

**Comments on TransGas Development Systems LLC
Coal-to-Gasoline Plant, Mingo County, West Virginia
Draft Permit R13-2791**

by

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December 17, 2009*

TECHNICAL APPENDIX

*As supplemented by Technical Appendix Section VII submitted to the West Virginia Department of Environmental Protection, Division of Air Quality via electronic mail on December 18, 2009.

TECHNICAL APPENDIX

Supporting assumptions and calculations

I. Particulate Matter Emissions from Flaking Liquid Sulfur

The Applicant submitted several documents describing the production of elemental sulfur in liquid form and states that sulfur can be delivered in liquid or solid form.¹ Yet nowhere in the Application and accompanying documents, Draft Permit or Engineering Evaluation is there a description of and quantification of emissions associated with the production of solid sulfur from liquid sulfur.

Sulfur may be solidified as flakes, slates, prills, nuggets, granules, pastilles, and briquettes. In flaking, molten sulfur cooled on a rotating drum flaker. Drum flaking systems consist of an overflow weir feeder and a steel belt cooler. The heated weir distributes the product over the steel belt and forms a film that is taken up by the running steel belt. The liquid product solidifies to an even layer on the steel belt, which is cooled by spraying water from the underside. Retaining strips of Neoprene or rubber prevent the product from spilling over the edges of the steel belt. At the cooler end, a crusher breaks the solid product layer into small irregular flakes. After leaving the crusher, the flakes are fed into a chute for further processing.

Flaking liquid sulfur is a similar process as drum granulating urea. Using the emission factor for PM_{filterable} for a urea drum granulator (SCC 30104004) given by EPA's FIRE 6.25 database and assuming that the liquid sulfur mass flow rate is at least that of solid sulfur given on page N21 of the Application,² the uncontrolled annual PM_{filterable} emissions associated with flaking the elemental sulfur solution can be calculated as follows:

$$\begin{aligned} & (241 \text{ lb PM/ton of sulfur produced}) \times (\text{ton PM}/2,000 \text{ lb PM}) \times \\ & (2,669.53 \text{ kg solid sulfur/hr}) \times (2.20462 \text{ lb solid S/kg solid S}) \times \\ & (\text{ton solid S}/2,000 \text{ lb solid S}) \times (8,760 \text{ hours/year}) = \end{aligned}$$

3,106.2 tpy of PM_{filterable, uncontrolled} from flaking dried sulfur

¹ See, for example, UHDE, TransGas Development Systems, LLC, CTL Project, Process Description, September 2008, at 25.

² Reported purities are 99.5 to 99.999 wt%; see, e.g., www.chemicaland21.com/arokorhi/industrialchem/inorganic/SULFUR.htm, accessed July 28, 2009 and www.radiochemistry.org/periodictable/elements/16.html, accessed July 28, 2009.

Assuming installation of control equipment on the granulator with 99%, 99.5% or 99.9% control efficiency, the potential controlled emissions of filterable PM from flaking sulfur would be:

$$3,106.2 \text{ tpy of PM}_{\text{filterable, uncontrolled}} \text{ from flaking dried sulfur} \times (1 - n\% \text{ control efficiency}) =$$

99.0% control efficiency: 31.06 tons/year of PM_{filterable, controlled}

99.5% control efficiency: 15.53 tons/year of PM_{filterable, controlled}

99.9% control efficiency: 3.1 tons/year of PM_{filterable, controlled}

Based on the same assumptions and the emission factor from U.S. EPA's FIRE 6.25 database for PM_{10filterable}, the uncontrolled annual PM_{10filterable} emissions associated with drying the elemental sulfur solution can be calculated as follows:

$$(4.82 \text{ lb PM}_{10}/\text{ton of sulfur produced}) \times (\text{ton PM}_{10}/2,000 \text{ lb PM}_{10}) \times (2,669.53 \text{ kg solid sulfur}/\text{hr}) \times (2.20462 \text{ lb solid S}/\text{kg solid S}) \times (\text{ton solid S}/2,000 \text{ lb solid S}) \times (8,760 \text{ hours}/\text{year}) =$$

62.1 tpy of PM_{10filterable, uncontrolled} from flaking dried sulfur

Assuming installation of control equipment on the granulator with 99%, 99.5% or 99.9% control efficiency, the potential controlled emissions of filterable PM₁₀ from flaking sulfur would be:

$$62.1 \text{ tpy of PM}_{10\text{filterable, uncontrolled}} \text{ from flaking dried sulfur} \times (1 - n\% \text{ control efficiency}) =$$

99.0% control efficiency: 0.62 tons/year of PM_{10filterable, controlled}

99.5% control efficiency: 0.31 tons/year of PM_{10filterable, controlled}

99.9% control efficiency: 0.1 tons/year of PM_{10filterable, controlled}

II. Particulate Matter Emissions from Loading Solid Sulfur Flakes onto Trucks

The Draft Permit's estimates of particulate matter emissions from transfer points and conveyors fail to account for emissions associated with loading the solid sulfur flakes onto trucks for off-site transport.³ The Application indicates that the Project would produce 25,782 tons/year of

³ See Application, Attachment N at N13.

sulfur.⁴ Assuming a moisture content of 0.25% for the solid sulfur flakes and an 80% control efficiency, emissions from loading trucks with solid sulfur flakes can be estimated as follows:

$$E = k \times 0.0032 \times ((U/5)^{1.3} / (M/2)^{1.4}) \times (1 - \text{control efficiency})$$

where

- E emission factor (lb particulate matter/ton sulfur product)
- k 0.74 particle size multiplier for PM
- k 0.35 particle size multiplier for PM10
- U 7 mph mean wind speed in West Virginia
- M 0.25% moisture content

$$E_{PM} = 0.0674 \text{ lb PM}_{\text{uncontrolled}}/\text{ton sulfur}$$

$$E_{PM10} = 0.0319 \text{ lb PM10}_{\text{uncontrolled}}/\text{ton sulfur}$$

PM emissions:

$$(0.0674 \text{ lb PM}_{\text{uncontrolled}}/\text{ton sulfur}) \times (25,782 \text{ tons/year}) \times (\text{ton}/2,000 \text{ lb}) \times (1-0.8) =$$

$$\mathbf{0.174 \text{ tons PM}_{\text{controlled}}/\text{year}}$$

$$\text{PM10 emissions: } (0.0319 \text{ lb PM10}_{\text{uncontrolled}}/\text{ton sulfur}) \times (25,782 \text{ tons/year}) \times (\text{ton}/2,000 \text{ lb}) \times (1-0.8) =$$

$$\mathbf{0.082 \text{ tons PM10}_{\text{controlled}}/\text{year}}$$

⁴ Application, Attachment N at N14: (2,669.53 kg/hour sulfur) × (2.205 lb/kg) × (8,760 hours/year) = 25,782 tons/year sulfur.

III. TANKS 4.0.9d Output for Methanol Storage Tank

TANKS 4.0.9d Emissions Report - Summary Format Tank Identification and Physical Characteristics

Identification

User Identification: IFR Methanol Tank
 City: Charleston
 State: West Virginia
 Company: TransGas Development
 Type of Tank: Internal Floating Roof Tank
 Description:

Tank Dimensions

Diameter (ft): 100.00
 Volume (gallons): 2,000,000.00
 Turnovers: 350.00
 Self Supp. Roof? (y/n): Y
 No. of Columns: 0.00
 Eff. Col. Diam. (ft): 0.00

Paint Characteristics

Internal Shell Condition: Light Rust
 Shell Color/Shade: White/White
 Shell Condition: Good
 Roof Color/Shade: White/White
 Roof Condition: Good

Rim-Seal System

Primary Seal: Mechanical Shoe
 Secondary Seal: Shoe-mounted

Deck Characteristics

Deck Fitting Category: Typical
 Deck Type: Welded

Deck Fitting/Status

Quantity

Access Hatch (24-in. Diam.)/Unbolted Cover, Ungasketed	1
Automatic Gauge Float Well/Unbolted Cover, Ungasketed	1
Roof Leg or Hanger Well/Adjustable	32
Sample Pipe or Well (24-in. Diam.)/Slit Fabric Seal 10% Open	1
Vacuum Breaker (10-in. Diam.)/Weighted Mech. Actuation, Gask.	1
Meterological Data used in Emissions Calculations: Charleston, West Virginia (Avg Atmospheric Pressure = 14.25 psia)	

TANKS 4.0.9d
Emissions Report - Summary Format
Liquid Contents of Storage Tank

IFR Methanol Tank - Internal Floating Roof Tank
Charleston, West Virginia

Mixture/Component	Month	Daily Liquid Surf. Temperature (deg F)			Liquid Bulk Temp (deg F)	Vapor Pressure (psia)			Vapor Mol. Weight	Liquid Mass Fract.	Vapor Mass Fract.	Mol. Weight	Basis for Vapor Pressure Calculations
		Avg.	Min.	Max.		Avg.	Min.	Max.					
Methyl alcohol	All	56.67	51.31	62.04	55.00	1.2977	N/A	N/A	32.0400			32.04	Option 2: A=7.897, B=1474.08, C=229.13

TANKS 4.0.9d
Emissions Report - Summary Format
Individual Tank Emission Totals

Emissions Report for: Annual
IFR Methanol Tank - Internal Floating Roof Tank
Charleston, West Virginia

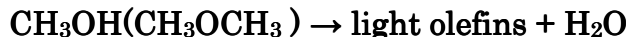
Components	Losses(lbs)				Total Emissions
	Rim Seal Loss	Withdrawl Loss	Deck Fitting Loss	Deck Seam Loss	
Methyl alcohol	122.31	1,563.02	245.39	0.00	1,930.73

IV. Applicability of 40 CFR 60 Subpart NNN

DME is a byproduct created through chemical reaction as follows⁵:



Figure 1 below shows how light olefins are produced in the MTG process as follows:



“Light olefins” is a synonym for light alkenes which include ethylene, propylene, and butene⁶ all of which are 40 CFR 60.667-listed chemicals.

The production rates of propylene and butenes are as follows:⁷
Hydrocarbon⁸ = gasoline production / (0.60) = (87,400 kg/hour) / (0.60) = 145,667 kg/hr

Production of propylene: (0.05 kg/kg hydrocarbon product) × (145,667 kg/hr) = 7,283 kg propylene/hour = 63.8 Gg/yr

Production of butenes: (0.073 kg/kg product) × (145,667 kg/hour) = 10,633 kg/hr = 93.2 Gg/yr

The total amount of NNN-regulated products produced in the MTG process is 157 Gigagram/year (Gg/yr), which exceeds the applicability threshold in 40 CFR 60.660(c)(5).

⁵ Lee, S., Methane and Its Derivatives, Marcel Dekker Inc. (1997) at 297; <http://snipurl.com/tqb5w> [books_google_com].

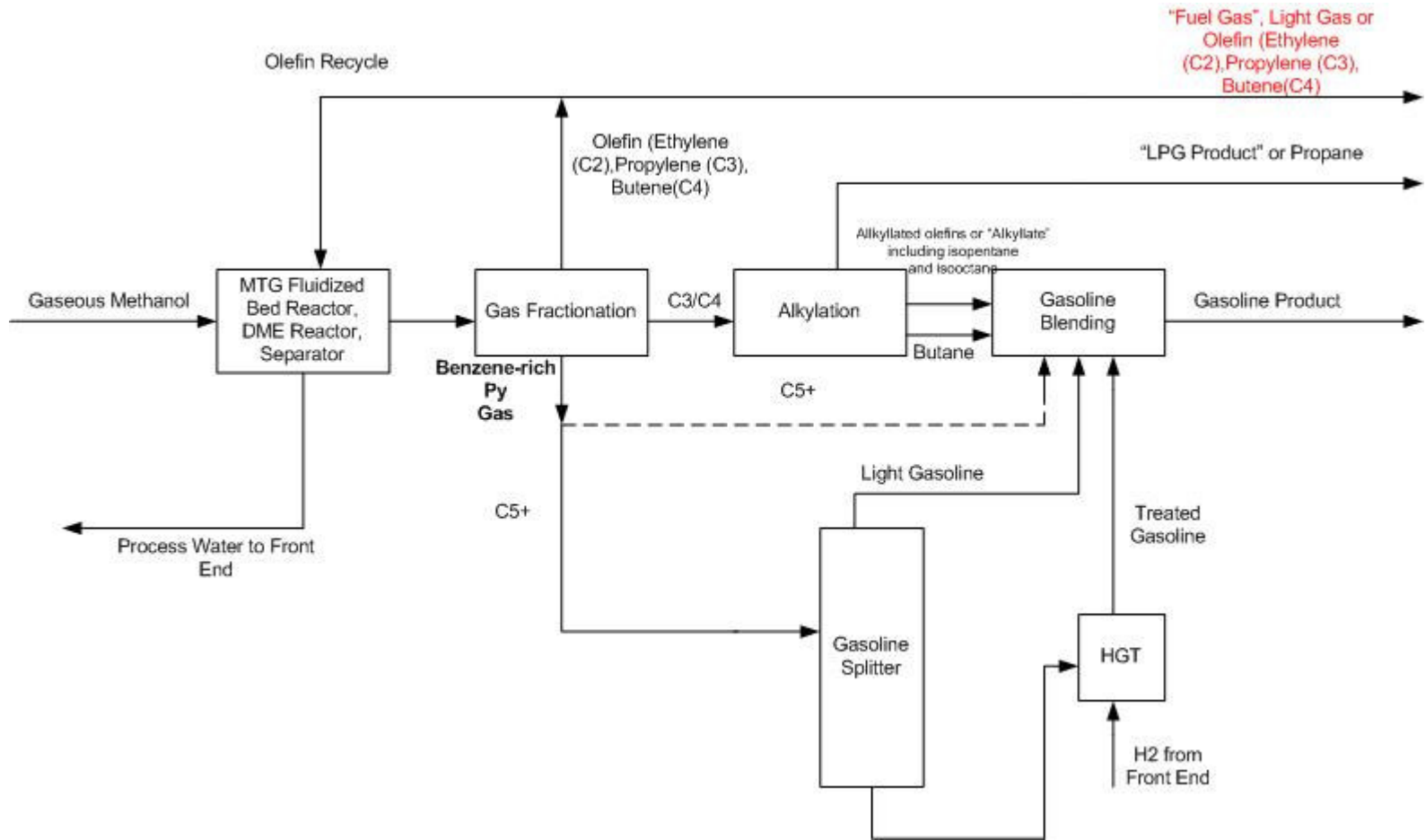
⁶ Wikipedia Online Encyclopedia, Alkenes; <http://en.wikipedia.org/wiki/Alkene>.

⁷ Weight percentages of propylene and butenes in the MTG product are taken from “Selected Technical and Economical Comparisons” Part 5, Chapter 3, Table 3.9 at page 3-30; <http://www.princeton.edu/~ota/disk3/1982/8224/822405.PDF>.

⁸Id. (weight percentage of gasoline).

Figure 1. Udhe MTG and HGT Process Showing Production of Propylene and Butene

Source: DM Biddy, *et al*, eds., *Methane Conversion* (1988) (adapted from Figure 4, p. 278).



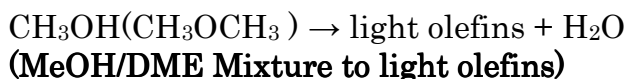
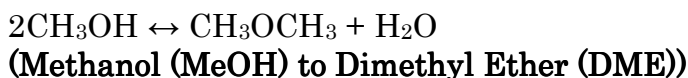
V. Applicability of 40 CFR 61 Subpart J and V

The MTG process produces a gasoline which contains 0.3 vol% of benzene.⁹ TransGas intends to produce 31,500 gallons per hour of gasoline.¹⁰ Therefore, TransGas has the intention of producing and using the following amount of benzene annually:

$$(0.003 \text{ gal benzene/gal gasoline}) \times (31,500 \text{ gal gasoline/hr}) \times (8,760 \text{ hours/year}) = 827,820 \text{ gal/yr of benzene}$$

$$(827,820 \text{ gal benzene/year}) \times (0.8765 \text{ g benzene/cm}^3 \text{ benzene}) \times (2.6417\text{E}+04 \text{ cm}^3/\text{gal}) \times (\text{Mg}/10^6 \text{ g}) = \mathbf{19,168 \text{ Mg benzene/year}}$$

Furthermore, the MTG process has streams which service mixtures containing benzene at 10wt% or greater. The MTG process includes heavy gasoline treatment ("HGT"). The HGT process includes reactions such as dealkylation (deethanizer) or cracking.¹¹ Reactions in the Methanol synthesis and MTG processes, including HGT, can be described as follows:¹²



Light olefins → heavy olefins

Heavy olefins → paraffins + aromatics + naphthenes

⁹Brandl, A., Heinritz, M., Hindman A., McGihon, R., Tabak, S. and Zhao, X., An Alternative Route for Coal to Liquid Fuel: Applying the Exxon Mobil to Methanol to Gasoline (MTG) Process, presented by ExxonMobil and Udhe at the 2008 Gasification Technologies Conference, Washington, D.C., October 5 through 8, 2008, Slide 9.

¹⁰ Application, Appendix N at 21.

¹¹ Bibby, D.M., R.F. Howe, S. Yurchak, Studies in Surface Science and Catalysis, Vol.36, Methane Conversion, Vol. 36, Elsevier Publishing Co. Inc., New York, NY, 1988, at 298; <http://snipurl.com/tqb7x> [books_google.com].

¹² Lee, S., Methane and Its Derivatives, "Chapter 3: Methane Derivatives Via Synthesis Gas", ISBN Marcel Dekker Inc., New York, NY, 1997, at 145; <http://snipurl.com/tqb89> [books_google.com], accessed November 18, 2009.

The mixture of paraffins, aromatics, and naphthenes is commonly referred to as naphtha or crude gasoline.

Gas fractionation is the process for producing olefins (ethylene and other alkenes) from aliphatic hydrocarbons such as methanol/dimethyl ether mixtures. Gas fractionation produces a benzene-rich liquid by-product called “pyrolysis gasoline”. In the Uhde MTG process, the benzene rich stream is used as a gasoline additive or may be sent to the HGT process (see Figure 1). Prior to any alkylation, the pyrolysis gasoline contains **at least 40 wt% benzene**.¹³ Since the MTG process has the capacity to produce or use more than 1000 Mg per year of benzene as a byproduct and there exist streams in the MTG process that service benzene at a mass fraction of 10% or greater, the TransGas MTG process is “in benzene service” per §60.111. TransGas does not qualify for any of the exemptions in 40 CFR 60.110(b) and (c), and TransGas’s MTG process must comply with the provisions of 40 CFR 61.112(a) which require compliance with the leak detection and repair program under 40 CFR Part 61 Subpart V.

VI. Other Underestimated Emissions

Underestimation of Particulate Matter Emissions

1. **The steady-state particulate matter (PM, PM10) emissions from the methanol-to-gasoline process are underestimated**

The “Block Flow Diagram” provided by Uhde indicates that tail gas from the methanol-to-gasoline (“MTG”) process is vented to the [CO₂](#) purification process with process stream 31. The CO₂ purification process vents to the atmosphere at C1. The [CO₂](#) purification process will involve a mixture including coke byproduct, which cannot be controlled to 100% by scrubbing. While TransGas has redacted information indicating the amount of methanol fed to the MTG process, literature indicates that 43.5% of the methanol charged to the MTG process yields hydrocarbons and that 60% by weight of those hydrocarbons are saleable gasoline. Therefore, the charge of methanol to the MTG process can be back-calculated as follows:

$$\text{Charge methanol: } (87,400 \text{ kg/hour}) / (0.435 \times 0.60) = 334,866 \text{ kg/hr}$$

¹³ Nexant ChemSystem’s, Process Evaluation/Research Development Program for the PERP program, Benzene/Toluene (02/03-5)”, October 2003; <http://www.chemsystems.com/reports/search/docs/abstracts/0203-5-abs.pdf>, accessed November 20, 2009.

Coke is estimated to be 0.2% by weight of the methanol charged to the MTG.¹⁴ Based on the mass flow rate of 334,866 kg/hour provided by the Applicant,¹⁵ the emission rate of particulate matter associated with coke byproduct may be calculated as follows:

Uncontrolled coke in vent streams (E1 and E2 or E5):
 $(0.002) \times (334,866 \text{ kg/hour}) \times (2.205 \text{ lbs/kg}) / (2,000 \text{ lbs/ton}) =$
6,467 tons of petroleum coke byproduct as PM

Assuming 99% control efficiency, the controlled emissions of coke are 64.67 tons/year.

Since stream 31 is not shown as having pressure relief devices in Attachment A to the Draft Permit (requiring a closed system on pressure relief devices), stream 31 has the potential to release 64.67 tons of petroleum coke byproduct as PM to the atmosphere.

2. Particulate matter (PM and PM10) emissions are underestimated because they do not include emissions of ammonium sulfate and ammonium carbonate from the CO₂ wash column

TransGas has indicated that the acid gas removal (“AGR”) is synonymous with the “Rectisol wash system,” which consists of a “methanol wash section, recycle gas compression, CO₂ product recovery section (CO₂ wash column or CO₂ stripper), hot generation section, and methanol/water separation”.¹⁶ These processes are shown in process flow diagram 235 of the Application.

The overhead stream from the solvent flash II column is mostly CO₂ with impurities of methanol, H₂S, CO, and hydrogen cyanide (“HCN”). Without an additional wash column for the removal of ammonia (“NH₃”) preceding the CO₂ wash column, NH₃ and H₂S will form ammonium sulfide salts¹⁷ (“NH₂COOH”) in the CO₂ wash column. It is evident from this diagram and the process description¹⁹ that TransGas has not applied for the construction of an additional wash column between Solvent Flash II Column and the CO₂ Wash column. Ammonium sulfide is highly unstable and will likely exist as a mixture of NH₃ and ammonium hydrosulfide (“(NH₄)SH”) salts.

¹⁴ www.chemicaland21.com/arokorhi/industrialchem/inorganic/SULFUR.htm, accessed July 28, 2009 and www.radiochemistry.org/periodictable/elements/16.html, accessed July 28, 2009

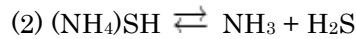
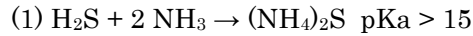
¹⁵ It should be noted that the mass flow rate provided by the Application on electronic page 245 for Stream 6 is less than the sum of Streams 31, 7, 8, and 20 given on electronic page 246. Furthermore, no stream 28 is shown in the accompanying “Block Flow Diagram”.

¹⁶ Application at 15 (electronic page 365).

¹⁷ <http://www.gasification.org/Docs/Conferences/2008/32KEREST.pdf>, “Handling of Trace Components for Rectisol Wash Units” Presented by Tomas Haberle and Ulvi Kerestecioglu in Washington, DC on October 08, 2008 and accessed on 11/16/2009, Slide 21.

¹⁸ <http://en.wikipedia.org/wiki/Carbamate>, “Carbamate”, Wikipedia Online Encyclopedia, Accessed on 11/16/2009

¹⁹ Application, at pages 15 and 16 of the “Process Description” (electronic pages 365 and 366).



Some of these salts will likely become entrained in the stream exiting the top of the CO₂ wash column as particulate matter less than ten microns in diameter. Using equilibrium calculations, the availability of ammonium sulfide salt can be calculated as follows, based on the mass flow rate of process stream 16 (PL16)^{20,21,22,23}:

$$\begin{aligned} & (\text{mol NH}_4\text{SH/mol H}_2\text{S}) \times (5 \text{ mol H}_2\text{S}/10^6 \text{ mol of PL16}) \times \\ & (462,593.08 \text{ kg PL16/hour}) \times (68.154 \text{ g NH}_4\text{SH/mol}) \times (1000\text{g/kg}) \times \\ & (\text{mol PL16}/28 \text{ g PL16}) \times (\text{lb}/453.6 \text{ g}) \times (\text{ton}/2,000 \text{ lb}) \times (8,760 \text{ hours/year}) \\ & = \mathbf{54.36 \text{ tons/year PM}_{10}} \text{ (as ammonium hydrosulfide salt)} \end{aligned}$$

Underestimated NO_x Emissions

3. NO_x emissions from the flare are underestimated because the flow rate is underestimated

The Applicant takes credit for an “industrial standard”²⁴ post-flare NO_x concentration of 250 ppmv. The Department has restricted TransGas to the corresponding pound-per-hour and ton-per-year emission rates associated with a 250 ppmv, exhaust NO_x concentration.

However, calculations of NO_x emissions are based on a flare exhaust rate of 296,000 m³n/hr, whereas other parts of the Application used flare inlet flow rates with exhaust pollutant concentrations.²⁵

²⁰ The mass flow rate of Process Line 16 is reported on page 22 (electronic page 246) of Appendix N, to the “(Redacted Application) Regulation 13 Permit Application for the Construction of a Coal to Gasoline Plant in Mingo County, West Virginia” Prepared for TransGas Development Systems by Potesta and Associates, Inc. and submitted to the WVDEP on December 2008

²¹ Lurgi, co-creators of the Rectisol process, reports that the sulfur content on the CO₂ byproduct of the Rectisol process is approximately 5 ppm in the document entitled “Lurgi’s MPG Gasification Plus Rectisol Gas Purification – Advanced Process Combination For Reliable Syngas Production Gasification Technologies 2005 San Francisco, October 9 – 12, 2005 prepared by Ulrich Koss and Holger Schlichting of Lurgi AG, Germany

²² The formation of ammonium sulfide requires an excess of ammonia. Therefore, it is assumed that hydrogen sulfide is the limiting reagent in the formation ammonium hydrosulfide.

²³ Due the expected high concentration of CO₂ in Stream Line 16 the average molecular weight of this stream is assumed to be equivalent to that of CO₂.

²⁴ Application, Attachment 2 to Appendix N at 15 (electronic page 305).

²⁵ “Section 3.7: CO₂ acid gas removal: CO assumes equal inlet and outlet flare flow rates by applying a CO “offgas” concentration to the “flue gas rate” or syngas to the flare”.

As demonstrated elsewhere, the Draft Permit condition restricting the flow rate to the flare during startup is neither technically feasible nor practically enforceable. Based on a raw syngas molar flow rate of 62,869 lbmol/hour (639,917 m³n/hour), the NO_x emission rate associated with emission points B2, B3, C2, or E5 at 30 startups per year per gasifier at 1 hour per startup can be calculated as follows:

$$\begin{aligned} & (250 \text{ lb-mol NO}_2) / (10^6 \text{ lb-mol flare exhaust}) \times \\ & (62,869 \text{ lb-mol flare exhaust/gasifier}) \times (46 \text{ lb NO}_2/\text{lbmol NO}_2) \times \\ & (1 \text{ hour/startup}) \times (30 \text{ startups/year}) / (2,000 \text{ lb/ton}) \\ & = \mathbf{10.8 \text{ tons NO}_x \text{ per year}} \end{aligned}$$

Underestimated CO Emissions

4. The steady-state CO byproduct emissions from the methanol-to-gasoline process are underestimated

The Applicant's emission estimates do not properly account for CO emissions from the methanol-to-gas ("MTG") process. Contrary to statements by Uhde on behalf of TransGas on page 13 of "Response on DEP Questions," the "Block Flow Diagram" provided in the same document indicates, that, indeed, there are indeed emissions of MTG tail gas to atmosphere: process stream 31 from the MTG reaction vents to the CO₂ purification process; the CO₂ purification process vents to the atmosphere as process stream 17 through C1.²⁶ The Applicant quantifies CO emissions in process stream 31 by assuming reduction of CO in the CO₂ purification process to 1 ppmv or 0.014 tons/year using catalytic purification. As such, TransGas has estimated total CO emissions from the MTG process (stream C1) at 0.014 tons/year.²⁷ However, TransGas has applied for the CO₂ purification process to be comprised of a CO₂ wash column or catalytic purification.²⁸ The CO₂ purification column uses demineralized water as a scrubbant which favors absorption of highly soluble components in the mixture, such as methanol, over CO. The column has no control efficiency leaving a mixture containing CO.²⁹ The CO/CO₂ mixture in process stream 31 is estimated to be 0.1% by weight of the charge to the MTG process.³⁰

²⁶ Application Attachment N, Uhde, Response on DEP Questions, Section 3.12, page 24 (electronic page 278).

²⁷ Id. at 17.

²⁸ TransGas indicated their intent to use "CO₂ stripping" (synonymous with a CO₂ wash column) "or catalytic purification" in item 1 of Attachment L: CO₂ Purification (CO₂P) of Appendix L to the "(Redacted Application) Regulation 13 Permit Application for the Construction of a Coal to Gasoline Plant in Mingo County, West Virginia" Prepared for TransGas Development Systems by Potesta and Associates, Inc. and submitted to the WVDEP on December 2008

²⁹ Even though Application Attachment N, Uhde, Response on DEP Questions, Section 3.6 at 15 and 16 (electronic page 269 and 270) indicates that the AGR process (CO₂ Rectisol) and the CO₂

While TransGas has redacted information indicating the amount of methanol fed to the process, literature indicates that 43.5% of the methanol charged to the MTG process yields hydrocarbons and that 60% by weight of those hydrocarbons are saleable gasoline. Therefore, the mass flow of methanol to the MTG process can be calculated as follows:

$$\text{Methanol flow to MTG} = (87,400 \text{ kg/hr}) / (0.435 \times 0.60) = 334,866 \text{ kg/hr}$$

Based on the methanol mass flow rate of 334,866 kg/hr,³¹ the amount of CO/CO₂ mixture directed to CO₂ purification may be calculated as follows:

$$\text{CO/CO}_2 \text{ mixture in process stream 31: } (334,866 \text{ kg/hr}) \times (0.001) \times (0.4536 \text{ kg/lb}) \times (2,000 \text{ lb/ton}) \times (8760 \text{ hours/year}) = 3,233 \text{ tons/year}$$

With average bed temperatures for the MTG process of 775 F³² (686°K) the concentration of CO in the stream to CO₂ purification is expected to be approximately 2.5 mol% according to concentration versus temperature data for Boudouard's Equilibria³³ and data from other sources³⁴:

$$\text{CO in process stream 31: } (0.025 \text{ lb-mol CO/lb-mol mixture}) \times (3,233 \text{ tons/year}) \times (28 \text{ lb CO/lb-mol CO}) / ((0.025 \times 28 \text{ lb CO/lb-mol CO}) + (1-0.025) \times (44 \text{ lb CO}_2\text{/lb-mol CO}_2)) = \mathbf{67.2 \text{ tons per year of CO}}$$

purification process (CO₂ wash column) used by TransGas to purify CO₂ can both reduce CO to less than 1 ppmv, the same document at 18 (electronic page 368) and process flow diagram 235 "CO₂/H₂S removal" (electronic page 37) of the same document indicate that CO₂ purification is accomplished through a CO₂ wash column which separates CO₂ from methanol due to methanol's volatility. The CO₂ wash column or Rectisol wash column does not involve any "state-of-the-art" catalytic process. The "methanol-rich" stream, which contains CO, is flashed to remove CO and CO is sent back to the gasifier as sluicing gas, process stream 26, while the other CO₂-rich vent stream, c1, containing CO impurities is vented to atmosphere.

³⁰ Ibid

³¹ It should be noted that the mass flow rate provided by TransGas' application on page 245 for Stream 6 is less than the sum of Streams 31, 7, 8, and 20 given on page 246. Furthermore, no stream 28 is shown in the accompanying "Block Flow Diagram" or Section 4.1 (electronic page 285). Either these values are in error or this is not a steady-state process.

³² <http://www.princeton.edu/~ota/disk3/1982/8224/822405.PDF>, "Selected Technical and Economical Comparisons" Part 5, Chapter 3, Table 3.9, page 3-30, Accessed 07/25/2008.

³³ http://www.jfe-21st-cf.or.jp/chapter_2/2b_2_img.html, JFE 21st Century Foundation, "2B(2) Equilibria among C, CO, and CO₂ (Boudouard's Equilibria)

³⁴ Handling of Trace Components for Rectisol Wash Units, presented by Tomas Haberle and Ulvi Kerestecioglu in Washington, DC, on October 8, 2008 at slide 26 indicates that CO₂ purity is 98.5% or more; <http://www.gasification.org/Docs/Conferences/2008/32KEREST.pdf>, accessed November 16, 2009.

Due to the infinite solubility of methanol in water, little of the CO/CO₂ mixture will be contained in the bottoms, methanol-rich stream from the CO₂ wash column to be flashed off and used as sluicing gas in the gasifier. Therefore, most of the CO/CO₂ in process stream 31 will be emitted with stream c1.

Since C1 is not shown as a pressure relief device in Attachment A to the Draft Permit (which requires a closed system on pressure relief devices) C1 has the potential to release 67.2 tons of CO to the atmosphere. In addition to the other process emissions of CO estimated by the Applicant, the total emissions of CO from the TransGas facility amount to 136.4 tons/year.³⁵ Therefore, the facility is a major source for CO emissions.

5. The fugitive CO emissions from the gasification process are underestimated because Applicant assumed that the stream was composed of organic compounds only

The Applicant estimated fugitive equipment leaks of CO using “Approach 1: Average Emission Factor” from EPA 453/R-95-017, “Protocol for Equipment Leak Emission Estimation” (1995). The Applicant discounted leak emissions for “connectors” by 30%, indicating that this is the mass concentration of carbon monoxide in the entire gaseous stream following gasification and including scrubbing.³⁶ However, this stream will also contain inorganics and methane. In accordance with EPA guidance, the leak emission of carbon monoxide must be calculated as a percentage of the concentration of the stream that is organic excluding methane, not 100%, as follows:³⁷

$$E_x = E_{\text{TOC}} \times \text{WP}_x / \text{WP}_{\text{TOC}}$$

where

E_x = mass emissions of organic chemical “x” from the equipment (kg/hour);

E_{TOC} = The TOC mass emissions from the equipment (kg/hour) calculated from either the average emission factor, screening ranges, EPA correlation, or unit-specific correlation approaches;

WP_x = The concentration of organic chemical x in the equipment in weight percent; and

WP_{TOC} = The TOC concentration in the equipment in weight percent.

³⁵ (69.26 tons CO/year) + (67.2 tons CO/year) =

³⁶ Application, Attachment 3 to Attachment N at 02 (electronic page 308).

³⁷ U.S. Environmental Protection Agency, Preferred and Alternative Methods For Estimating Fugitive Emissions From Equipment Leaks, November 1996, Volume II: Chapter 4 at 4.3-6.

The facility's raw syngas stream has a worst-case TOC (excluding methane) concentration of only 63 mol%³⁸ (79% by weight), not 10% by weight. Furthermore CO concentrations in raw syngas are approximately 60 mol% (73%), not 30% by weight. Scrubbers following gasifiers do not have any efficiency for removing CO. CO will not be mitigated until and unless, under SSM conditions, the gasified stream reaches the flare. Therefore, the connectors between the gasifier exhaust and the scrubber exhaust will service a stream containing 73% by weight CO. The Applicant cannot assume that only 30% of the equipment leak is CO for this group of components.

While it is true that Draft Permit Condition No. 4.1.9.2 requires leak detection and repair ("LDAR") programs for non-welded connectors, the control efficiency associated with an LDAR depends, in part, on how the leak is defined for a given pollutant.³⁹ The Department has cited a 10,000 ppmv leak detection definition that was developed for organic compounds, not CO, using a flame ionization detector ("FID"). In fact, CO leak monitoring would require the use of a non-dispersion infrared sensor ("NDIR").⁴⁰ Therefore, TransGas could have numerous leaks before a 10,000 ppmv reading is obtained on an FID. Because no monitor suitable for the measurement of CO leaks is required in the permit, Condition No. 4.1.9.2 is not practically enforceable for CO, and no control efficiency is warranted for a leak detection and repair programs for CO. The potential and actual CO emissions from this group of components should be calculated as follows:

$$\begin{aligned}
 E_{CO} &= (0.00183 \text{ kg/hour/connector}) \times (500 \text{ connectors}) \times \\
 &(\text{lb}/0.45359237 \text{ kg}) \times (8,760 \text{ hours/year}) \times (\text{ton}/2,000 \text{ lb}) \times (0.73/0.79) \\
 &= \mathbf{8.16 \text{ tons/year}}
 \end{aligned}$$

Underestimated VOC and HAP Emissions

³⁸ The Application made several references to their Puertollano, Spain project as "lessons learnt" (electronic page 269). Page 9 of the Uhde brochure entitled "PRENFLO™ Gasification" indicates that the worst-case, non-methane total organic compound (NMTOC) volume (mole) concentration in raw syngas is as follows:

$$\begin{aligned}
 \text{CO}_2 &= 2.9 \text{ vol\%} \\
 \text{CO} &= \mathbf{59.9 \text{ vol\%}} \\
 62.8 &\approx 63 \text{ vol\% (mol\%)}
 \end{aligned}$$

Using the molar composition given in the same Uhde brochure, the average molecular weight of the raw gas stream is 22.88 lb/lbmol resulting in a weight percent of CO and NMTOC is 73 and 79%, respectively.

³⁹ U.S. Environmental Protection Agency, Preferred and Alternative Methods For Estimating Fugitive Emissions From Equipment Leaks, November 1996, Volume II: Chapter 4 at 4.2-8.

⁴⁰ U.S. Environmental Protection Agency, 40 CFR Part 60, Appendix A, Test Method 10A

6. The steady-state VOC and HAP emissions from the MTG process are underestimated because they do not account for emissions of methanol and dimethyl ether from this process.

Methanol (“MeOH”) is both a VOC and a HAP. Dimethyl ether (“DME”) is a VOC.

Literature indicates that approximately 0.2% by weight of the total outlet streams from the MTG process is a mixture of methanol and DME.⁴¹ This byproduct stream is identified by the Applicant as process stream 31.

The mass flow rate of MeOH/DME mixture may be calculated as follows:

$$\begin{aligned} &\text{Methanol/DME in Vent Streams (E1 and E2 or E5):} \\ &(0.002) \times (344,866 \text{ kg/hour}) (8,760 \text{ hours/year}) / (2,000 \text{ lbs/ton}) \\ &= \mathbf{6467 \text{ tons of MeOH/DME/year}} \end{aligned}$$

While it is true that this stream will be vented to a CO₂ purification system which uses demineralized water to separate volatiles from CO₂, the Department has not required the use of catalytic purification and there is no reactive species included in the demineralized water scrubbing solution of the CO₂ wash column. Therefore, mass transfer of CO₂ contaminants occurs as a function of solubility in the demineralized water.⁴² The solubility of DME is only 328 g/L at 20°C,⁴³ as opposed to an infinite methanol solubility in water.⁴⁴ The vapor pressure of DME is much greater than that of methanol,⁴⁵ so any absorption of DME would quickly

⁴¹ Lee, S., Methane and Its Derivatives, Chapter 3: Methane Derivatives Via Synthesis Gas, Marcel Dekker Inc., New York, NY, 1997 at 147; <http://snipurl.com/tnnug> [books_google_com], accessed November 12, 2009.

⁴² Jaeger Products, Inc., Scrubbing Pollutants from Vent Streams, at 2 and 6 of indicates that mass transfer occurs when “the scrubbing liquid exhibits high solubility for the contaminants in the gas and these migrate from the gas into the liquid” unless “the liquid contains a reactive solute that enhances the degree of absorption by reacting with the contaminant once it dissolves and effectively removing it chemically. This chemical absorption process allows for effective scrubbing of fairly insoluble gases.” Mass transfer is governed by “solubility when no reaction takes place”; <http://www.jaeger.com/Brochure/gasscrubbing.pdf>, accessed on November 18, 2009.

⁴³ Arko Holdings Inc., Dimethyl Ether; <http://www.chemicaland21.com/petrochemical/DIMETHYL%20ETHER.htm>, accessed November 18, 2009.

⁴⁴ Perry, Robert H. and Don W. Green, Perry’s Chemical Engineering Handbook, 7th Ed., Table 2-2 “Physical Properties of Organic Compounds” at 2-40.

⁴⁵ The vapor pressure of methyl alcohol (methanol) is given as 200 mmHg at 34.8°C while the vapor pressure of dimethyl ether is 760 mmHg at temperature of only -23.7°C according to pages 2-67 and 2-70 of Table 2-8 “Vapor Pressure of Organic Compounds, up to 1 atm” in Perry’s Chemical Engineering Handbook, 7th Ed., by Robert H. Perry and Don W. Green.

volatilize.⁴⁶ As such, it can be expected that DME will not be absorbed by the scrubbing solution and will be released to the atmosphere.

The dehydrogenation of methanol (“CH₃OH”) to dimethyl ether (“CH₃OHCH₃”) is described by the following⁴⁷:



Since DME is not favored over Methanol for scrubbing in the CO₂ Wash Column due to its lower solubility, stream C1 has the potential to release 6,367 tons/year of DME to the atmosphere or a mixture of MeOH and DME in the same amount.

7. The VOC emissions are underestimated because they fail to account for fugitive VOC emissions from the CO₂ wash column.

The bottoms stream from the CO₂ wash column is a methanol-rich stream of wash water containing some CO and CO₂ impurities that are flashed off and recycled back to the gasifier.⁴⁸ Methanol-rich wash water stream is pumped, warmed-up, and directed to the methanol/water separator (distillation) for methanol recovery. This pumping, heating, distillation of methanol, and recycling is associated with numerous piping components in light liquid and vapor service. Yet the Application does not estimate any fugitive emissions associated with the bottoms stream leaving the CO₂ wash column, with the product streams from methanol/water separation, or with the regenerated methanol stream, which are all shown in process flow diagram 235 of the Application.

8. The hazardous air pollutants carbonyl sulfide and hydrogen cyanide and the NSR-regulated pollutants hydrogen sulfide and total reduced sulfurs from the proposed facility

The Applicant based their calculations on practical experience at the Puertollano, Spain facility. The ultimate analysis of syngas for that facility reveals sulfur may be present as carbonyl sulfide or hydrogen sulfide at 0.17 mol% and that nitrogen may be present as diatomic nitrogen, ammonia, or hydrogen cyanide at

⁴⁶ Jaeger Products, Inc., Scrubbing Pollutants from Vent Streams, at 6 of indicates that “mass transfer will also occur from the liquid to the gas if conditions are favorable”; <http://www.jaeger.com/Brochure/gasscrubbing.pdf>, accessed on November 18, 2009.

⁴⁷ Lee, S., Methane and Its Derivatives, Chapter 3: Methane Derivatives Via Synthesis Gas, Marcel Dekker Inc., New York, NY, 1997 at 148; <http://snipurl.com/tnnug> [books_google_com], accessed November 12, 2009.

⁴⁸ Application at electronic page 368.

15 mol%. When these mol percentages are multiplied by the molar flow rate applied for by TransGas and multiplied by their respective molecular rates, the following mass flow rates are obtained which exceed the mass flow rates on which Uhde based TransGas potential emissions:

COS:

$$\begin{aligned} & (0.0017 \text{ lb-mol COS/lb-mol syngas}) \times (62,869 \text{ lb-mol syngas/hour}) \times \\ & (60 \text{ lb COS/ lb-mol COS}) \times (0.453 \text{ kg/lb COS}) \\ & = 2905 \text{ kg/hour} \gg 224.1 \text{ kg/hour} \end{aligned}$$

H₂S:

$$\begin{aligned} & (0.0017 \text{ lb-mol H}_2\text{S/lb-mol syngas}) \times (62,869 \text{ lb-mol syngas/hour}) \times \\ & (34 \text{ lb H}_2\text{S/lb-mol H}_2\text{S}) \times (0.453 \text{ kg/lb H}_2\text{S}) \\ & = 1646 \text{ kg/hour} \gg 1163.5 \text{ kg/hour} \end{aligned}$$

HCN:

$$\begin{aligned} & (0.15 \text{ lb-mol HCN/lb-mol syngas}) \times (62,869 \text{ lb-mol syngas/hour}) \times \\ & (28 \text{ lb HCN/ lb-mol HCN}) \times (0.453 \text{ kg/lb HCN}) \\ & = 119,615 \text{ kg/hour} \gg 51.6 \text{ kg/hour} \end{aligned}$$

VII. Underestimated CO Emissions from the Flare

The Applicant has indicated that the flare is “non-assisted”⁴⁹ and that the control efficiency of the flare is 98% by weight.^{50,51} Yet, the Applicant based potential emissions of CO on a destruction efficiency of 99.5 mol%^{52, 53} and a volumetric flow rate of 100,000 m³n of CO per startup. (As discussed elsewhere, the Applicant erroneously assumes that there is only 100,000 m³n/hour of CO during a 1-hour startup.) The flow rate of CO is 60% by volume (mole)^{54, 55} of the total flow to the flare⁵⁶. Therefore, the CO flow rate is 37,721.3 lb-mol/hour

⁴⁹ Application, Attachment M, Item 4, Page M1 (electronic page 194): “Air Pollution Control Device Sheet (Flare System).”

⁵⁰ *Ibid*, Item 7.

⁵¹ Application, Appendix N.

⁵² The Applicant (Uhde) used 99.5% in conjunction with a volume or mole %, therefore, one can only conclude that 99.5% is a molar percentage.

⁵³ Application, Appendix N, Attachment 2, Page 14 (electronic page 304).

⁵⁴ *Ibid*.

⁵⁵ Based on information for the Puertollano Spain IGCC plant provided by Uhde in “PRENFLO Gasification”; http://www.uhde.eu/cgi-bin/byteserver.pl/archive/upload/uhde_brochures_pdf_en_11.00.pdf, and corrected for the ultimate analysis of the coal used for startup (PRB at 0.5% sulfur) at TransGas.

⁵⁶ The total flow rate to the flare can be calculated as follows:

(1,056,196 lb/hour and 383,505 m³n/hour⁵⁷). Assuming a destruction efficiency of 98% by weight (2% by weight CO emitted to atmosphere) and a CO flow rate of 37,721.3 lb-mol/hour (1,056,196 lb/hour and 383,505 m³n/hour)⁵⁸ the resulting CO emission rate during startup of B2 or C2 is 21,124 lb/startup, resulting in 317 tons/year of CO emissions from startups.⁵⁹

It should be noted that the Draft Permit has not required that the flare be assisted. Without assistance, flare combustion efficiency decreases at heat contents less than 300 Btu/ft³ and when the flare gas contains nitrogen, at heat contents less than 365 Btu/ft³. Therefore, we believe that the assumed 98% combustion efficiency is an overestimation and that emission of CO during startup may be higher than the previously calculated 317 tons/year. At 95% efficiency, the annual CO emissions increase to 792 tons/year.⁶⁰

$$(28,516.8 \text{ kmol/hour}) \times (1,000 \text{ mol/kmol}) \times (1 \text{ gmol/mol}) \times (\text{lb-mol}/453.59237 \text{ gmol}) = 62,869 \text{ lb-mol/hour.}$$

⁵⁷ The volumetric flow rate can be calculated as follows:

$$(28,516.8 \text{ kmol/hour}) \times (22.414 \text{ m}^3\text{n/kmol}) \times (0.60 \text{ m}^3 \text{ CO/m}^3 \text{ raw syngas}) = 383,505 \text{ m}^3\text{n/hour.}$$

$$\text{⁵⁸ Uncontrolled CO: } (37,721.3 \text{ lb-mol/hour})(28 \text{ lb/lb-mol}) = 1,056,196 \text{ lb CO /hour}$$

$$\text{⁵⁹ } (21,124 \text{ lb CO/startup}) \times (30 \text{ startups}) = 316.86 \text{ tons CO/year.}$$

⁶⁰ At 95% by weight destruction efficiency, controlled CO emissions can be calculated as follows:

$$(1 - (95 \text{ lb CO controlled})/(100 \text{ lb CO})) \times (1,056,196 \text{ lb CO /hr}) \times (\text{hr/startup}) \times (30 \text{ startups/year}) \times (\text{ton controlled CO}/2,000 \text{ lb controlled CO}) = 792 \text{ tons/year.}$$