APPENDIX J

Effect of Low Sulfur Diesel Fuel on Greenhouse Gas Emissions

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IMPACT OF THE PROPOSED AMENDMENTS ON THE GREENHOUSE EFFECT

Earth's atmospheric gases serve to maintain higher terrestrial surface temperatures than would occur if the Earth had no atmosphere. This phenomenon is known as the "greenhouse effect," as the gases have a warming effect similar to the glass of a greenhouse in transmitting incoming solar radiation and blocking outgoing terrestrial radiation. The combustion of fossil fuels results in the formation of carbon dioxide (CO_2) and water vapor (H_2O), along with the release of chemical potential energy as heat. Carbon dioxide and water vapor are known as greenhouse gases (GHGs), due to their transparency to sunlight and their opacity to certain wavelengths of infrared radiation emitted from the Earth's surface. Other GHGs include methane (CH_4), carbon monoxide (CO), ozone (O_3), and nitrous oxide (N_2O).

By the end of the twentieth century, scientists around the world had become concerned that GHGs emitted by processes of anthropic origin are the cause of what seems to be global warming. The contribution of anthropically generated GHGs, emitted since 1765, to global warming is known as "radiative forcing." The radiative forcing for CO_2 is estimated to be 1.56 Watts per square meter (W/m^2). The total radiative forcing for all GHGs except water is estimated to be 2.45 W/m^2. Since H_2O condenses at atmospheric temperatures, and because clouds reflect some wavelengths of solar radiation, the effect of water vapor emissions on global warming is uncertain. The heat released in the combustion of fossil fuels and in the condensation of water vapor has a direct local warming effect on the atmosphere. However, this effect is not as persistent as radiative forcing.

Figure H-1 presents a simplified life-cycle schematic for refinery fuel products showing the various processes from which GHGs are emitted. Implementation of the proposed amendments will cause increases in GHG emissions for various processes in the life-cycle of California diesel fuel. These changes are due to an increase in gas production, hydrogen production process chemistry, and an increase in refinery process electricity and fuel requirements, compared to the current statewide diesel fuel composite. Methane emissions are expected to increase due to natural gas production and distribution losses. Methane losses will be small compared to the additional carbon dioxide emissions generated due to the additional gas production and refinery processing; however, methane emissions have 21 times the radiative forcing impact as carbon dioxide emissions. A smaller amount of additional methane and nitrous oxide will be emitted in the natural gas combustion process. We have estimated the incremental carbon dioxide emissions and carbon dioxide equivalent (CO_2 Eq.) methane and nitrous oxide emissions, which will result from the production of low-sulfur California diesel fuel. These emission increases should be substantially offset by a reduction in CO_2 emissions due to combustion of the low-sulfur, lower carbon diesel fuel. There should be no change in GHG emissions due to distribution of the low-sulfur California diesel fuel.

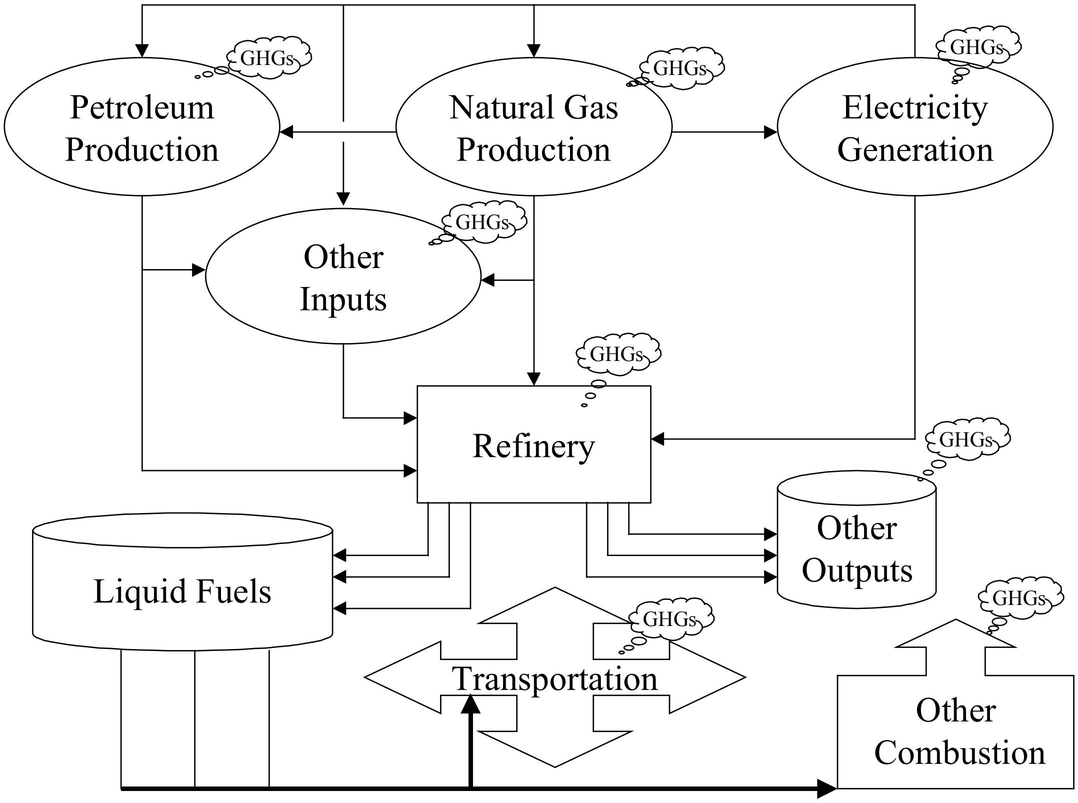

Figure 1: **Life-Cycle Schematic for GHG Emissions for Refinery Products**

Carbon Dioxide Emission Assumptions and Analysis

Table H-1. Table of Gross Assumptions
CARB Diesel Production and Delivery (→ $C_{14}H_{27}S_{0.00074}$) is assumed to be 80 percent efficient with respect to carbon dioxide emissions; i.e., approximately 25 percent more CO_2 emissions are attributable to the use of CARB Diesel than its end use combustion[1]. Additional CO_2 Eq. emissions include 2 percent of CO_2 from production and 1 percent of CO_2 from combustion.
Natural Gas Production and Delivery (→ $0.775CH_4 + 0.160C_2H_6 + 0.065CO_2$) is assumed to be 91 percent efficient with respect to carbon dioxide emissions; i.e., approximately 10 percent more CO_2 emissions are attributable to the use of natural gas than its end use combustion[1]. Additional CO_2 Eq. emissions of 6.5 percent weight of gas are lost as CH_4 or emitted as CH_4 and N_2O in combustion.
Sulfur Reduction Model $\mathbf{C_{14}H_{27}S_{0.00074}} + 0.025H_2 =$ $0.974926C_{14}H_{27.334345} + 0.024334C_{14}H_{14} + 0.00074C_{14}H_{14}S + 0.025H_2$ $\rightarrow 0.974926C_{14}H_{27.334345} + 0.05C_7H_8 + 0.000074C_{14}H_{14}S + 0.000666S$ $= 1.025\mathbf{C_{13.658537}H_{26.390244}S_{0.000072195122}} + 0.000666S$
Additional energy will be required for gas production, compression, and heating; steam production; heat input for endothermic reactions; and hydrogen compression and heating. These additional energy requirements will result in CO_2 (and CO_2 equivalent) emissions due to the production, distribution, and combustion of natural gas. No additional energy will be required for pumping or heating of distillate blending components, no heat will be recovered from exothermic reactions, and energy consumption associated with the additional sulfur recovery and handling will be relatively insignificant.

Table H-2. Combustion Data for Fuels and Fuel Components	Natural Gas	CARB Diesel	Dibenzyl	Dibenzyl Sulfide	Toluene	Low-S CARB
CO_2 Factors (lbmols/lbmol)	1.16	14	14	14	7	13.6585
CO_2 Factors (lbs/lb)	2.540	3.1535	3.381	2.875	3.344	3.1530
Net Heating Value (Btus/lbmol)	368000	3602800	3092000	3398000	1610000	3517850
Net Heating Value (Btus/lb)	18300	18439	17000	15850	17500	18452
CO_2 Factors (lbmols/mmBtu)	3.15	3.8859	4.53	4.12	4.35	3.8826
CO_2 Factors (lbs/mmBtu)	139	171.02	199	181	191	170.88

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[1] This analysis does not account for energy loss due to incomplete combustion or the impacts of carbon monoxide (CO) or soot emissions on global warming; however, we expect that these factors will be offset substantially by the associated reduction in CO_2 emissions.

Table H-3. Heats of Formation of Reactants and Products Involved in Hydrogen Production, Hydrodesulfurization, and Sulfur Production

Compound	Formula	Weight	State	Btu/lbmol	Btu/lb
Methane	CH_4	16.04	Gas	-32000	-2000
Ethane	C_2H_6	30.07	Gas	-36000	-1200
Water	H_2O	18.02	Gas	-104000	-5769
Carbon Monoxide	CO	28.01	Gas	-47510	-1696
Carbon Dioxide	CO_2	44.01	Gas	-169200	-3844
Hydrogen	H_2	2.02	Gas	0	0
Dibenzyl	$C_{14}H_{14}$	182.26	Gas	58300	320
Dibenzyl Sulfide	$C_{14}H_{14}S$	214.33	Gas	83000	390
Toluene	C_7H_8	92.14	Gas	21500	230
Hydrogen Sulfide	H_2S	34.08	Gas	-8810	-259
Oxygen	O_2	32.00	Gas	0	0
Sulfur Dioxide	SO_2	64.06	Gas	-127600	-1992
Sulfur	S	32.07	Liquid	795	25
Water	H_2O	18.02	Gas	-104000	-5769

Table H-4. Reactions and Heats of Reactions Involved in Hydrogen Production, Hydrodesulfurization, and Sulfur Production

Process	Reaction	Btu/lbmol	Btu/lb
Steam Reforming & Shift Conversion	$\mathbf{CH_4} + H_2O \rightarrow CO + 3H_2$	88500	5520
	$\mathbf{C_2H_6} + 2H_2O \rightarrow 2CO + 5H_2$	149000	4950
	$CO + H_2O \rightarrow \mathbf{CO_2} + H_2$	17700	402
Hydrotreatment & desulfurization	$\mathbf{C_{14}H_{14}} + H_2 \rightarrow 2C_7H_8$	-15300	-84
	$\mathbf{C_{14}H_{14}S} + 2H_2 \rightarrow 2C_7H_8 + H_2S$	-48800	-228
Sulfur Production	$2H_2S + 2O_2 \rightarrow SO_2 + \mathbf{S} + 2H_2O$	-317200	-9890
	$2H_2S + SO_2 \rightarrow 3\mathbf{S} + 2H_2O$	-20100	-628

Table H-5. Process Conditions and Energy Requirements

Process Reactants	From	To	Btu/lbmol	Btu/lb
Natural Gas	1 atm, 80 °F	600 psig, 1500 °F	22200	1100
Reformer Steam	1 atm, 60 °F	600 psig, 1500 °F	31807	1765
Conversion Steam	1 atm, 60 °F	600 psig, 650 °F	23304	1293
Hydrogen	Cooled to 80 °F (constant volume)	900 psig, 800 °F	5070	2510

Based on the composition of natural gas, the steam reforming and shift conversion reactions, and the process reactant energy requirements; we can combine all of the direct CO_2 emissions, energy requirements, and indirect CO_2 and CO_2 Eq. emissions into a single equation for the production of high-pressure hydrogen gas from natural gas and water.

22200 Btu[2] +
0.775 CH_4 + 0.775*(31807 Btu[2]) + 0.775 H_2O + 0.775*(88500 Btu[3]) +
0.160 C_2H_6 + 0.320*(31807 Btu[2]) + 0.320 H_2O + 0.160*(149000 Btu[3]) +
1.095*(23304 Btu[2]) + 1.095 H_2O + 1.095*(17700 Btu[3]) +
0.065 CO_2 + 2.325*(5070 Btu[2]) + 0.800*(5070 Btu[2]) + 1.095*(5070 Btu[2])

→ 2.325 H_2 + 0.800 H_2 + 1.095 CO_2 + 1.095 H_2 +
{[22200 + (0.775 + 0.320)*(31807) + 0.775*(88500) + 0.160*(149000) + 1.095*(23304 + 17700) +(2.325 + 0.800 + 1.095)*(5070)] Btu
/(process energy efficiencies)/(natural gas production efficiency)}
*[CO_2 + CO_2 Eq. emission factors] +
0.065 CO_2

Assuming that gas compression and heating combined is 32 percent efficient[4], gross heat basis, and that steam production and process heating are each 80 percent efficient, gross heat basis; applying the efficiency of gas production and delivery, the CO_2 emission factor for the combustion of natural gas, and the CO_2 Eq. emission factor for CH_4 and N_2O emissions;

→ 4.22 H_2 + 1.16 CO_2 +
[22200/0.32/0.91 + 172156/0.80/0.91 + 21395/0.32/0.91] Btu/1.105
*[0.00000315 CO_2/Btu + (0.065/44.01/18300) CO_2 Eq./Btu],

where the gross energy requirements have been divided by 1.105 for application net energy CO_2 factors; and simplifying,

→ 4.22 H_2 + 1.16 CO_2 direct process emissions +
(1.10 CO_2 + 0.03 CO_2 Eq.) indirect process emissions,

→ 4.22 H_2 + 2.29 (CO_2 + CO_2 Eq.) total emissions.

For every molecule of high-pressure hydrogen gas produced for hydrotreating, 0.543 molecules of carbon dioxide and carbon dioxide equivalent are emitted to the

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[2] Taken from Table H-5.
[3] Taken from Table H-4.
[4] We have based the assumption on a 50 percent energy transfer due to gas compression, assumed to be 20 percent efficient, and a 50 percent energy transfer due to heating, assumed to be 80 percent efficient (0.50/0.20 + 0.50/0.80 = 1.00/0.32).

atmosphere. On a mass basis, 11.8 pounds of carbon dioxide, and equivalent, are emitted per pound of high-pressure hydrogen gas produced.

From the sulfur reduction model and combustion data for CARB Diesel, the sulfur reduction will require 0.0250 molecules of hydrogen per molecule of CARB Diesel or 0.0140 pounds of hydrogen per million Btu of CARB Diesel. The additional hydrogen production will result in additional CO_2 and CO_2 Eq. emissions of 0.166 pounds per million Btu of CARB Diesel. This represents and increase of 0.0767 percent over the estimated 216 pounds per million Btu[5], currently emitted in the production, delivery, and combustion of CARB Diesel.

From the sulfur reduction model and combustion data, we estimate that the combustion of low-sulfur CARB Diesel will emit 170.88 pounds of CO_2 per million Btu of fuel. This is 0.14 pounds per million Btu less than the 171.02 pounds per million Btu emitted in the combustion of the current fuel. This reduction represents a 0.065 percent decrease in CO_2, and equivalent, emissions attributable to the production, distribution, and use of CARB Diesel, and will substantially offset the emission increase due to the production of the low-sulfur fuel. The net CO_2, and equivalent, emission increase is therefore expected to be about 0.026 pounds per million Btu, a 0.012 percent increase in emissions from California diesel fuel use[6].

The outcome of this analysis is sensitive to efficiency assumptions. If the energy transfer processes for hydrogen production are, on average, 20 percent more efficient than assumed; then, the additional CO_2 and CO_2 Eq. emissions from those processes will be 16.7 percent less than estimated. The production and use of low-sulfur CARB Diesel will then result in a net CO_2, and equivalent, emission increase of about 0.012 pounds per million Btu from the current statewide composite diesel fuel. This represents only a 0.0057 percent increase in CO_2, and equivalent, emissions from California diesel fuel use.

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[5] [1.02*0.25 + 1.01*1.00]*(171.02 lbs/mmBtu) = 216.34 lbs/mmBtu

[6] Changes to GHG emissions other than carbon dioxide, which may occur due to combustion of low-sulfur CARB Diesel, have not been studied but would likely have a minor impact on the analysis.

Other Effects

Because suspended PM scatters solar radiation, a substantial portion of the radiation incident to the Earth's trosposphere is returned to space, thereby decreasing the net insolation at the Earth's surface. Due to this phenomenon, particulate sulfate is estimated to exert a global average cooling effect of -0.67 W/m^2. However, particulate black carbon (BC) (soot) from diesels and other sources absorbs solar radiation, as well as terrestrial infrared radiation, thereby warming the atmosphere. In addition to these direct scattering and absorption effects, there are also indirect effects associated with diesel PM and other aerosols. Tropospheric PM emissions may affect the size distribution of cloud droplets, altering the radiative properties of clouds and increasing their reflectivities. Particulate matter may also inhibit rainfall by increasing cloud lifetimes.

Black carbon aerosol causes positive climate forcing (warming) that is very uncertain in magnitude, but appears to be about 0.5 to 1 W/m^2. Black carbon may be the second most important component of global warming after CO_2, in terms of direct radiative forcing. The reduction of diesel particulate emissions with exhaust after-treatment or other means will help to reduce the BC component of global warming. Reducing soot emissions has the potential to slow global warming sooner than reducing carbon dioxide, methane, or other GHGs; because soot has a major impact on global warming and has a very short atmospheric lifetime compared to carbon dioxide. Reducing soot emissions has the additional benefit of reducing human health risk.

Nitrous oxide is produced as a byproduct of NO reduction and CO/HC oxidation on noble metal catalysts in gasoline vehicle exhaust systems. The effects of catalyzed diesel particulate filters and other diesel exhaust after-treatment devices on N_2O emissions are unknown. To the extent that regulated- pollutant, emission-equivalent diesel engines may replace gasoline engines in the future, a reduction or less rapid increase in N_2O emissions may result. Catalyzed after-treatment of diesel engines for PM control should also reduce methane and other hydrocarbon (HC) emissions from diesel engines.