

Combined pre-treatment technologies for cleaning biogas before its upgrading to biomethane: an Italian full-scale anaerobic digester case study

Supplementary materials

Table S1: analytical details (pg. 2 – 4)

Table S2: bio-CH₄ specification (pg. 5)

Table S1: analytical details

#		analyzed compound	CAS number	formula	unit	method	LOQ ^a
1		methane	74-82-8	CH ₄	%	on-line measurement	0.01
2		carbon dioxide	124-38-9	CO ₂	%	on-line measurement	0.01
3		oxygen	7782-44-7	O ₂	%	on-line measurement	0.01
4		hydrogen sulfide	7783-06-4	H ₂ S	ppmv	on-line measurement	1
5	terpenes	limonene	5989-27-5	C ₁₀ H ₁₆	mg/Nm ³	UNI CEN/TS 13649	0.1
6		α-pinene	80-56-8	C ₁₀ H ₁₆	mg/Nm ³	UNI CEN/TS 13649	0.1
7		β-pinene	127-91-3	C ₁₀ H ₁₆	mg/Nm ³	UNI CEN/TS 13649	0.1
8		p-cymene	99-87-6	C ₁₀ H ₁₄	mg/Nm ³	UNI CEN/TS 13649	0.1
9		m-cymene	535-77-3	C ₁₀ H ₁₄	mg/Nm ³	UNI CEN/TS 13649	0.1
10		camphene	79-92-5	C ₁₀ H ₁₆	mg/Nm ³	UNI CEN/TS 13649	0.1
11		myrcene	123-35-3	C ₁₀ H ₁₆	mg/Nm ³	UNI CEN/TS 13649	0.1
12		phellandrene *	99-83-2, 555-10-2	C ₁₀ H ₁₆	mg/Nm ³	UNI CEN/TS 13649	0.1
13		Δ-3-carene	13466-78-9	C ₁₀ H ₁₆	mg/Nm ³	UNI CEN/TS 13649	0.1
14		terpinene *	99-86-5, 99-84-3, 99-85-4	C ₁₀ H ₁₆	mg/Nm ³	UNI CEN/TS 13649	0.1
15		camphor	76-22-2	C ₁₀ H ₁₆ O	mg/Nm ³	UNI CEN/TS 13649	0.1
16		menthol *	2216-51-5, 89-78-1	C ₁₀ H ₂₀ O	mg/Nm ³	UNI CEN/TS 13649	0.1
17		aliphatic hydrocarbons	propane	74-98-6	C ₃ H ₈	mg/Nm ³	UNI CEN/TS 13649
18	butane		106-97-8	C ₄ H ₁₀	mg/Nm ³	UNI CEN/TS 13649	0.1
19	pentane		109-66-0	C ₅ H ₁₂	mg/Nm ³	UNI CEN/TS 13649	0.1
20	hexane		110-54-3	C ₆ H ₁₄	mg/Nm ³	UNI CEN/TS 13649	0.1
21	heptane		142-82-5	C ₇ H ₁₆	mg/Nm ³	UNI CEN/TS 13649	0.1
22	octane		111-65-9	C ₈ H ₁₈	mg/Nm ³	UNI CEN/TS 13649	0.1
23	decane		124-18-5	C ₁₀ H ₂₂	mg/Nm ³	UNI CEN/TS 13649	0.1
24	cyclopentane		287-92-3	C ₅ H ₁₀	mg/Nm ³	UNI CEN/TS 13649	0.1
25	2-methylpentane		107-83-5	C ₆ H ₁₄	mg/Nm ³	UNI CEN/TS 13649	0.1
26	cyclohexane		110-82-7	C ₆ H ₁₂	mg/Nm ³	UNI CEN/TS 13649	0.1
27	methylcyclohexane		108-87-2	C ₇ H ₁₄	mg/Nm ³	UNI CEN/TS 13649	0.1
28	isoprene		78-79-5	C ₅ H ₈	mg/Nm ³	UNI CEN/TS 13649	0.1
29	aromatic hydrocarbons	benzene	71-43-2	C ₆ H ₆	mg/Nm ³	UNI CEN/TS 13649	0.1
30		toluene	108-88-3	C ₇ H ₈	mg/Nm ³	UNI CEN/TS 13649	0.1
31		ethyl-benzene	100-41-4	C ₈ H ₁₀	mg/Nm ³	UNI CEN/TS 13649	0.1
32		xylene *	1330-20-7	C ₈ H ₁₀	mg/Nm ³	UNI CEN/TS 13649	0.1
33		styrene	100-42-5	C ₈ H ₈	mg/Nm ³	UNI CEN/TS 13649	0.1
34		4-vinyltoluene	622-97-9	C ₉ H ₁₀	mg/Nm ³	UNI CEN/TS 13649	0.1
35		trimethyl-benzene *	108-67-8, 526-73-8, 95-63-6	C ₉ H ₁₂	mg/Nm ³	UNI CEN/TS 13649	0.1
36		tetramethyl-benzene *	488-23-3, 95-93-2, 527-53-7	C ₁₀ H ₁₄	mg/Nm ³	UNI CEN/TS 13649	0.1
37	cumene	98-82-8	C ₉ H ₁₂	mg/Nm ³	UNI CEN/TS 13649	0.1	
38	ketones	acetone	67-64-1	C ₃ H ₆ O	mg/Nm ³	UNI CEN/TS 13649	0.1
39		methyl ethyl ketone	78-93-3	C ₄ H ₈ O	mg/Nm ³	UNI CEN/TS 13649	0.1
40		methyl propyl ketone	107-87-9	C ₅ H ₁₀ O	mg/Nm ³	UNI CEN/TS 13649	0.1
41		methyl isopropyl ketone	563-80-4	C ₅ H ₁₀ O	mg/Nm ³	UNI CEN/TS 13649	0.1
42		methyl butyl ketone	591-78-6	C ₆ H ₁₂ O	mg/Nm ³	UNI CEN/TS 13649	0.1
43		cyclohexanone	108-94-1	C ₆ H ₁₀ O	mg/Nm ³	UNI CEN/TS 13649	0.1

44	halocarbon compounds	chloromethane	74-87-3	CH ₃ Cl	mg/Nm ³	UNI CEN/TS 13649	0.1
45		vinyl chloride	75-01-4	C ₂ H ₃ Cl	mg/Nm ³	UNI CEN/TS 13649	0.1
46		chloroethane	75-00-3	C ₂ H ₅ Cl	mg/Nm ³	UNI CEN/TS 13649	0.1
47		dichloromethane	75-09-2	CH ₂ Cl ₂	mg/Nm ³	UNI CEN/TS 13649	0.1
48		dichloroethane *	75-34-3, 107-06-2	C ₂ H ₄ Cl ₂	mg/Nm ³	UNI CEN/TS 13649	0.1
49		dichloroethylene *	75-35-4, 540-59-0	C ₂ H ₂ Cl ₂	mg/Nm ³	UNI CEN/TS 13649	0.1
50		dichloropropane *	78-87-5, 142-28-9, 594-20-7	C ₃ H ₆ Cl ₂	mg/Nm ³	UNI CEN/TS 13649	0.1
51		1,3-dichloropropene	542-75-6	C ₃ H ₄ Cl ₂	mg/Nm ³	UNI CEN/TS 13649	0.1
52		dichlorobenzene *	95-50-1, 541-73-1, 106-46-7	C ₆ H ₄ Cl ₂	mg/Nm ³	UNI CEN/TS 13649	0.1
53		chloroform	67-66-3	CHCl ₃	mg/Nm ³	UNI CEN/TS 13649	0.1
54		trichloroethane *	71-55-6, 79-00-5	C ₂ H ₃ Cl ₃	mg/Nm ³	UNI CEN/TS 13649	0.1
55		trichloropropane	96-18-4	C ₃ H ₅ Cl ₃	mg/Nm ³	UNI CEN/TS 13649	0.1
56		trichloroethylene	79-01-6	C ₂ HCl ₃	mg/Nm ³	UNI CEN/TS 13649	0.1
57		tetrachloroethylene	127-18-4	C ₂ Cl ₄	mg/Nm ³	UNI CEN/TS 13649	0.1
58		tetrachloroethane *	630-20-6, 79-34-5	C ₂ H ₂ Cl ₄	mg/Nm ³	UNI CEN/TS 13649	0.1
59		carbon tetrachloride	56-23-5	CCl ₄	mg/Nm ³	UNI CEN/TS 13649	0.1
60		pentachloroethane	76-01-7	C ₂ HCl ₅	mg/Nm ³	UNI CEN/TS 13649	0.1
61		hexachloroethane	67-72-1	C ₂ Cl ₆	mg/Nm ³	UNI CEN/TS 13649	0.1
62		tribromomethane	75-25-2	CHBr ₃	mg/Nm ³	UNI CEN/TS 13649	0.1
63		dibromoethane *	557-91-5, 106-93-4	C ₂ H ₄ Br ₂	mg/Nm ³	UNI CEN/TS 13649	0.1
64		bromodichloromethane	75-27-4	CHBrCl ₂	mg/Nm ³	UNI CEN/TS 13649	0.1
65	dibromochloromethane	124-48-1	CHBr ₂ Cl	mg/Nm ³	UNI CEN/TS 13649	0.1	
66	esters	ethyl acetate	141-78-6	C ₄ H ₈ O ₂	mg/Nm ³	UNI CEN/TS 13649	0.1
67		methyl acetate	79-20-9	C ₃ H ₆ O ₂	mg/Nm ³	UNI CEN/TS 13649	0.1
68		butyl acetate	123-86-4	C ₆ H ₁₂ O ₂	mg/Nm ³	UNI CEN/TS 13649	0.1
69		methyl propionate	554-12-1	C ₄ H ₈ O ₂	mg/Nm ³	UNI CEN/TS 13649	0.1
70		ethyl propionate	105-37-3	C ₅ H ₁₀ O ₂	mg/Nm ³	UNI CEN/TS 13649	0.1
71		methyl butanoate	623-42-7	C ₅ H ₁₀ O ₂	mg/Nm ³	UNI CEN/TS 13649	0.1
72		ethyl butanoate	105-54-4	C ₆ H ₁₂ O ₂	mg/Nm ³	UNI CEN/TS 13649	0.1
73		methyl pentanoate	624-24-8	C ₆ H ₁₂ O ₂	mg/Nm ³	UNI CEN/TS 13649	0.1
74		ethyl pentanoate	539-82-2	C ₇ H ₁₄ O ₂	mg/Nm ³	UNI CEN/TS 13649	0.1
75		ethyl isovalerate	108-64-5	C ₇ H ₁₄ O ₂	mg/Nm ³	UNI CEN/TS 13649	0.1
76	2-methoxyethyl acetate	110-49-6	C ₅ H ₁₀ O ₃	mg/Nm ³	UNI CEN/TS 13649	0.1	
77	acetonitrile	75-05-8	C ₂ H ₃ N	mg/Nm ³	UNI CEN/TS 13649	0.1	
78	alcohols	methanol	67-56-1	CH ₄ O	mg/Nm ³	UNI CEN/TS 13649	0.1
79		ethanol	64-17-5	C ₂ H ₆ O	mg/Nm ³	UNI CEN/TS 13649	0.1
80		propanol *	71-23-8, 67-63-0	C ₃ H ₈ O	mg/Nm ³	UNI CEN/TS 13649	0.1
81		buthanol *	71-36-3, 75-65-0, 78-83-1	C ₄ H ₁₀ O	mg/Nm ³	UNI CEN/TS 13649	0.1
82		pentanol *	71-41-0, 6032-29-7, 584-02-1	C ₅ H ₁₂ O	mg/Nm ³	UNI CEN/TS 13649	0.1
83		2-methoxyethanol	109-86-4	C ₃ H ₈ O ₂	mg/Nm ³	UNI CEN/TS 13649	0.1
84	nitro compounds	nitromethane	75-52-5	CH ₃ NO ₂	mg/Nm ³	UNI CEN/TS 13649	0.1
85		nitroethane	79-24-3	C ₂ H ₅ NO ₂	mg/Nm ³	UNI CEN/TS 13649	0.1
86		nitropropane *	108-03-2, 79-46-9	C ₃ H ₇ NO ₂	mg/Nm ³	UNI CEN/TS 13649	0.1
87		nitrobenzene	98-95-3	C ₆ H ₅ NO ₂	mg/Nm ³	UNI CEN/TS 13649	0.1
88		dinitrobenzene *	25154-54-5	C ₆ H ₄ N ₂ O ₄	mg/Nm ³	UNI CEN/TS 13649	0.1

89	ethers	tetrahydrofuran	109-99-9	C ₄ H ₈ O	mg/Nm ³	UNI CEN/TS 13649	0.1
90		1,4-dioxane	123-91-1	C ₄ H ₈ O ₂	mg/Nm ³	UNI CEN/TS 13649	0.1
91		dimethyl ether	115-10-6	C ₂ H ₆ O	mg/Nm ³	UNI CEN/TS 13649	0.1
92		diethyl ether	60-29-7	C ₄ H ₁₀ O	mg/Nm ³	UNI CEN/TS 13649	0.1
93		methylfuran *	534-22-5, 930-27-8	C ₅ H ₆ O	mg/Nm ³	UNI CEN/TS 13649	0.1
94		ethylfuran *	3208-16-0, 67363-95-5	C ₆ H ₈ O	mg/Nm ³	UNI CEN/TS 13649	0.1
95		dimethylfuran *	625-86-5, 3710-43-8	C ₆ H ₈ O	mg/Nm ³	UNI CEN/TS 13649	0.1
96		methyl tert-butyl ether	1634-04-4	C ₅ H ₁₂ O	mg/Nm ³	UNI CEN/TS 13649	0.1
97	siloxanes	hexamethylcyclotrisiloxane	541-05-9	((CH ₃) ₂ SiO) ₃	mg/Nm ³	UNI CEN/TS 13649	0.1
98		octamethylcyclotetrasiloxane	556-67-2	((CH ₃) ₂ SiO) ₄	mg/Nm ³	UNI CEN/TS 13649	0.1
99		decamethylcyclopentasiloxane	541-02-6	((CH ₃) ₂ SiO) ₅	mg/Nm ³	UNI CEN/TS 13649	0.1
100		dodecamethylcyclohexasiloxane	540-97-6	((CH ₃) ₂ SiO) ₆	mg/Nm ³	UNI CEN/TS 13649	0.1
101		pentamethyldisiloxane	1438-82-0	C ₅ H ₁₆ Si ₂ O	mg/Nm ³	UNI CEN/TS 13649	0.1
102		hexamethyldisiloxane	107-46-0	C ₆ H ₁₈ Si ₂ O	mg/Nm ³	UNI CEN/TS 13649	0.1
103		octamethyltrisiloxane	107-51-7	C ₈ H ₂₄ Si ₃ O ₂	mg/Nm ³	UNI CEN/TS 13649	0.1
104		decamethyltetrasiloxane	141-62-8	C ₁₀ H ₃₀ Si ₄ O ₃	mg/Nm ³	UNI CEN/TS 13649	0.1
105	dodecamethylpentasiloxane	141-63-9	C ₁₂ H ₃₆ Si ₅ O ₄	mg/Nm ³	UNI CEN/TS 13649	0.1	
106	aldehydes	acetaldehyde	75-07-0	C ₂ H ₄ O	mg/Nm ³	UNI CEN/TS 13649	0.1
107		propanal	123-38-6	C ₃ H ₆ O	mg/Nm ³	UNI CEN/TS 13649	0.1
108		butanal	123-78-8	C ₄ H ₈ O	mg/Nm ³	UNI CEN/TS 13649	0.1
109		pentanal	110-62-3	C ₅ H ₁₀ O	mg/Nm ³	UNI CEN/TS 13649	0.1
110		hexanal	66-25-1	C ₆ H ₁₂ O	mg/Nm ³	UNI CEN/TS 13649	0.1
111		heptanal	111-71-7	C ₇ H ₁₄ O	mg/Nm ³	UNI CEN/TS 13649	0.1
112		octanal	124-13-0	C ₈ H ₁₆ O	mg/Nm ³	UNI CEN/TS 13649	0.1
113		benzaldehyde	100-52-7	C ₇ H ₆ O	mg/Nm ³	UNI CEN/TS 13649	0.1
114	sulfur compounds	dimethyl sulfide	75-18-3	C ₂ H ₆ S	mg/Nm ³	UNI CEN/TS 13649	0.1
115		dimethyl trisulfide	3658-80-8	C ₂ H ₆ S ₃	mg/Nm ³	UNI CEN/TS 13649	0.1
116		dimethyl tetrasulfide	5756-24-1	C ₂ H ₆ S ₃	mg/Nm ³	UNI CEN/TS 13649	0.1
117		carbon disulfide	75-15-0	CS ₂	mg/Nm ³	UNI CEN/TS 13649	0.1
118		methanethiol	74-93-1	CH ₄ S	mg/Nm ³	UNI CEN/TS 13649	0.1
119		ethanethiol	75-08-1	C ₂ H ₆ S	mg/Nm ³	UNI CEN/TS 13649	0.1
120		propanethiol	107-3-9	C ₃ H ₈ S	mg/Nm ³	UNI CEN/TS 13649	0.1
121		buthanethiol *	109-79-5, 75-66-1	C ₄ H ₁₀ S	mg/Nm ³	UNI CEN/TS 13649	0.1
122	thiophenol	108-98-5	C ₆ H ₆ S	mg/Nm ³	UNI CEN/TS 13649	0.1	
123	inorganics	nitrogen	7727-37-9	N ₂	mg/Nm ³	UNI CEN/TS 13649	0.1
124		hydrogen chloride	7647-01-0	HCl	mg/Nm ³	Ministerial Decree 2000/08/25	0.001
125		hydrogen fluoride	7664-39-3	HF	mg/Nm ³	Ministerial Decree 2000/08/25	0.001
126		ammonia	7664-41-7	NH ₃	mg/Nm ³	UNICHIM 632	0.01

* Sum of isomers. ^a Limit of quantification.

Analytical instrumentation:

- # 1 – 4: stationary biogas analyzer, SWG 100 – MRU.
- # 5 – 103: portable micro GC-MS, micro-GC Fusion – Inficon
- # 104 – 105: ion chromatograph, 930 Compact IC Flex - Metrohm
- # 106: UV-VIS spectrophotometer, V-630 - Jasco

Table S2: bio-CH₄ specification

trace compounds concentration in bio-CH ₄ exiting the upgrading unit and injected in the natural gas grid						
trace compound	formula	unit	method	LOQ ^a	content in bio-CH ₄	legislation limit
hydrogen	H ₂	%	UNI EN ISO 6974	0.0001	≤ LOQ	≤ 0.5
oxygen	O ₂	%	UNI EN ISO 6974	0.0001	0.0330	≤ 0.6
nitrogen	N ₂	%	UNI EN ISO 6974	0.0001	0.2550	not provided
carbon oxide	CO	%	UNI EN ISO 6974	0.0001	0.0021	≤ 0.1
carbon dioxide	CO ₂	%	UNI EN ISO 6974	0.0001	1.6620	≤ 2.5
hydrogen sulfide	H ₂ S	mg/Sm ³	UNI EN ISO 6974	0.0001	0.0075	≤ 5
total sulfur	S	mg/Sm ³	UNI EN ISO 19739	0.01	≤ LOQ	≤ 6
total silicon	Si	mg/Sm ³	UNI CEN/TS 13649	0.0001	0.0010	≤ 1
ammonia	NH ₃	mg/Sm ³	UNICHIM 632	0.01	0.17	≤ 10
total amines	//	mg/Sm ³	NIOSH 2010	0.001	≤ LOQ	≤ 10
fluorine	F ₂	mg/Sm ³	Ministerial Decree 2000/08/25	0.001	≤ LOQ	≤ 3
chlorine	Cl ₂	mg/Sm ³	Ministerial Decree 2000/08/25	0.001	0.011	≤ 1
water Dew Point at 70 bar	//	°C	UNI EN ISO 6327	0.01	-60.05	≤ -5

^a Limit of quantification