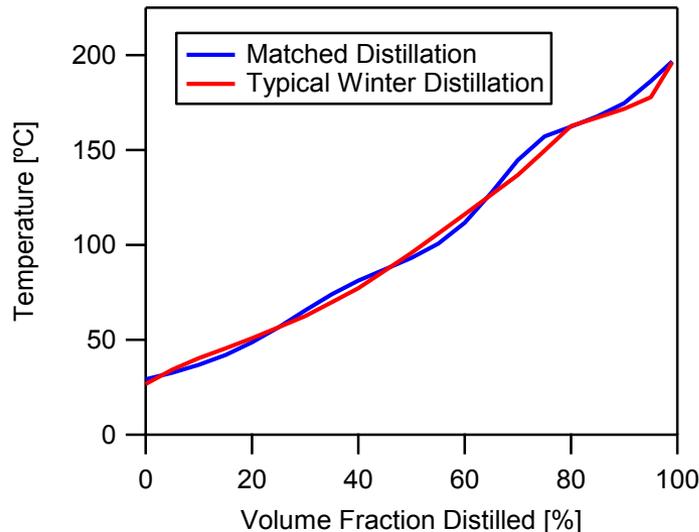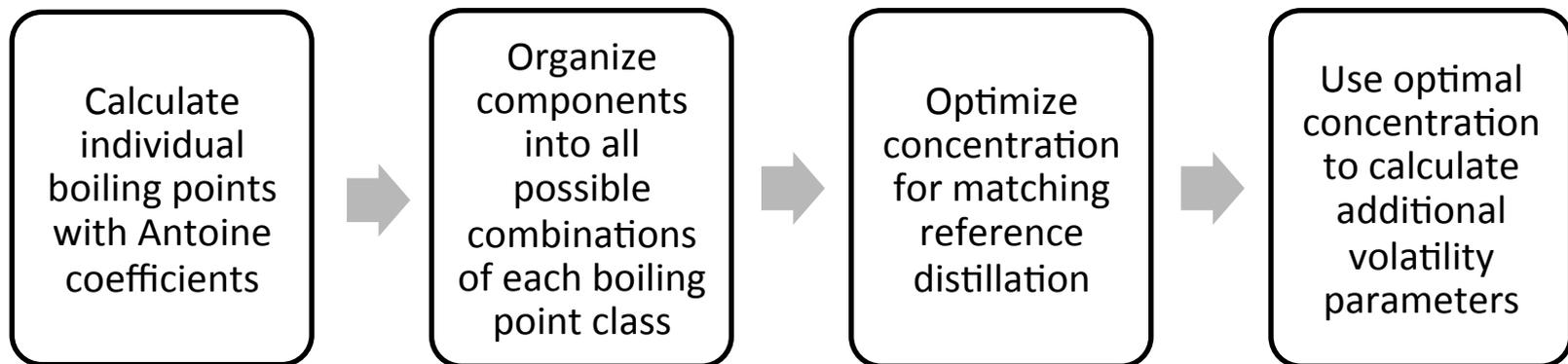

Manually matched typical winter ASTM D86 distillation with components butane, hexene, nonene, and undecane.
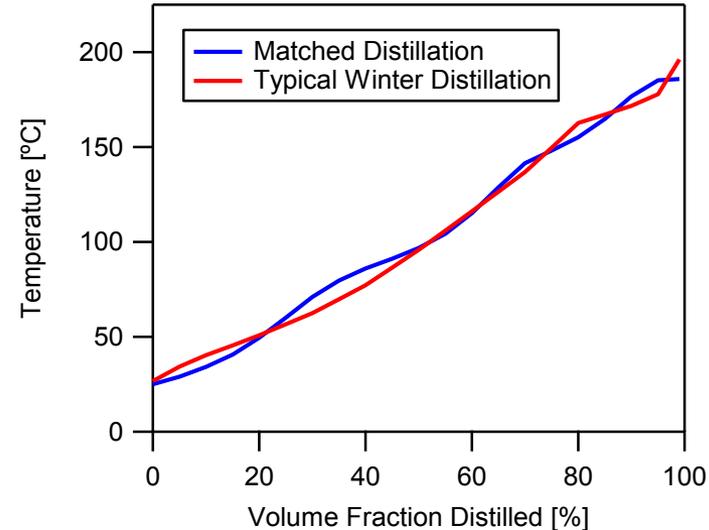
Manually matched typical winter ASTM D86 distillation with components butene, hexene, methyl pentanoate, and pentanoic acid.

Application of Volatility Model:
Model Structure

✕ Levenberg Marquardt algorithm used to optimize component concentrations in each run

| Calculate individual boiling points with Antoine coefficients | → | Organize components into all possible combinations of each boiling point class | → | Optimize concentration for matching reference distillation | → | Use optimal concentration to calculate additional volatility parameters |

Calculation process of volatility model

Application of the Volatility Model:
Initial Results

- ✕ Initial round showed inadequacy of matching ASTM D86 distillation with a thermodynamic model (investigated further with laboratory testing)

  - Matching summer distillation gave typical autumn to winter gasoline results

  - Matching winter distillation gave results that were too volatile

  - Increased initial boiling point of reference summer distillation curve to attempt to correct overall shape of the reference distillation curve to be more representative of an equilibrium curve

Application of the Volatility Model:
Distillation Matches

✖ Top distillation matches from running volatility model

| Match Rank	Component 1		Component 2		Component 3		Component 4		MSE
	name	mole fraction	name	mole fraction	name	mole fraction	name	mole fraction	
1	n-butane	0.126	n-hexene	0.506	2,2,5,5-tetramethyl-3-hexene	0.268	γ-valerolactone	0.100	14
2	n-butane	0.131	n-hexene	0.475	2,2,5-trimethylhexane	0.290	γ-valerolactone	0.103	14
3	n-butane	0.119	n-hexene	0.516	2,2,5,5-tetramethyl-3-hexene	0.265	γ-valerolactone	0.100	15
4	n-butane	0.122	n-hexene	0.489	2,2,5-trimethylhexane	0.286	γ-valerolactone	0.103	15
5	isobutane	0.105	n-hexene	0.530	2,2,5,5-tetramethyl-3-hexene	0.265	γ-valerolactone	0.100	17
6	n-butene	0.097	2,3-dimethylbutane	0.491	2,2,5-trimethylhexane	0.310	γ-valerolactone	0.103	17
7	isobutane	0.088	2,3-dimethylbutane	0.499	2,2,5-trimethylhexane	0.309	γ-valerolactone	0.104	17
8	n-butane	0.165	cyclohexane	0.517	p-xylene	0.248	γ-valerolactone	0.070	17
9	isobutane	0.108	n-hexene	0.503	2,2,5-trimethylhexane	0.286	γ-valerolactone	0.103	17
10	n-butane	0.106	2,3-dimethylbutane	0.477	2,2,5-trimethylhexane	0.313	γ-valerolactone	0.104	17
11	n-butane	0.167	cyclohexane	0.508	ethylbenzene	0.256	γ-valerolactone	0.069	18
12	n-butane	0.114	n-hexene	0.470	methyl pentanoate	0.332	γ-valerolactone	0.084	18
13	isobutane	0.085	2,3-dimethylbutane	0.520	2,2,5,5-tetramethyl-3-hexene	0.295	γ-valerolactone	0.100	18
14	n-butene	0.093	2,3-dimethylbutane	0.512	2,2,5,5-tetramethyl-3-hexene	0.294	γ-valerolactone	0.100	19
15	n-butene	0.111	n-hexene	0.477	methyl pentanoate	0.328	γ-valerolactone	0.084	19
25	n-butene	0.113	n-hexene	0.475	methyl pentanoate	0.338	ethyl levulinate	0.074	23

Application of the Volatility Model:
Volatility Properties of Top Distillation Matches

✕ Volatility properties of top distillation matches from running volatility model

Match Rank	RVP (kPa)	T_{10} (°C)	T_{50} (°C)	T_{90} (°C)	T_{end} (°C)	$T_{V/L=20}$ (°C)	SER $DI_{A/F=11}$ (°C)	SER $DI_{\Phi=1.3}$ (°C)	ASTM DI (°C)	Distillation and Vapor Lock Class
1	63	65	102	168	215	60	600	595	571	A-1
2	64	65	102	168	215	60	570	555	572	B-1
3	67	66	102	168	215	59	603	586	572	B-1
4	68	66	102	169	215	59	572	556	572	B-1
5	71	68	101	168	215	59	596	590	573	B-1
6	64	66	102	167	215	61	556	546	571	B-1
7	65	67	102	167	215	61	552	542	572	B-1
8	74	62	103	166	215	56	615	606	568	C-1
9	71	68	101	169	215	59	566	551	573	B-1
10	59	65	102	167	215	62	554	545	572	A-1
11	74	62	103	167	214	56	613	604	569	C-1
12	65	65	101	164	214	60	657	570	564	B-1
13	65	66	102	166	215	61	583	574	571	B-1
14	62	66	102	166	215	61	588	578	571	A-1
15	66	66	101	164	214	60	661	572	565	B-1
25	67	65	101	168	207	59	662	577	570	B-1

Application of the Volatility Model:
Investigation of Poor Driveability

✖ Poor predicted driveability for match number 8 and number 11 were explored

✖ Poor driveability fuels had higher distillation temperatures in the 20 to 40% distilled range

- This fraction needs to vaporize during cold starts and higher temperatures indicate more energy required

- Validates findings by Geng et al. [8]
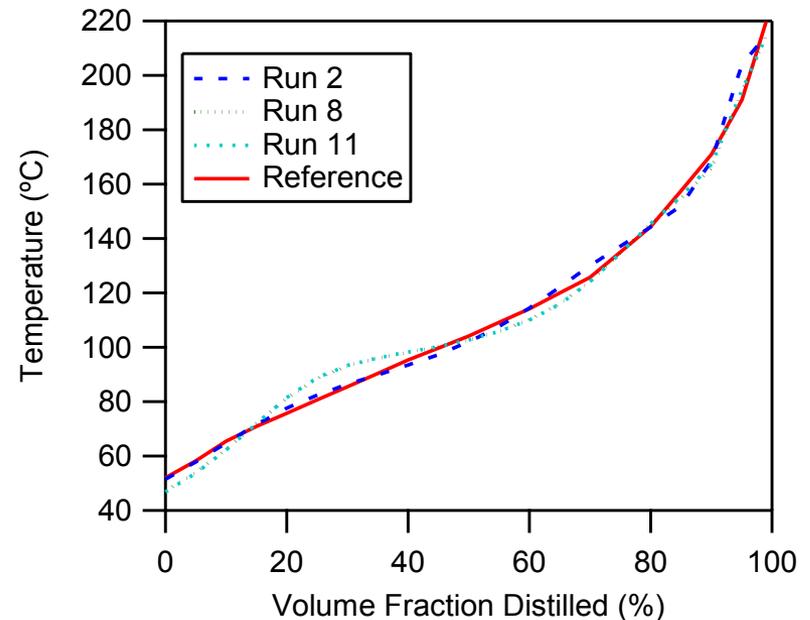
Comparison of good driveability case and poor driveability case predicted by the distillation optimization

[8]   Geng, SAE 2007-01-4073

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Application of the Volatility Model:
Biofuel Mixture Compositions

✦ Two biofuel mixtures chosen for further testing

  ▪ Mixtures chosen because components could be purchased and produced through lignocellulosic biomass conversion processes

Properties of biofuel mixture 1

*Assumes ideal solution. **For liquids at 20 ˚C or for gases at the boiling point of the liquified gas.

Components	Liquid mole fraction xi	MW (kg/kmol)	*Volume fraction	**Density (kg/L)
n-butene	0.111	56.106	0.083	0.595
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γ-valerolactone	0.084	100.116	0.067	1.0794

Properties of biofuel mixture 2

*Assumes ideal solution. **For liquids at 20 ˚C or for gases at the boiling point of the liquified gas.

Components	Liquid mole fraction xi	MW (kg/kmol)	*Volume fraction	**Density (kg/L)
n-butene	0.113	56.106	0.086	0.595
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methyl pentanoate	0.338	116.158	0.352	0.8947
ethyl levulinate	0.074	144.168	0.085	1.0111

Experimental Setup:
Volatility Testing

✗ ASTM D86 certified distillation apparatus

✗ RVP/$T_{V/L=20}$ testing chamber

 ▪ Designed to meet ASTM D5188 ($T_{V/L=20}$) and ASTM D5191 (RVP)

✗ Volatility testing apparatuses made/ purchased by Alison Ferris

✗ All following distillation, RVP, and $T_{V/L=20}$ tests run by Alison Ferris


ASTM D86 Distillation Apparatus

Reid vapor pressure and $T_{V/L=20}$ testing chamber

Laboratory Volatility Testing Results:
Investigation of Equilibrium vs D86 Curves

✖ Could thermometer in ASTM D86 be replaced by a RTD?

✖ What was the cause of the differences between ASTM D86 and an equilibrium curve?
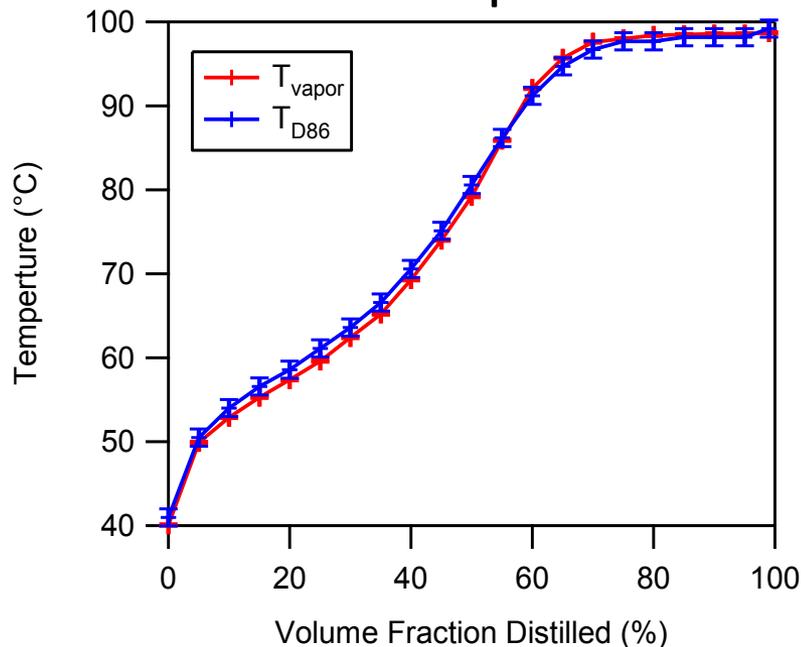
Distillation of 50/50 n-pentane/n-heptane. RTD compared to D86 thermometer
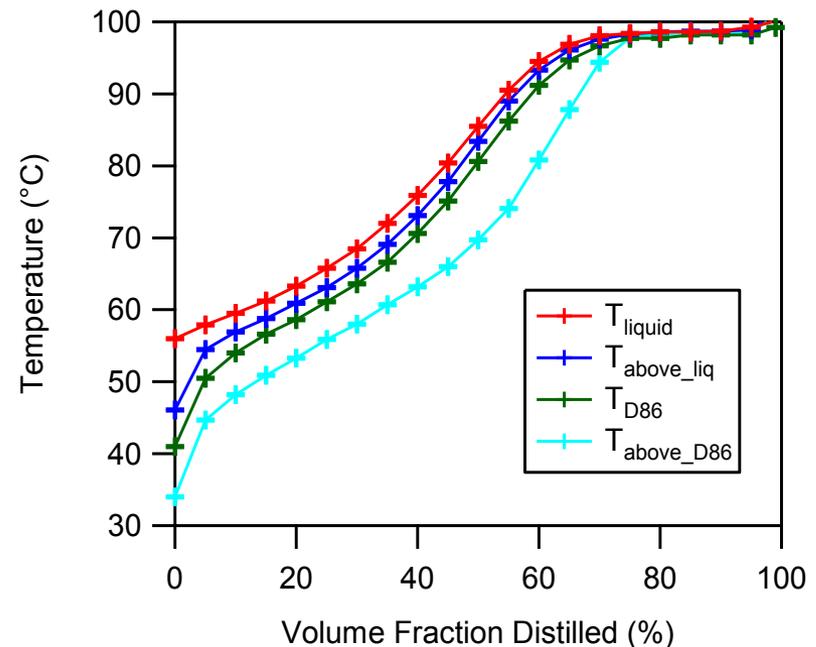
Distillations measured at different heights above the liquid

Laboratory Volatility Testing Results:
Comparison of Model With Equilibrium Curve

�֊ Comparison of distillation of 50/50 mixture with model for verification

✖ Equilibrium curve appears to be shifted 6% to the left from the calculated curve

- Phenomenon documented by Huber et al. [9] and attributed to liquid in transit

- Shift ignored due to unreasonable amount of liquid expected to be in transit

- Model predicts equilibrium distillation within 4 °C
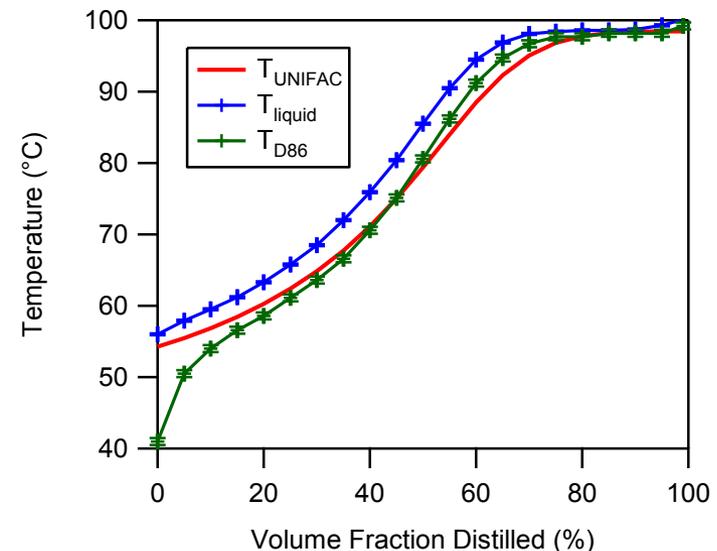
Liquid distillation, D86 distillation, and modeled distillation comparison for 50/50 molar mixture of n-pentane/n-heptane
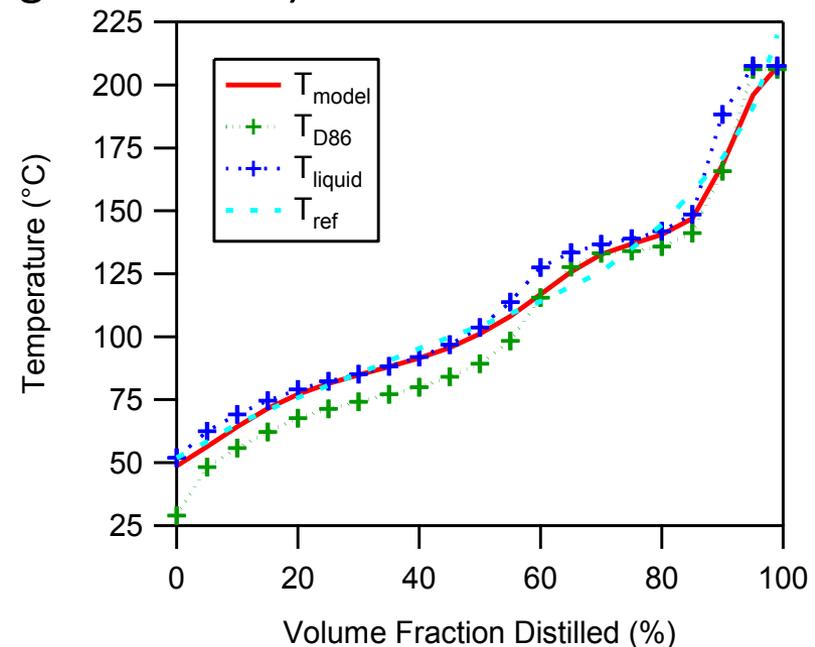
[9] Huber et al. Energy & Fuels, 2008

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Laboratory Volatility Testing Results:
Distillation of Biofuel Mixtures

✖ Distillations for biofuel mixture 1 and biofuel mixture 2

- ▪ MSE biofuel 1 = 19 (4.4 °C average deviation)
- ▪ MSE biofuel 2 = 41 (6.4 °C average deviation)
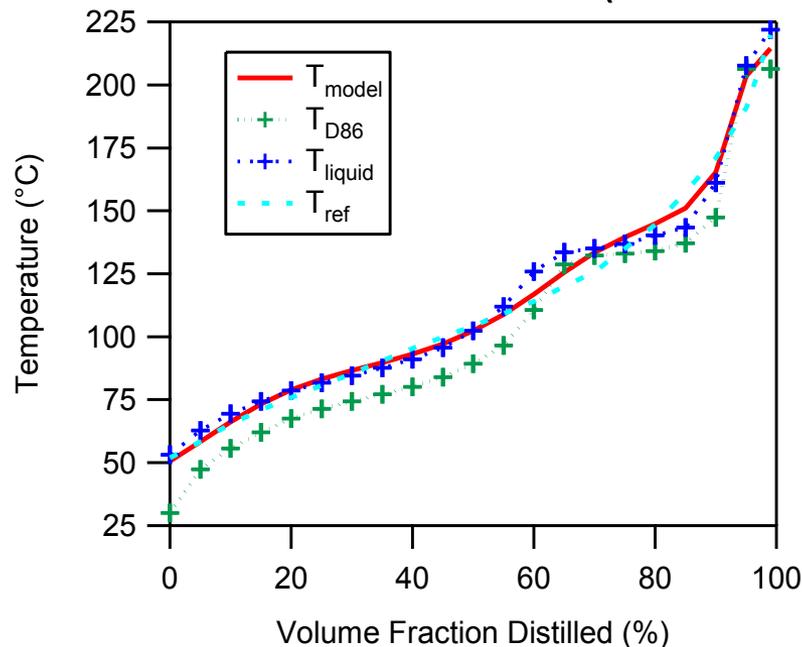
Distillation results of biofuel mixture 1

Distillation results of biofuel mixture 2

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Laboratory Volatility Testing Results:
RVP and $T_{V/L=20}$

✖ Laboratory volatility results for both biofuel mixture 1 and biofuel mixture 2

RVP results

	Biofuel Mixture 1	Biofuel Mixture 2
RVP Experimental (kPa)	65.0 ± 3.0	75.8 ± 3.0
RVP Model (kPa)	66.0 ± 1.0	69.6 ± 0.7

$T_{V/L=20}$ results

	Biofuel Mixture 1	Biofuel Mixture 2
$T_{V/L=20}$ Experimental (°C)	59.5 ± 0.3	57.2 ± 0.3
$T_{V/L=20}$ Model (°C)	59.7 ± 0.5	57.8 ± 0.4

Laboratory results for measuring biofuel mixture 1 and biofuel mixture 2

Biofuel Mixture	RVP (kPa)	T_{10} (°C)	T_{50} (°C)	T_{90} (°C)	T_{end} (°C)	$T_{V/L=20}$ (°C)	Distillation and Vapor Lock Class
1	65.0	55.6	89.3	147.4	206.3	59.5	B-1
2	75.7	55.8	89.3	165.7	206.2	57.4	C-1

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Experimental Setup:
Combustion Characteristics
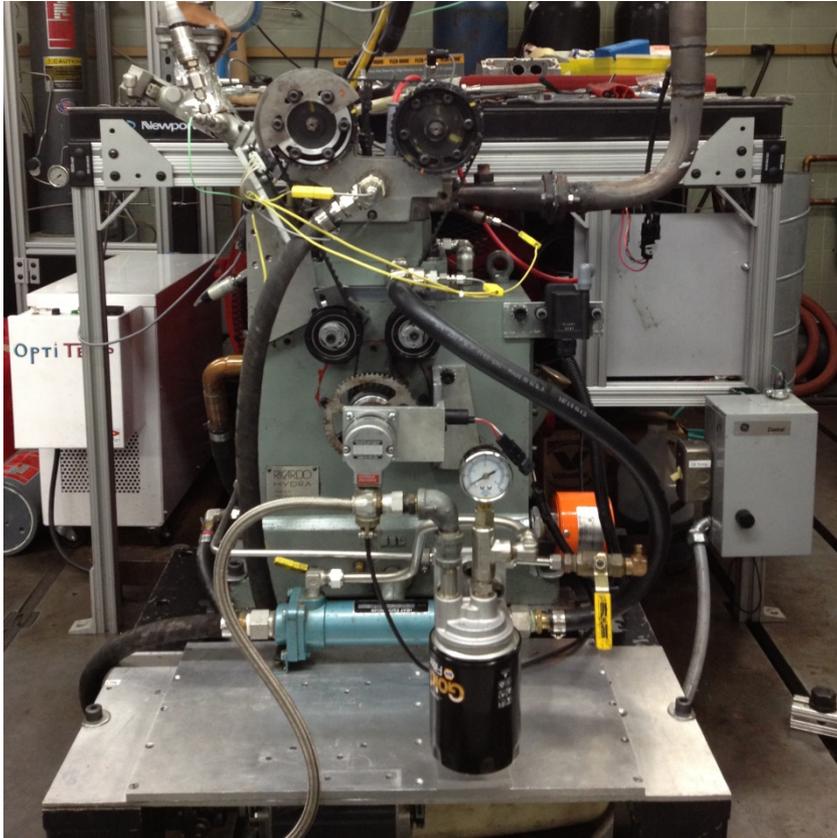
Single-cylinder direction-injection spark-ignition engine

Engine Specifications	
Engine Type	Ricardo Hydra base 4-Stroke, 4-Valve, SI
Combustion Chamber Geometry	Pentroof
Displacement (cm^3)	696
Compression Ratio	12:1
Bore (mm)	90.20
Stroke (mm)	108.89
Connecting rod length (mm)	161.72
Clearance Volume (cm^3)	64.3
Squish Height (mm)	1.01
IVC (CAD ATDC)	-133
EVO (CAD ATDC)	153

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Experimental Setup:
Laboratory Systems

- Fuel System
  - Direct injection system
  - Dual port fuel injectors
  - Syringe Pump and ultrasonic nozzle
- Emissions
  - Horiba 5 gas emissions bench (CO, CO_2, NO_x, HC, O_2)
- Engine Control
  - Mototron ECU
  - Drivven injector control
- Data acquisition
  - NI compact Daq
  - High speed measurements 0.25 CAD resolution
  - Many low-speed measurements
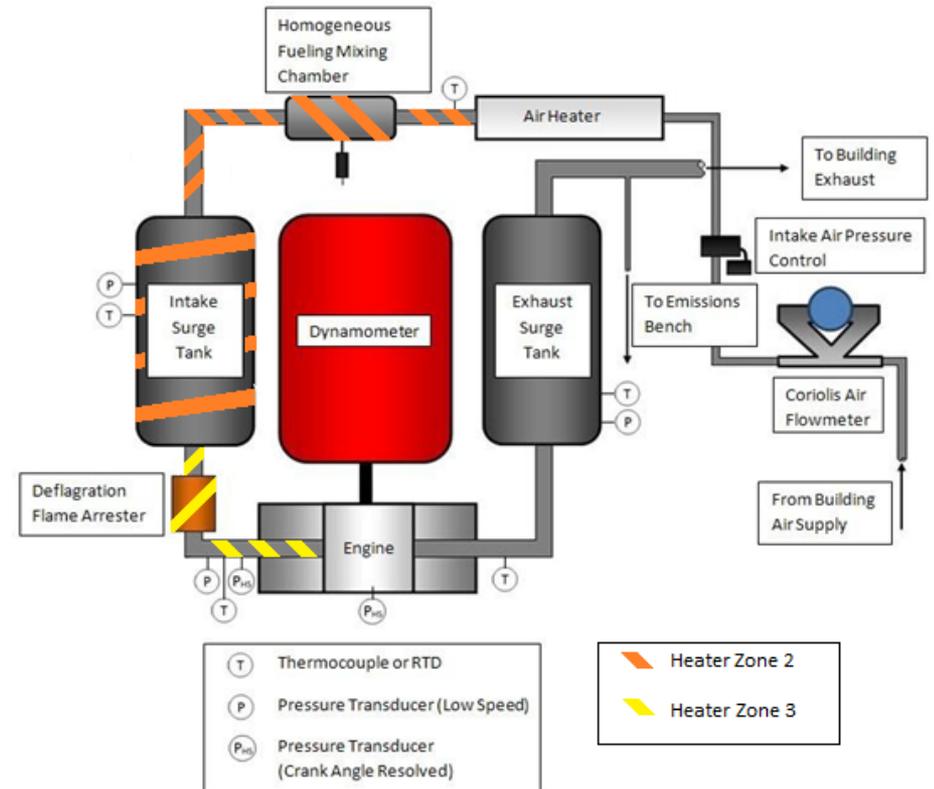
Lab Layout showing intake and exhaust

Engine Testing:
Knock Limit Definition

- The knock-limited spark advance (KLSA) compared for the biofuel mixtures relative to EEE gasoline

- KLSA defined as spark advance where 10 % of recorded engine cycles had a knocking intensity (KI) greater than 100 kPa on a 5-15 kHz bandpass filtered cylinder pressure trace
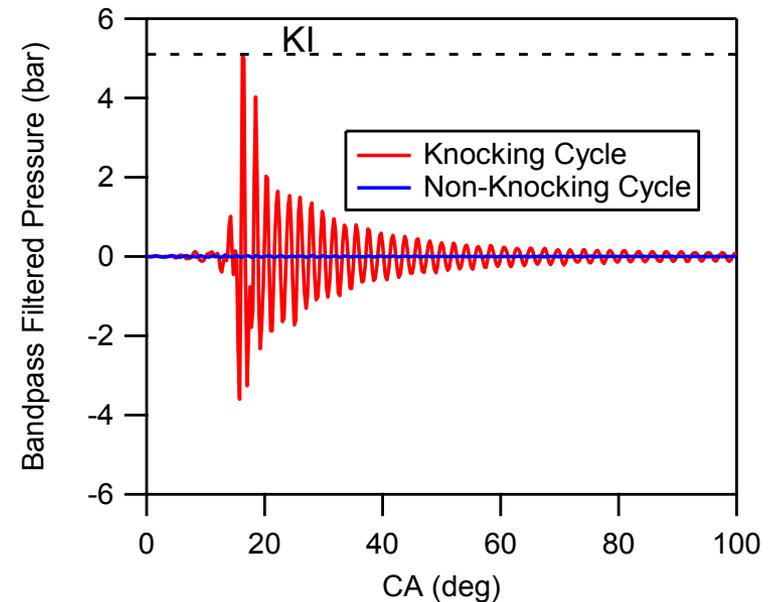
Bandpass filtered pressure data, showing a knocking and a non-knocking cycle. Cylinder pressure acquired from a knocking case for biofuel mixture 1. Conditions: 80 kPa IMAP, 40 °C intake air temperature, and -12.0 deg ATDC spark timing.

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Engine Testing:
Properties of Biofuel Mixtures

✖ Energy density estimated from LHV of individual components

✖ Octane number estimated using linear volumetric blending approximation

Relevant properties for characterizing combustion of the biofuel mixtures relative to EEE certification gasoline. * Values assuming linear volumetric blending of octane number. **Values measured from mixed fuels. [1]Calculated from neat values [10] and [11].

Property	EEE	Biofuel Mixture 1	Biofuel Mixture 2
RON/MON	96.5/88.6	*90/79	*91/80
Net heat of combustion (LHV)			
Gravimetric [MJ/kg]	43.0	36.1[1]	36.0[1]
Volumetric [MJ/L]	31.9	27.5	28.1
Density (293 K) [kg/L]	0.742	**0.760	**0.780
Reid vapor pressure (311K) [kPa]	63.4	65.0	75.8
Stoichiometric A/F ratio	14.53	12.01	11.88
H/C [mol/mol]	1.847	1.9697	1.9748
O/C [mol/mol]	0.00	0.1485	0.1528

[10]   Christensen et al. Energy & Fuels, 2011
[11]   Turns, McGraw Hill, 2000

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Engine Testing:
Engine Operating Conditions

✗ Conditions matched between DISI and homogeneous SI for 100 ℃ intake air temperature to compare relative difference in combustion phasing relative to EEE gasoline

✗ Change in relative combustion phasing between homogeneous SI and DISI indicates significant vaporization effects

Engine Operating conditions

	DISI Conditions				Homogeneous SI Conditions	
Intake Air Temperature (˚C)	100	100	40	40	100	100
Intake Air Pressure (kPa)	40	60	60	80	40	60
Engine Speed (rpm)	2000	2000	2000	2000	2000	2000
Equivalence Ratio	1.0	1.0	1.0	1.0	1.0	1.0
Spark Timing	MBT	KLSA	MBT	KLSA	MBT	KLSA
End of Injection (dBTDC)	270	270	270	270	-	-
Injection Pressure (MPa)	10	10	10	10	-	-
Exhaust Pressure (kPa)	101	101	101	101	101	101
Coolant Temperature (˚C)	80	80	80	80	80	80

Engine Testing:
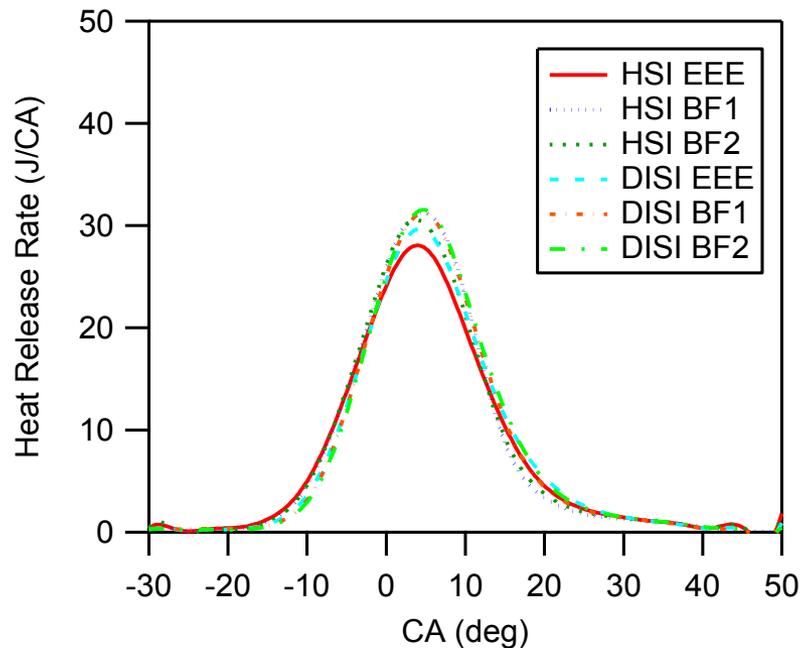## Matched DISI and Homogeneous SI Conditions
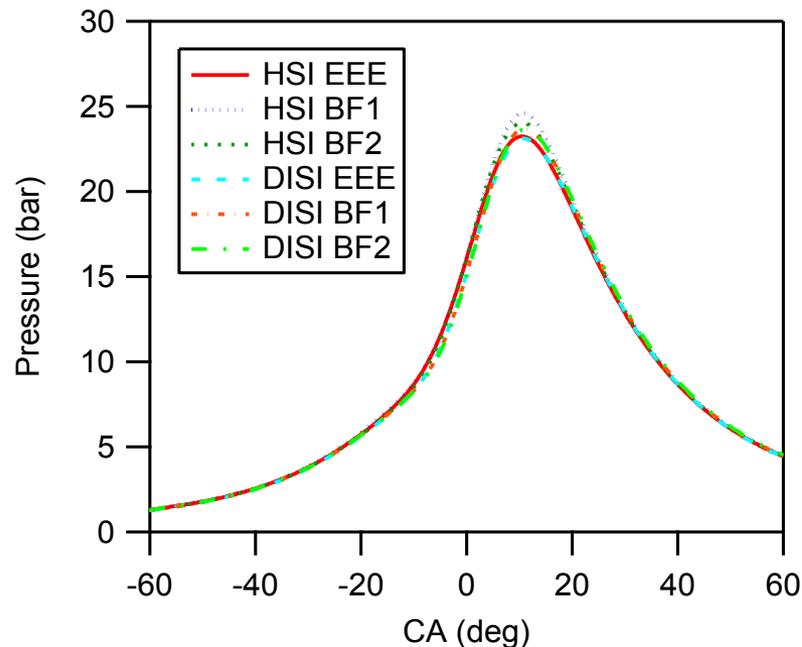
Cylinder pressure vs crank angle.
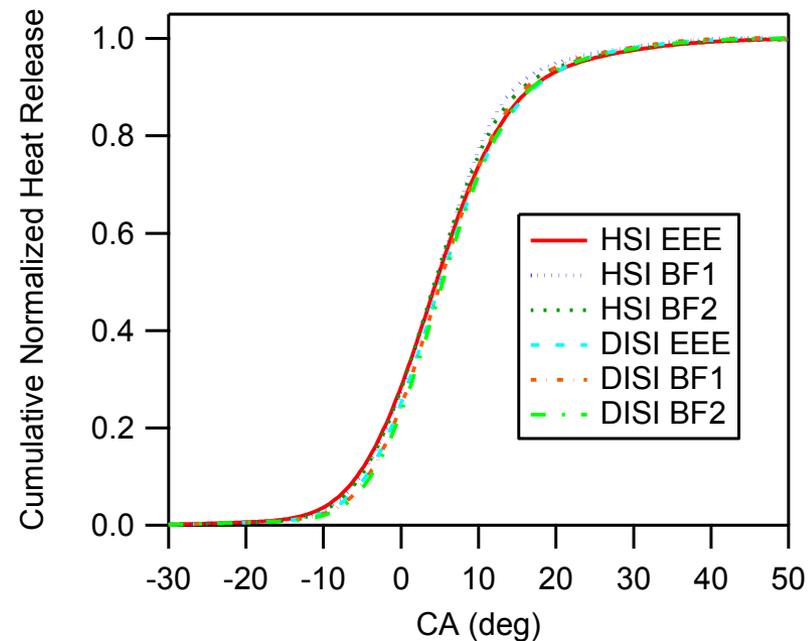**Conditions: 40 kPa IMAP 100 ℃ intake air temperature**
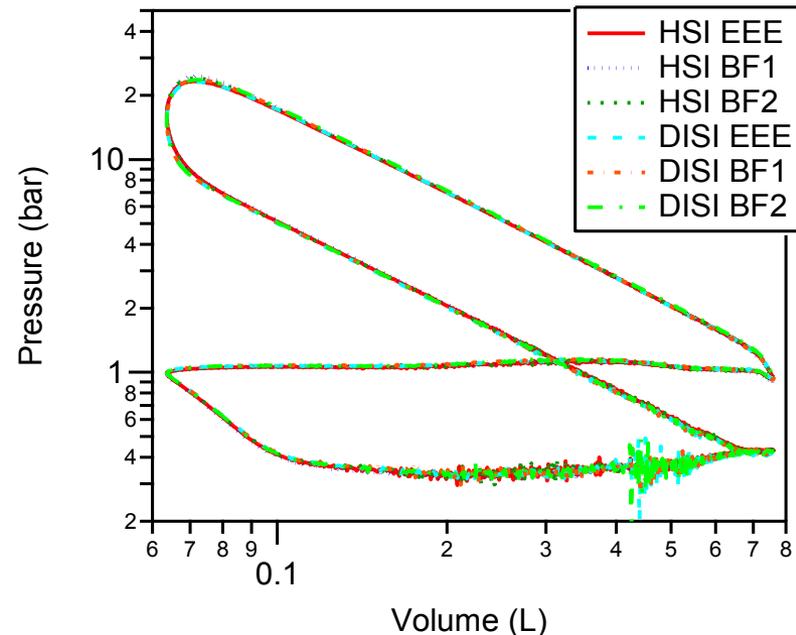
Log pressure vs log volume.
Conditions: 40 kPa IMAP 100 ℃ intake air temperature

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Engine Testing:
Matched DISI and Homogeneous SI Conditions

Heat release rate. Conditions: 40 kPa
IMAP 100 $^\circ$C intake air temperature

Cumulative normalized heat release.
Conditions: 40 kPa IMAP 100 $^\circ$C intake
air temperature

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Engine Testing:
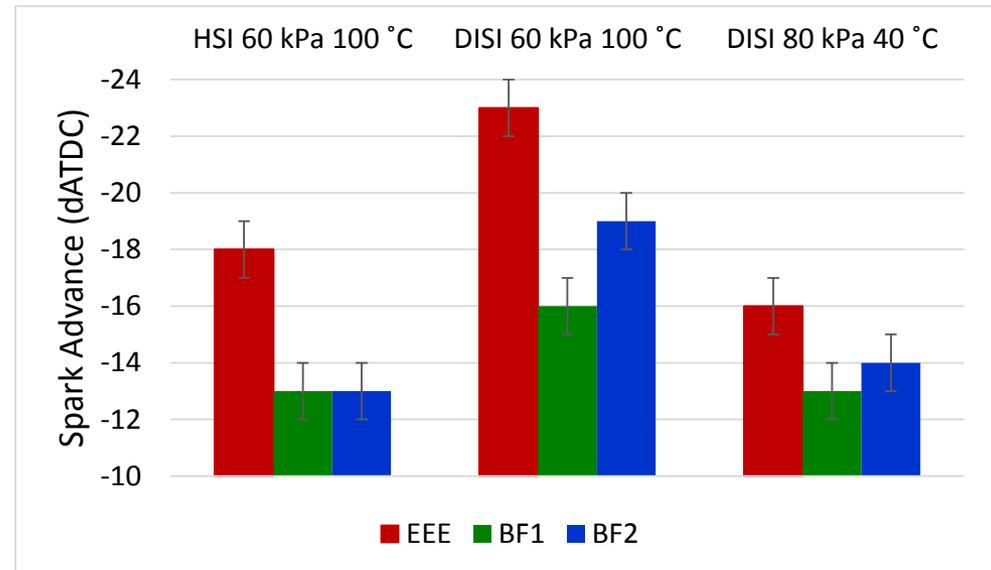## Relative Spark Timing for Location of CA$_{50}$

- Relative spark timing for the same CA$_{50}$ tabulated for all engine runs

- Flame speeds shown to be comparable from heat release analysis
  - Spark timing for the same location of CA$_{50}$ used to compare relative KLSA between fuels

- 40 kPa IMAP homogeneous SI and DISI cases show no vaporization effects

- Possible vaporization effects seen for 60 kPa IMAP homogeneous SI and DISI cases

Relative spark timings to EEE for the same location of CA$_{50}$ for both biofuel blends at all operating conditions

Engine Operating Condition	Spark Advance (EEE-Biofuel 1) (CAD)	Spark Advance (EEE-Biofuel 2) (CAD)
Homogeneous SI (40 kPa 100 °C)	-2.2	-2.0
DISI (40 kPa 100 °C)	-2.4	-1.9
Homogeneous SI (60 kPa 100 °C)	-1.3	-1.3
DISI (60 kPa 100 °C)	-2.1	-1.8
DISI (60 kPa 40 °C)	-1.5	-1.2
DISI (80 kPa 40 °C)	-1.4	-0.9

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Engine Testing:
Knock Limited Spark Advance Results

✕ KLSA compared for knocking cases for all fuels

✕ Changed spark timings for biofuel mixtures to match location of CA_{50} of EEE

✕ 80 kPa IMAP 40 °C intake cases closest to RON test

  ▪ Every degree in spark advance corresponds to 0.5 to 1.0 increase in RON [12]

  ▪ Expect RON on the order of 93 to 95 for these biofuel mixtures

[12]   Leppard, SAE 820074, 1982

KLSA for three operating conditions where knocking was experienced. Both biofuel mixtures and EEE compared. Spark timings changed for biofuel mixtures to have equivalent location of CA_{50} for EEE.

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Engine Testing:
Emissions Results

✦ Indicated specific emissions compared for the different fuels for the non-knocking operating conditions

✦ Emissions show no obvious trends for each operating condition, showing no advantage for any fuel
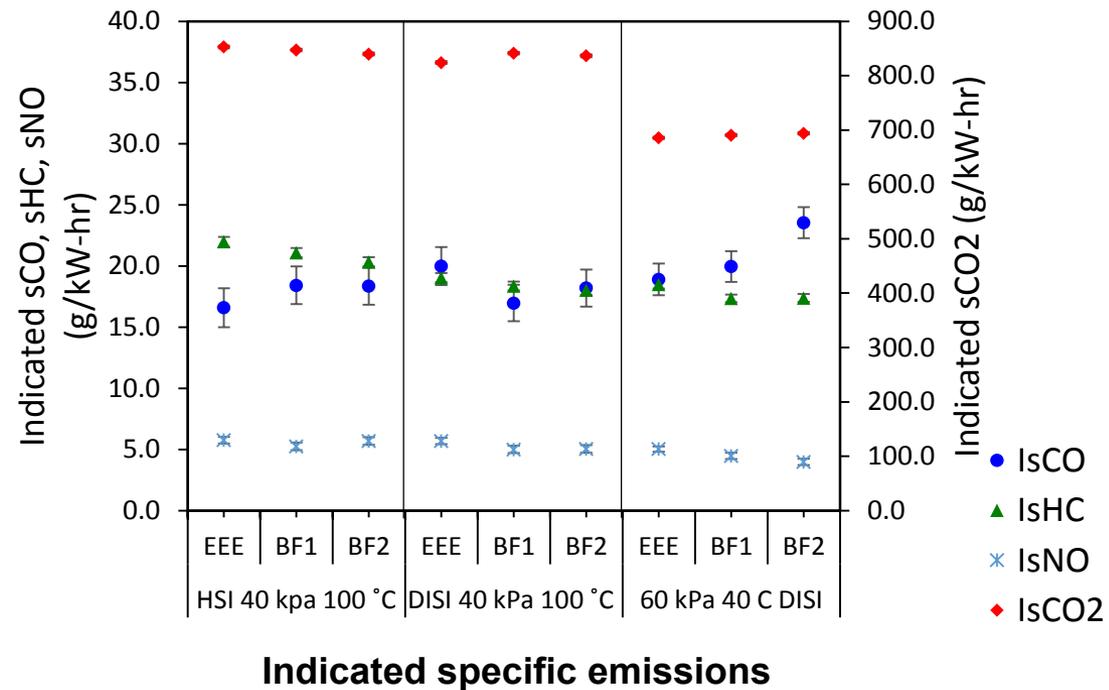
Indicated specific emissions

Conclusions

✗ Distillation was found to be an effective criterion for matching gasoline volatility

✗ Four component mixtures were found to be the minimum required to meet ASTM D4814 requirements for SI engine fuel

✗ Modeled gasoline volatility did not correspond to the expected volatility from the reference distillation curves

   ▪ An equilibrium distillation curve was modeled

   ▪ ASTM D86 gives significantly lower distillation temperatures (especially for the IBP) causing increased volatility for the model fuels

   ▪ Increasing the IBP for this particular reference curve was found to give volatility properties that were within ASTM specifications

✗ ASTM D86 and equilibrium distillation curves were shown to be able to be measured simultaneously

✗ Differences in ASTM D86 and equilibrium distillation curves were attributed to heat transfer

✗ Engine testing showed faster flame development time, and slightly faster flame speeds for the biofuel blends

✗ Average corrected KLSA for biofuel 1 was 5 CAD less than EEE and for biofuel 1 was 4 CAD less than EEE

✗ Likely sufficient ON for 87 AKI fuels

✗ No perceivable vaporization effects for 40 kPa IMAP cases. Measurable change for 60 kPa IMAP.

Recommendations for Future Work

✗ Development of heat transfer model to model ASTM D86 and equilibrium distillation curve
  ▪ Volatility specifications more fairly analyzed
  ▪ Could start with ASTM D86 reference distillation curves

✗ Distill multiple non-oxygenated gasoline blends to determine better equilibrium reference distillations

✗ Extend the driveability index model to model the processes that are occurring in the engine (PFI or DI instead of carburetor)

✗ Development of a group contribution theory for predicting octane number of mixtures

✗ Extend optimization function used to optimize distillations to other volatility parameters and octane number if an octane number model is developed

✗ Development of a methodology/model for materials compatibility

✗ Development of a model for solubility

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- ✕ ERC Faculty, Students, and Staff

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- ✕ Special thanks to Ralph Braun for being available for engine troubleshooting

- ✕ Special thanks to my wife for putting up with me being busy and encouraging me through highs and lows of research

- ✕ This work was funded by the DOE Great Lakes Bioenergy Research Center (DOE BER Office of Science DE-FC02-07ER64494)

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Questions?