## AUTO ALLIANCE

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## California LEVIII E10 Certification Gasoline -Alliance Fuels Group Position

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California Phase 3 Reformulated Gasoline (CaRFG3) E10 Certification Gasoline and Marketplace E85 Workshop

Sacramento, CA, Cal/EPA Headquarters Bldg.

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Alliance of Automobile Manufacturers

### California Fuel Quality - "Past Marketplace Fuel Composition vs. Future Direction"

Alliance & SGS N. America Surveys (CY 2008 and 2009 Combined)											
0	(										
Summer	(n = 37)										
	<b>Density</b>	<u>RVP</u>	<u>T10</u>	<u>T50</u>	<u>T90</u>	<u>Ethanol</u>	<b>Aromatics</b>	<u>Benzene</u>	<u>Olefins</u>	<u>Sulfur</u>	Octane Sensitivity
	<u>(kg/m3)</u>	(psi@100F)	<u>(deg. F)</u>	<u>(deg. F)</u>	<u>(deg. F)</u>	<u>(Vol.%)</u>	<u>(Vol.%)</u>	<u>(wt.%)</u>	<u>(Vol.%)</u>	<u>(ppm)</u>	(S = RON - MON)
25tile	738	6.9	136	210	301	5.4	20.2	0.5	3.6	5	8.5
50tile	740	7.0	137	212	307	5.5	22.5	0.5	4.8	6	8.7
75tile	745	7.1	138	213	311	5.7	24.5	0.6	6.2	11	8.9



#### Calif. Aromatics (vol. %) Summer Fuels



## **Background – Boxplot Interpretation**

A graphical summary of the distribution of a sample that shows its shape, central tendency, and variability.

The default boxplot display consists of the following:

*	1 Outlier (*) - Observation that is beyond the upper or lower whisker
*1	2 Upper whisker - Extends to the maximum data point within 1.5 box heights from the top of the box
2	<ul> <li>Interquartile range box - Middle 50% of the data</li> <li>Top line - Q3 (third quartile). 75% of the data are less than or equal to this value.</li> <li>Middle line - Q2 (median). 50% of the data are less than or equal to this value.</li> </ul>
4	<ul> <li>Bottom line – Q1 (first quartile). 25% of the data are less than or equal to this value.</li> </ul>
	4 Lower whisker – Extends to the minimum data point within 1.5 box heights from the bottom of the box

Boxplots can help you understand your distribution. For example, the boxplot above represents hold times for customer support calls. The outlier at the upper end and longer upper whisker and upper part of the box indicate positive skewness, which makes sense because at the lower end of the distribution, no hold times can be less than zero.

Boxplots are also useful for comparing several distributions. For example, a quality engineer compares the diameter of plastic pipes produced weekly over three weeks. The boxplot below represents the results.

# Alliance Proposal Summary – Relative to ARB Proposal (yellow = differences, green = no difference)

Parameter	Unite	California Cert	CARB LEVIII Proposed	Alliance Proposal -	
Farameter	Units	Gasoline "Phase II"	Targets	Ambient Standard	
Octane					
RON, min.	RON				
MON, min.	MON				
AKI, min.	Calc.	91	91	91, min.	
Sensitivity, min	Calc.	7.5	7.5	10.0, min.	
Volatility					
RVP	nsi	67-70	6.9 - 7.2	6.70 - 6.95	
RVP Evan	nsi				
	psi				
RVP AILILUUE	psi				
	deg. F				
110	deg. F	130 - 150		130 - 150	
Т50	deg. F	200 - 210	205 - 215	195 - 205	
T90	deg F	290 - 300	<b>310 - 320</b>	290 - 300	
FBP, max.	deg. F	390	390. max.	390. max.	
Residue max	vol %	2.0	2.0 max.	2.0	
Driveability Index			2.0, 110.	Report	
Chemical Composition / O	ther Physical				
chemical composition / o					
Aromatics, max.	vol. %	22 - 25	20 - 22	18 - 22	
Aromatics, Multi-					
substituted Alkyl	vol. %	12 - 14		10, max.	
Olefins. max.	vol. %	4.0 - 6.0	4-6	4-6	
Saturates	vol. %			Report	
MTBE	vol. %	10.8 - 11.2	0.05, max.		
Ethanol	vol. %		9.8 - 10.0	9.8 - 10.0	
Total Oxygen	wt. %		3.5	3.5, min.	
Benzene	vol. %	0.8 - 1.0	0.6 - 0.8	0.6 - 0.8	
Sulfur	ppm m/m	30 - 40	8 - 11	8, max.	
Lead	g/gal	0 - 0.01	0.0 - 0.01	0.0 - 0.01	
Phosphorus	g/gal	0.005	0.005, max.	0.005, max.	
Additives <sup>(3)</sup>			Title 13, CCR, Sec. 2257	Title 13, CCR, Sec. 2257	
Copper Corrosion		No. 1.	No. 1	No. 1	
Existent Gum, Washed.					
max.	mg/100ml	3.0	3.0, max.	3.0, max.	
Oxidation Stability, min.		4000	1000		
	minutes	1000	1000, min.	1000, min.	
Specific Gravity	minutes 	No limit, report	1000, min.	1000, min. Report	
Specific Gravity Heat of Combustion	minutes 	No limit, report No limit, report		1000, min. Report Report	
Specific Gravity Heat of Combustion Carbon	minutes   wt. %	No limit, report No limit, report No limit, report	 	1000, min. Report Report Report	

### **Evaporative Emissions – Ethanol Effects**

• The addition of 10vol% ethanol even with RVP control results in a more severe EVAP Standard because of ethanol's ability to increase permeability of vehicle fuel system elastomeric materials

#### • EVAP Standard needs a "Test Procedure Adjustment" to compensate

Hot Soak ("True Hot Soak") Permeation <sup>(a)</sup> – The Hot Soak emissions as defined in this report are the net increase in permeation rate following vehicle operation. We measured the mass increase in the SHED for one hour immediately following vehicle operation, and subtracted the previously measured static (or normal) permeation at the same temperature. While this is not the traditional Code of Federal Regulations (CFR) definition, we feel it is appropriate for the intent of this project.

"There was a large increase in the hot soak value with the E10 fuel compared to the E0. " (p. 22)





Ref. (a): CRC Report No. E77-2, "Enhanced Evaporative Emissions Vehicles," Harold M.<sup>5</sup> Haskew and Thomas F. Liberty, March 2010

## **Multi-substituted Alkyl Aromatics**

• The multi-substituted alkyl aromatics should continue to be controlled in the ARB's LEV III cert fuel to minimize variation in fuel composition effects on tailpipe emissions.

• As emissions regulations become more stringent, the emissions certification fuel will need to be equally controlled to ensure the measured emissions are a result of vehicle hardware and calibration effects and not spurious fuel formulation shifts.

## • A Total Aromatics limit alone in the cert fuel spec does not preclude the blending of relatively high molecular weight aromatics that can lead to increased HC and PM emissions.

• The proposed Distillation T90 and FBP serve to control high molecular weight HCs, but will not be exact enough.

• Very generally, multi-substituted alkyl aromatics (MSAA) can be the building blocks of high levels of particulate matter.

• The higher the concentration of MSAA hydrocarbons the greater likelihood of reaction between benzylic partial oxidation species of substituted aromatic fuel molecules and the 1,3-butadiene, ethylene and acetylene partial oxidation species, also known as soot precursors.

•References:

• Zhang, Hongzhi R., et. al., Univ. of Utah, "Pollutant Emissions from Gasoline Combustion. 1. Dependence of Fuel Structural Functionalities.", Environmental Science Technology., 2008, Vol. 42, pp. 5615-5621

• Kayes, David and Simone Hochgreb, MIT, "Mechanisms of Particulate Matter Formation in Spark-Ignition Engines., 2. Effect of Fuel, Oil, and Catalyst Parameters," Environmental Sci. Tech., 1999, Vol. 33, pp. 3968 – 3977

• Baral, Bivek and Robert Raine, Univ. of Auckland, "Performance and Emission of a Spark Ignition Engine Running on Gasoline Adulterated with Kerosene.", SAE 2009-28-0014

## Alliance Proposal - California LEVIII E10 Cert Fuel Specification

	Parameter	Units	ASTM Test Method (in CFR)	Alternative Test Method List	Alliance Proposal - Ambient Standard	
	Octane					
	RON, min.	RON	D2699			
	MON, min.	MON	D2700			
	AKI, min.	Calc.	(R+M)/2		91, min.	
	Sensitivity, min	Calc.	RON - MON		10.0, min.	
	Volatility					
			0 2224		6.70 - 6.95	
		psi	D 3231	D5190, D5191, or D5482		
		psi	D 3231	D5190, D5191, or D5482		
	RVP Altitude (*)	psi	D 3231	D5190, D5191, or D5482		
	IBP (2)	deg. F	D86			
	T10	deg. F	D86		130 - 150	
	T50	deg. F	D86		195 - 205	
	Т90	deg. F	D86		290 - 300	
	FBP, max.	deg. F	D86		390, max.	
	Residue, max.	vol. %	D86		2.0	
	Driveability Index		D4814		Report	
	Chemical Composition / Ot	her Physical				
	Aromatics, max.	vol. %	D1319		18 - 22	
	Aromatics, Multi-	vol %	DHA single column cap GC' (Johansen,		10, max.	
	Olofing may	vol. %	1992) D1210		16	
	Saturates	vol. %	D1319		Report	
	MTRF	vol. %				
	Fthanol	vol. %	D4815		9.8 - 10.0	
ĺ	Total Oxygen	wt. %			3.5, min.	
	Benzene	vol. %		D3606, D5580	0.6 - 0.8	
	Sulfur	ppm m/m	D3120	D2622, D3120, or D5453	8, max.	
ľ	Lead	g/gal	D3237	D3227 or D5059	0.0 - 0.01	
ľ	Phosphorus	g/gal	D3231		0.005, max.	
	Additives (3)				Note 5	
ľ	Copper Corrosion			D130	No. 1	
ĺ	Existent Gum, Washed,	mg (100m)		2004	3.0, max.	
	Midstion Stability and	mg/100ml		D381	1000	
	Oxidation Stability, min. minute			D525	1000, min.	
	Specific Gravity			D340 D4900	Report	
				D240, D4809	Report	
	Larbon Hydrogon	WT. %			Report	
	nyulogen	WT. %			Report	

The Alliance of Automobile Manufacturers Thanks the Air Resources Board for their consideration!



#### Contact

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**Back-up Material** 

## **Octane Sensitivity – Ethanol Effects**

- For the LEVIII Cert Fuel, the octane sensitivity value should be set higher (10, min.)
  - Fuel Survey Data show the California marketplace Octane Sensitivity (50<sup>th</sup> Percentile) is nominally already 9 when ethanol is at 5.5v% (Slide 2)
  - Ethanol's Sensitivity is 19 and ethanol concentration is moving from 5.5v% to 10 v%.

Octane Sensitivity of Pure Hydrocarbons <sup>(d)</sup>								
Hydrocarbon	Туре	RON	MON	Sensitivity				
Isooctane <sup>(a)</sup>	Paraffin	100	100	0				
Isopentane <sup>(a)</sup>	Paraffin	92	90	2				
Neohexane <sup>(a)</sup> (2,2-DiM-butane)	Paraffin	92	93	-1				
2-M-2-Pentene <sup>(a)</sup>	Olefin	98	83	15				
2,3-DiM-2- Pentene <sup>(a)</sup>	Olefin	98	80	18				
Toluene <sup>(a)</sup>	Aromatic	120	104	16				
1-M-3-E-Benzene <sup>(a)</sup>	Aromatic	112	100	12				
Ethanol <sup>(b)</sup>	Oxygenate	109	90	19				
Methanol <sup>(b)</sup>	Oxygenate	109	89	20				

Notes:

(a)API Research Project 45, "Summary of Data on the Knock Ratings of Hydrocarbons", Technical Data on Fuel by J.W. Rose and J.R. Cooper, 7<sup>th</sup> Ed., The British National Committee, World Energy Conf., 1977.

(b)Automotive Fuels Reference Book, Keith Owen & Trevor Coley, 1995, p. 591

(c)Values reported are for pure hydrocarbons, not blending numbers, which are reported higher. Octane numbers for ethanol verified by GM Fuels Group using standard CFR engine with modifications to carburetor fixed jet and intake air heater to stay within prescribed requirements of ASTMD2699 & D2700.