TECHNICAL SUPPORT DOCUMENT FOR THE PETROLEUM REFINING SECTOR: PROPOSED RULE FOR MANDATORY REPORTING OF GREENHOUSE GASES

Office of Air and Radiation
U.S. Environmental Protection Agency

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CONTENTS

1. Industry Description

Petroleum refineries are facilities that are engaged in producing liquefied petroleum gases (LPG), motor gasoline, jet fuels, kerosene, distillate fuel oils, residual fuel oils, lubricants, asphalt (bitumen), and other products through distillation of crude oil or through redistillation, cracking, or reforming of unfinished petroleum derivatives. There are three basic types of refineries: topping, hydroskimming, and upgrading (also referred to as "conversion" or "complex"). Topping refineries have a crude distillation column and produce naphtha and other intermediate products, but not gasoline. There are only a few topping refineries in the U.S., predominately in Alaska. Hydroskimming refineries have mild conversion units such as hydrotreating units and/or reforming units to produce finished gasoline products, but they do not upgrade heavier components of the crude oil that exit near the bottom of the crude distillation column. Some topping/hydroskimming refineries specialize in processing heavy crude oils to produce asphalt. There are 8 operating asphalt plants and approximately 20 other hydroskimming refineries operating in the U.S. as of January 2006 (EIA, 2006a). The vast majority (approximately 75 to 80 percent) of U.S. refineries are upgrading/conversion refineries. Upgrading/conversion refineries have cracking or coking operations to convert long-chain, high molecular weight hydrocarbons ("heavy distillates") into smaller hydrocarbons that can be used to produce gasoline product ("light distillates") and other higher value products and petrochemical feedstocks. The U.S., Western Europe, and Asia are the largest and most sophisticated producers of refined petroleum products. The U.S. produced 23 percent of the world's refinery products in 2003 (U.S. DOE, 2007).

There are 150 petroleum refineries in 35 States and 2 U.S. territories, eight of which are considered asphalt refineries. The majority of oil distillation capacity in the U.S. is at large, integrated companies with multiple refining facilities. About 30 percent of all facilities are small operations producing fewer than 50,000 barrels per day, representing about 5 percent of the total output of petroleum products annually. As of January 2006, the combined operating crude capacity for the 150 U.S. refineries (including those in U.S. territories) was 17.9-million barrels per calendar day (bbls/cd). The combined operating crude capacity for the 148 refineries within the U.S. States is just over 17.3-million bbls/cd; the 2 refineries located in U.S. territories had a combined capacity of 572,900 bbls/cd (EIA, 2006b). The average crude capacity utilization rate for U.S refineries was 90.6 percent in 2005. In 2005, the U.S. refineries (not including U.S. territories) produced 2,225 million barrels (MMbbl) of motor gasoline, 1,443 MMbbl of diesel fuel oil, 564 MMbbl of jet fuel, 305 MMbbl of petroleum coke, 229 MMbl of residual fuel oil, and 209 MMbbl of LPG, as well as other products (EIA, 2006a). Table 1 includes a list of the 150 refineries within the U.S. and its territories along with crude oil distillation capacities and process charge or production capacities for various process units as of January 2006.

Petroleum refining is a very energy-intensive industry. In 2002, it accounted for about 7 percent of the total U.S. energy consumption, making it the nation's second-highest industrial consumer (U.S. DOE, 2007).

Table 1. Petroleum Refineries in the United States.[a]

Facility Name	City	State	Crude Capacity (bbl/cd)	Charge capacity (bbl/sd)				Production capacity	
				FCCU	CRU	Fluid Coking	Delayed Coking	Hydrogen (MMcfd)	Sulfur (short tons/d)
BP	Prudhoe Bay	AK	12,500	0	0	0	0	0	0
ConocoPhillips Alaska	Kuparuk	AK	14,000	0	0	0	0	0	0
Flint Hills Resources	North Pole	AK	210,000	0	0	0	0	0	0
Petro Star Inc.	North Pole	AK	17,000	0	0	0	0	0	0
Petro Star Inc.	Valdez	AK	48,000	0	0	0	0	0	0
Tesoro Petroleum Corp.	Kenai	AK	72,000	0	13,000	0	0	13	20
Goodway Refining LLC	Atmore	AL	4,100	0	0	0	0	0	0
Gulf Atlantic Operations LLC	Mobile Bay	AL	16,700	0	0	0	0	0	0
Hunt Refining Co.	Tuscaloosa	AL	34,500	0	7,200	0	14,000	6	80
Shell Chemical LP	Saraland	AL	80,000	0	20,000	0	0	0	35
Cross Oil & Refining Co. Inc.	Smackover	AR	7,200	0	0	0	0	3	0
Lion Oil Co.	El Dorado	AR	70,000	19,900	14,800	0	0	0	157
Big West of CA	Bakersfield	CA	66,000	0	16,300	0	22,000	25	105
BP	Carson	CA	260,000	102,500	52,000	0	65,000	105	350
Chevron USA Inc.	El Segundo	CA	260,000	74,000	49,000	0	66,000	77	600
Chevron USA Inc.	Richmond	CA	242,901	90,000	71,300	0	0	181	789
ConocoPhillips	LA - Carson/ Wilmington	CA	139,000	50,280	36,750	0	52,200	105	370
ConocoPhillips	SF - Rodeo	CA	76,000	0	32,000	0	27,000	84	310
ConocoPhillips	Arroyo Grande (Santa Maria)	CA	44,200	0	0	0	23,400	0	120
Edgington Oil Co.	Long Beach	CA	26,000	0	0	0	0	0	0
ExxonMobil Corp.	Torrance	CA	149,500	100,000	20,000	0	54,600	138	400
Greka Energy	Santa Maria	CA	9,500	0	0	0	0	0	0

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Kern Oil & Refining Co.	Bakersfield	CA	26,000	0	3,300	0	0	0	5
Lunday-Thagard Co. (aka World Oil Co.)	South Gate	CA	8,500	0	0	0	0	0	0
Paramount Petroleum Corp.	Paramount	CA	50,000	0	8,500	0	0	0	40
San Joaquin Refining Co., Inc.	Bakersfield	CA	15,000	0	0	0	0	4	3
Shell Oil Products US	Martinez	CA	155,600	73,000	31,000	22,500	27,500	107	364
Shell Oil Products US	Wilmington	CA	98,500	36,000	34,000	0	40,000	15	280
Ten By Inc.	Oxnard	CA	2,800	0	0	0	0	0	0
Tesoro	Golden Eagle	CA	166,000	71,000	42,000	48,000	0	82	200
Valero Energy (Ultramar, Inc.)	Wilmington	CA	80,887	52,000	17,000	0	29,000	0	230
Valero Energy Corp.	Benicia	CA	144,000	75,300	37,200	29,500	0	141	303
Valero Energy Corp.	Wilmington	CA	6,200	0	0	0	0	0	0
Suncor Energy	Commerce City	CO	62,000	20,000	10,500	0	0	0	106
Suncor Energy	Denver	CO	32,000	10,000	10,000	0	0	0	2
Valero Energy Corp.	Delaware City	DE	181,500	87,000	43,800	53,000	0	40	596
Citgo Petroleum	Savannah	GA	28,000	0	0	0	0	0	0
Chevron USA Inc.	Honolulu (Barber's Point)	HI	54,000	22,000	0	0	0	3	0
Tesoro Hawaii Petrol.	Kapolei	HI	93,500	0	13,000	0	0	18	34
ConocoPhillips	Wood River	IL	306,000	101,000	96,500	0	18,000	57	504
ExxonMobil Corp.	Joliet	IL	238,500	98,000	52,200	0	59,100	0	660
Marathon Petroleum Co. LLC	Robinson	IL	192,000	49,000	74,500	0	29,400	0	202
PDV Midwest Refining	Lemont	IL	167,000	70,000	31,200	0	44,000	12	400
BP	Whiting	IN	410,000	169,000	90,000	0	36,000	31	550

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Countrymark Cooperative, Inc.	Mt. Vernon	IN	23,000	8,400	6,500	0	0	0	9
Coffeyville Refining	Coffeyville	KS	112,000	32,500	17,000	0	19,500	0	146
Frontier Oil Corp.	El Dorado	KS	106,000	39,000	30,000	0	19,000	6	230
National Cooperative Refinery Association	McPherson	KS	81,200	24,500	23,500	0	22,000	0	81
Marathon Petroleum Co. LLC	Catlettsburg	KY	222,000	99,000	50,000	0	0	0	448
Somerset Refinery Inc.	Somerset	KY	5,500	0	1,000	0	0	0	0
Calcasieu Refining Co.	Lake Charles	LA	30,000	0	0	0	0	0	0
Calumet Lubricants Co.	Shreveport	LA	42,000	10,500	8,000	0	0	6	10
Calumet Lubricants Co.	Cotton Valley	LA	13,020	0	0	0	0	2	0
Calumet Lubricants Co.	Princeton	LA	8,300	0	0	0	0	5	3
Citgo Petroleum Corp.	Lake Charles	LA	429,500	150,000	110,800	0	104,000	0	640
ConocoPhillips	Westlake	LA	239,400	50,000	44,000	0	64,000	0	860
ConocoPhillips	Belle Chasse	LA	247,000	104,000	44,600	0	27,000	0	125
ExxonMobil Corp.	Baton Rouge	LA	501,000	241,000	78,000	0	118,500	0	800
ExxonMobil Corp.- Chalmette	Chalmette	LA	188,160	71,600	49,400	0	35,000	0	935
Marathon Petroleum Co. LLC	Garyville	LA	245,000	131,000	48,500	0	37,400	0	790
Motiva Enterprises	Norco	LA	226,500	114,000	62,000	0	23,600	60	169
Motiva Enterprises	Convent	LA	235,000	92,000	40,000	0	0	63	728
Murphy Oil USA Inc.	Meraux	LA	120,000	37,000	32,000	0	0	0	31
Pelican Refining Co. LLC	Lake Charles	LA	0	0	0	0	0	0	0
Placid Refining Inc.	Port Allen	LA	56,000	20,500	11,000	0	0	0	28
Shell Chemical Co.	St. Rose	LA	55,000	0	0	0	0	0	0
Valero Energy Corp.	Krotz Springs	LA	80,000	34,000	13,000	0	0	0	0

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Valero Energy Corp.	Norco	LA	185,003	105,380	25,000	0	70,400	0	393
Marathon Petroleum Co. LLC	Detroit	MI	100,000	30,000	20,000	0	0	0	147
Flint Hills Resources	Rosemount	MN	279,300	86,500	51,300	0	70,800	115	999
Marathon Petroleum Co. LLC	St. Paul Park	MN	70,000	26,000	20,500	0	0	9	112
Chevron USA Inc.	Pascagoula	MS	330,000	67,000	96,000	0	105,000	230	1,300
Ergon Refining Inc.	Vicksburg	MS	23,000	0	0	0	0	8	0
Hunt Southland Refining	Sandersville	MS	11,000	0	0	0	0	0	0
Cenex Harvest States	Laurel	MT	55,000	13,500	12,000	0	0	30	130
ConocoPhillips	Billings	MT	58,000	21,490	13,550	0	19,950	20	246
ExxonMobil Corp.	Billings	MT	60,000	23,500	12,500	10,400		24	0
Montana Refining Co.	Great Falls	MT	8,200	2,500	1,030	0	0	2	0
Tesoro	Mandan	ND	58,000	30,600	12,100	0	0	0	17
Chevron USA	Perth Amboy	NJ	80,000	0	0	0	0	0	0
Citgo Asphalt Refining Co.	Paulsboro	NJ	32,000	0	0	0	0	0	0
ConocoPhillips	Linden	NJ	238,000	145,000	32,000	0	0	10	180
Hess Corporation	Port Reading	NJ	0	65,000	0	0	0	0	10
Sunoco, Inc.	Westville	NJ	145,000	57,000	30,000	0	0	0	80
Valero Energy Corp.	Paulsboro	NJ	160,000	55,000	30,000	0	27,000	9	206
Giant Refining Co.	Bloomfield	NM	16,800	6,500	4,000	0	0	0	3
Giant Refining Co.	Gallup	NM	20,800	11,500	6,800	0	0	0	2
Navajo Refining Co.	Artesia + Lovington	NM	75,000	27,000	18,000	0	0	0	130
Foreland Refining Co.	Tonopah/ Eagle Springs	NV	2,000	0	0	0	0	0	0

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BP PLC	Toledo	OH	131,000	55,000	43,000	0	34,000	33	340
Marathon Petroleum Co. LLC	Canton	OH	73,000	25,000	19,000	0	0	0	110
Sunoco, Inc.	Toledo	OH	160,000	79,000	48,000	0	0	45	62
Valero Energy Corp.	Lima	OH	146,900	40,000	55,000	0	23,000	58	110
ConocoPhillips	Ponca City	OK	194,000	69,802	54,190	0	27,660	35	34
Sinclair Oil Corp.	Tulsa	OK	70,300	27,750	16,800	0	0	0	28
Sunoco, Inc.	Tulsa	OK	85,000	0	24,000	0	11,000	0	0
Valero Energy Corp.	Ardmore	OK	83,640	30,000	21,350	0	0	26	243
Wynnewood Refining Co.	Wynnewood	OK	54,000	21,000	15,000	0	0	0	36
Chevron USA	Portland	OR	0	0	0	0	0	0	0
American Refining Group	Bradford	PA	10,000	0	1800	0	0	0	0
ConocoPhillips	Trainer (Marcus Hook)	PA	185,000	53,000	50,000	0	0	0	41
Sunoco, Inc.	Marcus Hook	PA	175,000	105,000	20,000	0	0	0	33
Sunoco, Inc. (combined Sun & Chevron)	Phil. (Girard Pt & Pt Breeze)	PA	335,000	123,500	86,000	0	0	0	260
United Refining Co.	Warren	PA	65,000	26,000	14,000	0	0	0	70
Valero Energy Corp.	Memphis	TN	180,000	70,000	36,000	0	0	0	116
AGE Refining & Manufacturing	San Antonio	TX	12,200	0	0	0	0	0	0
Alon USA Energy Inc.	Big Spring	TX	67,000	25,000	21,000	0	0	0	150
BP	Texas City	TX	437,000	189,300	138,000	0	43,000	0	1,400
Citgo	Corpus Christi	TX	156,000	81,800	52,500	0	43,500	0	357
ConocoPhillips	Borger	TX	146,000	72,300	26,900	0	0	91	340
ConocoPhillips	Sweeny	TX	247,000	119,000	37,500	0	74,100	155	595

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Delek Refining Ltd	Tyler	TX	58,000	20,250	17,500	0	6,000	0	15
ExxonMobil Corp.	Beaumont	TX	348,500	117,700	155,000	0	50,700	55	636
ExxonMobil Corp.	Baytown	TX	562,500	221,000	126,000	42,000	46,500	0	1,796
Flint Hills Resources	Corpus Christi	TX	288,126	106,700	71,600	0	14,000	0	237
Lyondell-Citgo Refining Co.	Houston	TX	270,200	100,000	37,000	0	105,000	0	803
Marathon Petroleum Co. LLC	Texas City	TX	72,000	55,000	11,000	0	0	0	0
Motiva Enterprises	Port Arthur	TX	285,000	90,000	48,000	0	57,500	0	711
Pasadena Refining Systems Inc.	Pasadena	TX	100,000	56,000	23,000	0	12,500	0	28
Shell Oil Products US - Deer Park Refining Limited Partnership	Deer Park	TX	333,700	75,000	72,000	0	88,000	108	1,150
South Hampton Resources Inc.	Silsbee	TX	0	0	1,500	0	0	2	0
Total SA	Port Arthur	TX	232,000	75,000	39,600	0	0	0	300
Trigeant Ltd.	Corpus Christi	TX	0	0	0	0	0	0	0
Valero Energy Corp.	Corpus Christi	TX	142,000	114,500	69,000	0	18,500	195	1,288
Valero Energy Corp.	Houston	TX	83,000	65,000	11,500	0	0	0	110
Valero Energy Corp.	Texas City	TX	213,750	83,000	16,500	0	50,000	0	924
Valero Energy Corp.	Three Rivers	TX	90,000	24,000	33,000	0	0	12	62
Valero Energy Corp.	Sunray	TX	158,327	54,465	47,400	0	0	0	60
Valero Energy Corp.	Port Arthur	TX	260,000	78,600	53,800	0	103,000	0	1,197
Western Refining	El Paso	TX	116,000	34,000	25,000	0	0	0	40
Big West Oil Co.	Salt Lake City	UT	29,400	11,000	7,300	0	0	0	4
Chevron USA	Salt Lake City	UT	45,000	14,000	8,000	0	8,500	0	21
Holly Corp.	Woods Cross	UT	24,700	8,900	7,700	0	0	0	10

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Silver Eagle Refining Inc.	Woods Cross	UT	10,250	0	2,200	0	0	1	0
Tesoro	Salt Lake City	UT	58,000	25,200	12,600	0	0	0	18
Giant Refining	Yorktown	VA	58,600	30,200	12,100	0	19,000	0	39
BP	Ferndale	WA	225,000	0	63,000	0	64,000	128	242
ConocoPhillips	Ferndale	WA	96,000	33,500	17,400	0	0	0	55
Shell Oil Products US	Anacortes	WA	145,000	57,900	32,700	0	25,700	0	350
Tesoro	Anacortes	WA	120,000	48,000	26,000	0	0	0	0
US Oil & Refining Co.	Tacoma	WA	37,850	0	6,500	0	0	0	10
Murphy Oil USA Inc.	Superior	WI	34,300	11,000	8,000	0	0	0	34
Ergon-West Virginia Inc.	Newell (Congo)	WV	20,000	0	3,400	0	0	1	1
Frontier Oil & Refining Co.	Cheyenne	WY	47,000	12,000	9,200	0	10,000	6	101
Little America Refining Co.	Evansville (Casper)	WY	24,500	11,000	6,000	0	0	0	0
Silver Eagle Refining Inc.	Evanston	WY	3,000	0	2,150	0	0	0	0
Sinclair Oil Corp.	Sinclair	WY	66,000	21,806	12,500	0	0	26	47
Wyoming Refining Co.	Newcastle	WY	12,500	5,500	2,750	0	0	0	4
Total in US States			**17,333,014**	**6,275,123**	**3,859,070**	**205,400**	**2,305,510**	**2,823**	**32,421**
Shell Chemical Yabucoa Inc.	Yabucoa	P.Rico	77,900	0	20,000	0	0	0	22
Hovensa LLC	Kingshill (St. Croix)	V.Isl	495,000	150,000	115,000	0	61,000	0	550
Grand Total			**17,905,914**	**6,425,123**	**3,994,070**	**205,400**	**2,366,510**	**2,823**	**32,993**

[a] EIA, 2006. Tables 3 and 4. Abbreviation for capacity units are: bbl/cd = barrel per calendar day = maximum capacity considering scheduled maintenance over 365 calendar days; bbl/cd = barrel per stream day = maximum capacity for a single, operating day; MMcfd = million cubic feet per day.

2. Total Emissions

The petroleum refining industry is the nation's second-highest industrial consumer of energy. Nearly all of the energy consumed is fossil fuel for combustion; therefore, the petroleum refining industry is a significant source of greenhouse gas (GHG) emissions. In addition to the combustion-related sources (e.g., process heaters and boilers), there are certain processes, such as fluid catalytic cracking units (FCCU), hydrogen production units, and sulfur recovery plants, that have significant process emissions of carbon dioxide (CO_2). Methane (CH_4) emissions from a typical petroleum refinery arise from process equipment leaks, crude oil storage tanks, asphalt blowing, and delayed coking units. System blow down and flaring of waste gas also contributes to the overall CO_2 and CH_4 emissions at the refinery. Additional detail on process-specific sources of GHG emissions is provided in Section 3.

Because much of the GHG emissions from petroleum refineries are characterized as fossil fuel combustion in the overall energy sector of the Inventory of U.S. Greenhouse Gas Emissions and Sinks, it is difficult to obtain a clear GHG emission estimate for petroleum refineries from the U.S. Inventory (EPA, 2008). Therefore, a separate industry profile was used to estimate the total GHG emissions from petroleum refineries (Coburn, 2007). This profile included estimates of CO_2, CH_4, and nitrous oxide (N_2O) from combustion sources (including coke combustion in FCCU), flares, and fugitive emission sources (equipment leaks, storage tanks, and wastewater treatment). The profile was updated to include GHG emissions from hydrogen production units, sulfur recovery units, asphalt blowing operations, and blowdown systems using the following emission factors:

- Hydrogen production: 6.05 metric tons CO_2/million cubic feet hydrogen produced
- Sulfur production: 0.366 metric tons CO_2/short ton sulfur produced
- Asphalt blowing: 2,555 standard cubic feet CH_4/thousand barrels asphalt blown
- Blow down systems: 137 standard cubic feet CH_4/thousand barrels crude throughput

The hydrogen production emission factor was based on the mass of CO_2 produced being 2.5 times the mass on hydrogen produced as reported in the "Hydrogen Fact Sheet" (see: http://www.getenergysmart.org/Files/HydrogenEducation/6HydrogenProductionSteamMethaneReforming.pdf). The sulfur production emission factor was based on engineering estimate after evaluating tail gas flow rates for sulfur recovery plants reported in EPA, 1998. The asphalt and blow down system emission factors were taken from the U.S. Inventory (EPA, 2008). Based on the updated industry profile, U.S. petroleum refineries have onsite GHG emissions of 204.75 million metric tons (mmt) of CO_2 equivalents (CO_2e). When accounting for electricity and steam purchases, petroleum refineries are also responsible for indirect GHG emissions of 26.0 mmt CO_2e.

Figure 1 presents the breakdown of onsite GHG emissions by source. As seen in Figure 1, combustion sources, direct process emissions, and flaring account for 99 percent of the onsite GHG emissions (on a CO_2e basis).
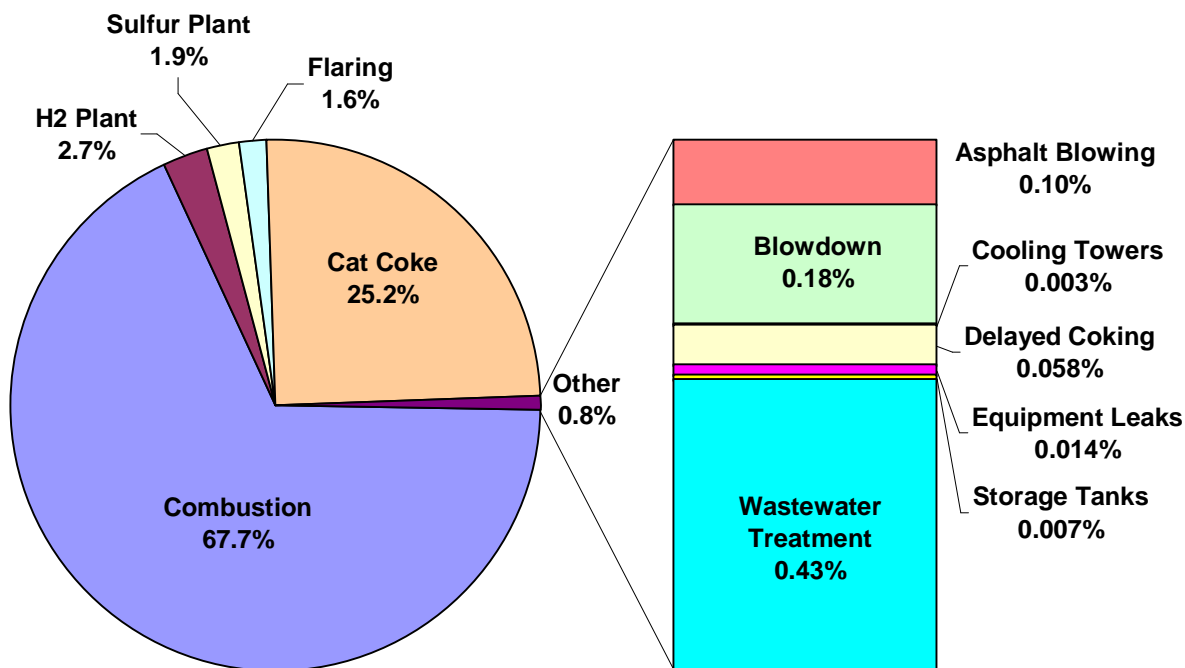
Figure 1. Relative importance of refinery GHG emission sources evaluated on CO$_2$e basis.

3. Emission Sources

This section includes brief descriptions of the sources and process units that generate significant greenhouse gases at a refinery. More complete descriptions of the entire refining process are available in other locations (U.S. EPA, 1995; U.S. EPA, 1998; U.S. DOE, 2007).

3.1 Stationary Combustion Sources

As seen in Figure 1, the combustion of fuels in stationary combustion sources is a significant source of GHG emissions at petroleum refineries. Combustion sources include process heaters, boilers, combustion turbines, and similar devices. Nearly all refinery process units use process heaters. In addition to direct process heat, many refinery processes also have steam and electricity requirements. Some refineries purchase steam to meet their process's steam requirements; others use dedicated on-site boilers to meet their steam needs. Similarly, some refineries purchase electricity from the grid to run their pumps and other electrical equipment; other refineries have co-generation facilities to meet their electricity needs and may produce excess electricity to sell to the grid. Refineries that produce their own steam or electricity will have higher on-site fuel usage, all other factors being equal, than refineries that purchase these

utilities. Combustion sources primarily emit CO_2, but they also emit small amounts of CH_4 and N_2O.

The predominant fuel used at petroleum refineries is refinery fuel gas (RFG), which is also known as still gas. RFG is a mixture of light C1 to C4 hydrocarbons, hydrogen, hydrogen sulfide (H_2S), and other gases that exit the top (overhead) of the distillation column and remain uncondensed as they pass through the overhead condenser. RFG produced at different locations within the refinery is typically compressed, treated to remove H_2S (if necessary), and routed to a common, centralized location (i.e., mix drum) to supply fuel to the various process heaters at the refinery. This RFG collection and distribution system is referred to as the fuel gas system.

The fuel gas generated at the refinery is typically augmented with natural gas to supply the full energy needs of the refinery. Depending on the types of crude oil processed and the process units in operation, the amount of supplemental natural gas needed can change significantly. Topping and hydroskimming refineries that process heavier crude oils generate limited amounts of RFG and may use natural gas for 70 percent or more of their energy needs. Upgrading/conversion refineries, especially those processing lighter crude oils, may need very little supplemental natural gas or may even produce more fuel gas than needed for basic operations. Depending on the quantities of propane and butane (C3 and C4 hydrocarbons) produced and local market conditions, upgrading/conversion refineries will typically have light gas plant to recover propane and butane for sale as products or for use as petrochemical or gas blending feedstocks. In these refineries, the hydrocarbon content of the RFG will be dominated by C1 or C2 hydrocarbons. Consequently, there may be significant variability in the fuel gas composition between different refineries. Within a given refinery, the variability in the refinery fuel gas composition should be somewhat less because most refinery process units are continuous. However, delayed coking units, which are significant fuel gas producers, are batch processes, so refineries with these units may have more variability in RFG composition than other refineries. Additionally, certain process units may cycle operations (notably hydrotreating units and catalytic reforming units) and other units are occasionally taken off-line for maintenance so that occasional variability in fuel gas composition within a refinery is inevitable.
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3.2 Flares

Flares are commonly used in refineries as safety devices to receive gases during periods of process upsets, equipment malfunctions, and unit start-up and shutdowns. "Emergency" flares receive only low flows of "sweep" gas to prevent air (oxygen) from entering the flare header and possibly the fuel gas system while maintaining the readiness of the flare in the event of a significant malfunction or process upset. Some flares may receive excess process gas on a frequent or routine basis; these flares act as pressure relief systems for the refinery's fuel gas system and may also be used to combust other low pressure gas streams generated at the refinery. Some flares may be used solely as control devices for regulatory purposes. As with stationary combustion sources, the combustion of gas in a flare results predominately in emissions of CO_2 along with small amounts of CH_4 and N_2O. In the 2002 National Emissions Inventory (NEI), emissions were reported for 252 flares at 77 refineries (EPA, 2006). Based on these data, each refinery is expected to have 3 flares on average.

3.3 Catalytic Cracking Units

In the catalytic cracking process, heat and pressure are used with a catalyst to break large hydrocarbons into smaller molecules. The fluid catalytic cracking unit (FCCU) is the most common type of catalytic cracking unit currently in use. Based on process-specific data collected in the development of emission standards for petroleum refineries, there are approximately 125 FCCU in the petroleum refining industry. In this type of reactor, the feed is pre-heated to between 500 and 800 degrees Fahrenheit (°F) and contacted with fine catalyst particles from the regenerator section, which are at about 1,300°F in the feed line ("riser"). The feed vapor, which is heavy distillate oil from the crude or vacuum distillation column, reacts when contacted with the hot catalyst to break (or crack) the large hydrocarbon compounds into a variety of lighter hydrocarbons. During this cracking process, coke is deposited on the catalyst particles, which deactivates the catalyst. The catalyst separates from the reacted ("cracked") vapors in the reactor; the vapors continue to a fractionation tower and the catalyst is recycled to the regenerator portion of the FCCU to burn-off the coke deposits and prepare the catalyst for reuse in the FCCU riser/reactor (U.S. EPA, 1998).

The FCCU catalyst regenerator generates GHG through the combustion of coke, which is essentially solid carbon with small amounts of hydrogen and various impurities that were deposited on the catalyst particles during the cracking process. CO_2 is the primary GHG emitted; small quantities of CH_4 and N_2O are also emitted during "coke burn-off." An FCCU catalyst regenerator can be designed for complete or partial combustion. A complete-combustion FCCU operates with sufficient air to convert most of the carbon to CO_2 rather than carbon monoxide (CO). A partial-combustion FCCU generates CO as well as CO_2, so most partial-combustion FCCUs are typically followed by a CO boiler to convert the CO to CO_2. Most refineries that operate an FCCU recover useful heat generated from the combustion of catalyst coke during catalyst regeneration; the heat recovered from catalyst coke combustion offsets some of the refinery's ancillary energy needs.

Thermal catalytic cracking units (TCCU) are similar to FCCUs except that the catalyst particles are much bigger and the system uses a moving bed reactor rather than a fluidized system. The generation of GHG, however, is the same. Specifically, GHG are generated in the regenerator section of the TCCU when coke deposited on the catalyst particles is burned-off in order to restore catalyst activity.

3.4 Catalytic Reforming Units

In the catalytic reforming unit (CRU), low-octane heavy hydrocarbons, generally gasoline and naptha are reacted with a catalyst to produce aromatic compounds such as benzene. The feed to the CRU is usually treated with hydrogen to remove sulfur, nitrogen and metallic contaminants. The CRU usually has a series of three to six fixed-bed or moving bed reactors and may be operated continuously or as a semi-regenerative unit. As in the FCCU, coke is deposited on catalyst particles during the processing reaction, and this "catalyst coke" must be burned-off to reactivate the catalyst, generating CO_2, along with small amounts of CH_4 and N_2O. In a continuous CRU, the catalyst can be regenerated one reactor at a time, which avoids disrupting

the process. In a semi-regenerative CRU, all the reactors are shut down at one time for catalyst regeneration, usually after no more than 2 years of operation (U.S. EPA, 1998).

3.5 Fluid Coking Units

Coking is another cracking process, usually used at a refinery to generate transportation fuels, such as gasoline and diesel, from lower-value fuel oils. A desired by-product of the coking reaction is petroleum coke, which can be used as a fuel for power plants as well as a raw material for carbon and graphite products. The fluid coking process is continuous and occurs in a reactor rather than a coke drum like the delayed coking process. Fluid coking units produce a higher grade of petroleum coke than delayed coking units; however, unlike delayed coking units that use large process preheaters, fluid coking units burn 15 to 25 percent of the coke produced to provide the heat needed for the coking reactions (U.S. DOE, 2007). Like the FCCU and CRU, the combustion of the petroleum coke generates CO_2 along with small amounts of CH_4 and N_2O.

3.6 Sulfur Recovery Vents

Hydrogen sulfide is removed from the refinery fuel gas system through the use of amine scrubbers. While the selectivity of hydrogen sulfide removal is dependent on the type of amine solution used, these scrubbers also tend to extract CO_2 from the fuel gas. The concentrated sour gas is then processed in a sulfur recovery plant to convert the hydrogen sulfide into elemental sulfur or sulfuric acid. CO_2 in the sour gas will pass through the sulfur recovery plant and be released in the final sulfur plant vent. Additionally, small amounts of hydrocarbons may also be present in the sour gas stream. These hydrocarbons will eventually be converted to CO_2 in the sulfur recovery plant or via tail gas incineration. The most common type of sulfur recovery plant is the Claus unit, which produces elemental sulfur. The first step in a Claus unit is a burner to convert one-third of the sour gas into sulfur dioxide prior to the Claus catalytic reactors. GHG emissions from the fuel fired to the Claus burner are expected to be accounted for as a combustion source. After that, the sulfur dioxide and unburned hydrogen sulfide are reacted in the presence of a bauxite catalyst to produce elemental sulfur. Based on process-specific data collected in the development of emission standards for petroleum refineries, there are 195 sulfur recovery trains in the petroleum refining industry (U.S. EPA, 1998).

3.7 Hydrogen Plants

The most common method of producing hydrogen at a refinery is the steam methane reforming (SMR) process. Methane, other light hydrocarbons, and steam are reacted via a nickel catalyst to produce hydrogen and CO. Excess CH_4 is added and combusted to provide the heat needed for this endothermic reaction. The CO generated by the initial reaction further reacts with the steam to generate hydrogen and CO_2 (U.S. DOE, 2007). According to EIA's Refinery Capacity Report 2006 (EIA, 2006), 54 of the 150 petroleum refineries have hydrogen production capacity.

3.8 Fugitive Emission Sources

Fugitive CH_4 emission sources are projected to only contribute 0.8 percent of a typical refinery's total GHG emissions. The largest four fugitive emission sources are projected to be blow down systems, delayed coking unit depressurization and coke cutting, asphalt blowing, and wastewater treatment (including sludge digestion). Methane emissions from process equipment leaks are expected to be small compared to other GHG emission sources at a typical refinery. Unless the

refinery receives unstabilized crude, CH_4 emissions from crude oil loading and storage are expected to be negligible, as are CH_4 emissions from cooling towers. These processes are described in further detail in Appendix A.

4. Review of Existing Programs and Methodologies

In developing GHG monitoring and reporting options for petroleum refineries, a number of existing programs and guideline methodologies were reviewed. Specifically, the following resources were examined:

1. 2006 Intergovernmental Panel on Climate Change (IPCC) Guidelines for National Greenhouse Gas Inventories. Volume 2, Chapters 2 and 4.

2. European Union (EU) Emissions Trading Scheme (2007). *2007/589/EC: Commission Decision of 18 July 2007 Establishing Guidelines for the Monitoring and Reporting of Greenhouse Gas EmissionsPpursuant to Directive 2003/87/EC of the European Parliament and of the Council. Available at:* http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=CELEX:32007D0589:EN:NOT.

3. U.S. Department of Energy (DOE). 2007. Technical Guidelines: Voluntary Reporting Of Greenhouse Gases (1605(B)) Program.

4. API (American Petroleum Institute). 2004. *Compendium of Greenhouse Gas Emissions Methodologies for the Oil and Gas Industry.* February.

5. CARB (California Air Resource Board). 2008. *Regulation For The Mandatory Reporting of Greenhouse Gas Emissions: Second 15-Day Modified Regulatory Language For Public Comment.* May 15.

6. Environment Canada (2006). Technical Guidance Manual on Reporting Greenhouse Gas Emissions. http://www.ghgreporting.gc.ca/GHGInfo/Pages/page15.aspx?lang=E.

Each of these sources was reviewed to determine the types of emissions to be reported, the facility reporting thresholds, and the monitoring methodologies recommended. The reporting and monitoring options presented in Sections 5, 6, and 7 are commensurate with the methodologies used in these existing programs and guidelines.

5. Types of Information to be Reported

5.1 Types of Emissions to be Reported

Based on the existing programs and the emission sources at petroleum refineries, GHG reporting for refineries are limited to CO_2, CH_4, and N_2O. Table 2 summarizes the refinery emission sources expected to have appreciable GHG emissions and the GHG expected to be emitted for each refinery emission source.

Figure 2 presents the breakdown of onsite GHG emissions by pollutant. Figure 2 indicates that CH_4 and N_2O emissions from petroleum refineries account for less than 1 percent of the total GHG emissions (evaluated on a CO_2e basis).

Table 2. Summary of Refinery GHG Emission Sources Considered for Reporting

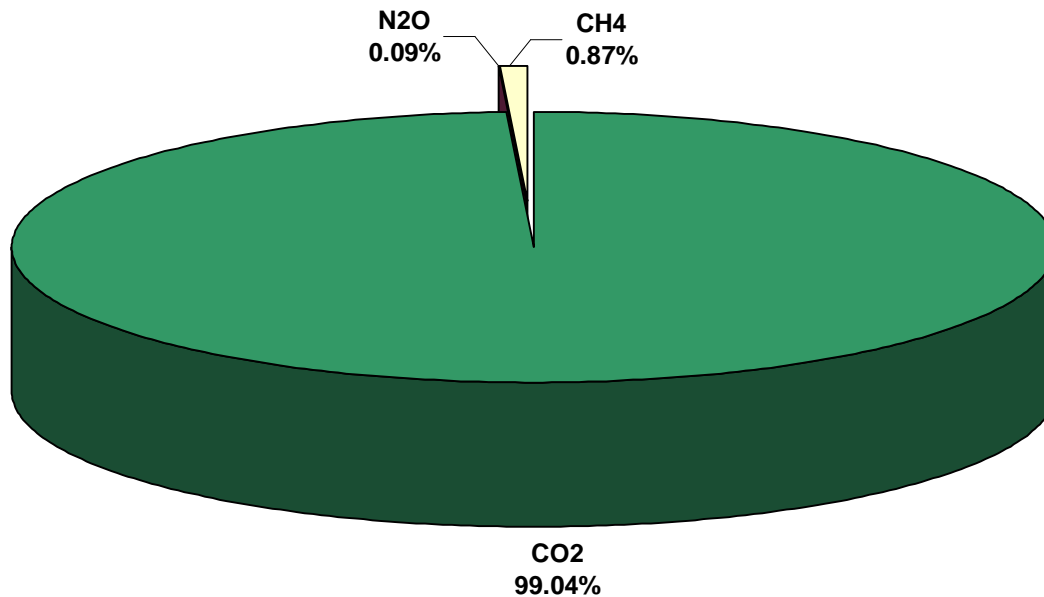| Emission Source	GHG Emitted
Stationary combustion sources	CO_2, CH_4, and N_2O
Coke burn-off emissions from catalytic cracking units, fluid coking units, catalytic reforming units, and coke calcining units	CO_2, CH_4, and N_2O
Flares	CO_2, CH_4, and N_2O
Hydrogen plant vent	CO_2 and CH_4
Sulfur recovery plant	CO_2
On-site wastewater treatment system	CO_2 and CH_4
On-site land disposal unit	CH_4
Asphalt blowing	CO_2 or CH_4
Uncontrolled blowdown systems	CH_4
Process vents not otherwise specified	CO_2, CH_4, and N_2O
Delayed coking units	CH_4
Process equipment leaks	CH_4
Storage tanks	CH_4
Loading operations	CH_4

Figure 2. Relative importance of CO_2, CH_4, and N_2O in the total nationwide refinery GHG emissions inventory (evaluated on a CO_2e basis).

5.2 Other Information to be Reported

In order to check the reported GHG emissions for reasonableness and for other data quality considerations, additional information about the emission sources is needed. Although the exact information required is somewhat source dependent, the following is a general list of additional information that must be reported.

(1) The unit identification number (if applicable);

(2) A description of the type of unit (RFG-fired process heater, flare, FCCU, TCCU, sulfur recovery plant, etc.);

(3) Maximum rated throughput of the unit (MMBtu/hr; bbl/stream day, tons sulfur produced/stream day, etc.);

(4) The calculated CO_2, CH_4, and N_2O emissions for each unit (as applicable), expressed in both metric tons of pollutant emitted and metric tons of CO2e; and

(5) A description of the method used to measure and/or calculate the GHG emissions for each unit.

6. Options for Reporting Threshold

Several options were evaluated as potential reporting thresholds. These options include:

Option 1. All refineries with facility-wide GHG emissions exceeding 1,000 metric tons of CO_2e ($mtCO_2e$) must report.
Option 2. All refineries with facility-wide GHG emissions exceeding 10,000 $mtCO_2e$ must report.
Option 3. All refineries with facility-wide GHG emissions exceeding 25,000 $mtCO_2e$ must report.
Option 4. All refineries with facility-wide GHG emissions exceeding 100,000 $mtCO_2e$ must report.

Table 3 presents the number of refineries and the GHG emissions included for each threshold option. The analysis presented in Table 3 only considers the direct (on-site) GHG emissions at the refineries. Essentially all refineries are expected to have direct emissions exceeding a 10,000 mtCO2e threshold. If indirect GHG emissions are included, all U.S. petroleum refineries are expected to exceed a 25,000 $mtCO_2e$ emission threshold.

Table 3. Evaluation of Alternative Threshold Options (considering direct emissions only)

Option/Threshold Level	Emissions Covered		Facilities Covered	
	mmt CO_2e/year	Percent	Number	Percent
Option 1: >1,000 $mtCO_2e$	204.75	100	150	100
Option 2: >10,000 $mtCO_2e$	204.74	99.995	149	99.3
Option 3: >25,000 $mtCO_2e$	204.69	99.97	146	97.3
Option 4: >100,000 $mtCO_2e$	203.75	99.51	128	85.3

7. Options for Monitoring Methods

7.1 Stationary Combustion Sources

There are four basic monitoring options for combustion units. Option 1 is to use annual fuel consumption (based on company records), default higher heating value (HHV) for the fuel, and a fuel-specific emission factor. Because of the variability in refinery fuel gas composition, this method has high uncertainty when applied to a specific refinery. The carbon content or HHV of other fuel products used at a refinery, such as diesel fuel or directly purchased and used natural gas, will have much less variability both within the refinery and across different refineries than refinery fuel gas. As such, Option 1 can yield reasonably accurate CO_2 emission estimates for these non-RFG fuel types. However, these are expected to be only a small portion of a refinery's total fuel combustion. Option 2 is similar to Option 1, but the HHV is measured periodically (daily or weekly measurement frequencies were evaluated) and fuel consumption quantities (based on company records) are estimated over the same intervals as the HHV measurements. This option should reduce the uncertainty associated with Option 1 since a higher sampling frequency yields lower uncertainties. However, since hydrogen combustion does not produce

CO_2, it is important to note that a measure of HHV does not necessarily improve the estimation of CO_2 emissions since some of the heat content of RFG is from hydrogen and only carbon content measurements can accurately estimate carbon dioxide emissions for fuel gas streams with significant hydrogen content. Option 3 uses direct volumetric flow measurements and routine carbon content measurements (daily or weekly) to estimate CO_2 emissions. Like Option 2, this option will have less uncertainty than Option 1 since a higher sampling frequency yields lower uncertainties. Option 3 is preferred to Option 2 in that some of the heat content of refinery fuel gas is from hydrogen (again, only carbon content measurements can accurately estimate CO_2 emissions for fuel gas streams with significant hydrogen content). Therefore, routine measurement of the carbon content provides a better correlation to the resulting CO_2 emissions than HHV. Also, in Option 3 direct fuel flow measurements are made using calibrated flow meters, whereas Option 2 allows less rigorous estimates of fuel consumption. As a variant to Option 3, the use of a continuous carbon content monitor was also evaluated. Option 4 uses a continuous emission monitoring system (CEMS) for CO_2 and exhaust flow rate. These options (or Tiers) are described in more detail in the Stationary Combustion TSD (EPA-HQ-OAR-2008-0508-004).

7.2 Flares

Three general options were considered for flares, which follow Options 1 through 3 for stationary combustion sources; as flares do not have enclosed exhaust stacks, an exhaust CEMS (Option 4) is not technically feasible for flares. Stationary combustion source Options 1 and 2 can provide reasonable estimates of the "sweep" gas or routine flare gas GHG emissions but cannot be used to provide accurate estimates of the GHG emissions released during periods of start-up, shutdown, or malfunction (SSM) because the flow rate and composition of the gases released to the flare during SSM events can vary so widely. As such, Options 1 and 2 for flares require separate engineering calculation of the GHG emissions from flares that occur during SSM events. Due to the variability in flow rates and potential gas composition for flares, Option 3, especially the variant of Option 3 that requires both continuous flow and continuous composition monitoring, provides significantly more accurate emission estimates than Options 1 or 2; however, this variability places additional requirements on the types of monitors that can be used for Option 3. Dual range monitors will generally be required to monitor the low flow rates associated with maintaining the readiness of the flare and the high flow rates that can occur during periods of process upsets, which adds additional costs to the monitoring system.

7.3 Process Emissions

Four processes are considered in this section; a fifth process, hydrogen production by steam reforming, is considered in a separate Hydrogen Production TSD (EPA-HQ-OAR-2008-0508-016). Three of the processes considered here, the FCCU, the catalytic reforming unit (CRU), and the fluid coking unit vents, are all associated with petroleum coke combustion. As described previously, the emissions generated from these processes are the result of coke combustion, so the monitoring methods are similar to those in the combustion section, but they are tailored by process considering the relative quantity of coke burned by each process and the typical measurement locations and controls used for each type of process.

Three monitoring options were considered for these process emissions sources. Option 1 is to use process feed rates and default coke burn-off factors and coke carbon content to estimate CO_2 emissions. This option does not account for differences in coke deposition rates by type of crude or severity of the cracking conditions used by a given unit, and therefore is expected to have high uncertainties. Option 2 is to monitor coke burn-off rates using gas composition analyzers and to estimate flow rate by air blast rates and flow correlations. This option is required for many FCCU to comply with Part 60 and Part 63 standards and provides accurate estimates of the CO_2 emissions rate from the FCCU regenerator. Due to these regulatory requirements, it is estimated that approximately 90 percent of FCCUs already have gas compositional monitors in-place. Option 3 is the use of a CEMS for CO_2 and exhaust gas flow rate. For partial combustion units, this may lead to additional monitoring needs to prevent double counting the GHG process emissions from the FCCU and GHG combustion emissions from RFG fired in the CO boiler.

A fourth process vent source is the sulfur recovery vent. As described previously, some CO_2 and trace amount of hydrocarbons will enter the sulfur recovery plant in the sour gas. It is expected that the total sour gas flow rate is metered at the plant as it is necessary for proper operation of the sulfur recovery plant. Option 1 entails periodic sampling of the sour gas for carbon content at the inlet to the sulfur recovery plant. Option 2 is the use of a CEMS capable of measuring the carbon content and flow rate in the sour gas feed stream at the inlet to the sulfur recovery plant. Option 2 would have less uncertainty than Option 1 due to the higher measurement frequency. Option 3 is the use of a CEMS for measuring the CO_2 and flow rate of the final sulfur recovery plant tail gas stack. Option 3 has the advantage of including the CO_2 emissions from the first-stage Claus burner as well as the tail gas incinerator, if one is used. However, this option could result in double counting because fuel used in the Claus burner would also contribute to the CO_2 emissions in the final tail gas stack. If a refinery is using "common-pipe" fuel gas consumption measurements, it will have no way of knowing how much of the exhaust CO_2 is from the combustion of fuel gas in the Claus burner. In this case, the refinery would have to measure fuel flow and composition directly at the Claus burner in addition to the stack CEMS measurements. Given the issues related in properly accounting for the sulfur plant process emissions and combustion emissions, Option 3 may not provide any improvement in the overall accuracy of the process-related GHG emissions estimate for sulfur recovery plants.

7.4 Fugitive Emission Sources
There are a variety of GHG emission sources at the refinery, which include: asphalt blowing, delayed coking unit depressurization and coke cutting, coke calcining, blowdown systems, process vents, process equipment leaks, storage tanks, loading operations, wastewater treatment, and waste disposal. To fully account for the refinery's GHG emissions, the emissions from these sources should be reported; however, the emissions from these sources are expected to be only about 1 percent of the refinery's total GHG emissions. Therefore, Option 1 – use of default emission factors – is appropriate for these sources. Where applicable, more stringent options (such as using Method 21 monitoring for process equipment leaks, using the TANKS model and compositional data for storage tanks, and using the number of delayed coking unit vessel size and cycle activity data) were also considered. If a refinery is already monitoring high CH_4-containing process lines, or is already using the TANKS model to estimate methane emissions from storage tanks, etc., then these options can be used. For purposes of the current regulatory

activity, additional monitoring of these fugitive CH_4 emission sources is not specified given the high cost and high uncertainty associated with the fugitive monitoring or estimation methods and the small contribution these emissions make to the total GHG emissions from the refinery.

8. Options for Estimating Missing Data

A complete record of all measured parameters used in the GHG emissions calculations is required (e.g., concentrations, flow rates, fuel heating values, carbon content values, etc.). Therefore, whenever a quality-assured value of a required parameter is unavailable (e.g., if a CEMS malfunctions during unit operation or if a required fuel sample is not taken), a substitute data value for the missing parameter shall be used in the calculations.

In general, it is recommended that the average of the data measurements before and after the missing data period be used to calculate the emissions during the missing data period. If, for a particular parameter, no quality-assured data are available prior to the missing data incident, the substitute data value should be the first quality-assured value obtained after the missing data period. Missing data procedures are applicable for heat content, carbon content, gas and liquid fuel flow rates, stack gas or air blast flow rates, and compositional analysis data (CO_2, CO, O_2, CH_4, N_2O, and H_2O content, as applicable).

9. QA/QC Requirements

To ensure the quality of the reported GHG emissions, the following quality assurance/quality control (QA/QC) activities are considered important:

(1) Developing and maintaining a Quality Assurance Project Plan (QAPP) that documents the measurements made, their accuracy, and explains the quality assurance procedures applied for each measurement used to quantify GHG emissions. The QAPP and the appropriate records of quality assurance checks should be retained on-site for a minimum of 5 years.

(2) All fuel flow meters, gas composition monitors, and/or heating value monitors that are used to provide data for the GHG emissions calculations should be calibrated prior to the first reporting year, using a suitable method published by a consensus standards organization (e.g., ASTM, ASME, API, AGA, etc.). Alternatively, calibration procedures specified by the flow meter manufacturer may be used. Fuel flow meters, gas composition monitors, and/or heating value monitors shall be recalibrated either annually or at the minimum frequency specified by the manufacturer.

(3) Documentation of the procedures used to ensure the accuracy of the estimates of fuel usage, gas composition, and/or heating value including, but not limited to, calibration of weighing equipment, fuel flow meters, and other measurement devices should maintained. The estimated accuracy of measurements made with these devices should also be recorded, and the technical basis for the estimates should be provided.

(4) All CO_2 CEMS and flow rate monitors used for direct measurement of GHG emissions should comply with QA procedures for daily calibration drift checks and quarterly or annual

accuracy assessments, such as those provided in Appendix F to Part 60 or similar QA procedures.

10. References

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Appendix A. Derivation of Calculation Methods

Most of the calculation methods being considered for the reporting of GHG emissions from refineries are fairly straight-forward and are documented elsewhere.[1, 2] This section provides additional information for a few of the methods being evaluated and were specifically developed to reduce the burden for estimating fugitive emission from sources that are not expected to contribute significantly to the overall GHG inventory for U.S. petroleum refineries.

A.1 Equipment Leaks

The *Equipment Leaks Protocol Document* contains a variety of methods that may be used to estimate fugitive emissions from leaking process equipment.[3] To use these methods for estimating methane emissions, the average methane concentration of the various refinery process streams would need to be measured or estimated, and the number of equipment components would need to be determined. Many refineries already have these data, and can use the methods in the *Protocol Document* directly. For refineries that do not have these data readily available, a simple method of estimating these emissions was developed. First, methane emissions from fugitive equipment leaks were estimated using:

- ¡ A set leak fraction of 2 percent (1.4 percent with leaks greater than 10,000 ppmv but less than 100,000 ppmv, and 0.6 percent with leaks greater than 10,000 ppmv).

- ¡ The zero and pegged value leak equations from the *Protocol Document* as provided in Table A-1 of this report.

- ¡ Model refinery equipment component counts from EPA's *Locating and Estimating Emission of Benzene* document as well as estimated component counts for fuel gas systems as provided in Tables A-2 and A-3 of this report.[4]

- ¡ An estimated methane composition for each model process unit as provided in Table A-4.

Table A-4 also summarizes the methane emissions per model process unit.

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[1] EPA, 2008. *Inventory of Greenhouse Gas Emissions and Sinks: 1990-2006.* EPA-430-R-08-005. Office of Atmospheric Programs, Washington, DC. April 15.

[2] API, 2004. Compendium of Greenhouse Gas Emissions Methodologies for the Oil and Gas Industry. February.

[3] U.S. EPA (Environmental Protection Agency). 1995. *Protocol for Equipment Leak Emission Estimates.* EPA-453/R-95-017. Office of Air Quality Planning and Standards, Research Triangle Park, NC.

[4] U.S. EPA (Environmental Protection Agency). 1998a. *Locating and Estimating Air Emissions from Sources of Benzene.* EPA-454/R-98-011. Office of Air Quality Planning and Standards, Research Triangle Park, NC.

Table A-1. Fugitive Equipment Leak Rate for Refinery Equipment Components.[a]

Equipment Type (All Services)	Default Zero Emission Rate (kg/hr/source)	Pegged Emission Rates (kg/hr/source)	
		10,000 ppmv	100,000 ppmv
Valve	7.8E-06	0.064	0.140
Pump	2.4E-05	0.074	0.160
Other[b]	4.0E-06	0.073	0.110
Connector	7.5E-06	0.028	0.030
Flange	3.1E-07	0.085	0.084
Open-Ended Line	2.0E-06	0.030	0.079

[a] As reported in U.S. EPA (1995, see footnote 3)

[b] The "other" equipment type was developed from instruments, loading arms, pressure relief devices, stuffing boxes, vents, compressors, dump lever arms, diaphragms, drains, hatches, meters, and polished rods. This "other" equipment type should be applied to any equipment other than connectors, flanges, open-ended lines, pumps, or valves.

As seen by the estimated emissions for the model process units in Table A-4, the fuel gas system and the hydrogen plant are expected to produce the majority of the refinery's methane emissions. From the results presented in Table A-4, the average methane emissions between the small and large model plants for fuel gas systems and hydrogen plants is 6.0 and 4.3 mt/yr, respectively. For crude oil distillation columns, the average methane emissions rate is approximately 0.4 mt/yr. Several process units in Table A-4 were projected to have average emission rates of approximately 0.2 mt/yr, and several other process units were projected to have average emission rates of approximately 0.1 mt/yr.

Based on this analysis, Equation 1 was developed to provide a very quick and simple method for estimating methane emissions from fugitive equipment leaks at a refinery.

$$CH_4 = \left(0.4 * N_{CD} + 0.2 * N_{PU1} + 0.1 * N_{PU2} + 4.3 * N_{H2} + 6 * N_{FGS}\right)$$ (Equation 1)

Where:
CH_4 = annual methane emissions from fugitive equipment leaks (mtCH$_4$/yr)
N_{CD} = number of atmospheric crude oil distillation columns at the facility
N_{PU1} = cumulative number of catalytic cracking units, coking units (delayed or fluid), hydrocracking, and full-range distillation columns (including depropanizer and debutanizer distillation columns) at the facility
N_{PU2} = cumulative number of hydrotreating/hydrorefining units, catalytic reforming units, and visbreaking units at the facility
N_{H2} = total number of hydrogen plants at the facility
N_{FGS} = total number of fuel gas systems at the facility

Table A-2. Median Equipment Leak Component Counts for Small Model Processes.[a]

Process Unit	Valves			Pumps		Com-pres-sors	Pressure Relief Valves			Flanges			Open-Ended Lines	Sampling Connec-tions
	Gas	Light Liquid	Heavy Liquid	Light Liquid	Heavy Liquid		Gas	Light Liquid	Heavy Liquid	Gas	Light Liquid	Heavy Liquid		
Crude Distillation	75	251	216	8	8	2	6	6	5	164	555	454	39	10
Alkylation (sulfuric acid)	278	582	34	18	10	1	12	15	4	705	1296	785	20	16
Alkylation (HF)	102	402	62	13	3	2	12	13	0	300	1200	468	26	8
Catalytic Reforming	138	234	293	8	5	3	5	3	3	345	566	732	27	6
Hydrocracking	300	375	306	12	9	2	9	4	4	1038	892	623	25	10
Hydrotreating/Hydrorefining	100	208	218	5	5	2	5	3	5	290	456	538	20	6
Catalytic Cracking	186	375	450	13	14	2	8	8	7	490	943	938	8	8
Thermal Cracking (visbreaking)	206	197	0	7	0	0	4	0	0	515	405	0	0	4
Thermal Cracking (coking)	148	174	277	9	8	2	7	16	13	260	322	459	13	8
Hydrogen Plant	168	41	0	3	0	2	4	2	0	304	78	0	8	4
Asphalt Plant	120	334	250	5	8	2	5	10	9	187	476	900	16	6
Product Blending	67	205	202	6	11	1	10	6	22	230	398	341	33	14
Sulfur Plant	58	96	127	6	6	3	3	88	15	165	240	345	50	3
Vacuum Distillation	54	26	84	6	6	2	2	5	2	105	121	230	16	4
Full-Range Distillation	157	313	118	7	4	2	5	4	6	171	481	210	20	6
Isomerization	270	352	64	9	2	2	7	10	1	432	971	243	7	8
Polymerization	224	563	15	12	0	1	10	5	3	150	450	27	5	7
MEK Dewaxing	145	1208	200	35	39	3	10	14	4	452	1486	2645	19	17
Other Lube Oil Processes	153	242	201	7	5	2	5	5	5	167	307	249	60	6
Fuel Gas System[b]	120	0	0	0	0	2	5	0	0	300	0	0	20	5

[a] Process component counts (except for fuel gas system) as presented in the Benzene L&E document (U.S. EPA, 1998; see footnote 4) for refineries with crude capacities less than 50,000 bbl/cd

[b] Fuel gas system component counts estimated using engineering judgment.

Table A-3. Median Equipment Leak Component Counts for Large Model Processes.[a]

Process Unit	Valves			Pumps		Com-pres-sors	Pressure Relief Valves			Flanges			Open-Ended Lines	Sampling Connec-tions
	Gas	Light Liquid	Heavy Liquid	Light Liquid	Heavy Liquid		Gas	Light Liquid	Heavy Liquid	Gas	Light Liquid	Heavy Liquid		
Crude Distillation	204	440	498	15	14	2	7	5	12	549	982	1046	75	9
Alkylation (sulfuric acid)	192	597	0	21	0	2	13	4	0	491	1328	600	35	6
Alkylation (HF)	104	624	128	13	8	1	9	11	1	330	1300	180	40	14
Catalytic Reforming	310	383	84	12	2	3	8	11	0	653	842	132	48	9
Hydrocracking	290	651	308	22	12	2	10	12	0	418	1361	507	329	28
Hydrotreating/Hydrorefining	224	253	200	7	6	2	9	4	8	439	581	481	49	8
Catalytic Cracking	277	282	445	12	12	2	11	9	13	593	747	890	59	15
Thermal Cracking (visbreaking)	110	246	130	7	6	1	6	3	15	277	563	468	30	7
Thermal Cracking (coking)	190	309	250	12	11	1	8	5	10	627	748	791	100	10
Hydrogen Plant	301	58	0	7	360	3	4	139	0	162	148	0	59	21
Asphalt Plant	76	43	0	4	0	0	3	7	0	90	90	0	24	24
Product Blending	75	419	186	10	10	2	9	16	6	227	664	473	24	8
Sulfur Plant	100	125	110	8	3	1	4	4	4	280	460	179	22	7
Vacuum Distillation	229	108	447	2	12	1	5	1	4	473	136	1072	0	7
Full-Range Distillation	160	561	73	14	2	2	7	8	2	562	1386	288	54	6
Isomerization	164	300	78	9	5	2	15	5	2	300	540	265	36	7
Polymerization	129	351	82	6	2	0	7	12	28	404	575	170	17	9
MEK Dewaxing	419	1075	130	29	10	4	33	6	18	1676	3870	468	0	7
Other Lube Oil Processes	109	188	375	5	16	3	8	6	20	180	187	1260	18	9
Fuel Gas System[b]	120	0	0	0	0	2	5	0	0	300	0	0	20	5

[a] Process component counts (except for fuel gas system) as presented in the Benzene L&E document (U..S. EPA, 1998; see footnote 4) for refineries with crude capacities of 50,000 bbl/cd of greater.

[b] Fuel gas system component counts estimated using engineering judgment.

Table A-4. Estimated Methane Concentration and Fugitive Emission Rates for Model Refinery Process Units.

Process Unit	Concentration of Methane (weight fraction)[a]		Methane Emission Rate (tonnes CH$_4$/yr)	
	Gas Stream	Light Liquid Stream	Small Model Plant	Large Model Plant
Crude Distillation	0.05	0.000005	0.185	0.570
Alkylation (sulfuric acid)	0	0	0	0
Alkylation (HF)	0	0	0	0
Catalytic Reforming	0.01	0	0.074	0.146
Hydrocracking	0.02	0	0.403	0.216
Hydrotreating/hydrorefining	0.01	0	0.059	0.101
Catalytic Cracking	0.02	0	0.205	0.265
Thermal Cracking (visbreaking)	0.01	0	0.109	0.059
Thermal Cracking (coking)	0.02	0	0.125	0.247
Hydrogen Plant	0.6	0.0001	4.300	4.264
Asphalt Plant	0	0	0	0
Product Blending	0	0	0	0
Sulfur Plant	0.001	0	0.003	0.006
Vacuum Distillation	0.001	0	0.002	0.011
Full-Range Distillation	0.02	0	0.101	0.218
Isomerizaiton	0	0	0	0
Polymerization	0	0	0	0
MEK Dewaxing	0	0	0	0
Other Lube Oil Processing	0	0	0	0
Aromatics	0	0	0	0
Fuel Gas System	0.7	0	4.472	7.468

[a] Methane concentrations for heavy liquids were assumed to be negligible.

A.2 Storage Tanks

Methane (CH$_4$) emissions can occur from petroleum refinery storage tanks. Crude oil storage tanks are expected to be the primary contributor to the GHG emissions from storage tanks. Most other intermediate and final product storage tanks are expected to have negligible CH$_4$ emissions as the stored liquids typically do not contain any CH$_4$. When crude oil is initially pumped from the well, the crude oil can contain significant amounts of CH$_4$ because the crude is stored under pressure within the oil reservoir. When the oil is first stored at atmospheric conditions at the well site, significant amounts of light organics, including CH$_4$, are released from the crude oil, commonly referred to as flashing losses. After the light volatiles have flashed from the crude oil, the "stabilized" crude oil is then transported to the refineries for further processing. As such, most of the CH$_4$ emissions from crude oil storage typically occur upstream of the petroleum

refinery. If the crude oil is transported under pressure (e.g., via pipeline) before the crude oil is stabilized, significant CH_4 emissions can occur at the refinery from flashing losses in the crude oil storage tanks.

The TANKS model is a tool that implements the AP-42 emission estimation methods (developed by API) for organic liquid storage.[5] The TANKS model is not applicable for estimating the emissions from unstabilized crude oil. The *API Compendium of Greenhouse Gas Emissions Methodologies for the Oil and Gas Industry* contains a variety of methods that may be used to estimate flashing losses from storage tanks.[6] One of the simpler correlation equation methods presented in the *API Compendium* and one of the few that is applicable to refinery storage tanks is referred to as the EUB (Energy and Utilities Board) Rule-of-Thumb approach. The EUB Rule-of-Thumb correlation equation estimates the volume of gas released. Using the molar volume of gas at standard conditions and the CH_4 content of the gas, the EUB Rule-of-Thumb approach can be used to calculate flashing losses from storage tanks as follows:

$$CH_4 = (0.995 * Q_{un} * \Delta P) * MF_{CH4} * \frac{16}{MVC} * 0.001 \qquad \text{(Equation 2)}$$

Where:
   CH_4 = emission rate of methane from storage tanks (mtCH_4/yr)
   Q_{un} = quantity of unstabilized crude oil received at the facility (bbl/yr)
   ΔP = pressure differential from the previous storage pressure to atmospheric pressure (pounds per square inch)
   MF_{CH4} = mole fraction of CH_4 in vent gas from the unstabilized crude oil storage tank from facility measurements; use 0.27 as a default if measurement data are not available.
   0.995 = correlation equation factor (scf gas per bbl per psi)
   16 = molecular weight of CH4 (kg/kg-mole).
   MVC = molar volume conversion factor (849.5 scf/kg-mole).
   0.001 = conversion factor (mt/kg).

For stabilized crude oil, the TANKS model (current version is 4.09D) can be used to estimate CH_4 emissions from crude oil storage tanks. The TANKS model generally outputs total hydrocarbon losses, so the CH_4 content of the released vapor must be determined. It is important not to use the liquid phase composition for this estimate as the vapors will have much higher relative CH_4 concentrations than in the liquid phase. The TANKS model was used to estimate the hydrocarbon losses for crude oil using the default crude oil properties pre-loaded in the TANKS model (Crude oil with a Reid vapor pressure of 5 psi and average molecular weight of vapor of 50 g/mol). Concentrations of C5 through C8 hydrocarbons in the crude oil were estimated based on average crude oil compositions reported in Potter and Simmons.[7]

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[5] U.S. EPA (Environmental Protection Agency). 1995a. *Compilation of Air Pollutant Emission Factors. Sections 7.* AP-42. Office of Air Quality Planning and Standards, Research Triangle Park, NC.

[6] API, 2004. Compendium of Greenhouse Gas Emissions Methodologies for the Oil and Gas Industry. February.

[7] Potter, T.L., and K.E. Simmons. 1998. *Composition of Petroleum Mixtures*. Total Petroleum Hydrocarbon Criteria Working Group Series, Volume 2. May.

Concentrations of C1 through C4 hydrocarbons in the crude oil were estimated based on best engineering judgment and adjusted so that the average molecular weight of the equilibrium gas mixture was 50 g/mol (to match the TANKS model assumption). Although the estimated CH_4 concentration in the crude oil was only 5 parts per million by weight (ppmw), the vapor phase was projected to contain just under 8 percent CH_4. Therefore the total hydrocarbon emissions rates estimated using the TANKS model were multiplied by 8 percent to estimate a CH_4 emissions factor for crude oil storage tanks. Several crude oil storage tanks with different floating roof seal designs and component fittings were evaluated. All of the tanks were 200 ft diameter, 7.5-million gallon capacity tanks, with an estimated throughput of 20,000 to 25,000 bbls per day (40 to 50 turnovers per year). The tanks were evaluated at a number of meteorological locations. Based on this evaluation, an emission factor of 0.1 Mg CH_4/million bbls of crude throughput was developed. The uncertainty of this default emission factor is large, roughly factor of 2 or 3, based on the results for different tank runs. Nonetheless, it provides a very simple means of estimating CH_4 emissions from crude oil storage tanks, and presumably all storage tanks at the refinery, and is appropriate given the small contribution of storage tank emissions in the overall GHG emissions inventory for a petroleum refinery.

A.3 Delayed Coking Unit Coke Cutting

Methane emissions have been found in recent delayed coking vessel depressurization vent tests, and the tests noted that significant emissions appeared to occur when the coke vessel was opened.[8, 9, 10, 11] Additionally, other test data indicate that significant emissions continue to occur during the coke cutting operations.[12] From the delayed coking vessel depressurization vent tests, methane is approximately 30 percent of the gas volume on a dry basis. However, water is added to the coking drum to cool the coke, and the water vaporizes. Consequently, the coker depressurization vent stream is 90 percent or more water vapor. It is unknown how much of the void space within the coke drum is well purged with steam and what fraction is trapped and only released to the atmosphere during the coke cutting operations. Any trapped gas is expected to have high concentrations of methane (roughly 30 percent by volume).

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[8] South Coast Air Quality Management District. 2004a. *Source Test Report 03-194 Conducted at Chevron / Texaco Refinery, El Segundo, California—Volatile Organic Compound (VOC), Carbon Monoxide (CO), and Particulate Matter (PM) Emissions From a Coke Drum Steam Vent.* May 14.

[9] South Coast Air Quality Management District. 2004b. Source Test Report 03-197 Conducted at Conoco-Phillips Refinery, Carson, California—Volatile Organic Compound (VOC), Carbon Monoxide (CO), and Particulate Matter (PM) Emissions From a Coke Drum Steam Vent. July 23.

[10] South Coast Air Quality Management District. 2004c. *Source Test Report 03-198 Conducted at Exxon Mobil Refinery, Torrance, California—Volatile Organic Compound (VOC), Carbon Monoxide (CO), and Particulate Matter (PM) Emissions From a Coke Drum Steam Vent.* March 4.

[11] South Coast Air Quality Management District. 2004d. Source Test Report 03-200 Conducted at Shell Oil Refinery, Wilmington, California—Volatile Organic Compound (VOC), Carbon Monoxide (CO), and Particulate Matter (PM) Emissions From a Coke Drum Steam Vent. July 1.

[12] Chambers, A., and M. Strosher. 2006. *Refinery Demonstration of Optical Technologies for Measurement of Fugitive Emissions and for Leak Detection.* Prepared for Environment Canada, Ontario Ministry of the Environment, and Alberta Environment. Project No. CEM 9643-2006. March 31.

Although some of the coke drum is filled with coke, the coke is quite porous, so a rough estimate of the gas within the coke drum can be estimated by the dimensions of the coke drum vessel itself. A default methane concentration of 3 percent by volume is recommended based on the typical methane dry composition of 30 percent by volume and the lower range of water content in the depressurization purge vent. If a facility has data for the coker drum purge vent (but not during periods of active steaming), then that concentration can be used to estimate the vapor-phase concentration within the coker drum. While using the direct volume of the coke drum vessel will over-estimate the amount of gas released, the actual concentration of the gas within the vessel is expected to be somewhat higher than the purge vent concentrations because of the likelihood of trapped gas pockets. Thus, the combination of the purge vent concentration combined with the entire vessel volume assumption is expected to provide a reasonable estimate of the methane emissions when the coke drum vessel is opened and subsequently de-coked. Consequently, Equation 3 was developed to estimate the methane emissions from opening the coke drum vessel and subsequent coke cutting operations.

$$CH_4 = \left(N * H * \frac{p * D^2}{4} * \frac{16}{MVC} * MF_{CH4} * 0.001 \right)$$
(Equation 3)

Where:
CH_4 = annual CH_4 emissions from the delayed coking unit vessel opening (mtCH$_4$/yr)
N = total number of vessel openings for all delayed coking unit vessels of the same dimensions during the year
H = height of coking unit vessel (ft)
D = diameter of coking unit vessel (ft)
16 = molecular weight of CH_4 (kg/kg-mole)
MVC = molar volume conversion (849.5 scf/ kg-mole)
MF_{CH4} = mole fraction of methane in coking vessel gas; default value is 0.03
0.001 = conversion factor – kg to metric tonnes.