APPENDIX G

Oxygenate Contaminants in Alkylates

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A. Background

Alkylate is a mixture of high-octane, low vapor pressure, branched chain paraffinic hydrocarbons. Alkylate is produced mainly through two processes – alkylation and dimerization with hydrogenation.

Traditional alkylation processes react light olefins, such as propene and butene, produced in catalytic crackers and cokers, with isobutane in the presence of a strong acid catalyst (sulfuric acid or hydrofluoric acid) to form alkylate product. The primary alkylation reaction between isobutane and butene forms the high octane, 2,2,4 trimethyl pentane isomer (isooctane). In the dimerization process, iso-butene reacts with itself or with other C_3-C_5 olefins, in the presence of a solid catalyst, to form isooctene and other heavier iso-olefins. The mixture of iso-olefins is then hydrogenated to form a high-octane paraffinic gasoline blendstock that is similar to alkylate.

$$(CH_3)_2CHCH_3 + (CH_3)_2C{=}CH_2 \xrightarrow{H_2SO_4} (CH_3)_3CCH_2CH(CH_3)_2$$

Isobutane Isobutene 2,2,4-Trimethylpentane (Isooctane)

$$(CH_3)_2C{=}CH_2 + (CH_3)_2C{=}CH_2 \xrightarrow{H_2SO_4} \text{2,2,4-Trimethyl-2-pentene OR 2,2,4-Trimethyl-1-pentene}$$

Isobutene Isobutene (Isooctene)

B. Alcohol and Ether Formation in Alkylates

Side reactions may occur during alkylation to form alcohol and ether contaminants. Such reactions are possible because of the acidic environment during the alkylation process and the presence of small amounts of water. An olefin such as isobutene can react with water to form t-butyl alcohol. Once formed, alcohols can react with olefins to form ethers. Ethers can also be formed from the elimination of water between two alcohols in acidic solution. The product can contain heavier ethers but the majority are C8 ethers. Typical ethers are di-sec-butyl ether and isobutyl-sec-butyl ether.

C. Oxygenates in Alkylates

The CaRFG3 regulations require determination of the prohibited oxygenates by ASTM method D 4815-99 ("Standard Test Method for Determination of MTBE, ETBE, TAME, DIPE, tertiary –Amyl alcohol and C1 to C4 Alcohols in Gasoline by Gas Chromatography." Table 1 lists the target oxygenates.

Table 2 shows the results of an analysis of a commercial isooctane reported to ARB staff in units of volume percent oxygenate. The results were converted to weight percent oxygen using

Equation 1 below. The sample was analyzed by ASTM method D5441-98 “Standard Test Method for Analysis of Methyl tert-Butyl Ether (MTBE) by Gas Chromatography.”

The MTBE concentration in the commercial isooctane sample was 0.074 volume percent. In a gasoline in which this isooctane was present at 20 percent of the final volume, the MTBE concentration from this source would be 0.015 volume percent.

Table 3 shows the results of the analysis for alcohols and ethers in the isooctene intermediate from a pilot plant dimerization process. Total oxygen concentration in the isooctene from the alcohols and ethers containing 4 or more carbon atoms was 0.62 percent by weight. If this isooctene were present in a gasoline at 10 percent of the final volume, the total oxygen concentration from this source would be 0.06 weight percent.

The values shown in Table 4 are the oxygenate levels in the product obtained by hydrogenation of the isooctene intermediate for which oxygenate levels were reported in Table 3. The hydrogenation step reduced the total oxygen concentration from oxygenates from 0.62 percent by weight to 0.05 percent by weight. In a gasoline in which this isooctane was present at 20 percent of the final volume, the MTBE concentration from this source would be 0.01 volume percent.

Calculation of Weight Percent Oxygen

The oxygenate levels were converted from volume percent concentrations to equivalent percent oxygen levels using Equation 1.

Equation 1

$$\text{Wt\% Oxygen} = \frac{D \times V \times 16.0}{D_{fuel} \times M}$$

Where:
D = Density of the oxygenate (per
D_{fuel} = Density of the fuel (assumed to be 5.75 pounds per gallon)
V = Volume percent of the oxygenate
M Molecular mass of the oxygenate
16.0 = atomic mass of oxygen

Table 1

Alcohols and Ethers Analyzed by ASTM Test Method D4815-99

Methanol
Ethanol
Isopropanol
n-propanol
iso-Butanol
tert-Butanol
sec-Butanol
n-Butanol
Tert-pentanol (*tert*- amylalcohol)
Methyl *tert*-butylether (MTBE)
Ethyl *tert*-butylether (ETBE)
Diisopropylether (DIPE)
Tert-amylmethylether (TAME)

Table 2

Oxygenates Levels in a Commercial Isooctane

OXYGENATE	Concentration in Isooctane		Concentration in Gasoline[1]	
	Vol.% oxygenate	Wt. % oxygen	Vol.% oxygenate	Wt. % oxygen
Tert-pentanol (*tert*-amylalcohol)	0.0426	0.009	0.009	0.002
Methyl *tert*-butyl ether (MTBE)	0.0738	0.014	0.015	0.003
Sec-butyl methyl ether (MSBE)	0.1330	0.026	0.027	0.005
Tert-amylmethylether (TAME)	0.0398	0.007	0.008	0.001

[1] Assumes that the isooctane concentration in gasoline is 20 percent of the final volume

Table 3

Oxygenates in Isooctene Samples From a Dimerization Pilot Plant

OXYGENATE	Concentration in Isooctene		Concentration in Gasoline[1]	
	Vol.% oxygenate	Wt. % oxygen	Vol.% oxygenate	Wt. % oxygen
C4	0.50	0.11	0.05	0.011
C5	0.01	0.002	0.001	0.0002
C6	—	—	—	—
C7	0.04	0.01	0.004	0.001
C8	3.58	0.44	0.358	0.044
C9+	0.56	0.06	0.056	0.006
TOTAL	4.69	0.62	0.47	0.06

[1] Assumes that the isooctene concentration in gasoline is 10 percent of the final volume

Table 4

Oxygenates in Isooctane Samples From a Dimerization Pilot Plant

OXYGENATE	Concentration in Isooctene		Concentration in Gasoline[1]	
	Vol.% oxygenate	Wt. % oxygen	Vol.% oxygenate	Wt. % oxygen
C4	0.09	0.02	0.018	0.004
C5	—	—	—	—
C6	—	—	—	—
C7	0.02	0.003	0.004	0.001
C8	0.17	0.02	0.033	0.004
C9+	0.07	0.01	0.014	0.002
TOTAL	0.35	0.05	0.07	0.01

[1] Assumes that the isooctane concentration in gasoline is 20 percent of the final volume