

September 9, 2008

**TECHNICAL SUPPORT DOCUMENT FOR THE
PETROCHEMICAL PRODUCTION SECTOR:
PROPOSED RULE FOR MANDATORY
REPORTING OF GREENHOUSE GASES**

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

September 9, 2008

CONTENTS

1.0	INTRODUCTION.....	1
2.0	SOURCE DESCRIPTION.....	1
2.1	Acrylonitrile	1
2.2	Carbon Black.....	2
2.2.1	Furnace Black Process	3
2.2.2	Thermal Black Process	4
2.2.3	Acetylene Black Process.....	4
2.2.4	Lamp Black Process.....	5
2.3	Ethylene	5
2.4	Ethylene Dichloride.....	7
2.5	Ethylene Oxide.....	8
2.6	Methanol	9
2.6.1	Conventional Reforming Process	9
2.6.2	Coal Gasification	10
2.6.3	Partial Oxidation.....	11
3.0	TOTAL EMISSIONS.....	12
4.0	OPTIONS FOR REPORTING THRESHOLD.....	13
5.0	OPTIONS FOR MONITORING METHODS.....	14
5.1	Review of existing programs and methodologies	15
5.2	Discussion of options for monitoring methods	15
5.2.1	Option 1.....	15
5.2.2	Option 2.....	15
5.2.3	Option 3.....	17
6.0	Missing Data	18
6.1	Option 2	19
6.2	Option 3	19
7.0	Quality Assurance and Quality Control Requirements	19
7.1	Monitoring of Flow and Composition	20
7.2	CEMS	20
8.0	REFERENCES.....	20

1.0 INTRODUCTION

The petrochemical industry consists of numerous processes that use fossil fuel or petroleum refinery products as feedstocks. However, for this Greenhouse Gas (GHG) reporting rule, the petrochemical production source category only considers the production of acrylonitrile, carbon black, ethylene, ethylene dichloride, ethylene oxide, and methanol. The petrochemical source category includes all forms of carbon black (e.g., furnace black, thermal black, acetylene black, and lamp black) because their production is based on petrochemical feedstocks. The rule focuses on these six processes because production of GHGs from these processes has been recognized by the Intergovernmental Panel on Climate Change (IPCC) to be significant compared to other petrochemical processes.¹ For the purposes of this report, bone black is not considered to be a form of carbon black because it does not use petrochemical feedstocks.

As discussed in section 2 of this report, there are 88 facilities operating petrochemical processes in the United States, and 9 of these facilities are operating either two or three types of petrochemical processes (e.g., ethylene and ethylene oxide).

2.0 SOURCE DESCRIPTION

This section summarizes the processes and major emission points of GHGs for each of the six types of petrochemical processes identified in section 1.0. The facilities making each type of petrochemical are also listed. More complete descriptions of the processes are available in referenced documents.

2.1 Acrylonitrile

The primary use of acrylonitrile is in the production of acrylic and modacrylic fibers. It is also used in the production of various resins and in the production of adiponitrile and acrylamide. The five facilities that make acrylonitrile in the United States are listed in Table 1. All of these facilities manufacture acrylonitrile by direct ammoxidation of propylene with ammonia (NH₃) and oxygen over a catalyst.² This process is referred to as the SOHIO process, after the Standard Oil Company of Ohio (SOHIO). Although not commercialized in the United States, other methods to produce acrylonitrile include the ammoxidation of propane and the direct reaction of propane with hydrogen peroxide.³

Table 1. Acrylonitrile Production Facilities in the United States⁴⁻⁷

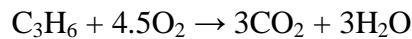
Facility	City	State	Capacity (mm lbs/yr) ^a
Cytec	Waggaman (Avondale)	LA	475
Lucite (formerly DuPont)	Beaumont	TX	308
Ineos Nitriles	Green Lake	TX	1,014
Ineos Nitriles	Lima	OH	410
Solutia	Alvin	TX	1,100

^aCapacities are presented in million pounds per year (mm lbs/yr).

The SOHIO process involves a gas-phase, fluidized bed reaction of chemical-grade propylene, ammonia, and oxygen (from air) over a catalyst.^{1,2} The catalyst is a mixture of heavy metal oxides (including bismuth and molybdenum). The ammoxidation of propylene converts only about 70 percent of the propylene feedstock to acrylonitrile, and about 15 percent is converted to acetonitrile and hydrogen cyanide (HCN). The remaining propylene feedstock is either converted to CO₂ by direct oxidation of the feedstock or converted to other hydrocarbons through side reactions. The exact yield of acrylonitrile at each facility depends in part on the type of catalyst used and the process configuration. The reaction governing the production of acrylonitrile is shown below.



The direct oxidation of propylene to generate CO₂ follows the reaction shown below.



After a series of heat recovery and neutralization steps, the product gas stream from the reactor passes through an absorber which uses water as the scrubbing fluid. Most of the acrylonitrile, HCN, acetonitrile, and other organic compounds are transferred to the water. Inert compounds, such as CO₂ and nitrogen, and small amounts of organic compounds remain in the gas stream that is vented from the absorber. This vent stream is routed to a thermal incinerator to control hydrocarbon emissions. The liquid stream from the absorber undergoes a series of distillations to obtain acrylonitrile and one or more byproducts of the desired purity. All 5 facilities in the United States recover HCN as a byproduct. All of the facilities also separate acetonitrile from water that is recycled to the absorber, but only the Lucite and Ineos Nitriles facilities recover the acetonitrile as a byproduct; the other two facilities burn the acetonitrile stream.^{2,5}

The gaseous stream from the absorber contains much of the CO₂ generated in the reactor. Small amounts of CO₂ may be lost through equipment leaks between the reactor and the absorber, and small amounts may be carried along with the primary process fluid and released from other process vents. Emission streams from these other process vents and storage tanks are routed to flares to control emissions of hydrocarbons. Supplemental fuel (natural gas) is used in the incinerators and flares as necessary to maintain operating temperatures.² Combustion of organic pollutants and supplemental fuel in the thermal incinerators and flares is another source of CO₂ emissions. Small amounts of unburned methane may be emitted from the combustion units, and small amounts of nitrous oxide (N₂O) may also be generated in and emitted from the combustion units. No supplemental fuel-fired boilers or process heaters are needed because excess heat from the exothermic ammoxidation reaction and incinerator exhaust is recovered to supply other energy needs in the process.

2.2 Carbon Black

Carbon black is a black powder or granular substance formed through a high temperature (1,320 °C to 1,540 °C) reaction of hydrocarbon fuel with a limited supply of combustion air. It is used primarily as a reinforcing agent in tires and other rubber compounds, and also has

applications as a pigment.¹ As shown in Table 2, 21 facilities produce carbon black in the United States. Most of these facilities use the furnace black process (also called the oil furnace process in some reference documents). Other production processes include the thermal black process, the acetylene black process, and the lamp black process. All of these processes are described in the sections below. Another process, the channel black process, has not been used in the United States since 1976 and is not discussed further in this report.⁸

Table 2. Carbon Black Production Facilities in the United States^{5,9}

Facility	City	State	Capacity (mm lbs/yr)	Process
Cabot Corp.	Franklin	LA	355	Furnace
Cabot Corp.	Pampa	TX	65	Furnace
Cabot Corp.	Ville Platte	LA	355	Furnace
Cabot Corp.	Waverly	WV	220	Furnace
Chevron Phillips	Cedar Bayou	TX	20	Acetylene
Columbian Chemicals Co.	El Dorado	AR	130	Furnace
Columbian Chemicals Co.	North Bend	LA	350	Furnace
Columbian Chemicals Co.	Proctor	WV	200	Furnace
Columbian Chemicals Co.	Ulysses	KS	115	Furnace
Continental Carbon Co.	Phenix City	AL	200	Furnace
Continental Carbon Co.	Ponca City	OK	285	Furnace
Continental Carbon Co.	Sunray	TX	190	Furnace
Degussa Engineered Carbons	Aransas Pass	TX	125	Furnace
Degussa Engineered Carbons	Belpre	OH	185	Furnace
Degussa Engineered Carbons	Borger	TX	290	Furnace, Thermal
Degussa Engineered Carbons	New Iberia	LA	250	Furnace
Degussa Engineered Carbons	Orange	TX	155	Furnace
General Carbon Co.	Los Angeles	CA	1	Lamp black
Sid Richardson Carbon Co.	Addis	LA	310	Furnace
Sid Richardson Carbon Co.	Big Spring	TX	235	Furnace
Sid Richardson Carbon Co.	Borger	TX	315	Furnace

2.2.1 Furnace Black Process^{1,8,10,11}

In the furnace black process a heavy aromatic liquid, also known as carbon black oil, is injected continuously into the combustion zone of a natural gas-fired furnace. Both the natural gas and a portion of the carbon black feedstock are oxidized to provide heat in the furnace, and the remainder of the carbon black feedstock is pyrolyzed to carbon black in an oxygen-depleted environment. In addition to the desired carbon black product, the vent gas from the furnace contains numerous compounds including CO₂, unburned CH₄, carbon monoxide, hydrogen, and various organic compounds. A water quench is used to cool the gas stream and stop the reactions. Both the combustion air and the carbon black oil are preheated before entering the

furnace. Some of the energy to preheat these streams may come from the furnace exhaust gas; the remainder is provided by combustion of off-gasses from downstream in the process or from supplemental fuels.

Carbon black is separated from the gas stream in a fabric filter. Typically, a portion of the exhaust, or tail gas, from the fabric filter is burned to provide heat for the product dryers, and the rest is burned in a thermal incinerator for pollution control. Hot exhaust from the thermal incinerator may be used to generate steam, and at least one facility uses the steam to run a steam turbine that generates electricity. Carbon black manufacturing facilities generally have several, perhaps many, furnaces. Furnaces that are used to make the same grade of product may all discharge to a single product processing train with one dryer. Although data for most facilities are not available, it is likely that each facility has only one thermal incinerator for burning all excess tail gas that is not needed to provide heat for dryers (there may be a backup device such as a flare for periods when the incinerator is out of service). The number of process heaters per facility is also unknown, but it is possible that steam generated by recovering heat from the tail gas incinerator is used without the need for additional combustion units.

Most of the CO₂ that is generated in the furnaces is released to the atmosphere in the exhaust from the thermal incinerator and the combustion units for each dryer. Small amounts also may be released through equipment leaks in the process. The thermal incinerator, combustion units for dryers, and any additional combustion units needed to supply heat for preheaters emit additional CO₂ that is generated by burning the tail gas (i.e., carbon monoxide and various hydrocarbons) and if necessary, supplemental fuel. Unburned CH₄ from the furnaces and supplemental fuel in other combustion units is also released to the atmosphere from the same emission points. Small amounts of N₂O also likely are generated in and released from each of the combustion units.

2.2.2 Thermal Black Process^{1,8}

In the thermal black process gaseous hydrocarbons or atomized petroleum oils are decomposed in a pair of furnaces in the absence of air. One furnace receives and cracks the carbon black feedstock while the other is being preheated by combustion of off-gas from the fabric filter used to recover the carbon black. Natural gas or another fuel may also be used to supplement the off-gas, if necessary. The off-gas is primarily hydrogen but also contains 6 percent CH₄ and 4 percent higher hydrocarbons. Once the first furnace becomes too cool to crack the feed, the flows to the reactors are switched. The GHGs emitted from this process are CO₂, CH₄, and N₂O, and all of the main emission points are combustion units, the same as for the furnace black process. As shown in Table 2, only one facility in the United States is making carbon black using the thermal black process, and this process accounts for only a portion of the carbon black produced at the facility. Information about the number of combustion sources at this facility in addition to the combustion needed to preheat the furnaces is not available.

2.2.3 Acetylene Black Process^{1,8}

In the acetylene black process, acetylene or acetylene-containing light hydrocarbons are fed into a preheated reactor where the acetylene is decomposed into carbon black. This is an

exothermic process and has a very high yield (95-99 percent). As shown in Table 2, acetylene black is produced by only one facility in the United States, and the amount produced accounts for less than one-half of one percent of the total carbon black capacity in the United States.

2.2.4 Lamp Black Process^{1,8}

For the lamp black process, carbon black feedstock is open-burned in shallow pans. Little data are available to indicate the efficiency of this process or the emissions generated by it. As shown in Table 2, lamp black accounts for less than one-tenth of one percent of the total carbon black capacity in the United States.

2.3 Ethylene

In the United States, all ethylene is produced by way of steam cracking. Ethylene (CH₂=CH₂) may be produced from steam cracking of a petrochemical feedstock in a petrochemical plant, or from cracking and other processes operated at petroleum refineries. A list of currently operating facilities that manufacture ethylene is displayed in Table 3.)

Table 3. Ethylene Production Facilities in the United States^{5,12,13}

Facility	City	State	Capacity (mm lbs/yr)
BASF Fina	Port Arthur	TX	1,830
Chevron Phillips	Cedar Bayou (Baytown)	TX	1,750
Chevron Phillips	Port Arthur	TX	1,750
Chevron Phillips	Sweeny	TX	2,034
Chevron Phillips	Sweeny	TX	1,480
Chevron Phillips	Sweeny	TX	600
Dow	Freeport	TX	1,390
Dow	Freeport	TX	2,226
Dow	Plaquemine	LA	1,146
Dow	Plaquemine	LA	1,630
Dow	Taft	LA	1,300
Dow	Taft	LA	904
DuPont	Orange	TX	1,500
Eastman	Longview	TX	1,847
Equistar	Channelview	TX	3,858
Equistar	Chocolate Bayou (Alvin)	TX	1,200
Equistar	Clinton	IA	1,049
Equistar	Corpus Christi	TX	1,700

Table 3. Ethylene Production Facilities in the United States^{5,12,13}

Facility	City	State	Capacity (mm lbs/yr)
Equistar	LaPorte	TX	1,740
Equistar	Morris	IL	1,212
ExxonMobil	Baton Rouge	LA	2,200
ExxonMobil	Baytown	TX	4,840
ExxonMobil	Beaumont	TX	1,800
ExxonMobil	Houston	TX	225
Formosa Plastics	Point Comfort	TX	3,375
Huntsman	Odessa	TX	800
Huntsman	Port Arthur	TX	1,400
Huntsman	Port Neches	TX	450
Ineos Olefins and Polymers	Chocolate Bayou (Alvin)	TX	3,860
Javelina	Corpus Christi	TX	333
Sasol North America	Lake Charles (Westlake)	LA	1,000
Shell	Deer Park	TX	3,100
Shell	Norco	LA	1,984
Shell	Norco	LA	1,446
Sunoco	Marcus Hook	PA	496
Westlake Petrochemicals	Calvert City	KY	450
Westlake Petrochemicals	Sulphur	LA	1,250
Westlake Petrochemicals	Sulphur	LA	1,150
Williams Olefins	Geismar	LA	1,350

In the United States, most ethylene is produced from steam cracking of ethane, propane, or naphtha. Some facilities also use butane, gas oil, or other feedstocks. Most facilities use more than one type of feedstock.¹³

Steam cracking petrochemical feedstocks to produce ethylene also produces other high value (saleable) petrochemical products, including propylene, butadiene, and aromatic compounds. The separation and purification of all of the products derived from the steam cracking operation are considered to be part of the ethylene process. The steam cracking process also generates CH₄, which is generally burned for energy recovery within the process along with hydrogen and other light ends that are not recovered as products.¹

All of the GHG emissions associated with the ethylene process are from combustion units. Carbon dioxide is the primary GHG, but small amounts of unburned CH₄ are also emitted, and small amounts of N₂O are likely generated in and emitted from the combustion units.

Except for processes using ethane or gas oil feedstocks, combustion of the off-gas from the process is sufficient to provide the steam for the cracking operation and any other energy needs in the process.¹ Small amounts of supplemental fuel are needed (and presumably mixed with the off-gas) when ethane or gas oil are used as the feedstock. The number of combustion units at each facility for energy purposes is not known because information about the number of steam cracking units at each facility is not available, and it is not known whether facilities have a centralized combustion unit to supply energy for all purposes or multiple units. Each facility, however, likely has a single fuel gas system (with or without supplemental natural gas) that supplies fuel to all combustion units.

In addition to combustion units for energy purposes, each ethylene production facility has a flare to control emissions from excess fuel gas production. For this analysis, it is assumed that each facility also has one thermal incinerator to control hydrocarbon emissions from process vents, storage tanks, and other emission points associated with production of ethylene and byproducts. As for combustion units used to supply energy, the primary GHG emitted from these combustion units is CO₂. Small amounts of CH₄ and N₂O are also emitted.

2.4 Ethylene Dichloride

Ethylene dichloride (1,2-dichloroethane) is produced from ethylene by direct chlorination, oxychlorination, or by a combination of the two processes (referred to as the “balanced process”). As shown in Table 4, most facilities in the United States use the balanced process.

Table 4. Ethylene Dichloride Production Facilities in the United States^{5,14}

Facility	City	State	Capacity (mm lbs/yr)	Process
Dow	Freeport	TX	1,650	Direct chlorination
Dow	Oyster Creek	TX	3,000	Balanced
Dow	Plaquemine	LA	2,800	Balanced
Formosa Plastics	Baton Rouge	LA	1,225	Balanced
Formosa Plastics	Point Comfort	TX	2,900	Balanced
Geismar Vinyls	Geismar	LA	1,180	Balanced
Georgia Gulf	Lake Charles	LA	1,700	Balanced
Georgia Gulf	Plaquemine	LA	2,530	Balanced
Occidental	Convent	LA	1,500	Direct chlorination
Occidental	Ingleside (Corpus Christi)	TX	1,500	Direct chlorination
Occidental (formerly Vulcan)	Geismar	LA	600	Direct chlorination
OxyMar	Ingleside (Corpus Christi)	TX	3,900	Balanced
OxyVinyls	Deer Park	TX	2,100	Balanced
OxyVinyls	La Porte	TX	3,900	Balanced
PPG Industries	Lake Charles	LA	2,700	Balanced
Westlake	Calvert City	KY	1,950	Balanced

The direct chlorination process involves gas-phase reaction of ethylene with chlorine to produce ethylene dichloride. The oxychlorination process involves gas-phase reaction of ethylene with hydrochloric acid (HCl) and oxygen to produce ethylene dichloride and water. Most facilities that produce ethylene dichloride use it as a feedstock in the production of vinyl chloride monomer. Cracking ethylene dichloride to produce vinyl chloride also produces HCl. This HCl can be used as a raw material in the oxychlorination process. Therefore, most ethylene dichloride/vinyl chloride monomer production facilities operate a ‘balanced process’ in which ethylene dichloride is produced using both the direct chlorination process and the oxychlorination process.^{1,15}

The oxychlorination process produces a small amount of CO₂ from the direct oxidation of the ethylene feedstock; most of this CO₂ is released to the atmosphere from a knockout drum that follows the oxychlorination reactor and quench.¹⁵ Most of the CO₂ emissions from the oxychlorination process and essentially all of the CO₂ emissions from the direct chlorination process are from combustion units.¹ Some of the energy needs are supplied by recovering heat from the incinerator that is used to control hydrocarbon emissions from process vents and storage tanks, and the rest is provided by burning supplemental fuels. The number of combustion units per facility is unknown, but it is likely that supplemental fuel from the same source is used in all of them. Organic liquid wastes are also disposed of by incineration.¹⁵ The CH₄ content of process vent emissions is considered to be negligible, but some unburned CH₄ is emitted from the combustion units that burn supplemental fuel.¹ Small amounts of N₂O are also likely emitted from the combustion units.

Because it includes the oxychlorination process, the ‘balanced process’ also emits CO₂ from the direct oxidation of the ethylene feedstock. Emissions from combustion units are comparable to those from the individual processes.

2.5 Ethylene Oxide

Ethylene oxide (C₂H₄O) is used as a feedstock in the manufacture of glycols, glycol ethers, alcohols, and amines. It is manufactured by reacting ethylene and oxygen over a catalyst. The oxygen may be supplied to the process through either an air or a pure oxygen stream. As shown in Table 5, almost all ethylene oxide manufacturers in the United States use the oxygen process.

The by-product CO₂, from the direct oxidation of the ethylene feedstock, is removed from the process vent stream using a recycled carbonate solution. The recovered CO₂ may be vented to the atmosphere or recovered for further utilization (e.g., food production).¹⁹

The ratio of metric tons of ethylene consumed per metric ton of ethylene oxide produced defines the selectivity of the ethylene oxide process. The combined ethylene oxide reaction and by-product CO₂ reaction is exothermic and generates heat, which is recovered to produce steam for the process. The ethylene oxide process also produces other liquid and off-gas by-products (e.g., ethane) that may be burned for energy recovery within the process. The amount of CO₂, other by-products, and steam produced from the process is dependent upon the selectivity of the process.¹

Table 5. Ethylene Oxide Production Facilities in the United States^{5,16-18}

Facility	City	State	Capacity (mm lbs/yr)	Process
BASF	Geismar	LA	485	Oxygen
Dow	Seadrift	TX	950	Air
Dow	Taft	LA	1,700	Air/Oxygen
Dow	Plaquemine	LA	620	Oxygen
Eastman	Longview	TX	230	Oxygen
Equistar	Bayport	TX	800	Oxygen
Formosa	Point Comfort	TX	550	Oxygen
Huntsman	Port Neches	TX	1,015	Oxygen
Old World Industries	Clear Lake	TX	780	Oxygen
PD Glycol	Beaumont	TX	700	Oxygen
Shell	Geismar	LA	920	Oxygen
Sunoco	Claymont	DE	120	Oxygen

2.6 Methanol

Methanol is most commonly synthesized in the gas phase over a heterogeneous catalyst from a synthesis gas (syngas), which is a mixture containing hydrogen, carbon monoxide, and carbon dioxide. One company also operates a liquid-phase conversion process. Several process techniques to produce syngas have been developed such as steam reforming of natural gas, coal gasification, partial oxidation of various hydrocarbon feedstocks, and combinations of these technologies. Although steam reforming of natural gas is the most common method of producing syngas worldwide, only two facilities in the United States use this method. Other facilities in the United States produce syngas using coal gasification or partial oxidation of natural gas. All of the facilities use only a portion of the syngas to produce methanol. The rest is used to produce other chemicals, some of which are in other GHG reporting source categories such as hydrogen and ammonia production. Table 6 lists currently operating methanol manufacturing facilities in the United States.

2.6.1 Conventional Reforming Process^{1,28-30}

The conventional reforming process for methanol production involves steam reforming to produce syngas (which may include either a single reformer unit or both a primary reformer unit and a secondary reformer unit) followed by conversion of the syngas to methanol. A typical steam reforming process begins with a preheated natural gas feedstock, which is then desulfurized, mixed with steam, and reformed and cooled before finally being compressed as feed to a methanol conversion unit.

Table 6. Methanol Production Facilities in the United States^{5,20-27}

Facility	City	State	Capacity (mm gpy)	Process to produce syngas	Other GHG source categories at facility
Dakota Gasification Company	Beulah	ND	2	Coal gasification	Ammonia, Carbon dioxide
Eastman	Kingsport	TN	102 ^a	Coal gasification	
Millenium	La Porte (Deer Park)	TX	210	Partial oxidation of natural gas	
Terra Industries	Woodward	OK	40	Steam reforming of natural gas	Ammonia
Praxair	Geismar	LA	30	Steam reforming of natural gas	Hydrogen

^aTotal capacity includes 70 million gal/yr unit based on conventional gas-phase methanol conversion and 32 million gal/yr unit based on a new liquid-phase conversion unit. Both units convert syngas produced in the coal gasification unit.

Off-gas from the methanol conversion unit includes methane feedstock that did not break down in the reformer and some syngas that was not converted to methanol in the methanol conversion unit. A portion of this gas is compressed and recycled to the methanol conversion unit. The remainder is purged to prevent buildup of noncondensable gases. The purged gas is used as fuel in the reformer. The methanol from the methanol conversion unit is purified in a series of distillation units. Light ends from the distillation unit are used as fuel in the reformer. Heavy liquid organic compounds from the final methanol distillation column are a hazardous waste, which may be burned if a permit is obtained, or this stream may be further processed. Water from the distillation column, which contains methanol and other organic compounds, is sent to biological treatment. A flare is used to control startup, shutdown, and malfunction emissions. Although no facilities in the United States are known to operate the conventional reforming process in this way, one option is to utilize CO₂ captured from other industrial processes as a supplemental feedstock to the methanol production process.

2.6.2 Coal Gasification^{26-28,31,32}

Coal gasification is accomplished by a combination of partial oxidation and hydrogasification of coal feedstock. The coal reacts with oxygen to produce carbon monoxide and with water to produce carbon monoxide and hydrogen. Carbon monoxide and water can then react to yield carbon dioxide and hydrogen, and the carbon dioxide can be reacted with coal to produce carbon monoxide.

The Dakota Gasification facility primarily produces synthetic natural gas, but they also produce a variety of other chemicals as byproducts. The facility uses 14 Lurgi moving bed gasifiers to convert lignite to a raw synthesis gas. Coal is fed to the top of each gasifier, and steam and oxygen are fed to the bottom of the gasifiers. As the steam and oxygen rise through the coal bed they react with the coal to form the raw syngas. After exiting the top of the

gasifiers, the raw gas is cooled in waste heat recovery boilers. A portion of the raw gas is sent to a shift conversion unit where some of the carbon monoxide in the gas reacts with water vapor to form hydrogen and carbon dioxide. The shifted gas is then recombined with the remainder of the raw gas. The mixed gas is sent to an acid gas unit where carbon dioxide, sulfur compounds, and naphtha are removed by a cold methanol wash. Most of the synthesis gas from the acid gas unit is sent to a methanation unit to produce synthetic natural gas. On average, about 10 percent of the syngas is diverted to an ammonia production unit. Purge gas from the ammonia process is used as fuel in boilers at the facility. A small amount of syngas is used to produce methanol. Methanol is not identified as a saleable product from the facility, so enough may be produced only to use as the absorbing fluid in the acid gas unit. The carbon dioxide from the acid gas unit is compressed and sold for use in enhanced oil recovery operations. Naphtha is also recovered from the acid gas unit and either sold as a product or used as fuel in boilers and superheaters at the facility. The gasification process also produces a significant amount of water vapor that is condensed in the waste heat recovery boilers and other cooling operations. This condensed water contains coal fines, tars, oils, phenolic compounds, and ammonia. The coal fines, tar, and tar oil are removed by gravity separation. Coal fines and tar are recycled to the gasifiers, and the coal tar is used as fuel in boilers and superheaters. The water stream is further processed to remove crude phenolic compounds and ammonia. The crude phenol stream is further processed to produce phenol and cresylic acid as saleable products. The ammonia is fed to a flue gas desulfurization scrubber that is used to remove sulfur dioxide from the boiler exhaust gas. The water stream from these units is used as make-up water in the plant's cooling tower. The facility has a total of three boilers and two superheaters.

The syngas that the Eastman facility produces from coal gasification is used to make methanol and other products derived from methanol. The Eastman facility uses two Texaco pressurized entrained-flow gasifiers (one on-line and the second on stand-by). A coal slurry and oxygen are fed to the gasifier. A portion of the raw gas from the gasifier is sent to a water shift reactor to produce hydrogen. The shifted gas and the unshifted raw gas are sent to separate acid gas units where most of the carbon dioxide and hydrogen sulfide are removed. The carbon dioxide is vented to the atmosphere. A portion of the syngas from one of the acid gas units is sent to a cryogenic unit to separate hydrogen from carbon monoxide. The hydrogen is combined with the rest of the syngas and sent to the methanol conversion units. The facility has both a conventional gas-phase conversion unit and a new liquid-phase unit. A portion of the gas that is not converted in the methanol conversion units is recycled to the units, and the rest is purged to be used as fuel. Overhead light ends from the methanol purification steps (distillation) are also collected and used as fuel. Bottoms from the distillation unit contain water, methanol, and a variety of other organic compounds. This stream is further processed to recover additional methanol. The methanol product is reacted with acetic acid to produce methyl acetate, and the methyl acetate is reacted with carbon monoxide from the cryogenic unit to produce acetic anhydride.

2.6.3 Partial Oxidation^{22,28}

Partial oxidation consists of the incomplete combustion of hydrocarbon to produce syngas. Steam is used to control the reaction temperature, which leads to additional hydrogen. Reaction conditions are typically around 1500°C and 150 atmospheres. This process is attractive

because it allows utilization of hydrocarbon feeds that could not be handled in the more conventional vapor-phase processes, such as steam reforming. Thus, partial oxidation typically is used to produce syngas from heavy hydrocarbon liquids, but other feedstocks can also be used. Disadvantages include the cost and soot formation due to thermal cracking of feedstock or the reversible reaction of carbon monoxide decomposition to carbon and carbon dioxide. Additionally, sulfur compounds have to be removed downstream before the syngas is converted to methanol.

The Millenium facility operates a partial oxidation unit that uses natural gas and oxygen as the feedstocks. A portion of the resulting syngas is separated into a carbon monoxide stream and a hydrogen-rich stream. The hydrogen-rich stream and the remaining syngas are fed to the methanol conversion unit. The carbon monoxide and methanol are used to make acetic acid.

3.0 TOTAL EMISSIONS

Petrochemical production accounts for an estimated 55 million metric tons (mmt) of CO₂ equivalent (CO₂e) emissions per year, representing less than 1 percent of the total U.S. GHG emissions of 7,054 million metric tons in 2006.³³ The emissions from petrochemical production operations were estimated by applying the IPCC's default Tier I emission factors for CO₂ and CH₄ to each petrochemical production facility in the United States.¹ The primary activity data needed to use these emission factors is the production capacity at the facility. Other important considerations are the type of feedstock or operating characteristics at each facility. For example, the CO₂ emissions per million pounds of ethylene oxide produced differ depending on whether the facility feeds oxygen or air to the reactor. Information about operating facilities, their production capacities, and types of processes was obtained from several resources as noted in section 2.0. Using this approach, about 95 percent of the CO₂e emissions are from CO₂, and 5 percent are from CH₄.

This approach potentially overstates the total CO₂e emissions because the actual production rate at a facility may be less than its design capacity. At the same time, the approach may underestimate the total CO₂e emissions because N₂O emissions from combustion are not estimated. In their discussion of combustion units, the IPCC estimates the mass of CH₄ emissions from burning natural gas or refinery gas to be nearly 10 times higher than the N₂O emissions. However, because the global warming potential (GWP) of N₂O is nearly 15 times greater than the GWP of CH₄, the total CO₂e emissions from N₂O may be as much as 1.5 times greater than the CO₂e emissions from CH₄. The default emission factors also do not account for emissions from flares, but these emissions are expected to be small relative to process emissions and emissions from combustion units used to supply energy. Another potential limitation is that the emission factors do not account for CH₄ emissions from onsite anaerobic wastewater treatment systems, but such emissions are expected to be minimal because petrochemical facilities are not known to use anaerobic wastewater treatment systems. It is not clear if the emission factors include CO₂ emissions from the conversion of organic compounds in aerobic wastewater treatment systems, but these emissions also are expected to be small. Finally, as discussed further in section 5 of this report, the uncertainty of the estimates obtained using this

approach for any individual facility is expected to be higher than for more site-specific approaches.

The total emissions include both process-based emissions and emissions from combustion of supplemental fuel. For the purposes of this analysis, process-based emissions take many forms. For example, CO₂ formed by direct oxidation of ethylene in an ethylene oxide reactor or the direct oxidation of propylene in an acrylonitrile reactor are process-based emissions. Methane in the off-gas from an ethylene process is a process-based emission if it is released unburned from process vents or a combustion unit. Similarly, CO₂ created by burning the off-gas from any petrochemical process is a process-based emission. Carbon dioxide emissions from an aerobic wastewater treatment system and the direct release of CO₂ and CH₄ in equipment leaks are other forms of process-based emissions. The only emissions that are not process-based are emissions (CO₂, CH₄, and N₂O) derived from the combustion of supplemental fuel. Based on available data it is difficult to estimate the percentage of emissions from specific process vents, supplemental fuel-fired combustion units, equipment leaks, and wastewater treatment systems for each process. However, it is clear that process-based emissions dominate for acrylonitrile, ethylene, and ethylene oxide processes. Both process-based and combustion-based emissions appear to be significant for carbon black and methanol processes. As noted in section 2 of this report, essentially all GHG emissions from ethylene dichloride processes are from combustion of supplemental fuel. Equipment leak and wastewater emissions (although considered to be a form of process-based emissions) are both estimated to be less than 1 percent of the total CO₂e emissions from petrochemical production.

4.0 OPTIONS FOR REPORTING THRESHOLD

The following four options were evaluated as potential reporting thresholds for petrochemical facilities:

- Option 1. All petrochemical facilities with facility-wide GHG emissions exceeding 1,000 mtCO₂e report
- Option 2. All petrochemical facilities with facility-wide GHG emissions exceeding 10,000 mtCO₂e report.
- Option 3. All petrochemical facilities with facility-wide GHG emissions exceeding 25,000 mtCO₂e report
- Option 4. All petrochemical facilities with facility-wide GHG emissions exceeding 100,000 mtCO₂e report

Table 7 illustrates the process and combustion-based GHG emissions from petrochemical operations at facilities that would be covered under the four options. Based on our analysis, 84 of the 88 petrochemical facilities have estimated GHG emissions greater than 100,000 metric tons of CO₂ equivalent (mtCO₂e)/yr, 87 of the 88 facilities have estimated GHG emissions greater than 25,000 mtCO₂e/yr, and all 88 facilities have estimated GHG emissions greater than 1,000 mtCO₂e/yr. This information shows the various thresholds do not have a significant effect on the amount of emissions or the number of facilities that would be covered. Given the uncertainty in the emissions estimation procedure, we are not certain that even the smallest

facilities have emissions as low as estimated. Furthermore, the emissions presented in Table 7 are not the total emissions from petrochemical facilities because many of the 88 facilities also have operations that are part of other source categories. For example, some petrochemical operations occur at petroleum refineries; the emissions from the refining operations at these facilities are not included in Table 7. In addition, numerous petrochemical manufacturing facilities produce other chemicals that are not subject to reporting. These facilities may have combustion sources for the non-petrochemical production processes that are not included in Table 7. Similarly, some petrochemical facilities may also make ammonia, hydrogen, or other products, but emissions from these non-petrochemical processes are not shown in Table 7.

Table 7. Thresholds for GHG evaluation.

Source Category	Threshold Level, mtCO ₂ e/yr	Total National Emissions (mmt CO ₂ e)	Number of Facilities	Emissions Covered		Facilities Covered	
				mmt CO ₂ e/year	Percent	Number	Percent
Petrochemical production	>1,000	54.83	88.0	54.83	100.0	88	100.0
	>10,000	54.83	88.0	54.82	99.98	87	98.9
	>25,000	54.83	88.0	54.82	99.98	87	98.9
	>100,000	54.83	88.0	54.82	99.7	84	95.5

5.0 OPTIONS FOR MONITORING METHODS

Three options were considered for estimating process-based emissions and emissions from combustion sources that supply energy to petrochemical processes. The options reflect a range of monitoring methodologies, and progressing from one option to the next decreases the amount of uncertainty in the emission estimates. Although other source categories may apply at certain petrochemical production facilities, such as petroleum refinery units or onsite wastewater treatment units, options for estimating emissions from these source categories are described in the technical support documents for the applicable source categories. Procedures for estimating combustion source emissions, however, are estimated as part of these options because process and combustion operations are closely related in this source category.

Option 1: Apply a default emission factor based on the type of process and an annual activity rate (measured or estimated production rate).

Option 2: Perform a carbon balance using all feedstocks and products/byproducts to estimate emissions containing CO₂ derived from the feedstocks, and measure flow and carbon content of supplemental fuel used in combustion devices that supply energy to a petrochemical process.

Option 3: Perform direct and continuous measurement of CO₂ emissions from each stack (process vent or combustion source, except flares) using a continuous emission monitoring system (CEMS) for CO₂ concentration and stack gas volumetric flow rate based on the requirements in 40 CFR part 75, and estimate emissions from flares using the same procedures as described for petroleum refineries (Subpart Y).

5.1 Review of existing programs and methodologies

Methodologies were reviewed for measuring or estimating GHG emissions for the petrochemical production source category developed by different international groups, U.S. agencies, and others. The 2006 IPCC Guidelines for National Greenhouse Gas Inventories (Chapter 3.9 *Petrochemical and Carbon Black Production*) provided methodologies for these processes.¹ Further, the instructions for Form EIA-1605 from the Department of Energy's Voluntary Reporting of Greenhouse Gases Program recommend using either direct measurement or IPCC default factors to estimate methane emissions from petrochemical production and CO₂ emissions from methanol production. No regulations apply to reporting greenhouse gas emissions from petrochemical processes.

5.2 Discussion of options for monitoring methods

5.2.1 Option 1

Option 1 is the same as the IPCC Tier 1 approach. Emissions would be calculated using default CO₂ and CH₄ emission factors published by IPCC. These emission factors express the emissions per metric ton of product produced. Thus, the option is easy to implement because the only activity data needed in the calculation are plant-specific production rates. In addition, the cost to implement the option should be low because the monitoring equipment needed to measure the volume or mass of product is likely already being used. A disadvantage of using default values instead of direct measurements is that the level of uncertainty is high; default factors cannot reflect site-specific differences in characteristics such as the type of feedstock, operating conditions, catalyst selectivity, and thermal/energy efficiencies. Furthermore, these default factors exclude emissions from process flares and in the case of acrylonitrile, exclude combustion of auxiliary fuel for process waste gas energy recovery as well. Thus, the use of default values is more appropriate for sector wide or national total estimates from aggregated activity data than for determining emissions from a specific facility.

5.2.2 Option 2

Option 2 is derived from IPCC Tier 2, though unlike the IPCC approach, Option 2 does not consider supplemental fuel as a feedstock in the carbon balance. The supplemental fuel is not included as a feedstock because these fuels generally do not mix with process fluids, which means emissions from combusting them can readily be estimated using procedures for combustion sources.

Inputs for the carbon balance are the flow and carbon content of each feedstock and product. The difference in carbon content between inputs and outputs is calculated as CO₂ emissions, which means that any carbon that is converted to carbon monoxide or CH₄ is assumed to be CO₂. Any hydrocarbons that are lost through equipment leaks or discharged to wastewater are also assumed to be converted to CO₂ emissions. Products include the intended petrochemical as well as byproducts and organic wastes. Feedstocks are generally only a single chemical at any

given time, but the feedstock may vary over time (particularly for ethylene production). Several potential issues with this option are described below.

Assuming carbon in VOC equipment leaks is lost as CO₂ means the carbon balance approach potentially overstates CO₂ emissions. To evaluate the significance of the error introduced by this assumption, we estimated VOC emissions from a model ethylene facility. We assumed this average facility has approximately 90,000 pumps, valves, and connectors. Total VOC emissions from this model facility were estimated to be about 140 Mg/yr based on operation for 8,400 hours/yr and using emission factors that were used to estimate VOC emissions from these types of equipment in analyses for the equipment leak NSPS in 40 CFR part 60, subpart VVa. For this analysis, we assumed that the average carbon fraction in the numerous products from an ethylene process can be characterized by the carbon fraction in propylene. As a result, if the carbon in the hydrocarbon equipment leaks is assumed to be lost as CO₂, then the CO₂ emissions from the model process are overstated by about 440 Mg/yr. Extrapolating to the 39 ethylene facilities nationwide results in estimated nationwide emissions of about 17,000 Mg/yr of CO₂. This represents only about 0.04 percent of the total estimated CO₂e emissions from ethylene production. Thus, VOC emissions in equipment leaks can be safely ignored when using a carbon balance to estimate CO₂ emissions, even if facilities are not controlling VOC emissions from equipment leaks to the level required by New Source Performance Standards in 40 CFR part 60, subpart VVa (or National Emission Standards for Hazardous Air Pollutants in several subparts in 40 CFR part 63). VOC emissions for other petrochemical processes are expected to be similar or of even lower magnitude because other petrochemical processes are expected to have fewer pieces of equipment.

Under this option, emissions from combustion of process off-gas to supply energy to the process are calculated as process emissions because the process off-gas is not a product (the option does not include these emissions in estimates of emissions from combustion sources because there is no easy way to exclude them from the carbon balance). A potential issue with this approach, however, is that the carbon balance calculates only CO₂ emissions, but not CH₄ and N₂O emissions, from the combustion of process off-gas. As a result, total CO₂e emissions are potentially understated, particularly since the GWPs of CH₄ and N₂O are much higher than for CO₂. Adding to the potential underestimation is the fact that any CH₄ emissions from unreacted CH₄ feedstock or unrecovered CH₄ byproduct are assumed to be CO₂. However, the underestimation in the overall CO₂e emissions estimate is expected to be small because the default emission factors for CH₄ and N₂O from the combustion of refinery gas (comparable to off-gas from petrochemical processes) are approximately 5 orders of magnitude lower than the default emissions factor for CO₂. Furthermore, although section 3.0 of this report indicates that about 5 percent of total CO₂e emissions are estimated to be from CH₄, an unknown portion of these emissions is from combustion of supplemental fuels in combustion units. Combustion of supplemental fuels does not contribute to the potential underestimation in total CO₂e because CH₄ and N₂O emissions from the combustion of supplemental fuels are estimated under this option in accordance with the procedures for combustion sources.

The uncertainty of emissions estimated using this option will depend on the accuracy of flow and carbon content measurements and the fraction of input carbon that ends up in products. A very small uncertainty in any of these measurements could produce large uncertainty in the

emissions estimate. If a large fraction of carbon from the feedstock ends up in the product(s), this could even result in negative emissions estimates. For most petrochemical processes, the amount of feedstock carbon that is emitted is estimated to be fairly high--between 15 and more than 30 percent. For the direct chlorination process to produce ethylene dichloride, however, only 2.5 percent of the input carbon may not end up in products. Carbon dioxide emitted from other processes may contain about 5 percent to 6 percent of the carbon in the feedstock. Typically, it is anticipated that compositional analyses and carbon content methods will be accurate to plus or minus 1 percent and flow measurements will be accurate to plus or minus 5 percent. Given that sales are based on the amount of material sold, the accuracy of product flow and compositional analyses may be better than these rates. Table 8 shows the estimated uncertainties associated with the mass balance approach for each of the petrochemical processes, assuming 2 percent uncertainty in the input and output flow measurements, 1 percent uncertainty in the inlet carbon content measurement, and 0.1 percent uncertainty in the product carbon content measurement. For processes that have high product carbon yields, such as ethylene dichloride, the mass balance approach has significant uncertainties.

5.2.3 Option 3

Option 3 would require all process vent emissions to be routed to one or more stacks for direct and continuous measurement of CO₂ emissions from each process vent stack (except flares) and each combustion source stack (i.e., combustion for energy purposes). Process vent stacks include uncontrolled stacks as well as stacks following emission control devices such as thermal incinerators (even if heat is recovered from the exhaust gas) and flares. For flares, this option requires emissions from combustion of the routine flare gas to be based on annual fuel consumption (based on company records), a default higher heating value (HHV) for the fuel, and a fuel-specific emission factor. This calculation method 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, this option requires a separate engineering calculation of the GHG emissions from flares that occur during SSM events. In addition to using CEMS to estimate CO₂ emissions from combustion sources, CH₄ and N₂O emissions from combustion sources would be estimated using applicable procedures for combustion sources, as described in the Technical Support Document for Combustion Sources (EPA-HQ-OAR-2008-004). Unlike Option 2, emissions from the combustion of both process off-gas and supplemental fuels would be estimated using the procedures for combustion sources. The uncertainty of this option is estimated to be about 8 percent, assuming uncertainty in measurements for stack velocity, stack cross-sectional area, CO₂ concentration, temperature, pressure, and moisture content of 5 percent, 2 percent, 5 percent, 0.5 percent, 1 percent, and 3 percent, respectively. This option is similar to the IPCC Tier 3 approach, except that the IPCC guidelines indicate that process vent emissions may be either estimated or measured, and the IPCC methods for estimating CH₄ emissions from flares are more rigorous.

Table 8. Uncertainty Calculations for Option 2 for Petrochemical Processes.

Petrochemical	Percentage of carbon in feedstock that ends up in product(s)	Data used to estimate percentage of input carbon that ends up in products¹	Estimated uncertainty of emissions estimated using mass balance
Acrylonitrile	76	0.83 ton CO ₂ per ton acrylonitrile when HCN is also recovered	12%
Ethylene	76 to 94 (used 85%)	Fraction in products depends on feedstock: 0.267 ton methane produced (and burned) per ton of propane feedstock. 0.061 ton methane produced (burned) per ton of ethane feedstock	19%
Ethylene dichloride	93.5 to 97.5+ (used 95%)	Fraction in products depends on process: for direct chlorination, 0.29 ton ethylene yields 1 ton EDC (and some of what is lost may really be hydrocarbons not CO ₂) for oxychlorination, 0.302 ton ethylene yields 1 ton EDC	58%
Ethylene oxide	71 to 85 (used 78%)	Fraction depends on process and catalyst selectivity: for lowest selectivity, 0.9 ton ethylene yields 1 ton EO; for highest selectivity, 0.75 ton ethylene yields 1 ton EO	12%
Methanol	67	According to IPCC, 36.5 GJ from natural gas needed to produce 1 metric ton of methanol, 15.3 kg C per GJ of natural gas, and 0.67 metric ton of CO ₂ produced per metric ton of methanol. This includes natural gas that is burned as well as natural gas converted in reformer. (Note that when synthesis gas is produced by partial oxidation of coal or natural gas, the fraction of carbon in the feedstock that ends up in the methanol may be different.)	8%
Carbon black	58	As for methanol, only factors are for CO ₂ per ton of product: 2.62 ton CO ₂ per ton of carbon black produced. So if carbon black is all carbon and the carbon in CO ₂ and carbon black accounts for all carbon output, then 58 percent of the carbon input ends up in the carbon black.	6%

6.0 MISSING DATA

A complete record of all measured parameters used in GHG emissions calculations is required. Therefore, whenever a quality-assured value of a required parameter is unavailable, a substitute data value for the missing parameter must be used in the calculations. The procedures for estimating missing data vary based on the required monitoring method. In all cases at least 75 percent of all data must be captured on an annual basis (i.e., substitute values may be estimated for no more than 25 percent of required measurement values).

6.1 Option 2

The recommended procedures for estimating substitute values to use in place of any missing feedstock and product flow and carbon content data are the same as for missing fuel flow and carbon content data, which are provided in the TSD for stationary fuel combustion sources. In addition, the same procedures are recommended to estimate missing supplemental fuel flow and carbon content data. For missing carbon content data, the substitute data value would be the arithmetic average of the quality-assured values of that parameter immediately preceding and immediately following the missing data incident. If, for a particular parameter, no quality-assured data are available prior to the missing data incident, the substitute data value would be the first quality-assured value obtained after the missing data period. For missing flows, the substitute value would be the best available estimate of the flow rate based on all available process data. The owner or operator would be required to keep records of the procedures used for all such estimates.

6.2 Option 3

Required measurement data under Option 3 are the CO₂ emissions concentration and the gas stream flow rate for each CEMS. Total fuel flow and possibly the higher heating value of the fuel are also required for each combustion unit. Recommended procedures for estimating missing values for these parameters are the same as for units using Tier 4 in the general stationary fuel combustion source category. For missing concentration data or fuel heating value, the substitute data value would be the arithmetic average of the quality-assured values of that parameter immediately preceding and immediately following the missing data incident. If, for a particular parameter, no quality-assured data are available prior to the missing data incident, the substitute data value would be the first quality-assured value obtained after the missing data period. For missing stack and fuel flow rates, the substitute value would be the best available estimate of the flow rate based on all available process data. The owner or operator would be required to keep records of the procedures used for all such estimates. An alternative to the recommended approach would be to implement the procedures described in Part 75.35(a), (b), and (d).

7.0 QUALITY ASSURANCE AND QUALITY CONTROL REQUIREMENTS

Facilities must conduct quality assurance and quality control (QA/QC) of the data used in calculating GHG emission estimates. All facilities are encouraged to prepare an in-depth quality assurance and quality control plan that contains checks on all information used to determine the GHG emissions, such as data accuracy (e.g. equipment calibration and data repeatability) and the calculations performed to estimate the GHG emissions (e.g. to ensure that there are no computational errors). Thorough QA/QC records should be kept, and these should be made available for inspection upon request. Examples of QA/QC procedures specific to the petrochemical source category are listed below. Other applicable procedures may be found in the TSD for stationary fuel combustion sources.

7.1 Monitoring of Flow and Composition

For facilities using the mass balance method, Option 2, the owner or operator must document the procedures used to ensure the accuracy of all measurements made in monitoring flow and composition of the feed and product streams, such as:

- Measurement of the mass rate of each solid feedstock and product, and volume of each gas and liquid feedstock and product,
- Calibration of all weighing equipment and measurement devices, both upon initial compliance and at regular increments thereafter,
- Weekly determination of the carbon content of the feedstock and product or of the composition by gas chromatograph,
- Documentation of accuracy of weighing equipment and measurement devices, and
- Documentation of equipment maintenance activities.

7.2 CEMS

Applicable QA/QC procedures for CEMS would be the same as for units complying with the Tier 4 requirements for stationary fuel combustion sources. These procedures include those that are related to: initial certification of the CO₂ and stack gas flow monitors, periodic calibrations and audits to ensure the continued accuracy of CO₂ monitors and flow meters, acquiring and recording data, computing emissions and other pertinent procedures. In addition, QA/QC procedures for the fuel flow rate and heating value measurements would be the same as for any other stationary combustion sources, as described in the TSD for stationary fuel combustion sources.

8.0 REFERENCES

1. Intergovernmental Panel on Climate Change. 2006 IPCC Guidelines for National Greenhouse Gas Inventories, Volume 3: Industrial Processes and Product Use. Chapter 3: Chemical Industry Emissions. Prepared by the National Greenhouse Gas Inventories Programme. Eggleston, H.S., Buendia L., Miwa K., Ngara T. and Tanabe K. (eds). Published: IGES, Japan. 2006.
2. "Locating and Estimating Air Emissions from Sources of Acrylonitrile." United States Environmental Protection Agency. EPA-450/4-84-007a. March 1984.
3. "Acrylonitrile (ACN) Uses and Market Data." June 2007.
<http://www.icis.com/v2/chemicals/9074882/acrylonitrile/uses.html>
4. "Acrylonitrile." August 2001. <http://www.the-innovation-group.com/ChemProfiles/Acrylonitrile.htm>
5. SRI International. 2005 Directory of Chemical Producers, United States of America. Menlo Park, California.

6. "Chemical Industry News from the US.: October 2005".
<http://www.cheresources.com/chexpress/chexpress18.shtml>
7. "INEOS Nitriles announces acrylonitrile capacity expansion." Press Release. February 26, 2007. http://www.ineos.com/new_item.php?id_press=153
8. "AP-42 Carbon Black Production, 6.1 Carbon Black." Organic Chemical Process Industry. May 1983.
9. "Carbon Black." June 2002. <http://www.the-innovation-group.com/ChemProfiles/Carbon%20Black.htm>
10. Allen, Raymond R. "Title V Major Modification and Prevention of Significant Deterioration (PSD) Air Permit Application Alternative Feedstocks and Fuels Project, Columbian Chemicals Company, North Bend Carbon Black Plant, Agency Interest No. 4998, Permits Nos 2660-00005-V3 and PSD-LA-580(M-4)." State of Louisiana Department of Environmental Quality. Dec. 7, 2006.
11. Brown, Chuck Carr. "Part 70 Operating Permit, Cabot Corp-Canal Plant, Cabot Corporation, Centerville, St. Mary Parish, Louisiana." State of Louisiana Department of Environmental Quality. 2006.
12. "Ethylene." Sept. 2003. <http://www.the-innovation-group.com/ChemProfiles/Ethylene.htm>
13. "International Survey of Ethylene From Steam Crackers-2007." Oil & Gas Journal. July 16, 2007.
14. "Ethylene Dichloride." Nov. 2003. <http://www.the-innovation-group.com/ChemProfiles/Ethylene%20Dichloride.htm>
15. "Locating and Estimating Air Emissions from Sources of Ethylene Dichloride." United States Environmental Protection Agency. EPA-450/4-84-007d. March 1984.
16. "Ethylene Oxide." April 2005. <http://www.dow.com/ethyleneoxide/news/20050405c.htm>
17. "Ethylene Oxide in the US." Focus on Surfactants. Elsevier Science. Vol. 2007, Issue 8. August 2007, p. 3-4.
18. "Ethylene Oxide." August 2001. <http://www.the-innovation-group.com/ChemProfiles/Ethylene%20Oxide.htm>
19. "Locating and Estimating Air Emissions from Sources of Ethylene Oxide." United States Environmental Protection Agency. EPA-450/4-84-007L. September 1986.
20. "Global Methanol Capacity." 2006.
<http://www.methanol.org/pdf/WorldMethanolPlantsEndOf2006.pdf>

21. "Methanol." December 2002. <http://www.the-innovation-group.com/ChemProfiles/Methanol.htm>
22. "Vinyl Acetate Monomer (VAM)."
<http://www.lyondellbasell.com/Products/ByCategory/basic-chemicals/Acetyls/VinylAcetateMonomer%28VAM%29/>
23. "Big synthetic fuel plant exploits design options." Chem. Eng. News, Vol/Issue 58:44. Nov. 1980. http://www.osti.gov/energycitations/product.biblio.jsp?osti_id=6281435
24. Brown, Chuck Carr. "Operating Permit Renewal, Geismar Plant, Praxair Inc., Geismar, Ascension Parish, Louisiana." State of Louisiana Department of Environmental Quality. 2007.
25. Terra Industries Inc – TRA Annual Report (Regulation S-K, item 405). March 20, 2001. <http://sec.edgar-online.com/2001/03/20/0000950131-01-500179/Section2.asp>
26. Smith, R., Eastman Chemical Company Kingsport Plant Chemicals From Coal Operations 1983-2000. Presented at the 2000 Gasification Technologies Conference, San Francisco, California. October 8-11, 2000.
27. Perry, Myria and Eliason, Daren. "CO2 Recovery and Sequestration at Dakota Gasification Company." Oct. 2004.
http://www.gasification.org/Docs/Conferences/2004/11ELIA_Paper.pdf
28. LeBlanc, J., Schneider, R. and Strait, R. "Chapter 3: Production of Methanol." Methanol Production and Use. Ed. W. Cheng and H. Kung. Marcel Dekker, 1994.
29. Kirk-Othmer Encyclopedia of Chemical Technology. Ed J. Kroschwitz. John Wiley & Sons, Inc, Fourth Edition, Volume 16, 1995. p. 541-549.
30. S. Lee. Methanol Synthesis Technology. CRC Press, Boca Raton, FL, 1990. p. 15-21.
31. Dittus, Miles and Johnson, Dale. "Dakota Gasification Company Great Plains Synfuels Plant, The Hidden Value of Lignite Coal." Gasification Technologies Conference. 2001
32. Clean Coal Technology. Commercial-Scale Demonstration of the Liquid Phase Methanol (LPMEOHTM) Process. April 1999. Topical Report Number 11.
http://www.fossil.energy.gov/programs/powersystems/publications/Clean_Coal_Topical_Reports/topical11.pdf
33. United States Environmental Protection Agency. Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990-2006. EPA 430-R-08-005. April 15, 2008. p. 2-1.

Attachment A

Estimated Equipment Leak Emissions for Ethylene Production

Ethylene process unit (assume subject to 40 CFR part 63, subpart UU)

Types of equipment	Equipment counts	Emission factor, kg/hr/unit
gas valves	19680	0.000203
light liquid valves	12800	0.000232
pumps	224	0.000695
flanges	60000	0.000162

Assumed operating time, hr/yr 8,400

Annual emissions, Mg/yr 141.5

Assume the emissions can be represented as propylene

MW 42
Carbon mass fraction 0.857

Annual CO2 emissions if leaks
were to be captured and burned,
Mg/yr 444.6

Nationwide number of units 39

Nationwide potential CO2 emissions,
Mg/yr 17,339