

A 2nd Opinion **On De Minimis MTBE**

For
CARB Fuels Workshop
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Agenda

- ***Why*** we are here
- ***Why*** we need definition
- ***Where*** we have been
- ***Where*** we need to be

Why We Are Here

- **Tanks leaked**
 - Repair mandate deadline 1998
 - Oxygenate mandate 1992
- **MTBE banned**
- **Need to define zero**

***Why* Is the De Minimus Definition Important?**

Could Limit Supply 

Sources of unintentional oxygenate content:

- Line flush & tank bottoms.
- Trace co-production in isooctane processes.
- Ethanol contamination.

No basis for de minimus levels for non-MTBE ethers and non-ethanol alcohols.
(CARB RFG3 manual on Prohibition of MTBE)

Poor definition could trigger World Trade Organization restraint of trade proceedings

Where We Have Been

- **USEPA and pipelines define non-oxygenated as less than 2 vol% MTBE**
- **Emotional definition zero**
- **Dilemma**
 - **Chemists too smart**
 - **Californians like driving**
- **Need to define zero**

CARB Proposed Converting MTBE De Minimis to Oxygen Equivalent

Volume Percent <u>MTBE</u>	Weight Percent <u>Oxygen</u>
0.30	0.06
0.15	0.03
0.05	0.01

Source: CARB 08/29/01

Oxygen Content Relative to MTBE

Oxygenate	Oxygen Content Relative to MTBE
MTBE	1.00
TAME	0.86
ETBE	0.86
DIPE	0.86
C8 Ether	0.68
Methanol	2.74
Ethanol	1.91
Propanols	1.47
Butanols	1.19

Creative – But Could Be Infeasible

**Co-production of trace oxygenates
could require zero or negative
MTBE concentration**

- **ASTM D4806 allows ethanol to contain 0.5 vol% methanol**
- **Water reacts with olefins in some refining processes to form alcohols**
- **Alcohols react with olefins to form ethers**

Methanol in Ethanol

- **When ASTM sets a specification for a contaminant in a pure product, it means it is usually there *naturally***
- **With the likely ethanol minus methanol price differential, CARB may want a "*no-intentional-addition*" specification**

Oxygenates in Isooctene

- **Refiners want to use isooctene to:**
 - Blend off ethanol RVP
 - Replace oxygenate octane
 - Blend around the Unocal patents
- **Isooctene process controls MTBE but:**
 - Oxygenate (H₂O, TBA, MTBE) controls T50
 - Water reacts with nC₄= to form alcohol
 - Alcohol reacts with iC₄= to form C₈ ethers
 - Oxygen content 0.4 to 0.8 wt%

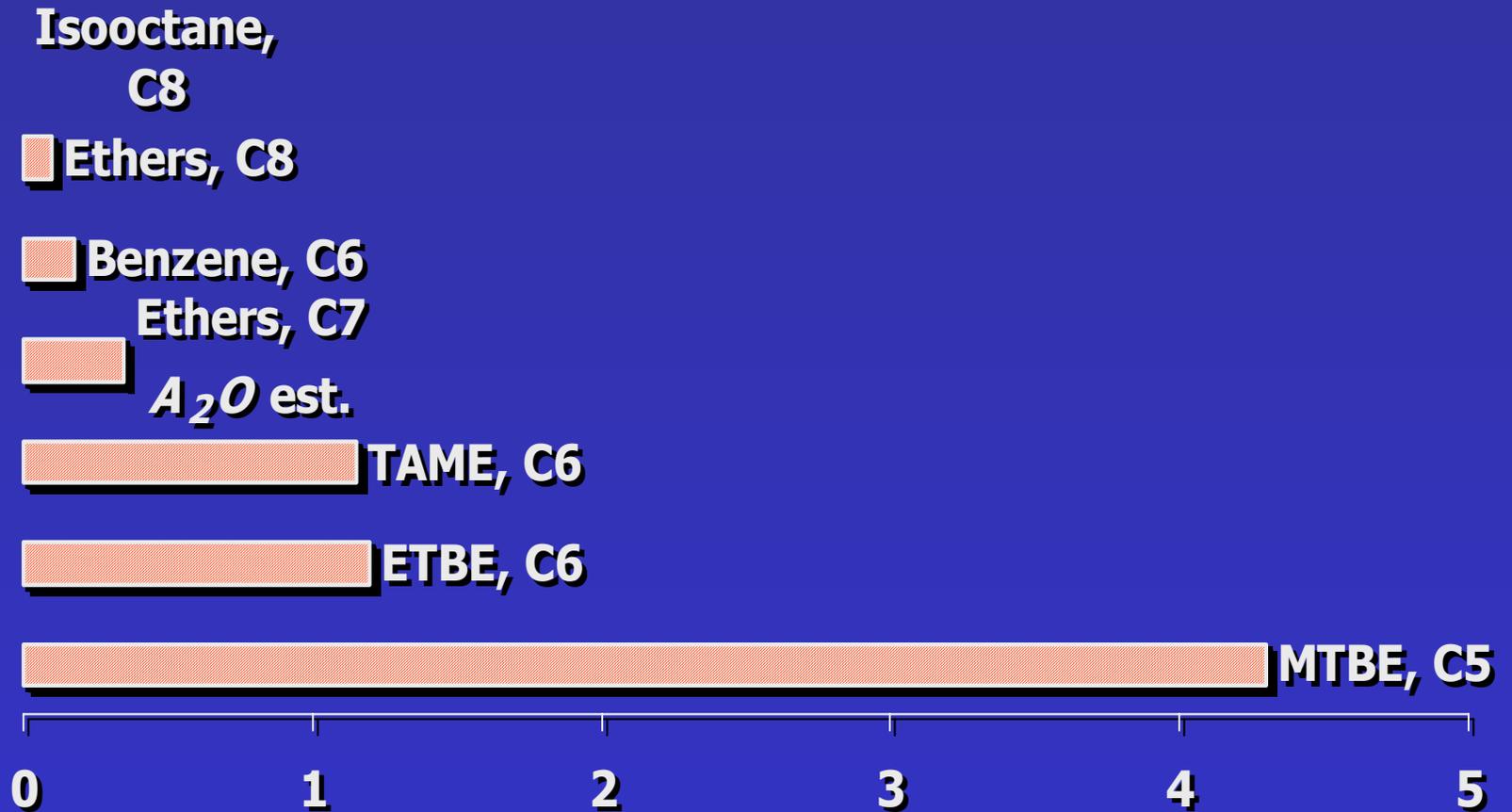
Water wash will not remove this oxygen



Oxygenates in Isooctane

- **Refiners want to use isooctane to:**
 - Blend off ethanol RVP
 - Replace oxygenate octane
- **Hydrogenation of isooctene lowers oxygen content to 0.04 - 0.07 wt%**
- **Raising hydrogenation severity would destroy isooctane**
- **Low solubility of C8 ethers in water prevents their removal via water wash**

Ethers' Solubility in Water, Wt %



***Why* is California Banning MTBE?**

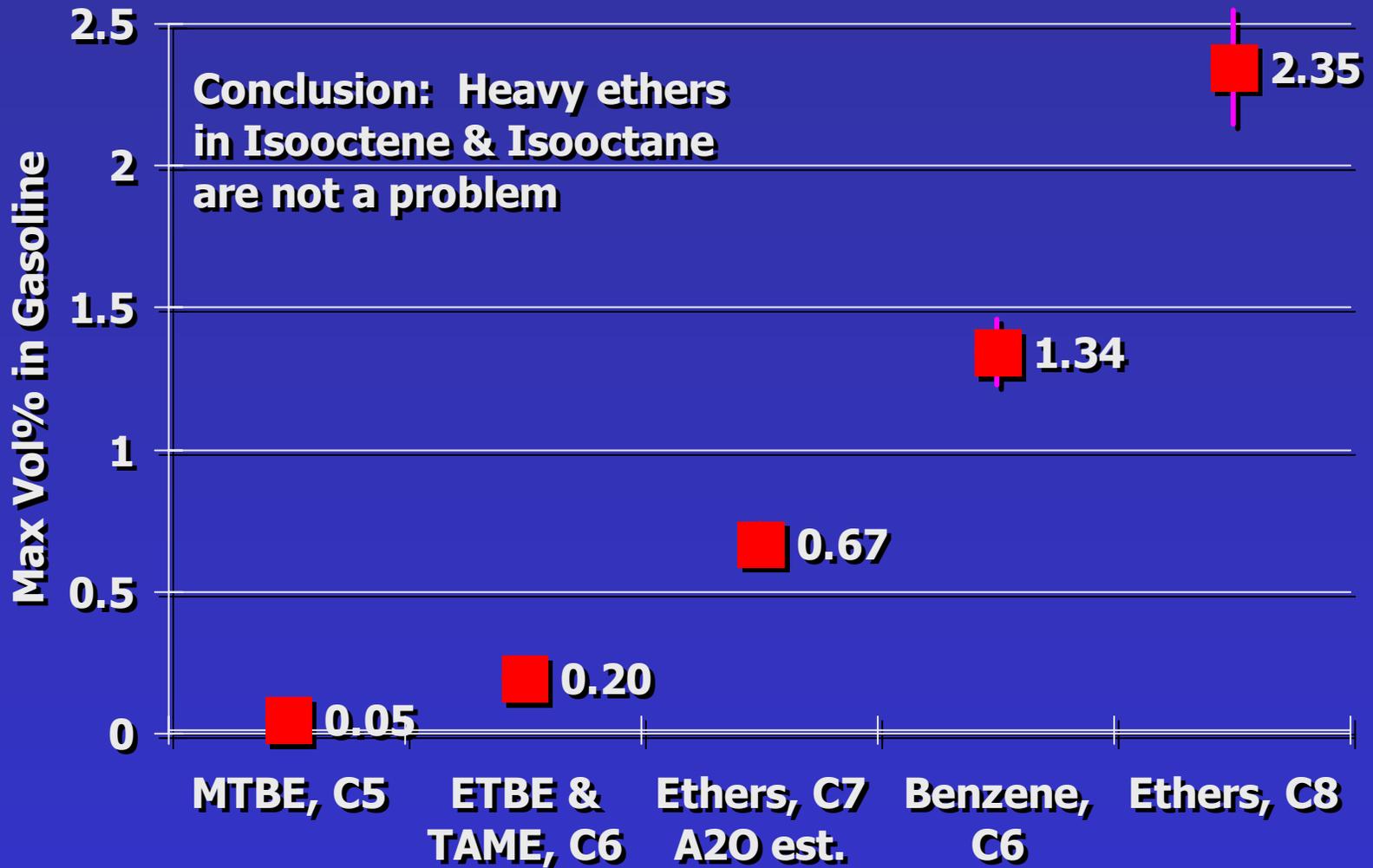
- **It gets into water**
- **People object to the taste and odor**
- **California apparently cannot solve its LUST problem**

**If MTBE 0.05 vol% Standard
is Correct, It Implies:**

- **Less soluble components can have a higher de minimus standard.**

(For example: 0.2 vol% would be OK for ETBE)

Maximum Ether in Gasoline Assuming MTBE Cap is Right



Where We Need to Be

- **Look before we leap**
- **Separate standard for non-MTBE ethers**
- **Separate standard for non-ethanol alcohols**
- ***No-intentional-addition* language that covers:**
 - **Co-production**
 - **Contamination**
 - **Blending off non-conforming product**

Look Before We Leap

- Evaluate feasibility of each proposed change in de minimis standard
- Delay implementation until actual data indicates feasibility
 - Commingling study showed problem with going to 0.3 vol% MTBE equivalent*
 - Commercial isooctane sample contained 0.055 wt% oxygen*
 - CARB isooctane consistent with my data

CARB 08/29/01 Decision to Delay was Good

Separate Standard for Non-MTBE Ethers

- **Most ethers less soluble in water than MTBE**
- **Individual ether standards can be greater than MTBE standard**
- **Simply converting to wt% oxygen equivalent of MTBE could:**
 - Limit imports of much needed blendstocks and products
 - Block imports from MTBE-using areas

Separate Standard for Non-ethanol Alcohols

- If the methanol content of ethanol is at the ASTM maximum, very few other oxygenates can be in gasoline
- Economics will drive methanol to max
- Need "*no-intentional-addition*" specification

"No-intentional-addition" **Language Must Cover**

- **Co-production**
- **Contamination**
- **Blending off non-conforming product**

Co-production

A gasoline or blendstock provider must be allowed to use confidential technical data showing that the oxygen content in excess of the standards was caused by co-production as a valid defense

Contamination

A gasoline provider must be allowed to document the source of unintentional oxygen content as tank bottoms, line flush or prior cargo and identify and promise to implement procedural changes to minimize re-occurrences as a valid defense

Blending Off Non-conforming Product

Non-conforming product and blendstock must be allowed to be blended with conforming products and blendstocks to bring the final product into compliance. This is to prevent someone from claiming that the oxygen in the non-conforming product was added intentionally.

Let the Predictive Model Control T50



This Will Improve Supply

- **Most of T50 increase due to MTBE rejection.**
- **$C_3 =$ used to make C_7 alkylate needed to balance T50 will go to petrochemicals.**
- **Butylenes from refining, petrochemicals and MTBE feedstocks are available.**
- **The C_8 isoparaffins produced have a T50 greater than the CaRFG3 cap.**
- **Adding alkylate reduces emissions.**

Summary

- **T50 cap needs to accommodate clean burning C8 isoparaffins.**
- **Some areas define unoxygenated as less than 2 vol% oxygenates.**
- **California needs to justify more stringent caps to avoid trade dispute.**
- **De minimis regulation needs flexibility to avoid unnecessary restriction of supply.**