Biomethane Quality

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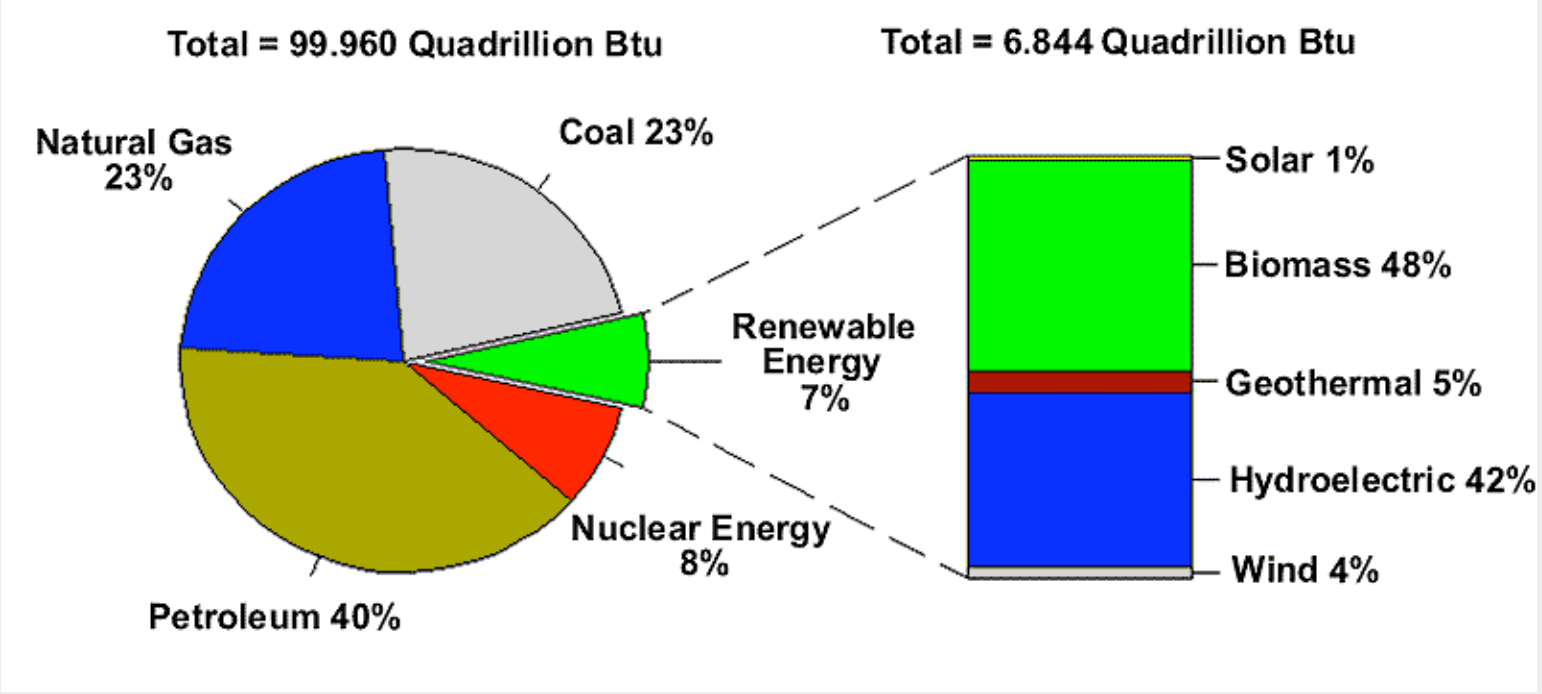
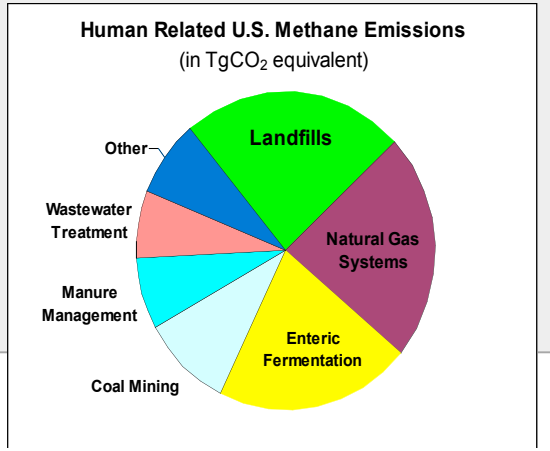
Energy Sources: US 2006



Natural Gas Perspectives

- Pressure to expand “renewable portfolio” *but* business opportunity
- Over 60% of human-related methane released through biological degradation of naturally-occurring materials
- LDCs/Transmission co.’s approached by biomethane developers to purchase gas
- Conservative approach to “new fuels”
- Interest is high



Sources of Biomass for Anaerobic Digestion

- Organic material from plants or animals:
  - Dairy Waste
  - Municipal solid wastes
  - Landfills
  - Food processing
  - Wineries/Agriculture
  - Others

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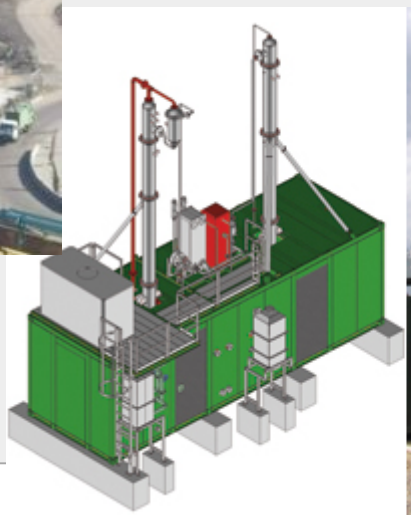
Anaerobic Digestion of Waste Yields Methane – *but what quality?*

- Specific to types of materials digested
- May be influenced by digester process
- May vary based upon cleanup/conditioning
- May be required to comply with specific specifications



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Definitions

- ***Biogas*** – The gaseous product from the digestion and/or volatilization of organic and inorganic waste material. Usually considered "raw" gas.
  - *Anaerobic digesters*
    - *Agricultural wastes*
    - *Dairy wastes*
    - *WWT*
    - *Co-digestion*
  - *Landfill gas*
- Not considered suitable for the pipeline network

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Definitions

- ***Biomethane*** – A “cleaned” or “conditioned” biogas product
  - A variety of processes may be used for gas cleanup
  - 5 basic designs of cleanup
- Biomethane *may* be suitable for introduction to the pipeline network
- Discerns this alternative fuel

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FERC Natural Gas Considerations/Tariffs – AGA Report 4A

- Hydrocarbons Liquids & Liquifiables
- H_2S and Total Sulfurs
- CO_2 and Total Non-Hydrocarbons
- Dust, Gums, Etc.
- Heating Value
- Oxygen
- Temperature
- Moisture Content
- Mercury
- Other

Natural Gas Industry Question:

- Are there any other components in biogas/biomethane which are not captured under general language of the existing tariffs which may impact:
  - Pipeline integrity /overall supply quality
  - Human health and safety
  - End use application
- Can these constituents be removed prior to introduction?

GTI Project

- To create Reference Documents for Dairy Waste Conversion, Landfill Gas and Wastewater Treatment Biomethane Guidance.
  - Dairy Waste followed by Landfill/WWT
- Funded by industry and PHMSA
- Serves to bring together parties for productive discussion on biomethane introduction to the pipeline network
- Not prescriptive

GTI Project Objectives

1) To Conduct:
   - Extensive Sample Collection
   - Laboratory Analysis

2) To Determine the gas quality of:
   - Raw Biogas
   - “Partially Cleaned” Biogas
   - Biomethane (cleaned biogas)

GTI Study Objectives, con't

3) To Verify biomethane against the following criteria:
   - > Against reported AGA Report 4A (Gas Quality) values
   - > Against the specific tariff which applied for each biomethane producer

4) To Investigate other compounds in the biomethane: selected analtyical review, concentrations recorded, "before and after" snapshot

5) To Serve as Template for other biomass investigations

Why Did We Select Dairy Waste Bioconversion First?

- Substrates (biomass) can be defined
- Least complex of the biomass substrates
- Relationship with Cornell University
- Dairy industry “speaks quality” and will accommodate
- Open access to sites
- High level of interest/involvement from Universities

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Sampling Design

Dairy Farm	Region	Biogas Production Technology	Biogas Clean Up Technology	Samples Collected
Dairy Farm 1	Midwestern	plug and flow digester	Moisture trap, iron sponge, water scrubber, oxygen stripper	raw biogas and biomethane
Dairy Farm 2	Western	complete mix digester	Pressure swing adsorption	raw biogas and biomethane
Dairy Farm 3	Eastern	plug and flow digester	Iron impregnated bark chip filter	raw and partially clean biogas
Dairy Farm 4	Eastern	plug and flow digester	Condenser	raw and partially clean biogas
Dairy Farm 5	Midwestern	plug and flow digester	Condenser	raw and partially clean biogas
Dairy Farm 6	Western	covered lagoon	Iron sponge	raw and partially clean biogas
Dairy Farm 7	Western	covered lagoon	Proprietary two-tank biodesulfurization system	raw and partially clean biogas
Dairy Farm 8	Midwestern	plug and flow digester	NA	raw biogas
Dairy Farm 9	Eastern	plug and flow digester	NA	raw biogas
Dairy Farm 10	Eastern	plug and flow digester	NA	raw biogas
Dairy Farm 11	Eastern	plug and flow digester	NA	raw biogas
Dairy Farm 12	Midwestern	plug and flow digester	NA	raw biogas
Dairy Farm 13	Western	covered lagoon	NA	raw biogas
Dairy Farm 14	Eastern	complete mix digester	NA	raw biogas

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Samples Collected: Dairy

> Collected 5 types of samples:

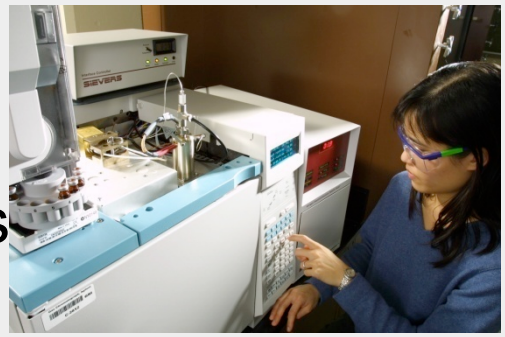
Summary of Samples Collected

Sample Type	Region Samples were Collected From	Samples Collected for Chemical Testing	Samples Collected for Biological Testing
Raw	Western, Eastern, and Midwestern	12 *(from 12 dairy farms)*	11 *(from 10 dairy farms)*
Partially Clean	Western, Eastern, and Midwestern	7 *(from 5 dairy farms)*	7 *(from 5 dairy farms)*
Biomethane	Western and Midwestern	23 *(from 2 dairy farms)*	22 *(from 2 dairy farms)*
Natural Gas	Midwestern	0	2 *(from one dairy farm and GTI Bio Lab)*
Air	Midwestern	0	1 *(from one dairy farm)*
Total	3 different U.S. regions	42	43

Chemical Testing and Biological Testing

Chemical Testing

- Two Tiers of Chemical Testing
  - ***First Tier Chemical Tests***
    - Major Components, Extended Hydrocarbons, Sulfur Compounds Halocarbons, Siloxanes, Metals
  - ***Second Tier Chemical Tests***
    - Volatile/Semi-volatile Organic Compounds, Pesticides, Polychlorinated Biphenyls, Pharmaceuticals



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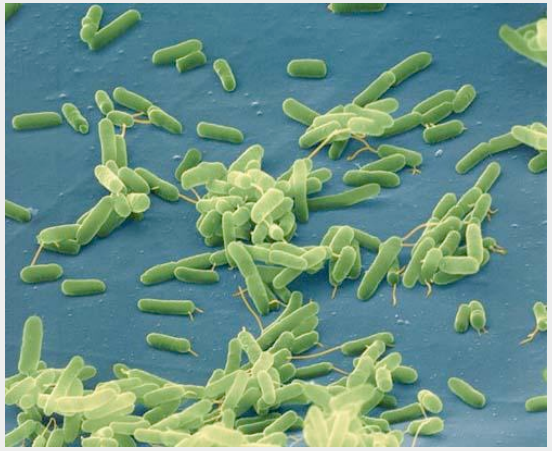
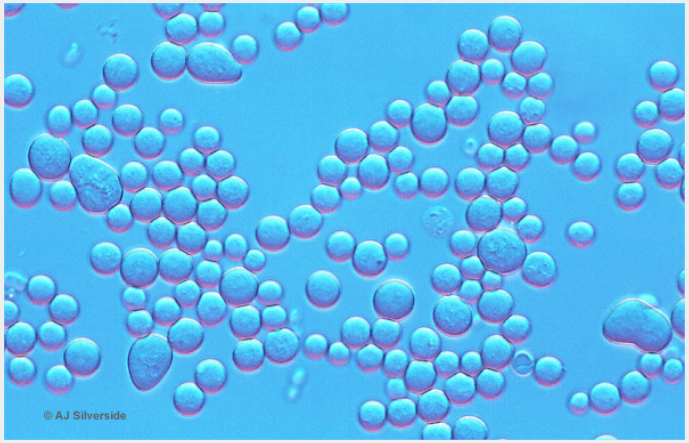
Biological Testing

- Biological Constituents
  - Total Bacteria
    - Live and Dead
  - Corrosion Causing Bacteria
    - Live and Dead
  - Spores
    - Live
  - Pathogens





Chemical Testing Results – All Samples, ave.

Sample Type	Raw Biogas	Partially Clean Biogas	Biomethane	Range of Tariff Values[1]
Gross HV (Dry) (Btu/ft^3)	615.3	598.7	986.7	967-1120 Btu/scf
Carbon Dioxide (Mol%)	35.5	32.3	0.54	2 – 3 (max)
Oxygen/Argon (Mol%)	0.74	1.64	0.91	0.001 – 0.2 (max)
Nitrogen (Mol%)	3.08	7.06	1.80	3 (max)
Methane (Mol%)	60.42	58.86	97.26	Not reported
Hexane Plus (Mol%)	0.0002	0.0001	0.0021	Not reported
Ammonia (Mol%)	0.004	NA	NA	Not reported
Hydrogen Sulfide (ppmv)	3085	2118	<0.05	0.25 – 0.3 grain per 100 scf
Total Sulfur (As Grains/100 SCF @ 14.73 psia, 60°F)	168	108	0.04	5 - 20
Total VOCs (ppbv)	221.4	189	55.83	Not reported
Total Pesticides (ppbv)	0.0675	0.17	0.52	Not reported

1American Gas Association. Transmission Measurement Committee. AGA Report No. 4A, Natural Gas Contract Measurement and Quality Clauses. Washington, DC: American Gas Association, 2001

First Tier Chemical Testing Results – *Biomethane* Samples

> Metals, Halocarbons, Siloxanes – below detection limit

Results from Major Components Analysis for 23 Biomethane Samples

Compound	Samples Above Detection Limit	Detection Limit(Mol%)	Average (Mol%)	Standard Deviation (Mol%)	Min (Mol%)	Max(Mol%)
Carbon Dioxide	23	0.03	0.54	0.35	0.06	0.95
Oxygen/Argon	10	0.03	0.91	0.51	0.39	1.99
Nitrogen	23	0.03	1.80	2.08	0.20	7.81
Methane	23	0.002	97.26	2.89	89.35	99.63
Ethane	1	0.002	0.11	NA	0.111	0.11
propane	1	0.002	0.028	NA	0.028	0.028
i-Butane	1	0.002	0.005	NA	0.005	0.005
n-Butane	1	0.002	0.005	NA	0.005	0.005
i-pentane	1	0.002	0.002	NA	0.002	0.002
Hexane Plus	1	0.0001	0.0021	NA	0.0021	0.000021
Carbonyl Sulfide	13	0.000005	0.000013	0.000016	0.000005	0.000053

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Tier I Example Specifics

Compound	Raw Samples Above Detection Limit	Raw Biogas Average (ppbv)	Partially Clean Samples Above Detection Limit	Partially Clean Biogas Average (ppbv)	Biomethane Samples Above Detection Limit	Biomethane Sample Average (ppbv)	OSHA Recommended Exposure Limit (ppbv)	NIOSH Recommended Exposure Limit (ppbv)
Benzene	10	4.20	6	5.85	1	27.09	1000	100
Carbon Tetrachloride	8	1.30	7	1.35	12	1.24	10000	2000
Pyridine	1	1.49	0	NA	0	NA	5000	5000
Toluene	10	43.27	7	22.25	13	12.52	200000	100000
1,1,2-Trichloroethane	4	31.62	3	24.19	0	NA	10000	10000
Tetrachloroethene	2	1.26	1	1.61	0	NA	100000	NA
Chlorobenzene	0	NA	1	1.48	0	NA	75000	75000
Ethylbenzene	9	10.94	7	9.75	4	1.83	100000	100000
m/p-Xylenes	8	9.80	6	2.98	12	2.60	100000	100000
Styrene	1	0.45	3	1.28	0	NA	100000	50000
o-Xylene	8	7.86	6	2.24	5	1.54	100000	100000
1,1,2,2-Tetrachloroethane	0	NA	1	0.68	0	NA	5000	1000
Isopropylbenzene	3	3.56	1	1.11	0	NA	50000	50000
n-Propylbenzene	4	5.74	2	1.42	0	NA	NA	NA
1,3,5-Trimethylbenzene	7	4.72	4	1.61	1	0.69	NA	25000
tert-Butylbenzene	3	3.26	1	1.02	0	NA	NA	NA
1,2,4-Trimethylbenzene	8	12.02	6	3.08	1	0.71	25000	NA
sec-Butylbenzene	6	3.83	2	0.96	0	NA	NA	NA
Phenol	6	9.68	5	10.53	0	NA	5000	5000
Aniline	2	21.34	2	12.87	0	NA	5000	NA
2-Chlorophenol	2	0.85	1	1.05	0	NA	NA	NA
p-Isopropyltoluene	9	3.26	6	20.13	0	NA	NA	NA
Benzyl Alcohol	3	5.08	4	46.26	1	2.10	NA	NA
3,4-Methylphenol (o,p-cresol)	7	17.97	3	7.45	0	NA	NA	NA

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Second Tier Chemical Testing Results – Biomethane Samples

- PCBs and Pharmaceuticals – below detection limit
- Only one sample collected from Dairy Farm 1 contained pesticides - 0.52 ppbv of gamma-chlordane. *The OSHA REL for gamma-chlordane is 30 ppb.*

Results from VOCs/SVOCs Analysis for 13 Biomethane Samples

Compound	Samples Above Detection Limit	Average (ppbv)	Standard Deviation	Min (ppbv)	Max (ppbv)
Benzene	1	27.09	NA	27.09	27.09
Carbon Tetrachloride	12	1.24	0.50	0.66	2.01
Toluene	13	12.52	28.91	1.67	107.54
Ethylbenzene	4	1.83	1.10	0.53	3.04
m/p-Xylenes	12	2.60	3.03	1.17	11.25
o-Xylene	5	1.54	1.30	0.48	3.36
1,3,5-Trimethylbenzene	1	0.69	NA	0.69	0.69
1,2,4-Trimethylbenzene	1	0.71	NA	0.71	0.71
Benzyl Alcohol	1	2.10	NA	2.10	2.10
N-nitroso-di-n-propylamine	7	2.92	0.75	1.45	3.60
Naphthalene	4	1.19	0.70	0.41	2.06
Di-n-butylphthalate	12	0.96	0.69	0.22	2.29
bis(2-Ethylhexyl)phthalate	13	0.44	0.19	0.20	0.81

Biological Testing Results – Biomethane Samples

Biological Results from 22 Biomethane Samples and 2 Natural Gas Samples

	Live Aerobic Bacteria	Live Anaerobic Bacteria	Spores	Total Bacteria	Total Acid-producing Bacteria	Total Iron-oxidizing Bacteria	Total Sulfate-reducing Bacteria
CFU/100 scf or #/100 scf							
Biomethane							
Mean	6.05E+02	2.52E+02	7.59E+02	3.87E+05	7.30E+03	1.53E+03	1.65E+02
Standard Deviation	1.22E+01	6.46E+00	8.03E+00	2.13E+01	5.72E+00	2.08E+00	NA
Minimum	5.74E+01	6.17E+01	1.24E+02	3.28E+03	9.69E+01	6.90E+02	1.65E+02
Maximum	3.55E+04	3.55E+04	1.37E+04	1.02E+07	9.80E+04	3.99E+03	1.65E+02
Samples Above the Detection Limit	7	10	4	22	18	6	1
Natural Gas and Ambient Air							
Natural Gas from Dairy Farm 5	9.25E+02	8.22E+01	6.16E+02	3.50E+06	BDL	4.30E+03	BDL
Natural Gas from GTI Lab	negative	negative	not detected	6.50E+05	1.40E+04	BDL	BDL
Ambient Air from Dairy Farm 1	negative	4.13E+01	not detected	7.90E+05	2.30E+03	BDL	BDL

Conclusions: Dairy Waste Biomethane Study

- Study data indicates that biomethane from dairy farm outputs can meet typical pipeline tariffs (Report 4A) and the particular tariff requirements (specific company).
- Other target compounds, not commonly found in natural gas, were detected in biomethane samples in very low concentrations (parts per billion). When compared against NIOSH and OSHA exposure limits, it may be concluded that specific trace concentrations of the compounds in biomethane are not of risk to public safety and health.

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Conclusions

- Results from biological testing were unclear.
- In samples tested, gas treatment technologies can effectively clean biogas to remove undesirable components to the specified contract requirements, which are within AGA Report 4A tariff boundaries.

Landfill and WWT Biogas/Biomethane

- 42 samples retrieved
- Natural gas samples (6) retrieved as well
- Analysis completed
- Results indicate higher level and greater variety in VOCs/SVOCs
- Greater potential for more constituents outside of natural gas profile
  - Aldehydes, ketones

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Natural Gas and Biomethane: Trace Constituents Detected

Highlighted Compounds:

- Found in biomethane but not in natural gas

or

- Found in biomethane in equal or greater amounts than in natural gas samples
- Less than OSHA and NIOSH exposure limits

Category	LF2 Biomethane	LF3 Biomethane	NG	WWTP1 Biomethane
Ammonia	BDL(<0.001%)	BDL(<0.001%)	BDL(<0.001%)	BDL(<0.001%)
Extended Hydrocarbons				
-Cycloalkanes	Cyclopentane; Methylcyclopentane; Cyclohexane	Cyclopentane; Methylcyclopentane; Cyclohexane; Methylcyclohexane	Cyclopentane; Methylcyclopentane; Cyclohexane; Methylcyclohexane	BDL (< 0.0001 mol%)
-Aromatics	BDL (< 1ppmv)	Benzene	Benzene; Toluene; Ethylbenzene; m,p-Xylene; o-Xylene; C3 Benzenes	BDL (< 0.0001 mol%)
-Paraffins	Hexanes	Hexanes; Heptanes	Hexanes; Heptanes; 2,2,4-Trimethylpentane; Octanes; Nonanes; Decanes	BDL (< 0.0001 mol%)
Organic Silicons	BDL (< 0.5 ppmv Si)	BDL (< 0.5 ppmv Si)	BDL (< 0.5 ppmv Si)	BDL (< 0.5 ppmv Si)
TO-14 Halocarbons	Dichlorodifluoromethane (CFC-12); 1,2-Dichlorotetrafluoroethane (CFC-114); Trichlorofluoromethane (CFC-11); Chloroethane; Chloroethene (Vinyl Chloride);	Dichlorodifluoromethane (CFC-12); 1,2-Dichlorotetrafluoroethane (CFC-114); Trichlorofluoromethane (CFC-11); Chloroethane; Chloroethene (Vinyl Chloride);	BDL (< 0.1 ppmv)	BDL (< 0.1 ppmv)
Mercury	BDL (< 0.02 µg/m3)	Yes*	BDL (< 0.02 µg/m3)	BDL (< 0.02 µg/m3)
Volatile Metals	Zinc	BDL (< 30 µg/m3)	Zinc	Zinc

Natural Gas and Biomethane: Trace Constituents Detected

Highlighted Compounds:
- Found in biomethane but not in natural gas or
- Found in biomethane in equal or greater amounts than in natural gas samples
- Less than OSHA and NIOSH exposure limits
- 0.00252 ppbv
- 0.00486 ppbv (mean value, 2 samples)

Category	LF2 Biomethane	LF3 Biomethane	NG	WWTP1 Biomethane
VOCs and SVOCs	Benzene; Carbon Tetrachloride; 1,2-Dichloropropane; Trichloroethene; Toluene; Ethylbenzene; m/p-Xylenes; o-Xylene; Isopropylbenzene; n-Propylbenzene; 1,3,5-Trimethylbenzene; 1,2,4-Trimethylbenzene; sec-Butylbenzene; 1,4-Dichlorobenzene; p-Isopropyltoluene; n-Butylbenzene; Naphthalene; 2-Methylnaphthalene; 1-Methylnaphthalene; Diethylphthalate; Di-n-butylphthalate;	Benzene; Carbon Tetrachloride; 1,2-Dichloropropane; Trichloroethene; Toluene; Tetrachloroethene; p-Isopropyltoluene; Diethylphthalate; Di-n-butylphthalate	Benzene; Carbon Tetrachloride; Toluene; Dibromochloromethane; Ethylbenzene; m/p-Xylenes; o-Xylene; Isopropylbenzene; n-Propylbenzene; 1,3,5-Trimethylbenzene; 1,2,4-Trimethylbenzene; sec-Butylbenzene; p-Isopropyltoluene; Benzyl Alcohol; n-Butylbenzene; Nitrobenzene; Naphthalene; 2-Methylnaphthalene; 1-Methylnaphthalene; Di-n-butylphthalate	Benzene; Carbon Tetrachloride; Toluene; Ethylbenzene; m/p-Xylenes; o-Xylene; 1,1,2,2-Tetrachloroethane; n-Propylbenzene; 1,3,5-Trimethylbenzene; sec-Butylbenzene; 1,4-Dichlorobenzene; p-Isopropyltoluene; n-Butylbenzene; Naphthalene; 2-Methylnaphthalene; 1-Methylnaphthalene; 4-Nitrophenol; Di-n-butylphthalate; bis(2-Ethylhexyl)phthalate
Pesticides	BDL (varies)	4,4'-DDT	BDL (varies)	4,4'-DDT
Aldehydes and Ketones	Formaldehyde; Acetaldehyde; Acetone; Propionaldehyde; Crotonaldehyde; 2-Butanone; Methacrolein; Butanal; Benzaldehyde	Formaldehyde; Acetaldehyde; Acetone; Propionaldehyde; 2-Butanone; Butanal	Formaldehyde; Acetaldehyde; Acetone; Propionaldehyde; 2-Butanone; Methacrolein; Butanal; Benzaldehyde; Pentanal	Acetaldehyde; Acetone
PCBs	BDL (varies)	BDL (varies)	BDL (varies)	BDL (varies)

Technical Challenge and Data Gaps

- Rapidly understand the fuel and its effects on pipeline infrastructure and overall gas quality
- Safely bring the new fuel to market with supportive data
- Supply supportive data to industry (to all parties)
- “Door Open” policy for this renewable product
- Common language and approach to analysis – Guidance

Short and Long Term Research Needs

- Constituents in Biomethane
  - More expanded profile
  - More data for comparison
  - Statistical profiling
  - Profiling over time
  - *Chemical and Biological*
- Effects of Biomethane Constituents on Pipeline Constituents
  - Trace constituents on metallic pipe
  - Trace constituents on non-metallic pipe
  - Synergistic effect of

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Short and Long Term Research Needs

- Effects of Biomethane Constituents on Pipeline Constituents
  - Trace constituents/biologicals on metallic pipe
  - Trace constituents/biologicals on non-metallic pipe
  - Synergistic effect of trace constituents and biologicals on pipe/components
  - Threshold concentrations
- Effects of Biomethane Constituents on Gas Quality
  - Trace constituents/biologicals on odorization
- Understanding natural gas for comparison

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Short and Long Term Research Needs

- Real-time analytical instrumentation for gas quality monitoring
- Common industry protocols and procedures

Short and Long Term Research Needs

- Biomethane Research Initiative
- Co-digestion: future of biomethane and waste management
  - "Recipe" formulations
    - Multitude of disciplines to harness energy potential
  - Waste management programs: Europe model
  - Economic development
- Committed monitoring programs: cause/effect
- Advancing these approaches to other new "interchangeable fuels" of the future
  - Gasification, etc.

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For further questions, please contact me. Thank you for your attention.

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