APPENDIX K

Low Sulfur Diesel Fuel and Water Quality

EFFECT OF THE PROPOSED AMENDMENTS ON WATER QUALITY

A. Introduction

California refiners are expected to meet the proposed 15 ppm sulfur content limit for diesel fuel by increasing their hydrotreating capacity. This hydrotreating for sulfur removal is called hydrodesulfurization. With the low sulfur limit additional hydrotreating will be needed to desulfurize the more difficult higher molecular weight aromatic sulfur compounds consisting of two aromatic rings. A key objective of hydrotreating for sulfur removal is to minimize hydrogen consumption and cracking reactions while achieving the desired sulfur reduction.[i] The newest hydrotreating catalysts are highly selective and allow sulfur removal while minimizing cracking reactions and the amount of aromatics saturation. Therefore, the impact of the additional hydrotreating on other fuel components and specifications is much reduced. However, some conversion of aromatic compounds to aliphatic compounds, and the conversion of the more polar sulfur-containing compounds to less polar hydrocarbons, should reduce the water solubility of the low sulfur fuel compared with the current diesel fuel.

B. Solubility of Low Sulfur Diesel Fuel

1. Background

Diesel fuels contain many different hydrocarbon compounds. Most of these compounds contain carbon numbers between 10 and 22. Table 1 below lists of typical compounds found in diesel fuels.

Hydrocarbon compounds in diesel fuel can be classified according to the ease with which they can be desulfurized. The aliphatic (n- and isoparaffins) and aromatic compounds with a single aromatic ring are relatively easy to desulfurize. While compounds that contain two or more rings are much more difficult to desulfurize. This is due to the fact that the aliphatic and single-ring aromatic molecules are sufficiently flexible so that the sulfur atom is in a position where it can make physical contact with the surface of the catalyst during the desulfulrization process. The more difficult compounds are contained in aromatics consisting of two aromatic rings. These compounds are typically in the C_{12}-C_{16} boiling range, particularly dibenzothiophenes ($C_{12}H_{14}$).

Table 1

Typical Diesel Fuel Hydrocarbons

Compound	Chemical formula	Hydrocarbon Class
Napthalene	$C_{10}H_8$	Aromatic
Tetralin	$C_{10}H_{12}$	Aromatic
cis-Decalin	$C_{10}H_{18}$	Napthene
1,3-Diethylbenzene	$C_{10}H_{14}$	Aromatic
n-Butylcyclohexane	$C_{10}H_{20}$	Napthene
n-Pentylcyclopentane	$C_{10}H_{20}$	Napthene
Decane	$C_{10}H_{22}$	n-Paraffin
Anthracene	$C_{14}H_{10}$	Aromatic
1-Pentylnathalene	$C_{15}H_{18}$	Aromatic
n-Nonylcylohexane	$C_{15}H_{30}$	Naphthene
n-Decylcyclopentane	$C_{15}H_{30}$	Naphthene
n-Pentadecane	$C_{15}H_{32}$	n-Paraffin
2-Methyltetradecane	$C_{15}H_{32}$	Isoparaffin
1-Decylnaphthalene	$C_{20}H_{28}$	Aromatic
n-Tetradecylcylohexane	$C_{20}H_{34}$	Naphthene
n-Tetradecylclopentane	$C_{20}H_{40}$	Naphthene
n-Pentadecylcyclopentane	$C_{20}H_{40}$	Naphthene
Eicosane	$C_{20}H_{42}$	Naphthene
2-Methylnonadecane	$C_{20}H_{42}$	n-Paraffin

Source: Technical Review: Diesel Fuels, Chevron Products Company

2. Properties

Typically, the solubilities of aromatic compounds in water are much higher than the solubilities of aliphatic compounds. The solubilities of aromatics that contain sulfur (thioaromatics) are expected be to somewhat higher than the solubilities of aromatic hydrocarbons, because sulfur-containing compounds are slightly more polar. However, the overall solubility of diesel fuel is not expected to change significantly due to the removal of sulfur compounds.

Assuming that only the sulfur is removed and no cracking occurs, then all of the thioaromatics are converted aromatics. This would result in a decrease in the water solubility of the fuel. If cracking does occur during the desulfurization process, some or all of the thioaromatic compounds could be converted to aliphatics, and aliphatic compounds are orders of magnitude less soluble in water than aromatic compounds. Table 2 below shows the water solubility of petroleum hydrocarbons by carbon number range and structure type.

Table 2: Water Solubility of Total Petroleum Hydrocarbons by Carbon Number Range (mg/l)

Carbon Number Range	Aliphatics	Aromatics
>C8-C10	0.430000	65.000
>C10-C12	0.034000	25.000
>C12-C16	0.000760	5.800
>C16-C21	-	0.650
>C16-C35	0.000003	-
>C21-C35	-	0.0066

3. Effect on Water Quality

The California and national diesel fuel regulations implemented in 1993 reduced the sulfur content of diesel fuel from about 3000 ppmw to about 300 ppmw (about 140 ppmw in California). As of this date, there are no reports of groundwater contamination related to the lower-sulfur diesel fuel. The proposed regulation would reduce the sulfur content from about 140 ppmw to less than 15 ppmw, a much smaller change in fuel sulfur content and solubility properties than caused by the previous sulfur reduction. Therefore, we do not anticipate that there would be any impacts on ground water associated with proposed low-sulfur diesel fuel.

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[i] Moncrief, T. Ian., Montgomery, W. David., Ross, Martin T., Charles River Associates Inc., Ory, Raymond E., Carney, Jack T., Baker and O'Brien Inc., An Assessment of the Potential Impacts of Proposed Environmental Regulations on U.S. Refinery Supply of Diesel Fuel, A study prepared by Charles River Associates Inc. and Baker and O'Brien Inc. for the American Petroleum Institute. August 2000.