Supplementary materials for paper 'Validation of two theoretically-derived equations for predicting pH in CO2 biomethanisation' by Yue Zhang, Sonia Heaven and Charles J. Banks

Results of application of Equations A and B to literature data

The following tables present the results of application of Equation A to data taken from the published literature on in situ and or hybrid CO_2 biomethanisation. Where possible i.e. where TAN and VFA data is available they also show results for Equation B.

The upper part of the table summarises values for key operating parameters. Nomenclature and definitions are based on Bywater et al. (2022) with minor modifications and corrections where required.

Nomenclature: NB parameters are listed in the order in which they appear in Tables S1-S4

Acronym	***Definition***	***Unit***
Temp	Digester operating temperature in degrees Celsius	
OLR	Organic loading rate, expressed as the mass of volatile solids (VS) or chemical oxygen demand (COD) added per unit of digester working volume per unit time	g VS L^{-1} day^{-1} or g COD L^{-1} day^{-1}
HRT	Hydraulic retention time, as reported or calculated from digester working volume divided by the daily volume of feed added	days
H_2 input	Volume of H_2 added per unit of digester working volume per unit time	L H_2 L^{-1} day^{-1}
SMP_{tot}	Specific methane production, defined as the volume of CH_4 produced from both anaerobic degradation of organic material and CO_2 biomethanisation (including from exogenous CO_2 where applicable), per unit of organic feed added	L CH_4 g^{-1} VS or L CH_4 g^{-1} COD
CH_4	Concentration of CH_4 in the output gas on a volumetric basis	%
TAN	Total ammonia nitrogen concentration in digestate	M or g N L^{-1}
VFA	Volatile fatty acid concentration in digestate	M or g COD L^{-1} or g L^{-1}
pH	pH value of digestate	-
pCO2	Partial pressure of CO_2 in digester headspace	-
a	Coefficient for Equation A derived from physical constants and baseline values	-
b	Coefficient for Equation A derived from physical constants and baseline values	-
Sig	Significance at 5% level as determined by t-test	-
n/r, n/a	Not reported, not applicable	-

The lower part(s) of the tables show the absolute value of the difference between the predicted and experimental pH values using Equation A or B for the specified conditions. These are presented as heatmaps corresponding to the definitions: good for a difference of < 0.1, reasonable for between 0.1-0.2, and poor for > 0.2.

Good	Reasonable	Poor

Bywater, A., Heaven, S., Zhang, Y. and Banks, C.J., 2022. Potential for Biomethanisation of CO2 from Anaerobic Digestion of Organic Wastes in the United Kingdom. *Processes*, *10*(6), p.1202.
Heaven, S., Zhang, Y., Bywater, A. and Banks, C., 2022. Dataset for 'Potential for biomethanisation of CO2 from anaerobic digestion of organic wastes in the UK'.

Table S1

Luo, G., Johansson, S., Boe, K., Xie, L., Zhou, Q. and Angelidaki, I., 2012. Simultaneous hydrogen utilization and in situ biogas upgrading in an anaerobic reactor. *Biotechnology and bioengineering*, *109*(4), pp.1088-1094.

		(i) With H_2	(ii) No H_2
Temp	°C	55	55
OLR	g VS L^{-1} day^{-1}	6.24	6.24
HRT	days	14.6	14.6
H_2 input	L L^{-1} day^{-1}	0.7	0.0
SMP_{tot}	L CH_4 g^{-1} VS	0.073	0.060
CH_4	%	65.0	62.0
TAN	mM	91.4	86.4
VFA	mM	28.8	8.7
pH	-	8.3	8.0
pCO_2	-	0.15	0.38
a x 10^8	-	1.88	1.89
b x 10^8	-	0.08	0.14
Difference between experimental and predicted pH based on Eqn A with coefficient *a*(x)			
a(i)	-	-	0.00
a(ii)	-	0.00	-
Difference between experimental and predicted pH based on Eqn B with coefficient *b*(x)			
b(i)	-	-	0.19
b(ii)	-	0.15	-

Cattle slurry, 55 °C CSTR, with or without H_2 addition

Equation A gives perfect agreement for real and predicted values. Agreement for Equation B is not as good, but the original paper notes that values for $NH4^+$ showed variability of up to 20% and that there was no significant difference in the mean values of $NH4^+$ for the two cases. pH values are reported to 1 dp.

Table S2

Luo, G. and Angelidaki, I., 2013. Hollow fiber membrane based H2 diffusion for efficient in situ biogas upgrading in an anaerobic reactor. Applied microbiology and biotechnology, 97(8), pp.3739-3744.

		(i)	(ii)	(iii)	(iv)	(v)	(vi)	RMSD	R^2	RMSE	Sig
	Phase	I		II		III					
		No H_2	With H_2	No H_2	With H_2	No H_2	With H_2				
Temp	°C	55	55	55	55	55	55	-	-	-	-
OLR	g VS L^{-1} day^{-1}	1.67	1.67	1.67	1.67	1.67	1.67	-	-	-	-
HRT	days	15	15	15	15	15	15	-	-	-	-
H_2 input	L L^{-1} day^{-1}	0	0.93	0	1.44	0	1.76	-	-	-	-
SMP_{tot}	L CH_4 g^{-1} VS	0.275	0.407	0.271	0.478	0.287	0.515	-	-	-	-
CH_4	%	54.2	78.4	53.1	90.2	55.4	96.1	-	-	-	-
TAN	mM	n/r	n/r	n/r	n/r	n/r	n/r	-	-	-	-
VFA	mM	1.6	4.3	1.7	11.8	1.9	37.8	-	-	-	-
pH	-	7.29	7.61	7.28	7.90	7.30	8.31	-	-	-	-
pCO_2	-	0.458	0.216	0.469	0.098	0.446	0.039	-	-	-	-
$a \times 10^8$	-	10.41	9.81	10.42	9.81	10.43	6.99	-	-	-	-
Difference between experimental and predicted pH based on Eqn A with coefficient *a*(x)											
a(i)	-	-	0.02	0.00	0.02	0.00	0.12	0.06	0.997	0.02	*
a(ii)	-	0.02	-	0.02	0.00	0.02	0.10	0.05	0.997	0.02	*
a(iii)	-	0.00	0.02	-	0.02	0.00	0.12	0.06	0.997	0.02	*
a(iv)	-	0.02	0.00	0.02	-	0.02	0.10	0.05	1.000	0.01	*
a(v)	-	0.00	0.02	0.00	0.02	-	0.12	0.06	0.997	0.02	*
a(vi)	-	0.16	0.13	0.16	0.12	0.16	-	0.15	1.000	0.00	*

55 °C CSTR with working volume 0.6 L, fed on cattle manure and whey, HRT 15 days. Varied H_2 addition rate

Equation A gives good agreement for most cases, though slightly less good for the experimental digester in phase III where there is some VFA. No TAN data. Also good agreement across all phases. Slope and intercept values (not shown) range from 0.875-0.925 and 0.71-0.94, respectively. All regression values are significant at the 5% level.

Note: Much of the information in this table is given in Table 1 in the main text, but is also included here for completeness and ease of reference.

Table S3

Luo, G. and Angelidaki, I., 2013. Co-digestion of manure and whey for in situ biogas upgrading by the addition of H2: process performance and microbial insights. Applied microbiology and biotechnology, 97(3), pp.1373-1381.

		(i)	(ii)	(iii)	(iv)	(v)	(vi)	RMSD	R^2	RMSE	Sig
Phase		1		2		3					
		No H_2	With H_2	No H_2	With H_2	No H_2	With H_2				
Diffuser		n/a	col	n/a	col	n/a	ceram	-	-	-	-
Mixing	rpm	150	150	300	300	150	150	-	-	-	-
Temp	^oC	55	55	55	55	55	55	-	-	-	-
OLR	g VS L^{-1} day^{-1}	1.67	1.67	1.67	1.67	1.67	1.67	-	-	-	-
HRT	days	15	15	15	15	15	15	-	-	-	-
H_2 input	L L^{-1} day^{-1}	0	1.7	0	1.7	0	1.7	-	-	-	-
SMP_{tot}	L CH_4 g^{-1} VS	0.287	0.452	0.299	0.501	0.295	0.529	-	-	-	-
CH_4	%	55	53	56	68	56.7	75	-	-	-	-
TAN	mM	36.9	35.7	37.1	36.4	37.5	38.0	-	-	-	-
VFA	mM	0.9	2.9	0.7	3.0	1.0	3.0	-	-	-	-
pH	-	7.28	7.74	7.33	7.84	7.31	7.89	-	-	-	-
pCO_2	-	0.45	0.13	0.44	0.088	0.433	0.066	-	-	-	-
$a \times 10^8$	-	10.86	11.53	9.81	12.94	10.48	14.99	-	-	-	-
$b \times 10^8$	-	0.39	0.37	0.36	0.42	0.38	0.51	-	-	-	-
Difference between experimental and predicted pH based on Eqn A with coefficient *a*(x)											
a(i)	-	-	0.02	0.04	0.06	0.01	0.11	0.06	0.995	0.02	*
a(ii)	-	0.02	-	0.07	0.04	0.04	0.09	0.06	0.996	0.02	*
a(iii)	-	0.04	0.06	-	0.10	0.03	0.15	0.09	0.995	0.03	*
a(iv)	-	0.07	0.04	0.11	-	0.09	0.05	0.08	0.993	0.02	*
a(v)	-	0.01	0.04	0.03	0.07	-	0.12	0.07	0.993	0.02	*
a(vi)	-	0.13	0.10	0.17	0.05	0.15	-	0.13	0.996	0.03	*
Difference between experimental and predicted pH based on Eqn B with coefficient *b*(x)											
b(i)	-		0.02	0.04	0.03	0.01	0.09	0.05	0.988	0.02	*
b(ii)	-	0.02		0.02	0.04	0.01	0.11	0.05	0.989	0.03	*
b(iii)	-	0.04	0.01		0.06	0.03	0.12	0.06	0.988	0.03	*
b(iv)	-	0.03	0.05	0.07		0.04	0.07	0.05	0.987	0.03	*
b(v)	-	0.01	0.01	0.03	0.04		0.10	0.05	0.987	0.02	*
b(vi)	-	0.11	0.12	0.15	0.07	0.12		0.12	0.995	0.03	*

55 ^oC CSTR, fed on cattle slurry and whey, different diffusers and mixing speeds

Equation A gives good agreement both within phases and phases, as indicated by R^2 values. Equation B gives a very slight improvement in RMSD, though not in R^2. Slope and intercept values (not shown) show a slight improvement from 1.14-1.20 and 0.99-1.53 for Equation A to 1.07-1.13 and 0.57-1.00 for Equation B, respectively. Note TAN measurements are only reported once for each stage: numerical values were estimated by scaling from Figure S3 in the supplementary materials of the original paper.

Table S4

Zhu, X., Chen, L., Chen, Y., Cao, Q., Liu, X. and Li, D., 2019. Differences of methanogenesis between mesophilic and thermophilic in situ biogas-upgrading systems by hydrogen addition. *Journal of Industrial Microbiology and Biotechnology*, *46*(11), pp.1569-1581.

		(i)	(ii)	(iii)	(iv)	(v)	(vi)	(vii)	(viii)
		Meso				Thermo			
	Phase	Ma	Mb	Mc	Md	Ta	Tb	Tc	Td
Temp	^oC	35	35	35	35	55	55	55	55
OLR	g VS L^{-1} day^{-1}	2	2	2	2	2	2	2	2
HRT	days	25	25	25	25	25	25	25	25
H_2 input	L L^{-1} day^{-1}	0.0	0.1	0.6	0.6	0.0	0.2	0.7	0.7
SMP_{tot}	L CH_4 g^{-1} VS	0.197	0.200	0.245	0.210	0.222	0.242	0.245	0.245
CH_4	%	62.0	59.8	38.1	39.1	66.0	68.9	52.1	68.3
TAN	mM	83.8	87.2	96.3	94.6	111.9	114.8	115.6	96.3
VFA	mM	23.6	22.2	22.8	25.1	43.4	43.4	43.4	43.4
pH	-	7.36	7.40	7.63	7.59	7.63	7.64	7.89	7.77
pCO_2	-	0.38	0.32	0.20	0.17	0.34	0.32	0.21	0.19
$a \times 10^8$	-	11.2	12.0	11.4	14.7	5.9	6.0	4.6	7.2
$b \times 10^8$	-	0.68	0.77	0.83	1.00	0.36	0.39	0.27	0.31
Difference between experimental and predicted pH based on Eqn A with coefficient *a*(x) - meso									
a(i)	-	-	0.03	0.01	0.11	-	-	-	-
a(ii)	-	0.03	-	0.02	0.08	-	-	-	-
a(iii)	-	0.01	0.02	-	0.10	-	-	-	-
a(iv)	-	0.12	0.08	0.11	-	-	-	-	-
Difference between experimental and predicted pH based on Eqn B with coefficient *b*(x) - meso									
b(i)	-	-	0.05	0.08	0.16	-	-	-	-
b(ii)	-	0.06	-	0.03	0.11	-	-	-	-
b(iii)	-	0.08	0.03	-	0.08	-	-	-	-
b(iv)	-	0.17	0.11	0.08	-	-	-	-	-
Difference between experimental and predicted pH based on Eqn A with coefficient *a*(x) - thermo									
a(i)	-	-	-	-	-	-	0.01	0.09	0.07
a(ii)	-	-	-	-	-	0.01	-	0.09	0.06
a(iii)	-	-	-	-	-	0.09	0.10	-	0.16
a(iv)	-	-	-	-	-	0.07	0.07	0.16	-
Difference between experimental and predicted pH based on Eqn B with coefficient *a*(x) - thermo									
b(i)	-	-	-	-	-	-	0.02	0.09	0.05
b(ii)	-	-	-	-	-	0.02	-	0.11	0.07
b(iii)	-	-	-	-	-	0.09	0.11	-	0.03
b(iv)	-	-	-	-	-	0.06	0.08	0.03	-

11.2 L working volume CSTRs fed on pig manure, at 35 and 55 ^oC. Varied amount of H_2 and mixing (intermittent in phases a-c, continuous in phase d). Note these experiments are reported in two other papers with additional conditions or analyses. The authors also kindly provided continuous data from their experiments. There were some minor inconsistencies between papers in values needed for Equation A and B. TAN values were taken from this paper apart from Td where the value from Zhu, Cao et al. (2019) was used. VFA values were taken from averages for daily data.

Equations A and B both show good agreement in almost all cases. Regression analysis only showed significance for *a(iii)* in mesophilic conditions and for *a(iii)*, *a(iv)* and *b(ii)* in thermophilic, reflecting the small number of phases: R^2 values (not shown) ranged from 0.996 to 1.000 for these cases.

Zhu, X., Cao, Q., Chen, Y., Sun, X., Liu, X. and Li, D., 2019. Effects of mixing and sodium formate on thermophilic in-situ biogas upgrading by H2 addition. J. Cleaner Production, 216, pp.373-381.
Zhu, X., Chen, L., Chen, Y., Cao, Q., Liu, X. and Li, D., 2020. Effect of H2 addition on the microbial community structure of a mesophilic anaerobic digestion system. Energy, 198, p.117368.

Table S5

Tao, B., Zhang, Y., Heaven, S. and Banks, C.J., 2020. Predicting pH rise as a control measure for integration of CO_2 biomethanisation with anaerobic digestion. *Applied Energy*, *277*, p.115535.

		(i) No H_2	(ii) With H_2	(iii) With H_2+CO_2
Temp	°C	37	37	37
OLR	g VS L^{-1} day^{-1}	4.14	4.14	4.14
HRT	days	25	25	25
H_2 input	L L^{-1} day^{-1}	0.0	3.7	10.9
SMP_{tot}	L CH_4 g^{-1} VS	0.561	0.776	1.215
CH_4	%	65.5	90.4	89.3
TAN	mM	337	n/r	n/r
VFA	g L^{-1}	0.90	n/r	n/r
pH	-	8.11	8.52	8.51
pCO_2	-	0.34	0.09	0.10
$a \times 10^8$	-	1.95	2.32	2.23
Difference between experimental and predicted pH based on Eqn A with coefficient *a*(x)				
a(i)	-	-	0.06	0.05
a(ii)	-	0.07	-	0.01
a(iii)	-	0.05	0.01	-

CSTR, 37 °C, commercial and industrial food wastes

Equation A gives good agreement for all conditions. Note that parameter values reported here were calculated from the original dataset to match the methods used in the current work and may differ slightly from those in the original paper. Regression analysis not carried out here as only 3 cases; results for whole dataset shown in Figure 1(c) and (d) and Figure A1 in the main paper.

Table S6

Tao, B., Zhang, Y., Heaven, S. and Banks, C.J., 2020. Predicting pH rise as a control measure for integration of CO2 biomethanisation with anaerobic digestion. *Applied Energy*, *277*, p.115535.

		(i) No H_2	(ii) With H_2
Temp	°C	37	37
OLR	g VS L^{-1} day^{-1}	3.64	3.64
HRT	days	15	15
H_2 input	L L^{-1} day^{-1}	0	2.7
SMP_{tot}	L CH_4 g^{-1} VS	0.309	0.437
CH_4	%	60.05	90.46
TAN	mM	108	n/r
VFA	g L^{-1}	n/r	n/r
pH	-	7.32	7.94
pCO_2	-	0.394	0.082
$a \times 10^8$	-	11.99	12.48
Difference between experimental and predicted pH based on Eqn A with coefficient *a*(x)			
a(i)	-	-	0.02
a(ii)	-	0.02	-

CSTR, 37 °C, co-settled primary and secondary sewage sludge

Equation A gives good agreement. Note that parameter values reported here were calculated from the original dataset to match the methods used in the current work and may differ slightly from those in the original paper. Regression analysis not carried out here as only 3 cases; results for whole dataset shown in Figure 1(a) and (b) in the main paper.

Table S7

Lovato, G., Alvarado-Morales, M., Kovalovszki, A., Peprah, M., Kougias, P.G., Rodrigues, J.A.D. and Angelidaki, I., 2017. In-situ biogas upgrading process: modeling and simulations aspects. *Bioresource technology*, *245*, pp.332-341.

		(i) No H_2	(ii) With H_2
Temp	°C	55	55
OLR	g VS L^{-1} day^{-1}	3.71	3.71
HRT	days	15	15
H_2 input	L L^{-1} day^{-1}	0	0.8
SMP_{tot}	L CH_4 g^{-1} VS	0.244	0.283
CH_4	%	65.6	72.7
TAN	mM	110	121
VFA	mM	1	1
pH	-	7.74	7.92
pCO_2	-	0.344	0.222
$a \times 10^8$	-	4.37	4.14
$b \times 10^8$	-	0.47	0.49
Difference between experimental and predicted pH based on Eqn A with coefficient *a*(x)			
a(i)	-	-	0.02
a(ii)	-	0.02	-
Difference between experimental and predicted pH based on Eqn B with coefficient *b*(x)			
b(i)	-	-	0.01
b(ii)	-	0.02	-

Cattle manure and whey 55°C as one of 3 case studies modelled

Equation A gives good agreement for average values in original paper; slightly less good for period selected in the current work from the data series kindly provided by author. Equation B gives a very small improvement, but note that this is using modelled TAN values in both cases.

Table S8

Lebranchu, A.; Blanchard, F.; Fick, M.; Pacaud, S.; Olmos, E.; Delaunay, S. Pilot-scale biomethanation of cattle manure using dense membranes. *Bioresource technology* **2019**, *284*, 430-436.

		(i) No H_2	(ii) With H_2	(iii) With H_2	(iv) With H_2	RMSD	R^2	RMSE	Sig
Temp	^oC	40	40	40	40	-	-	-	-
OLR	g VS L^{-1} day^{-1}	3.85	3.85	3.85	3.85	-	-	-	-
HRT	days	28	28	28	28	-	-	-	-
H_2 input	L L^{-1} day^{-1}	0	0.1728	0.288	0.4464	-	-	-	-
SMP_{tot}	L CH_4 g^{-1} VS	0.186	0.200	0.209	0.221	-	-	-	-
CH_4	%	57.4	61.6	64.4	68.3	-	-	-	-
TAN	mM	n/r	n/r	n/r	n/r	-	-	-	-
VFA	mM	n/r	n/r	n/r	n/r	-	-	-	-
pH	-	7.45	7.52	7.63	7.70	-	-	-	-
pCO_2	-	0.424	0.382	0.354	0.316	-	-	-	-
a x 10^8	-	8.02	7.52	6.21	5.87	-	-	-	-
Difference between experimental and predicted pH based on Eqn A with coefficient a(x)									
a(i)	-	-	0.03	0.11	0.13	0.10	0.942	0.01	no
a(ii)	-	0.03	-	0.08	0.10	0.08	0.986	0.01	no
a(iii)	-	0.11	0.08	-	0.02	0.08	0.993	0.00	no
a(iv)	-	0.13	0.10	0.02	-	0.10	0.953	0.01	no

100 L working volume CSTR at 40 ^oC fed on cattle manure, H_2 addition at 4 different rates

Agreement for individual values and RMSD generally good. A slight downward trend across the phases may reflect trends in baseline parameters, but no further supporting measurements were available to confirm this. The whole experiment lasted approx 2.5 HRT, so this may indicate some ongoing acclimatisation and stabilisation. No TAN or VFA values.

R^2 values between phases appear good but slope and intercept range from 0.40-0.47 and 3.94-4.61 respectively, and linear regression results not significant at 5% level, again possibly suggesting some drift between phases.

Table S9

Wahid, R., Mulat, D.G., Gaby, J.C. and Horn, S.J., 2019. Effects of H2: CO2 ratio and H2 supply fluctuation on methane content and microbial community composition during in-situ biological biogas upgrading. *Biotechnology for biofuels*, *12*(1), pp.1-15.

	From	(i)	(ii)	(iii)	(iv)
		Average		Endpoints	
		No H_2	With H_2	No H_2	With H_2
Temp	°C	37	37	37	37
OLR	g VS L^{-1} day^{-1}	0.1	0.1	0.1	0.1
HRT	Days	21	21	21.0	21.0
H_2 input	L L^{-1} day^{-1}	0.00	0.06	0.0	0.1
SMP_{tot}	L CH_4 g^{-1} VS	0.352	0.574	0.4	0.6
CH_4	%	66.7	94.47	66.7	94.5
TAN	mM	n/a	n/a	n/a	n/a
VFA	g L^{-1}	0.04	0.04	0.04	0.04
pH	-	7.07	7.64	6.95	7.80
pCO_2	-	0.333	0.031	0.395	0.046
$a \times 10^8$	-	25.18	70.21	28.08	32.01
Difference between experimental and predicted pH based on Eqn A with coefficient *a*(x)					
a(i)	-	-	0.41	-	-
a(ii)	-	0.44	-	-	-
a(iii)	-	-	-	-	0.05
a(iv)	-	-	-	0.06	-

n/a = not applicable

CSTR 37 °C, fed on glucose, 21-day HRT. Varied H_2 addition.

Equation A based on average values gave poor agreement in columns (i) and (ii), but there was some variation in pH and VFA and HCl was added on at least one occasion (see Figure 2 in original paper); thus averages may not have reflected final stable operating values. If final values from graphs in Fig 1 and 2 of original paper are used as in columns (iii) and (iv), agreement is good. Regression analysis not carried out as only two cases.

Table S10

Luo, G., Wang, W. and Angelidaki, I., 2013. Anaerobic digestion for simultaneous sewage sludge treatment and CO biomethanation: process performance and microbial ecology. *Environmental science & technology*, *47*(18), pp.10685-10693.

		(i)	(ii)	(iii)	(iv)	(v)	(vi)	(vii)	(viii)	RMSD	R^2	RMSE	Sig
	Phase	I		II		III		IV					
		With CO	No CO	With CO	No CO	With CO	No CO	With CO	No CO				
Temp	°C	55	55	55	55	55	55	55	55	-	-	-	-
OLR	g VS L^{-1} day^{-1}	3.35	3.35	3.35	3.35	3.35	3.35	3.35	3.35	-	-	-	-
HRT	days	10	10	10	10	10	10	10	10	-	-	-	-
CO input	L L^{-1} day^{-1}	1.12	0	2.46	0	4.87	0	9.48	0	-	-	-	-
SMP_{tot}	L CH_4 g^{-1} VS	0.281	0.204	0.367	0.188	0.541	0.201	0.595	0.187	-	-	-	-
CH_4	%	42.2	62	35.3	61.4	29.8	62.1	19.2	61	-	-	-	-
TAN	mM	n/r	n/r	n/r	n/r	n/r	n/r	n/r	n/r	-	-	-	-
VFA	mM	0.4	0.4	0.5	0.6	0.3	0.3	0.4	0.5	-	-	-	-
pH	-	7.10	7.25	7.03	7.28	7.03	7.24	7.17	7.29	-	-	-	-
pCO_2	-	0.565	0.369	0.634	0.386	0.689	0.366	0.445	0.383	-	-	-	-
$a \times 10^8$	-	13.40	14.25	14.13	12.66	13.00	14.73	14.36	12.45	-	-	-	-
Difference between experimental and predicted pH based on Eqn A with coefficient *a*(x)													
a(i)	-	-	0.03	0.02	0.02	0.01	0.04	0.03	0.03	0.03	0.938	0.03	*
a(ii)	-	0.03	-	0.00	0.05	0.04	0.01	0.00	0.06	0.03	0.943	0.02	*
a(iii)	-	0.02	0.00	-	0.04	0.03	0.02	0.01	0.05	0.03	0.929	0.03	*
a(iv)	-	0.02	0.05	0.05	-	0.01	0.06	0.05	0.01	0.04	0.949	0.02	*
a(v)	-	0.01	0.04	0.03	0.01	-	0.05	0.04	0.02	0.03	0.927	0.02	*
a(vi)	-	0.04	0.01	0.02	0.06	0.05	-	0.01	0.07	0.04	0.955	0.02	*
a(vii)	-	0.03	0.00	0.01	0.05	0.04	0.01	-	0.06	0.04	0.950	0.02	*
a(vii)	-	0.03	0.06	0.05	0.01	0.02	0.07	0.06	-	0.05	0.957	0.02	*

CSTR, 55 °C, sewage sludge with carbon monoxide addition (no H_2)

Equation A gives very good agreement in all cases, both within and across phases. No TAN data, little variation in VFA. Note absence of low pCO_2 values due to CO_2 produced from conversion of CO. Regression analysis across the different phases and cases gave slopes ranging from 0.933-1.024 and intercept values from -0.13 to 0.78, with all results significant at the 5% level.

Table S11

Wang, W., Xie, L., Luo, G., Zhou, Q. and Angelidaki, I., 2013. Performance and microbial community analysis of the anaerobic reactor with coke oven gas biomethanation and in situ biogas upgrading. *Bioresource technology*, *146*, pp.234-239.

		(i) With H_2	(ii) No H_2
Temp	^oC	37	37
OLR	g VS L^{-1} day^{-1}	1.1	1.1
HRT	days	10	10
SCOG input	L L^{-1} day^{-1}	0.00	0.65
SMP_{tot}	L CH_4 g^{-1} VS	0.256	0.404
CH_4	%	64.4	89.9
TAN	mM	n/r	n/r
VFA	mM	low	low
pH	-	7.0	7.5
pCO_2	-	0.34	0.09
a x 10^8	-	28.87	33.40
Difference between experimental and predicted pH based on Eqn A with coefficient *a*(x)			
a(i)	-	-	0.06
a(ii)	-	0.06	-

37 °C CSTR fed on wastewater biosolids plus increasing amounts of simulated coke oven gas (SCOG)

Equation A gave good agreement in phase I and II; phase III not shown as pH was controlled by chemical addition.

Table S12

Jing, Y., Campanaro, S., Kougias, P., Treu, L., Angelidaki, I., Zhang, S. and Luo, G., 2017. Anaerobic granular sludge for simultaneous biomethanation of synthetic wastewater and CO with focus on the identification of CO-converting microorganisms. *Water research*, *126*, pp.19-28.

		(i)	(ii)	(iii)	(iv)	(v)	(vi)	(vii)	(viii)	RMSD	R^2	RMSE	Sig
	Phase	I		II		III		IV					
		No CO	No CO	CO	No CO	CO	No CO	CO	No CO				
Temp	°C	37	37	37	37	37	37	37	37	-	-	-	-
OLR	g COD L^{-1} day^{-1}	5	5	5	5	5	5	5	5	-	-	-	-
HRT	days	3	3	3	3	3	3	3	3	-	-	-	-
CO input	L L^{-1} day^{-1}	0	0	2.5	0	2.5	0	5	0	-	-	-	-
SMP_{tot}	L CH_4 g^{-1} VS	0.304	0.299	0.342	0.306	0.424	0.316	0.536	0.312	-	-	-	-
CH_4	%			0.035		0.108		0.225		-	-	-	-
TAN	mM	n/r	n/r	n/r	n/r	n/r	n/r	n/r	n/r	-	-	-	-
VFA	mM	0.52	0.57	1.85	0.55	0.11	0.08	0.14	0.06	-	-	-	-
pH	-	7.51	7.56	7.41	7.54	7.32	7.65	7.28	7.67	-	-	-	-
pCO_2	-	0.249	0.267	0.238	0.250	0.517	0.246	0.553	0.245	-	-	-	-
$a \times 10^8$	-	11.92	9.86	15.82	11.05	9.02	8.61	9.26	8.23	-	-	-	-
Difference between experimental and predicted pH based on Eqn A with coefficient a(x)													
a(i)	-	-	0.08	0.12	0.03	0.12	0.13	0.11	0.15	0.11	0.679	0.08	*
a(ii)	-	0.08	-	0.20	0.05	0.04	0.06	0.03	0.07	0.09	0.656	0.09	*
a(iii)	-	0.12	0.20	-	0.15	0.24	0.25	0.23	0.27	0.22	0.873	0.05	*
a(iv)	-	0.03	0.05	0.15	-	0.09	0.10	0.07	0.12	0.10	0.658	0.09	*
a(v)	-	0.12	0.04	0.23	0.08	-	0.02	0.01	0.04	0.11	0.560	0.08	no
a(vi)	-	0.14	0.06	0.25	0.10	0.02	-	0.03	0.02	0.12	0.665	0.08	*
a(vii)	-	0.10	0.03	0.22	0.07	0.01	0.03	-	0.05	0.10	0.480	0.08	no
a(viii)	-	0.15	0.07	0.27	0.12	0.04	0.02	0.05	-	0.13	0.684	0.08	*

2 UASB 1-L working volume, 37 °C, one fed on glucose + BA medium, one also CO. Inflow rate initially 2.5, raised to 5.0 L L^{-1} day^{-1}. Injection plus recirculation due to low CO solubility.

Good agreement within and between phases apart from for experimental reactor in phase 2 when high VFA observed. No TAN data available. R^2 values between phases poor, probably due to relatively small variation in pH and pCO_2 overall as well as poor result for case *(iii)* when VFA present. Most results significant at the 5% level.

Table S13

Andreides, D., Quispe, J.I.B., Bartackova, J., Pokorna, D. and Zabranska, J., 2021. A novel two-stage process for biological conversion of syngas to biomethane. *Bioresource Technology*, *327*, p.124811.

		(i)	(ii)	(iii)	(iv)	(v)	(vi)	(vii)	(viii)	(ix)
	Phase	I		II		III		I	II	III
	Stage 1	No gas	Gas	No gas	Gas	No gas	No gas		Stage 2	
Temp	°C	55	55	55	55	55	55	42	42	42
OLR	g VS L^{-1} day^{-1}	2.6	2.6	2.6	2.6	2.6	2.6	-	-	-
HRT	days	18	18	18	18	18	18	-	-	-
Syngas	L L^{-1} day^{-1}	0	0.55	0	0.55	0	0.	-	-	-
SMP_{tot}	L CH_4 g^{-1} VS	0.20	0.22	0.17	0.18	0.19	0.21	0.19	0.19	0.22
CH_4	%	64.8	64.8	65.1	59.2	64.5	55.1	89.2	91.8	83.5
TAN	mM	n/r	n/r	n/r	n/r	n/r	n/r	n/r	n/r	n/r
TVFA	g L^{-1}	0.30	0.22	0.27	0.16	0.29	0.17	0.07	0.06	0.06
pH	-	7.82	7.77	7.80	7.71	7.80	7.68	7.54	7.64	7.64
pCO_2	-	0.35	0.34	0.35	0.35	0.36	0.36	0.11	0.08	0.16
$a \times 10^8$		3.42	4.02	3.65	4.62	3.58	4.96	25.6	26.6	13.1
Difference between experimental and predicted pH based on Eqn A with coefficient *a*(x)										
a(i)	-	-	0.06	0.02	0.11	0.02	0.14	-	-	-
a(ii)	-	0.06	-	0.04	0.05	0.04	0.08	-	-	-
a(iii)	-	0.02	0.04	-	0.09	0.01	0.11	-	-	-
a(iv)	-	0.11	0.05	0.09	-	0.09	0.03	-	-	-
a(v)	-	0.02	0.04	0.01	0.09	-	0.12	-	-	-
a(vi)	-	0.14	0.08	0.11	0.03	0.12	-	-	-	-
a(vii)	-	-	-	-	-	-	-	-	0.01	0.28
a(viii)	-	-	-	-	-	-	-	0.01	-	0.29
a(ix)	-	-	-	-	-	-	-	0.27	0.28	-

2-stage: first stage 55 °C CSTR fed on sewage sludge with syngas injection, second stage 42 °C trickle bed with H_2 injection. Varied syngas composition (H_2:CO:CO_2 ratios of 60:20:20 % v/v in phase I, 45:35:20 in phase II, and 30:50:20 in phase III).

Agreement in stage 1 reactor was good in phase I and II, good or reasonable in phase III; but little variation in pH or pCO_2 as no H_2 addition in this phase. The stage 2 reactor showed good agreement in phase I and II, poor in phase III. Regression analysis not carried out as only 3 cases for stage 2 with H_2 addition, and no variation in stage 1.

Table S14

Yang, Z., Liu, Y., Zhang, J., Mao, K., Kurbonova, M., Liu, G., Zhang, R. and Wang, W., 2020. Improvement of biofuel recovery from food waste by integration of anaerobic digestion, digestate pyrolysis and syngas biomethanation under mesophilic and thermophilic conditions. *Journal of Cleaner Production*, *256*, p.120594.

		(i)	(ii)	(iii)	(iv)	(v)	(vi)	(vii)	(viii)	(ix)	(x)
		Meso					Thermo				
	Phase	I	II	III	IV	V	I	II	III	IV	V
Temp	°C	37	37	37	37	37	55	55	55	55	55
OLR	g VS L^{-1} day^{-1}	3.52	3.52	3.52	3.52	3.52	3.52	3.52	3.52	3.52	3.52
HRT	days	20	20	20	20	20	20	20	20	20	20
Syngas	L L^{-1} day^{-1}	0	0.140	0.260	0.650	1.325	0	0.140	0.260	0.650	1.325
SMP_{tot}	L CH_4 g^{-1} VS	0.321	0.341	0.366	0.380	0.422	0.384	0.415	0.432	0.469	0.509
CH_4	%	62.2	61.5	62.4	62.2	61.1	63.5	64.3	63.5	63.8	64.0
TAN	mM	21.6	36.3	28.7	32.7	31.3	34.9	36.9	40.8	37.3	50.0
VFA	mM	3.3	3.3	3.3	3.3	3.3	6.7	5.0	3.3	3.3	3.3
pH	-	7.12	7.07	7.20	7.21	7.19	7.22	7.18	7.35	7.31	7.22
pCO_2	-	0.378	0.385	0.376	0.378	0.370	0.365	0.357	0.365	0.362	0.358
$a \times 10^8$	-	19.7	21.8	16.5	16.0	17.1	15.5	17.5	11.2	12.5	15.8
$b \times 10^8$	-	0.36	0.72	0.42	0.47	0.48	0.43	0.55	0.42	0.42	0.74
Difference between experimental and predicted pH based on Eqn A with coefficient *a*(x) - meso											
a(i)	-	-	0.04	0.08	0.09	0.06	-	-	-	-	-
a(ii)	-	0.04	-	0.12	0.13	0.10	-	-	-	-	-
a(iii)	-	0.08	0.12	-	0.01	0.02	-	-	-	-	-
a(iv)	-	0.09	0.13	0.01	-	0.03	-	-	-	-	-
a(v)	-	0.06	0.10	0.02	0.03	-	-	-	-	-	-
Difference between experimental and predicted pH based on Eqn B with coefficient *b*(x) - meso											
b(i)	-	-	0.07	0.06	0.11	0.12	-	-	-	-	-
b(ii)	-	0.07	-	0.01	0.04	0.05	-	-	-	-	-
b(iii)	-	0.06	0.01	-	0.05	0.06	-	-	-	-	-
b(iv)	-	0.11	0.04	0.05	-	0.01	-	-	-	-	-
b(v)	-	0.12	0.05	0.06	0.01	-	-	-	-	-	-
Difference between experimental and predicted pH based on Eqn A with coefficient *a*(x) - thermo											
a(i)	-	-	-	-	-	-	-	0.05	0.13	0.09	0.01
a(ii)	-	-	-	-	-	-	0.05	-	0.18	0.14	0.04
a(iii)	-	-	-	-	-	-	0.13	0.18	-	0.04	0.14
a(iv)	-	-	-	-	-	-	0.09	0.14	0.04	-	0.10
a(v)	-	-	-	-	-	-	0.01	0.04	0.14	0.10	-
Difference between experimental and predicted pH based on Eqn B with coefficient *b*(x) - thermo											
b(i)	-	-	-	-	-	-	-	0.10	0.01	0.01	0.21
b(ii)	-	-	-	-	-	-	0.10	-	0.11	0.11	0.12
b(iii)	-	-	-	-	-	-	0.01	0.11	-	0.00	0.23
b(iv)	-	-	-	-	-	-	0.01	0.11	0.00	-	0.22
b(v)	-	-	-	-	-	-	0.22	0.12	0.23	0.23	-

CSTR AD of food waste with added syngas to simulate that produced from digestate pyrolysis. One reactor at 37 °C and one at 55 °C.

The paper states that TVFA was always < 400 mg L^{-1}, but during mesophilic operation there was a peak of more than 8 g L^{-1}. VFA concentrations were estimated from Figures 1c and 2c in the original paper, with a value of 1 g L^{-1} assumed for mesophilic phase II. Equation A gave good or reasonable agreement in both mesophilic and thermophilic conditions. Equation B also performed well in mesophilic conditions. In thermophilic conditions it performed better than Equation A for phases 1-4 but less well in stage 5, perhaps indicating some other disturbance in this phase; although the paper suggests higher loading rates of H_2-deficient syngas could be achieved. Regression analysis between phases not carried out as little variation in pCO_2 or pH.

Table S15

Bassani, I., Kougias, P.G., Treu, L. and Angelidaki, I., 2015. Biogas upgrading via hydrogenotrophic methanogenesis in two-stage continuous stirred tank reactors at mesophilic and thermophilic conditions. Environmental science & technology, 49(20), pp.12585-12593.

		(i) Meso No H_2	(ii) With H_2	(iii) Thermo No H_2	(iv) With H_2
Temp	^oC	35	35	55	55
OLR	g VS L^{-1} day^{-1}	0.6	0.6	1.0	1.0
HRT	days	25 and 33	25 and 33	15 and 20	15 and 20
H_2 input	L L^{-1} day^{-1}	0	0.19	0	0.51
SMP_{tot}	L CH_4 g^{-1} VS	0.111	0.168	0.249	0.359
CH_4	%	69.7	88.9	67.1	85.1
TAN	mM	n/r	n/r	n/r	n/r
VFA	g L^{-1}	0.09	0.16	0.28	0.38
pH	-	7.73	8.17	7.89	8.49
pCO_2	-	0.303	0.088	0.329	0.066
$a \times 10^8$	-	5.80	6.59	3.01	2.22
Difference between experimental and predicted pH based on Eqn A with coefficient a(x)					
a(i)	-	-	0.05	-	-
a(ii)	-	0.05	-	-	-
a(iii)	-	-	-	-	0.09
a(iv)	-	-	-	0.10	-

Cattle manure, CSTR, 2-stage, mesophilic (35 ^oC) and thermophilic (55 ^oC). Continuous H_2 injection by diffuser into stage 2, no gas recirculation within or between stages.

Values here are for stage 2 reactors in control period before H_2 addition, and with H_2 addition: no gas recirculation in stage 2 or to stage 1. Good agreement, mesophilic slightly better than thermophilic. Regression analysis not carried out as only two cases at each temperature.

Table S16

Treu, L., Kougias, P.G., de Diego-Díaz, B., Campanaro, S., Bassani, I., Fernández-Rodríguez, J. and Angelidaki, I., 2018. Two-year microbial adaptation during hydrogen-mediated biogas upgrading process in a serial reactor configuration. *Bioresource technology*, *264*, pp.140-147.

		(i) Control period No H_2	(ii) Initial value With H_2	(iii) After 2 years With H_2
Temp	^{o}C	55	55	55
OLR	g VS L^{-1} day^{-1}	0.99	0.99	0.99
HRT	days	15 and 20	15 and 20	15 and 20
H_2 input	L L^{-1} day^{-1}	0.00	0.51	0.51
SMP_{tot}	L CH_4 g^{-1} VS	0.26	0.38	0.50
CH_4	%	66.90	86.50	98.70
TAN	mM	n/r	n/r	n/r
VFA	g L^{-1}	125	429	1144
pH	-	7.90	8.49	8.71
pCO_2	-	0.331	0.066	0.009
a x 10^8	-	2.90	2.22	7.23
Difference between experimental and predicted pH based on Eqn A with coefficient a(x)				
a(i)	-	-	0.08	0.23
a(ii)	-	0.09	-	0.29
a(iii)	-	0.34	0.35	-

Cattle manure, 55 ^{o}C, 2-stage: stage 1 with 15-day HRT fed on cattle manure, stage 2 with 20-day HRT fed on digestate and biogas from stage 1 plus H_2 (referred to as serial).

Good agreement between control period and initial H_2 addition. Poor agreement after 2 years, but note very low pCO_2 and higher VFA at this point. No TAN data. Regression analysis between phases not carried out due to small number of cases with presence of VFA in case *(iii)*.

Table S17

Hafuka, A., Fujino, S., Kimura, K., Oshita, K., Konakahara, N. and Takahashi, S., 2022. In-situ biogas upgrading with H2 addition in an anaerobic membrane bioreactor (AnMBR) digesting waste activated sludge. *Science of The Total Environment*, p.154573.

	Phase	(i) 2 No H_2	(ii) 3 No H_2	(iii) 4 With H_2	(iv) 5 With H_2	RMSD	R^2	RMSE	Sig
Temp	°C	37	37	37	37	-	-	-	-
OLR	g VS L^{-1} day^{-1}	0.21	0.27	0.26	0.28	-	-	-	-
HRT	days	33	30	30	29	-	-	-	-
H_2 input	L L^{-1} day^{-1}	0	0	0.033	0.090	-	-	-	-
SMP_{tot}	L CH_4 g^{-1} VS	0.24	0.19	0.28	0.31	-	-	-	-
CH_4	%	83.1	85.2	83.6	92.0	-	-	-	-
TAN	mM	42.8	42.8	42.8	42.8	-	-	-	-
VFA	mM	0.04	0.04	0.18	0.18	-	-	-	-
pH	-	7.18	7.18	7.10	7.40	-	-	-	-
pCO_2	-	0.169	0.148	0.164	0.08	-	-	-	-
$a \times 10^8$	-	38.35	43.79	47.67	48.21	-	-	-	-
$b \times 10^8$	-	1.64	1.87	2.03	2.06	-	-	-	-
Difference between experimental and predicted pH based on Eqn A with coefficient *a*(x)									
a(i)	-	-	0.06	0.09	0.10	0.08	0.984	0.02	no
a(ii)	-	0.06	-	0.04	0.04	0.05	0.915	0.04	no
a(iii)	-	0.09	0.04	-	0.00	0.06	0.972	0.02	no
a(iv)	-	0.10	0.04	0.00	-	0.06	0.091	0.02	no
Difference between experimental and predicted pH based on Eqn B with coefficient *b*(x)									
b(i)	-	-	0.06	0.09	0.09	0.08	0.985	0.02	no
b(ii)	-	0.06	-	0.03	0.04	0.04	0.917	0.04	no
b(iii)	-	0.09	0.03	-	0.00	0.06	0.972	0.02	no
b(iv)	-	0.10	0.04	0.00	-	0.06	0.107	0.02	no

Hollow Fibre Membrane AnMBR (operated as CSTR at start and end of experiment), 37 oC, fed weekly on WAS, daily on H2. 221 days, 7 phases with 5 as AnMBR, varied HRT and SRT.

Analysis of results is for phases 2-5 when reactor was configured as AnMBR: good agreement across all points. pH values for phases 4 & 5 are taken from Fig 3a in original paper. No real change between Equation A and B, both perform well. Regression analysis showed high R^2 values but was not significant at the 5% level, reflecting the small number of cases overall and the similar pH and pCO_2 values in cases *(i)* to *(iii)*.

Table S18

Bassani, I., Kougias, P.G. and Angelidaki, I., 2016. In-situ biogas upgrading in thermophilic granular UASB reactor: key factors affecting the hydrogen mass transfer rate. Bioresource technology, 221, pp.485-491.

	Gas transfer	-		Rashig		Rashig		Ceramic		Ceram + recirc		Ceram + recirc		Ceram + recirc		Ceram + recirc	
		(i) No H_2	(ii) No H_2	(iii) H_2	(iv) No H_2	(v) H_2	(vi) No H_2	(vii) H_2	(viii) No H_2	(ix) H_2	(x) No H_2	(xi) H_2	(xii) No H_2	(xiii) H_2	(xiv) No H_2	(xv) H_2	(xvi) No H_2
Liquid recirc	L $hour^{-1}$	4	4	4	4	7	7	7	7	7	7	7	7	7	7	7	7
Gas recirc	mL min^{-1}	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	4	0	6	0	6	0	6	0
Temp	^{o}C	55	55	55	55	55	55	55	55	55	55	55	55	55	55	55	55
OLR	g VS L^{-1} day^{-1}	3.73	3.73	3.73	3.73	3.73	3.73	3.73	3.73	3.73	3.73	3.73	3.73	3.73	3.73	3.73	3.73
HRT	days	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
H_2 input	L L^{-1} day^{-1}	0	0	3.477	0	2.636	0	2.629	0	2.144	0	1.834	0	1.768	0	1.828	0
SMP_{tot}	L CH_4 g^{-1} VS	0.336	0.342	0.410	0.362	0.401	0.329	0.394	0.299	0.366	0.311	0.318	0.351	0.280	0.205	0.307	0.279
CH_4	%	58.2	60.3	40.4	60.6	44.9	60.9	52	62.5	66.4	61.1	66	65	67.6	65	81.3	66.7
TAN	mM	n/r	n/r	n/r	n/r	n/r	n/r	n/r	n/r	n/r	n/r	n/r	n/r	n/r	n/r	n/r	n/r
VFA	g L^{-1}	1.69	1.21	3.4	1.41	3.6	2.26	2.81	2.37	5.11	3.24	3.66	2.37	4.34	3.21	3.87	2.36
pH	-	7.46	7.49	7.92	7.59	7.9	7.6	7.93	7.56	7.83	7.64	8.24	7.85	8.18	7.92	8.38	7.99
pCO_2	-	0.418	0.397	0.149	0.394	0.185	0.391	0.17	0.375	0.205	0.389	0.1835	0.35	0.188	0.35	0.102	0.332
$a \times 10^8$	-	7.46	7.27	6.09	5.67	5.20	5.56	5.19	6.43	5.71	5.03	1.87	3.16	2.21	2.59	2.11	2.23
Difference between experimental and predicted pH based on Eqn A with coefficient a(x)																	
a(i)	-	-	0.01	0.07	0.11	0.13	0.11	0.13	0.06	0.10	0.15	0.47	0.32	0.42	0.39	0.40	0.44
a(ii)	-	0.01	-	0.06	0.10	0.12	0.10	0.12	0.05	0.09	0.14	0.46	0.31	0.41	0.38	0.39	0.43
a(iii)	-	0.08	0.07	-	0.03	0.06	0.04	0.06	0.02	0.02	0.07	0.39	0.24	0.34	0.31	0.33	0.36
a(iv)	-	0.11	0.10	0.03	-	0.03	0.01	0.03	0.05	0.00	0.05	0.37	0.21	0.32	0.28	0.31	0.33
a(v)	-	0.14	0.13	0.06	0.03	-	0.03	0.00	0.08	0.03	0.01	0.34	0.18	0.29	0.25	0.28	0.30
a(vi)	-	0.11	0.10	0.03	0.01	0.02	-	0.02	0.06	0.01	0.04	0.36	0.21	0.31	0.28	0.30	0.33
a(vii)	-	0.14	0.13	0.06	0.03	0.00	0.03	-	0.08	0.03	0.01	0.34	0.18	0.29	0.25	0.28	0.30
a(viii)	-	0.06	0.05	0.02	0.05	0.08	0.06	0.08	-	0.04	0.09	0.41	0.26	0.36	0.33	0.35	0.38
a(ix)	-	0.10	0.09	0.02	0.00	0.03	0.01	0.03	0.05	-	0.05	0.37	0.22	0.32	0.29	0.31	0.34
a(x)	-	0.15	0.14	0.07	0.05	0.01	0.04	0.01	0.09	0.05	-	0.33	0.17	0.27	0.24	0.27	0.29
a(xi)	-	0.51	0.50	0.38	0.40	0.34	0.39	0.33	0.45	0.38	0.36	-	0.18	0.05	0.11	0.04	0.06
a(xii)	-	0.33	0.31	0.22	0.22	0.17	0.21	0.17	0.27	0.21	0.17	0.17	-	0.12	0.07	0.12	0.12
a(xiii)	-	0.45	0.44	0.33	0.34	0.29	0.34	0.28	0.39	0.32	0.30	0.05	0.13	-	0.06	0.01	0.00
a(xiv)	-	0.40	0.39	0.28	0.29	0.23	0.28	0.23	0.34	0.27	0.24	0.10	0.07	0.05	-	0.06	0.05
a(xv)	-	0.47	0.46	0.35	0.36	0.30	0.35	0.30	0.41	0.34	0.31	0.04	0.14	0.01	0.07	-	0.02
a(xvi)	-	0.45	0.44	0.33	0.34	0.28	0.33	0.28	0.39	0.32	0.30	0.06	0.12	0.00	0.05	0.02	-

Thermophilic 55 °C UASB, fed on potato starch wastewater, varied gas transfer (Rashid/ceramic) and gas and liquid recirculation.

Good or reasonable agreement across cases (i)-(x) and (xi)-(xvi). No clear single reason for the change between these two sets of results, though it could perhaps be related to changes in gas or liquid recirculation. Regression analysis across these cases confirmed good linear relationships, with R^2 ranging from 0.916-0.955 and 0.931-0.973 for (i)-(x) and (xi)-(xvi) respectively, RMSE values < 0.04 and all results significant at the 5% level. Table S18b shows RMSD, R^2, RMSE and significance for relationship between experimental pH and predicted pH value across the specified cases, excluding the baseline values used in deriving coefficient *a* in each case. Figure S1 gives an example of predicted versus experimental pH for cases (i)-(x) and (xi)-(xvi), using values for coefficient *a(x)* in Table S18: the shift between the two sets of is clearly seen.

Table S18b RMSD and linear regression results for cases in Table 18

Coefft	Case (i)-(x)				Case (xi)-(xvi)			
	RMSD	R^2	RMSE	Sig	RMSD	R^2	RMSE	Sig
a(i)	0.10	0.940	0.04	*	-	-	-	-
a(ii)	0.10	0.938	0.04	*	-	-	-	-
a(iii)	0.05	0.926	0.04	*	-	-	-	-
a(iv)	0.06	0.933	0.04	*	-	-	-	-
a(v)	0.07	0.922	0.04	*	-	-	-	-
a(vi)	0.06	0.936	0.04	*	-	-	-	-
a(vii)	0.07	0.916	0.04	*	-	-	-	-
a(viii)	0.06	0.928	0.04	*	-	-	-	-
a(ix)	0.05	0.926	0.04	*	-	-	-	-
a(x)	0.08	0.955	0.03	*	-	-	-	-
a(xi)	-	-	-	-	0.10	0.960	0.00	*
a(xii)	-	-	-	-	0.12	0.973	0.00	*
a(xiii)	-	-	-	-	0.07	0.946	0.00	*
a(xiv)	-	-	-	-	0.07	0.937	0.00	*
a(xv)	-	-	-	-	0.07	0.931	0.00	*
a(xvi)	-	-	-	-	0.06	0.960	0.00	*

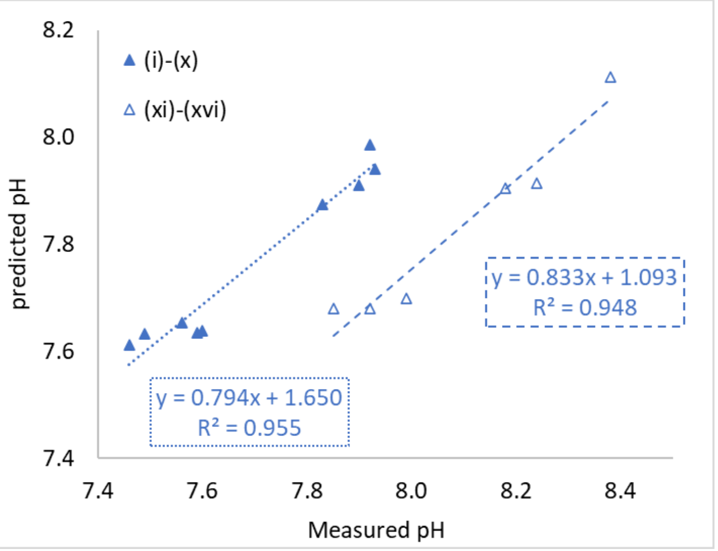

Figure S1 Predicted and experimental pH values from Table S18 cases (i)-(x) and (xi)-(xvi), based on Equation A with coefficient *a(x)*

Table S19

Illi, L., Lecker, B., Lemmer, A., Müller, J. and Oechsner, H., 2021. Biological methanation of injected hydrogen in a two-stage anaerobic digestion process. *Bioresource Technology*, *333*, p.125126.

		(i)	(ii)	(iii)
	H_2/CO_2 ratio	0	2	4
Temp	^oC	37	37	37
OLR	g VS L^{-1} day^{-1}	2.92	3.00	3.53
HRT	days	17.0	17.1	16.5
H_2 input	L L^{-1} day^{-1}	0.00	0.75	1.51
SMP_{tot}	L CH_4 g^{-1} COD	0.31	0.35	0.35
CH_4	%	66.14	62.67	56.69
TAN	mM	n/r	n/r	n/r
VFA	mM	very low	very low	very low
pH	-	7.91	8.17	8.55
pCO_2	-	0.28	0.18	0.12
a x 10^8	-	4.00	3.09	1.61
Difference between experimental and predicted pH based on Eqn A with coefficient a(x)				
a(i)	-	-	0.10	0.32
a(ii)	-	0.10	-	0.22
a(iii)	-	0.35	0.23	-

Anaerobic filters 37 ^oC fed on silage hydrolysate, acting as the second stage to thermophilic (60 ^oC) acidification reactor.

Good agreement for H_2/CO_2 ratios of 0 and 2, poor at ratio 4. Figure 4 of the original paper gives some VFA data, but values in effluent appear to be low. No TAN data.

Table S20

Thapa, A., Park, J.G., Yang, H.M. and Jun, H.B., 2021. In-situ biogas upgrading in an anaerobic trickling filter bed reactor treating a thermal post-treated digestate. Journal of Environmental Chemical Engineering, 9(6), p.106780.

		(i)	(ii)	(iii)	(iv)	RMSD
	Phase	I	II	III	IV	
	Day	0-50	51-85	86-93	94-120	
		No H_2	With H_2	With H_2	With H_2	
Temp	°C	37	37	37	37	-
OLR	g VS L^{-1} day^{-1}	1.88	1.88	1.88	1.88	-
HRT	days	10	10	10	10	-
H_2 input	L L^{-1} day^{-1}	0	2	1.4	1.5	-
SMP_{tot}	L CH_4 g^{-1} VS	0.239	0.362	0.415	0.452	-
CH_4	%	48.65	66.15	71.43	68.18	-
TAN	mM	n/r	n/r	n/r	n/r	-
VFA	g L^{-1}	0.19	1.69	1.98	2.21	-
pH	-	7.82	7.98	7.98	8.02	-
pCO_2	-	0.514	0.231	0.228	0.167	-
$a \times 10^8$	-	2.72	4.04	4.09	5.04	-
Difference between experimental and predicted pH based on Eqn A with coefficient $a(x)$						
a(i)	-	-	0.15	0.16	0.23	0.18
a(ii)	-	0.16	-	0.00	0.08	0.11
a(iii)	-	0.17	0.00	-	0.08	0.11
a(iv)	-	0.25	0.09	0.08	-	0.16

Trickle bed reactor, 37 °C. 1.1 L working volume, 2 kg COD m^{-3} day^{-1}, HRT 10 days based on liquid vol. Feed is thermally treated (120 °C for 30 min) food waste digestate. Phase I (day 0-50) no H_2, phase II (day 51-85) H_2 according to CO_2 in phase I. Phase III increased gas recirculation rate, phase IV altered H_2 flow rate. Unclear whether gas was recirculated in phase I.

Good agreement within and between phases II, III and IV; but note that pH was adjusted by HCl addition during part of the run. Poor agreement between phase I and other phases may indicate acclimatisation or other changes in operating mode before and after H_2 addition.

Table S21

Corbellini, V., Kougias, P.G., Treu, L., Bassani, I., Malpei, F. and Angelidaki, I., 2018. Hybrid biogas upgrading in a two-stage thermophilic reactor. Energy Conversion and Management, 168, pp.1-10.

		(i)	(ii)	(iii)	(iv)	(v)	(vi)
		Stage 1			Stage 2		
	Phase	I	II	III	I	II	III
		No H_2	With H_2	No H_2	No H_2	With H_2	No H_2
Temp	°C	53	53	53	53	53	53
OLR	g VS L^{-1} day^{-1}	1.68	1.68	1.80	-	-	-
HRT	days	15	15	15	28	28	28
H_2 input	L L^{-1} day^{-1}	0	0	0	0	0.55	0
SMP_{tot}	L CH_4 g^{-1} VS	-	-	-	0.211	0.214	0.198
CH_4	%	69.2	86.4	71.0	75.4	91.0	77.0
TAN	mM	n/r	n/r	n/r	n/r	n/r	n/r
VFA	g L^{-1}	0.2	2.7	0.6	0.0	0.1	0.1
pH	-	8.35	8.60	8.09	8.10	8.10	7.66
pCO_2	-	0.307	0.107	0.290	0.243	0.070	0.230
$a \times 10^8$	-	0.82	0.99	1.97	2.28	7.90	8.21
Difference between experimental and predicted pH based on Eqn A with coefficient *a*(x)							
a(i)	-	-	0.05	0.28	-	-	-
a(ii)	-	0.06	-	0.22	-	-	-
a(iii)	-	0.28	0.20	-	-	-	-
a(iv)	-	-	-	-	-	0.38	0.46
a(v)	-	-	-	-	0.45	-	0.01
a(vi)	-	-	-	-	0.46	0.01	-

2-stage (CSTR + upflow), 53 °C, fed on cattle manure and potato starch. H_2 added in stage 1 then recirculated between reactors. Stage 2 receives a small input of digestate from stage 1.

Good agreement in stage 1 CSTR in phase 1 & 2, and for second stage upflow reactor in phase 2 & 3. Surprisingly high pH in stage 1 given feedstock TKN of 1.74 g N L^{-1}. Operating period for each phase is < 3 HRT, so parameters may not have stabilised in each case. High VFA in stage 1 reactor in phase 2 as a result of which H_2 addition was ceased; no TAN data.

This research group also published the following paper related to the work in Table S25:
Corbellini, V., Feng, C., Bellucci, M., Catenacci, A., Stella, T., Espinoza-Tofalos, A. and Malpei, F., 2021. Performance Analysis and Microbial Community Evolution of In Situ Biological Biogas Upgrading with Increasing H2/CO2 Ratio. *Archaea*, *2021*.

In this work two CSTRs operated at 36.7 °C were fed on co-settled primary and secondary sewage sludge at a 22 day HRT and an OLR of 1.5 g COD/L-day, at increasing H_2/CO_2 ratios. Results are not analysed here as pH was controlled, making the experimental design unsuitable for the current purpose. The experiment also involved headspace addition which may have affected pCO_2 and pH.

Table S22

Díaz, I., Fdz-Polanco, F., Mutsvene, B. and Fdz-Polanco, M., 2020. Effect of operating pressure on direct biomethane production from carbon dioxide and exogenous hydrogen in the anaerobic digestion of sewage sludge. Applied Energy, 280, p.115915.

	Phase	(i) I	(ii) II	(iii) III	(iv) IV	RMSD
Pressure	kPa	200	250	300	300	-
Temp	^oC	37	37	37	37	-
OLR	g VS L^{-1} day^{-1}	0.92	0.00	0.00	4.83	-
HRT	days	20	20	20	20	-
H_2 input	L L^{-1} day^{-1}	0.45	0.45	0.45	0.64	-
SMP_{tot}	L CH_4 g^{-1} VS	0.332	0.359	0.336	0.418	-
CH_4	%	69.4	79.7	85.7	92.9	-
TAN	mM	46.0	43.3	62.2	51.4	-
VFA	mM	0.0	0.0	0.0	0.0	-
pH	-	6.60	6.80	6.80	7.00	-
pCO_2	-	0.304	0.320	0.378	0.221	-
a x 10^8	-	82.2	49.1	41.6	44.8	-
Difference between experimental and predicted pH based on Eqn A with coefficient *a*(x)						
a(i)	-	-	0.22	0.29	0.26	0.26
a(ii)	-	0.22	-	0.07	0.04	0.14
a(iii)	-	0.29	0.07	-	0.03	0.18
a(iv)	-	0.26	0.04	0.03	-	0.15
Difference between experimental and predicted pH based on Eqn B with coefficient b(x)						
b(i)	-	-	0.25	0.16	0.21	
b(ii)	-	0.25	-	0.08	0.03	0.21
b(iii)	-	0.16	0.08	-	0.05	0.15
b(iv)	-	0.21	0.03	0.05	-	0.11

Mixed sewage sludge, 35 ^oC, varied pressure and H_2 flow, no control conditions without H_2 or pressure.

Equations A and B both give good agreement apart from in Phase 1 where pH seems surprisingly low in comparison with other phases.: possible acclimatisation effect? pCO_2 is adjusted for applied pressure, TAN and VFA obtained from graphs.

Table S23

Agneessens, L.M., Ottosen, L.D.M., Voigt, N.V., Nielsen, J.L., de Jonge, N., Fischer, C.H. and Kofoed, M.V.W., 2017. In-situ biogas upgrading with pulse H2 additions: the relevance of methanogen adaption and inorganic carbon level. Bioresource Technology, 233, pp.256-263.

		(i)	(ii)	(iii)	(iv)	(v)	(vi)	RMSD	R^2	RMSE	Sig
H_2/CO_2		0	2	4	6	8	10		-	-	-
Temp	°C	38	38	38	38	38	38	-	-	-	-
OLR	g VS L^{-1} day^{-1}	0.77	0.77	0.77	0.77	0.77	0.77	-	-	-	-
HRT	days	20	20	20	20	20	20	-	-	-	-
H_2 input	L L^{-1} day^{-1}	0	0	0.62	0.93	1.24	1.55	-	-	-	-
SMP_{tot}	L CH_4 g^{-1} VS	0.293	0.399	0.451	0.571	0.571	0.442	-	-	-	-
CH_4	%	59.4	76.8	89.0	100.0	100.0	100.0	-	-	-	-
TAN	mM	n/r	n/r	n/r	n/r	n/r	n/r	-	-	-	-
VFA	mM	2.7	1.6	2.5	4.1	5.0	18.6	-	-	-	-
pH	-	7.91	7.89	7.90	7.91	8.18	8.43	-	-	-	-
pCO_2	-	0.213	0.206	0.21	0.168	0.118	0.079	-	-	-	-
$a \times 10^8$	-	5.20	5.65	5.41	6.59	4.64	3.44	-	-	-	-
Difference between experimental and predicted pH based on Eqn A with coefficient *a*(x)											
a(i)	-	-	0.03	0.02	0.09	0.04	0.15	0.08	0.961	0.03	*
a(ii)	-	0.03	-	0.02	0.06	0.07	0.18	0.09	0.949	0.03	*
a(iii)	-	0.02	0.02	-	0.08	0.06	0.16	0.08	0.953	0.03	*
a(iv)	-	0.09	0.06	0.08	-	0.13	0.23	0.13	0.992	0.01	*
a(v)	-	0.04	0.08	0.06	0.14	-	0.10	0.09	0.949	0.03	*
a(vi)	-	0.16	0.19	0.18	0.25	0.11	-	0.18	0.863	0.03	*

CSTR 38 °C fed on agro-waste digestate. Pulse addition of increasing amounts of H_2 to high stoichiometric ratios (10:1 H_2:CO_2 v/v)

Agreement good or reasonable until last set of conditions when some VFA is seen; but no TAN data available. Effect of pressure change due to increasing H_2 addition is uncertain. Note that pH points are clustered high and low. Good correlation for different H_2/CO_2 ratios. Slope and intercept values (not shown are between 0.64-0.72 and 2.11-2.84, respectively.

Table S24

Agneessens, L.M., Ottosen, L.D.M., Andersen, M., Olesen, C.B., Feilberg, A. and Kofoed, M.V.W., 2018. Parameters affecting acetate concentrations during in-situ biological hydrogen methanation. Bioresource technology, 258, pp.33-40.

Table S24a Initial values

		Initial values from Table 1 in paper	
		(i)	(ii)
Temp	^oC	38	38
pH	-	7.8	8.36
pCO_2	-	0.4	0.09
$a \times 10^8$	-	3.65	3.69
Difference between experimental and predicted pH based on Eqn A with coefficient *a*(x)			
	a(i)	-	0.00
	a(ii)	0.00	-

Mainly microbial and pathway results. Same feedstock and conditions as Agneessens et al. (2017) but varied H_2 additions to give low or high CO_2.

Good agreement at initial values

Table S24b Experimental values from paper and supplementary materials

		OLR 0.5, >25% CO_2		OLR 0.5, <7% CO_2		OLR 1.5, >25% CO_2		OLR 1.5, <7% CO_2	
All 38 ^oC		No H_2	With H_2	No H_2	With H_2	No H_2	With H_2	No H_2	With H_2
pH	-	7.89	7.84	8.32	8.32	8.07	8.08	8.34	8.18
pCO_2	-	0.54	0.40	0.53	0.42	0.48	0.35	0.47	0.34
$a \times 10^8$	-	2.16	3.30	0.70	0.89	1.53	2.04	0.75	1.61
[a]	No H_2	-	0.17	-	0.08	-	0.11	-	0.27
	With H_2	0.17	-	0.08	-	0.11	-	0.28	-
		OLR 2.0, >25% CO_2		OLR 2.0, <7% CO_2		OLR 2.0, <7 CO_2 [a]			
		No H_2	With H_2	No H_2	With H_2	No H_2	With H_2	-	-
pH	-	7.92	7.92	8.3	8.33	8.35	8.34	-	-
pCO_2	-	0.44	0.06	0.50	0.29	0.45	0.17	-	-
$a \times 10^8$	-	2.45	17.99	0.79	1.25	0.76	2.07	-	-
[a]	No H_2	-	0.71	-	0.25	-	0.33	-	-
	With H_2	0.83	-	0.17	-	0.37	-	-	-

[a] Comparison applicable only for same OLR and $\%CO_2$ level

[b] After acclimatisation (10 injections). Other values are for first injection.

CO_2 concentrations only provided for cases in Supplementary Materials. For values in the main paper CO_2 concentrations calculated by assuming $\%CO_2 + \%CH_4 = 100\%$.

Agreement poor apart from at low OLR and H_2 addition. Effect of experimental method including pressure changes due to increasing H_2 addition is uncertain.

Table S25

Corbellini, V., Catenacci, A. and Malpei, F., 2019. Hydrogenotrophic biogas upgrading integrated into WWTPs: enrichment strategy. Water Science and Technology, 79(4), pp.759-770.

	Phase	I			II			III			IV			V		
		No H_2	H_2	H_2	No H_2	H_2	H_2	No H_2	H_2	H_2	No H_2	H_2	H_2	No H_2	H_2	H_2
Temp	°C	35	35	35	35	35	35	35	35	35	35	35	35	35	35	35
OLR	g VS L^{-1} day^{-1}	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
HRT	days	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15
H_2 input	L L^{-1} day^{-1}	0	0	0	0	0.062	0.062	0	0.102	0.098	0	0.133	0.124	0	0.222	0.204
SMP_{tot}	L CH_4 g^{-1} VS	0.157	0.149	0.153	0.156	0.160	0.146	0.164	0.169	0.160	0.162	0.194	0.194	0.161	0.195	n/a
CH_4	%	72.6	73.0	72.4	72.2	73.5	74.5	72.5	75.2	76.3	71.3	77.2	77.0	71.3	80.2	75.3
TAN	mM	n/r	n/r	n/r	n/r	n/r	n/r	n/r	n/r	n/r	n/r	n/r	n/r	n/r	n/r	n/r
VFA	g HAc L^{-1}	0.834	0.314	0.943	0.632	0.348	2.56	0.313	0.275	1.09	0.269	0.412	0.274	0.209	0.184	1.012
pH	-	7.3	7.4	7.4	7.2	7.2	7.2	7.2	7.3	7.3	7.0	7.3	7.2	7.1	7.2	7.2
pCO_2	-	0.275	0.270	0.276	0.263	0.265	0.254	0.275	0.248	0.236	0.286	0.228	0.223	0.263	0.203	0.247
$a \times 10^8$	-	17.8	14.3	14.0	23.6	23.4	24.4	22.5	19.8	20.8	34.6	21.5	27.8	29.8	30.5	25.1
Difference between experimental and predicted pH based on Eqn A with coefficient a(x)																
a(i)	-	-	0.09	0.10	0.12	0.12	0.13	0.10	0.04	0.06	0.28	0.08	0.19	0.22	0.23	0.15
a(ii)	-	0.09	-	0.01	0.21	0.21	0.23	0.19	0.14	0.16	0.38	0.17	0.28	0.31	0.32	0.24
a(iii)	-	0.10	0.01	-	0.22	0.22	0.24	0.20	0.15	0.17	0.38	0.18	0.29	0.32	0.33	0.25
a(iv)	-	0.12	0.21	0.22	-	0.00	0.01	0.02	0.07	0.05	0.16	0.04	0.07	0.10	0.11	0.03
a(v)	-	0.12	0.21	0.22	0.00	-	0.02	0.02	0.07	0.05	0.17	0.04	0.07	0.10	0.11	0.03
a(vi)	-	0.13	0.23	0.24	0.01	0.02	-	0.03	0.09	0.07	0.15	0.05	0.06	0.09	0.10	0.01
a(vii)	-	0.10	0.19	0.20	0.02	0.02	0.03	-	0.06	0.03	0.18	0.02	0.09	0.12	0.13	0.05
a(viii)	-	0.04	0.14	0.15	0.08	0.07	0.09	0.06	-	0.02	0.24	0.04	0.15	0.18	0.18	0.10
a(ix)	-	0.07	0.16	0.17	0.05	0.05	0.07	0.03	0.02	-	0.22	0.01	0.12	0.15	0.16	0.08
a(x)	-	0.28	0.38	0.38	0.16	0.17	0.15	0.18	0.24	0.22	-	0.20	0.09	0.06	0.05	0.14
a(xi)	-	0.08	0.17	0.18	0.04	0.04	0.05	0.02	0.04	0.01	0.20	-	0.11	0.14	0.15	0.07
a(xii)	-	0.19	0.28	0.29	0.07	0.07	0.06	0.09	0.15	0.12	0.09	0.11	-	0.03	0.04	0.04
a(xiii)	-	0.22	0.31	0.32	0.10	0.10	0.09	0.12	0.17	0.15	0.06	0.14	0.03	-	0.01	0.07
a(xiv)	-	0.23	0.32	0.33	0.11	0.11	0.10	0.13	0.19	0.16	0.05	0.15	0.04	0.01	-	0.08
a(xv)	-	0.15	0.24	0.25	0.03	0.03	0.01	0.05	0.10	0.08	0.14	0.07	0.04	0.07	0.08	-

CSTR at 35 °C fed on sewage sludge semi-cts (5 days/week). Mainly good agreement within phases (results boxed and in red). Agreement between phases good or reasonable apart from in phase I experimental reactors and for control in phase IV. Little variation in pCO_2 and pH due to limited H_2 addition; pH reported to 1 dp. Experiment involves headspace pressurisation which may affect results. See Table S21 for information on a related paper by this group.

Table S26

Treu, L., Tsapekos, P., Peprah, M., Campanaro, S., Giacomini, A., Corich, V., Kougias, P.G. and Angelidaki, I., 2019. Microbial profiling during anaerobic digestion of cheese whey in reactors operated at different conditions. *Bioresource technology*, *275*, pp.375-385.

		(i)	(ii)	(iii)	(iv)
		Meso		Thermo	
	Days	0-88	97-146	125-155	155-272
		Whey	Whey+H_2	Whey+CM	Whey+CM+H_2
Temp	°C	37	37	54	54
OLR	g VS L^{-1} day^{-1}	2.2	2.2	2.2	2.2
HRT	days	25	25	15	15
H_2 input	L L^{-1} day^{-1}	0.00	0.90	0.00	0.84
SMP_{tot}	L CH_4 g^{-1} VS	0.296	0.434	0.412	0.444
CH_4	%	57.6	56.5	68.2	73.2
TAN	mM	n/r	n/r	n/r	n/r
VFA	mM	85.7	42.0	1.7	0.5
pH	-	7.21	7.59	7.76	8.03
pCO_2	-	0.424	0.250	0.318	0.216
$a \times 10^8$	-	14.23	9.89	4.51	3.13
Difference between experimental and predicted pH based on Eqn A with coefficient a(x)					
a(i)	-	-	0.15	-	-
a(ii)	-	0.15	-	-	-
a(iii)	-	-	-	-	0.13
a(iv)	-	-	-	0.13	-

CM = cattle manure

2-stage mesophilic and thermophilic CSTR fed on cheese whey with and without cattle manure and with various combinations of H_2 addition and buffering - only selected cases where there are comparable conditions shown here.

Equation A gave reasonable agreement but there were several changes in operating conditions (feedstock and buffering etc) during the trial, meaning that the experimental design was not ideal for the current purpose. In the mesophilic trial the digester was fed on Whey, Whey plus chemical buffer ($NaHCO_3$), Whey + H_2 and Whey + cattle manure + H_2 in consecutive phases; the thermophilic trial ran with Whey, diluted Whey, Whey + Cattle Manure and Whey + Cattle Manure + H_2. This experiment was continued by Palu et al. (2022) but numerical values for pH and pCO_2 were not reported.

Palù, M., Peprah, M., Tsapekos, P., Kougias, P., Campanaro, S., Angelidaki, I. and Treu, L., 2022. In-situ biogas upgrading assisted by bioaugmentation with hydrogenotrophic methanogens during mesophilic and thermophilic co-digestion. *Bioresource Technology*, *348*, p.126754.

Table S27

Voelklein, M.A., Rusmanis, D. and Murphy, J.D., 2019. Biological methanation: Strategies for in-situ and ex-situ upgrading in anaerobic digestion. Applied Energy, 235, pp.1061-1071.

		(i)	(ii)	(iii)	(iv)	RMSD
		Control period	Low capacity diffuser	Control period	Ceramic diffuser	
		No H_2	With H_2	No H_2	With H_2	
Temp	°C	55	55	55	55	-
OLR	g VS L^{-1} day^{-1}	4.0	4.0	4.0	4.0	-
HRT	days	46.0	46.0	46.0	46.0	-
H_2 input	L L^{-1} day^{-1}	0.00	5.05	0.00	5.29	-
SMP_{tot}	L CH_4 g^{-1} VS	0.388	0.461	0.382	0.64	-
CH_4	%	54.8	32.1	53.2	60.3	-
TAN	mM	n/r	n/r	n/r	n/r	-
VFA	g L^{-1}	0.47	1.90	0.62	7.81	-
pH	-	7.81	7.97	7.89	8.37	-
pCO_2	-	0.452	0.114	0.468	0.051	-
$a \times 10^8$	-	2.74	6.89	2.11	4.37	-
Difference between experimental and predicted pH based on Eqn A with coefficient *a*(x)						
a(i)	-	-	0.30	0.09	0.13	0.20
a(ii)	-	0.35	-	0.44	0.14	0.34
a(iii)	-	0.09	0.38	-	0.21	0.25
a(iv)	-	0.17	0.15	0.27	-	0.20

Study compared in situ and ex situ but only selected relevant cases considered here: in situ CSTR at 55 °C fed on ensiled ryegrass, with increasing H_2 input and changing diffusers

Equation A gave good agreement for control periods but otherwise poor, probably due to VFA accumulation during periods with H_2 addition (e.g. 7.8 g COD L-1 in phase 4). Some graphical data for VFA species but no TAN.

Table S28

Alfaro, N., Fdz-Polanco, M., Fdz-Polanco, F. and Díaz, I., 2019. H2 addition through a submerged membrane for in-situ biogas upgrading in the anaerobic digestion of sewage sludge. Bioresource technology, 280, pp.1-8.

		(i)	(ii)	(iii)	(iv)	(v)	(vi)	(vii)	(viii)	RMSD
	Phase	Start-up		1		2		3		
	Days	0-61		62-119		120-183		184-240		
		No H_2	No H_2	No H_2	With H_2	No H_2	With H_2	No H_2	With H_2	
Gas recirc	$L\ L^{-1}\ day^{-1}$	0	0	0	50	0	101	0	202	-
Temp	^oC	35	35	35	35	35	35	35	35	-
OLR	$g\ VS\ L^{-1}\ day^{-1}$	1.3	1.3	1.3	1.3	1.5	1.5	1.8	1.8	-
HRT	days	20	20	20	20	20	20	20	20	-
H_2 input	$L\ L^{-1}\ day^{-1}$	0	0	0	0.87	0	0.87	0	0.87	-
SMP_{tot}	$L\ CH_4\ g^{-1}\ VS$	0.315	0.323	0.338	0.415	0.213	0.313	0.211	0.300	-
CH_4	%	66	65.6	65.8	51.1	68	70.9	67.1	73.1	-
TAN	mM	55.7	52.0	49.4	47.8	50.1	51.5	54.0	56.7	-
VFA	mM	0.6	0.6	0.4	0.7	0.4	0.4	0.2	0.5	-
pH	-	7.45	7.23	7.41	7.28	7.42	7.80	7.41	8.09	-
pCO_2	-	0.344	0.344	0.341	0.124	0.32	0.114	0.329	0.197	-
$a \times 10^8$	-	10.0	16.8	11.1	41.4	11.5	13.0	11.5	3.6	-
Difference between experimental and predicted pH based on Eqn A with coefficient *a*(x)										
a(i)	-	-	0.22	0.04	0.59	0.06	0.11	0.06	0.41	0.29
a(ii)	-	0.22	-	0.18	0.38	0.16	0.11	0.16	0.62	0.31
a(iii)	-	0.04	0.18	-	0.55	0.02	0.06	0.02	0.45	0.28
a(iv)	-	0.61	0.39	0.56	-	0.55	0.48	0.55	1.01	0.62
a(v)	-	0.06	0.16	0.02	0.53	-	0.05	0.00	0.47	0.28
a(vi)	-	0.11	0.11	0.07	0.49	0.05	-	0.05	0.52	0.28
a(vii)		0.06	0.16	0.02	0.54	0.00	0.05	-	0.47	0.28
a(viii)		0.42	0.64	0.46	0.99	0.48	0.50	0.48	-	0.59
Difference between experimental and predicted pH based on Eqn B with coefficient *b*(x)										
b(i)		-	0.19	0.01	0.53	0.02	0.07	0.05	0.40	0.26
b(ii)		0.19	-	0.20	0.34	0.17	0.11	0.14	0.59	0.29
b(iii)		0.01	0.20	-	0.53	0.02	0.08	0.05	0.39	0.26
b(iv)		0.54	0.35	0.55	-	0.52	0.45	0.49	0.93	0.57
b(v)		0.02	0.17	0.02	0.51	-	0.06	0.03	0.42	0.26
b(vi)		0.08	0.11	0.08	0.45	0.06	-	0.03	0.48	0.26
b(vii)		0.05	0.14	0.05	0.48	0.03	0.03	-	0.45	0.26
b(viii)		0.41	0.60	0.41	0.92	0.43	0.46	0.46	-	0.55

Sewage sludge, 35 ^oC. Control and experimental digesters, gas addition in experimental reactor by Hollow Fibre Membrane. Gas recirculation rate varies from 50 - 202 $L\ L^{-1}\ day^{-1}$.

Agreement with Equation A poor apart from phase 2 of experiment, but agreement between experimental and control digesters is also poor in the start-up phase when there is no H_2 addition; and in general pH shows some variation within and between phases as seen by the standard deviations reported in Table 2 of the original paper are also quite high. Discrepancies could reflect variability in feedstock, which was collected periodically during the trial; and/or possible issues with pH measurement. Note that gas recirculation is only applied to the digester with H_2 injection. Equation B gives a slight improvement in agreement but does not resolve these issues. Regression analysis across all phases (results not shown) gave R^2 values ranging from 0.047-0.578 for Equation A and 0.112 to 0.647 for Equation B, respectively.

Table S29

Kim, S., Mostafa, A., Im, S., Lee, M.K., Kang, S., Na, J.G. and Kim, D.H., 2021. Production of high-calorific biogas from food waste by integrating two approaches: Autogenerative high-pressure and hydrogen injection. *Water Research*, *194*, p.116920.

Table 29a Results from paper

	Phase	(i) P1 No H_2	(ii) P3 No H_2	(iii) P5 With H_2	(iv) P6 With H_2	(v) P7 With H_2	RMSD
Pressure	Bar	1	5	5	5	5	-
Temp	°C	37	37	37	37	37	-
OLR	g COD L^{-1} day^{-1}	2.67	2.67	2.67	2.67	2.67	-
HRT	days	75	75	75	75	75	-
H_2 input	L L^{-1} day^{-1}	0	0	0.2547	0.377	0.54	-
SMP_{tot}	L CH_4 g^{-1} COD	0.28	0.26	0.28	0.29	0.28	-
CH_4	%	52.4	74.0	82.8	87.2	90.6	-
TAN	mM	n/r	n/r	n/r	n/r	n/r	-
Tot org acid	g COD L^{-1}	9.6	15.5	16.5	12.2	9.8	-
pH	-	7.5	7.2	7.2	7.4	7.8	-
pCO_2	-	0.470	1.275	0.875	0.630	0.375	-
a x 10^8	-	6.47	4.85	7.07	6.12	3.91	-
Difference between experimental and predicted pH based on Eqn A with coefficient a(x)							
a(i)	-	-	0.12	0.04	0.02	0.21	0.12
a(ii)	-	0.12	-	0.16	0.10	0.09	0.12
a(iii)	-	0.29	0.42	-	0.32	0.50	0.39
a(iv)	-	0.04	0.16	0.00	-	0.24	0.15
a(v)	-	0.02	0.10	0.06	0.00	-	0.06

Food waste with H_2 and/or pressure in CSTR at 37 °C

pCO_2 is adjusted for pressure. Reasonable or good agreement for some values but poor for others. The paper uses calculated pH values, and there are also changes in VFA (see Figs 1 & 2 in original paper). Some pressure-only cases (P2 and P4) are omitted from the table here, but these also showed generally poor agreement.

The calculated pH values use acid dissociation constants for 25 °C rather than for the operating temperature of 37 °C, and may also use the Henry's Law constant for CO_2 for 25 °C (although this is not explicitly stated in the paper). If Equation 4 in the original paper is used to calculate expected pCO_2 based on the calculated pH and the applied pressure, and assuming a Henry's constant for 25 °C, the expected CO_2 percentage values are far from the measured values apart from in phase 3 (see Table S29a). This may be explained by the fact that the molar concentrations of Na^+ and NH_4^+ used in Equation 4 were determined during phase 3. If Equation A is used to predict pH values based on measured CO_2 percentage, with a taken from phase 3 as in Table S29a, and these pH values are used in Equation 4, the calculated CO_2 percentages are much closer to the measured results, indicating that the pH calculations in this paper may need revision.

The calculations in section (a) using Equation 4 are based on the following constants: $[Na^+]$=0.12 M; $[NH_4^+]$=0.18 M as given in the paper; and Henry's constant for CO_2 K_H = 0.0339 mol L^{-1} atm^{-1} at 25 °C. Henry's constant for mesophilic conditions was also attempted for section (a), however the calculated CO_2 (%) in that case shows even less agreement and therefore is not included in the table.

Table S29b Comparison of pCO2 values calculated from Equation 4 in Kim et al. using (a) calculated pH values in Kim et al. (2021) and (b) predicted pH from Equation A with *a*(iii) from phase 3

Phase	P1	P3	P5	P6	P7
Pressure (bar)	1	5	5	5	5
Calculated pH	7.5	7.2	7.2	7.4	7.8
Measured CO_2 (%)	47	25.5	17.5	12.6	7.5
(a) pCO_2 from Equation 4 with calculated pH					
[H_2CO_3]	0.0212	0.0423	0.0423	0.0267	0.0106
Expected CO_2 (%)	63.3	25.3	25.3	15.9	6.3
(b) pH from Equation A with coefficient *a*(iii)	7.62	7.20	7.36	7.50	7.71
[H_2CO_3]	0.0161	0.0423	0.0293	0.0213	0.0130
Predicted CO_2 (%)	48.0	25.3	17.5	12.7	7.7

Table S30

Deschamps, L., Imatoukene, N., Lemaire, J., Mounkaila, M., Filali, R., Lopez, M. and Theoleyre, M.A., 2021. In-situ biogas upgrading by bio-methanation with an innovative membrane bioreactor combining sludge filtration and H2 injection. Bioresource Technology, 337, p.125444.

	Phase	(i) 0 No H_2	(ii) 1 With H_2	(iii) 2 With H_2	(iv) 3 With H_2	RMSD	R^2	RMSE	Sig
Temp	^oC	37	37	37	37	-	-	-	-
OLR	g VS L^{-1} day^{-1}	3.5	2.7	3.9	4.4	-	-	-	-
HRT	days	3.5	2.7	3.9	4.4	-	-	-	-
H_2 input	L L^{-1} day^{-1}	0	1.16	1.46	1.88	-	-	-	-
SMP_{tot}	L CH_4 g^{-1} VS	0.297	0.438	0.374	0.389	-	-	-	-
CH_4	%	74.7	97.4	82.8	97.9	-	-	-	-
TAN	mM	n/r	n/r	n/r	n/r	-	-	-	-
VFA	g L^{-1}	< 0.02	< 0.02	< 0.02	< 0.02	-	-	-	-
pH	-	7.3	7.8	7.7	7.9	-	-	-	-
pCO_2	-	0.253	0.015	0.043	0.014	-	-	-	-
$a \times 10^8$	-	19.32	97.75	43.60	81.61	-	-	-	-
Difference between experimental and predicted pH based on Eqn A with coefficient *a*(x)									
a(i)	-	-	0.61	0.33	0.54	0.51	0.793	0.09	no
a(ii)	-	0.70	-	0.34	0.07	0.45	0.997	0.03	*
a(iii)	-	0.35	0.32	-	0.24	0.31	0.981	0.08	no
a(iv)	-	0.62	0.07	0.26	-	0.39	0.969	0.09	no

Ethanol distillery wastewater, AnMBR, 37 ^oC

Generally poor agreement, although VFA accumulation seen only at highest H_2 loading. Operation without sludge wastage may have led to other changes in baseline conditions. No TAN data. pH of feedstock adjusted in phase 0. pH reported to 1 dp. Phases 4 and 5 not analysed here as unstable.

Regression analysis showed good agreement between phases (ii)-(iv) which was significant at the 5% level for coefficient *a*(ii); but values for slope and intercept ranged from 2.02 to 2.24 and from -7.78 to -9.70 respectively, indicating the results did not provide a useful working relationship.

Table S31

Khan, Alam, Sedrah Akbar, Valentine Okonkwo, Cindy Smith, Samiullah Khan, Aamer Ali Shah, Fazal Adnan, Umer Zeeshan Ijaz, Safia Ahmed, and Malik Badshah. "Enrichment of the hydrogenotrophic methanogens for, in-situ biogas up-gradation by recirculation of gases and supply of hydrogen in methanogenic reactor." *Bioresource Technology* 345 (2022): 126219.

	Phase	(i) No recirc No H_2	(ii) With recirc No H_2	(iii) No recirc With H_2	(iv) With recirc With H_2
Temp	^oC	37	0	0	0
OLR	g VS L^{-1} day^{-1}	3.5	3.5	3.5	3.5
HRT	days	10	10	10	10
H_2 input	L L^{-1} day^{-1}	0	0	1.6	1.6
SMP_{tot}	L CH_4 g^{-1} VS	0.300	0.425	0.500	0.897
CH_4	%	73.0	76.0	62.9	96.0
TAN	mM	n/r	n/r	n/r	n/r
VFA	g L^{-1}	0.50	0.35	1.20	0.40
pH	-	7.2	7.3	7.0	7.2
pCO_2	-	0.270	0.240	0.055	0.010
$a \times 10^8$	-	22.9	20.4	180.5	637.9
Difference between experimental and predicted pH based on Eqn A with coefficient *a*(x)					
a(i)	-	-	0.05	0.86	1.30
a(ii)	-	0.05	-	0.91	1.34
a(iii)	-	0.89	0.94	-	0.53
a(iv)	-	1.44	1.49	0.54	-

Cattle manure plus vegetable waste, 2-stage, 37 ^oC. H_2 injection into stage 2. Changed gas recirculation rates with or without H_2 addition.

Very poor agreement apart from variants without H2 addition. pH in second stage reactor appears to fall on addition of H_2, with or without gas recirculation. No clear explanation, although there is some increase in VFA when H_2 is added, particularly without recirculation.

Table S32

Wahid, R. and Horn, S.J., 2021. The effect of mixing rate and gas recirculation on biological CO2 methanation in two-stage CSTR systems. *Biomass and Bioenergy*, *144*, p.105918.

		(i)	(ii)	(iii)	(iv)	(v)	(vi)	(vii)	RMSD	R^2	RMSE	Sig
	Phase	1	2	3a	3b	3c	3d	3e				
	Start day	1	120	155	169	213	231	260				
	Mixing (rpm)	80	80	80	120	140	170	200				
	H_2/CO_2	0	2	4	4	4	4	4				
Temp	^oC	55	55	55	55	55	55	55	-	-	-	-
OLR	g VS L^{-1} day^{-1}	3.09	2.69	2.30	2.36	2.19	2.37	2.32	-	-	-	-
HRT	days	20	20	20	20	20	20	20	-	-	-	-
H_2 input	L L^{-1} day^{-1}	0.0	0.8	1.6	1.7	1.7	1.7	1.7	-	-	-	-
SMP_{tot}	L CH_4 g^{-1} VS	0.217	0.246	0.305	0.331	0.411	0.321	0.315	-	-	-	-
CH_4	%	62.2	37.8	31.6	38.3	40.3	41.9	40.2	-	-	-	-
TAN	mM	96.4	107.1	128.5	149.9	142.8	135.6	135.6	-	-	-	-
VFA	mM	5.4	6.0	8.3	11.0	12.2	15.6	15.3	-	-	-	-
pH	-	7.86	8.07	8.25	8.37	8.41	8.43	8.41	-	-	-	-
pCO_2	-	0.378	0.207	0.137	0.124	0.119	0.116	0.120	-	-	-	-
$a \times 10^8$	-	2.85	2.82	2.43	1.81	1.63	1.56	1.62	-	-	-	-
$b \times 10^8$	-	0.255	0.277	0.278	0.233	0.193	0.162	0.171	-	-	-	-
Difference between experimental and predicted pH based on Eqn A with coefficient *a*(x)												
a(i)	-	-	0.00	0.05	0.14	0.17	0.18	0.17	0.14	0.949	0.01	*
a(ii)	-	0.00	-	0.05	0.13	0.16	0.18	0.16	0.13	0.966	0.03	*
a(iii)	-	0.06	0.05	-	0.09	0.12	0.13	0.12	0.10	0.978	0.02	*
a(iv)	-	0.16	0.14	0.09	-	0.03	0.04	0.03	0.10	0.955	0.03	*
a(v)	-	0.19	0.17	0.12	0.03	-	0.01	0.00	0.12	0.956	0.03	*
a(vi)	-	0.21	0.19	0.13	0.04	0.01	-	0.01	0.13	0.958	0.03	*
a(vii)	-	0.19	0.18	0.12	0.03	0.00	0.01	-	0.12	0.957	0.03	*
Difference between experimental and predicted pH based on Eqn B with coefficient *b*(x)												
b(i)	-	-	0.03	0.03	0.03	0.08	0.12	0.11	0.08	0.853	0.03	*
b(ii)	-	0.03	-	0.00	0.05	0.10	0.15	0.13	0.09	0.940	0.04	*
b(iii)	-	0.03	0.00	-	0.05	0.10	0.15	0.13	0.09	0.963	0.03	*
b(iv)	-	0.03	0.06	0.05	-	0.05	0.10	0.08	0.07	0.941	0.04	*
b(v)	-	0.10	0.11	0.11	0.05	-	0.05	0.03	0.08	0.929	0.04	*
b(vi)	-	0.16	0.17	0.16	0.10	0.05	-	0.01	0.12	0.947	0.04	*
b(vii)	-	0.14	0.15	0.14	0.09	0.03	0.01	-	0.11	0.942	0.04	*

2-stage, 55 ^oC, cattle slurry, various mixing and gas recirculation rates. H_2 added to stage 2, no gas recirculation to stage 1. Results shown are for stage 2.

Equation A gives good agreement between phases 1, 2 and 3a and between phases 3b-3e. Equation B eliminates some of the larger discrepancies between predicted and experimental pH found using Equation A, with coefficient *b*(iv) giving good agreement across all phases. VFA and TAN values are approximate as estimated from acetic and propionic acid concentrations shown in Figure 4 in the original paper. Note the short duration of some phases, which may mean conditions had not fully stabilised.

Regression analysis across all phases showed good agreement ($R^2 > 0.9$, RMSE < 0.05) apart from for coefficient *b*(i). R^2 values were slightly lower and RMSE slightly higher for Equation B than Equation A, but slope and intercept values (not shown) were slightly better for Equation B. It can therefore be concluded both equations performed well.

Note: Much of the information in this table is given in Table 2 in the main text, but is also included here for completeness and ease of reference.

Table S33

Wahid, R. and Horn, S.J., 2021. Impact of operational conditions on methane yield and microbial community composition during biological methanation in in situ and hybrid reactor systems. *Biotechnology for Biofuels*, *14*(1), pp.1-15.

		(i)	(ii)	(iii)	(iv)	(v)	(vi)	(vii)	(viii)	(ix)	(x)	(xi)	(xii)	RMSD
Phase		I		II		III		IV		V		VI		
Days		1-64		65-78		79-85		93-113		114-140		141-172		
H_2/CO_2	-	0	0	0	2	0	2	0	2	0	2	0	4	-
Stir	rpm	80	80	80	80	140	140	80	80	80	80	80	80	-
CM/CW	w/w	9	9	9	9	9	9	8	8	9	9	9	9	-
Feeding	hours	24	24	24	24	24	24	24	24	48	48	24	24	-
Temp	^oC	55	55	55	55	55	55	55	55	55	55	55	55	-
OLR	g VS L^{-1} day^{-1}	4.1	4.1	4.1	4.1	4.1	4.1	4.2	4.2	4.1	4.1	4.1	4.1	-
HRT	days	20	20	20	20	20	20	20	20	20	20	20	20	-
H_2 input	L L^{-1} day^{-1}	0.0	0.0	0.0	0.7	0.0	0.7	0.0	0.7	0.0	0.7	0.0	1.4	-
SMP_{tot}	L CH_4 g^{-1} VS	0.145	0.144	0.146	0.185	0.134	0.133	0.142	0.204	0.142	0.194	0.134	0.165	-
CH_4	%	58.24	59.14	59.88	39.97	57.57	40.76	53.70	38.69	58.55	42.58	56.10	38.65	-
TAN	mM	177.1	179.9	183.5	197.8	237.0	205.6	222.8	226.3	199.9	206.3	189.2	199.9	-
VFA	mM	19.0	17.1	30.7	44.6	30.6	66.6	37.7	62.2	40.2	65.1	36.7	98.1	-
pH	-	7.92	7.94	7.94	8.10	8.15	8.28	7.91	8.11	7.82	8.04	7.77	7.95	-
pCO_2	-	0.418	0.409	0.404	0.286	0.424	0.262	0.463	0.280	0.415	0.231	0.439	0.191	-
$a \times 10^8$	-	2.17	2.10	2.12	1.86	1.08	1.15	2.02	1.84	2.90	2.76	3.15	4.36	-
$b \times 10^8$	-	0.33	0.33	0.30	0.24	0.20	0.10	0.35	0.24	0.43	0.31	0.45	0.29	-
Difference between experimental and predicted pH based on Eqn A with coefficient *a*(x)														
a(i)	-	-	0.01	0.01	0.05	0.24	0.20	0.03	0.05	0.10	0.08	0.13	0.23	0.13
a(ii)	-	0.01	-	0.00	0.04	0.22	0.19	0.01	0.04	0.12	0.09	0.15	0.24	0.13
a(iii)	-	0.01	0.00	-	0.04	0.23	0.19	0.02	0.05	0.11	0.09	0.14	0.24	0.13
a(iv)	-	0.05	0.04	0.04	-	0.18	0.15	0.03	0.00	0.16	0.13	0.19	0.28	0.14
a(iv)	-	0.24	0.22	0.23	0.17	-	0.02	0.21	0.17	0.34	0.30	0.37	0.44	0.27
a(vi)	-	0.21	0.20	0.20	0.15	0.02	-	0.19	0.15	0.32	0.28	0.35	0.42	0.25
a(vii)	-	0.03	0.01	0.02	0.03	0.21	0.18	-	0.03	0.13	0.10	0.16	0.25	0.13
a(viii)	-	0.06	0.04	0.05	0.00	0.18	0.15	0.03	-	0.16	0.13	0.19	0.28	0.14
a(ix)	-	0.10	0.11	0.11	0.15	0.34	0.30	0.13	0.15	-	0.02	0.03	0.14	0.17
a(x)	-	0.08	0.10	0.09	0.13	0.32	0.28	0.11	0.14	0.02	-	0.05	0.15	0.16
a(xi)	-	0.13	0.14	0.14	0.18	0.37	0.33	0.16	0.18	0.03	0.04	-	0.11	0.19
a(xii)	-	0.25	0.26	0.26	0.29	0.49	0.44	0.28	0.30	0.15	0.16	0.12	-	0.29

Table S33 ctd

		(i)	(ii)	(iii)	(iv)	(v)	(vi)	(vii)	(viii)	(ix)	(x)	(xi)	(xii)	RMSD
Phase		I		II		III		IV		V		VI		
Days		1-64		65-78		79-85		93-113		114-140		141-172		
Difference between experimental and predicted pH based on Eqn B with coefficient *b*(x)														
b(i)	-	-	0.00	0.03	0.09	0.15	0.30	0.02	0.09	0.09	0.01	0.11	0.03	0.12
b(ii)	-	0.00	-	0.03	0.09	0.15	0.30	0.02	0.08	0.09	0.01	0.11	0.03	0.12
b(iii)	-	0.03	0.03	-	0.06	0.12	0.27	0.05	0.06	0.12	0.01	0.14	0.01	0.11
b(iv)	-	0.10	0.10	0.07	-	0.06	0.21	0.11	0.00	0.19	0.07	0.21	0.04	0.12
b(iv)	-	0.16	0.16	0.12	0.05	-	0.16	0.17	0.05	0.24	0.12	0.26	0.09	0.16
b(vi)	-	0.36	0.36	0.32	0.23	0.20	-	0.37	0.22	0.44	0.28	0.46	0.22	0.33
b(vii)	-	0.02	0.02	0.05	0.11	0.17	0.31	-	0.10	0.07	0.03	0.09	0.04	0.12
b(viii)	-	0.10	0.10	0.07	0.00	0.06	0.21	0.11	-	0.19	0.07	0.21	0.04	0.12
b(ix)	-	0.09	0.09	0.12	0.17	0.24	0.38	0.07	0.17	-	0.09	0.02	0.10	0.17
b(x)	-	0.02	0.02	0.01	0.07	0.13	0.28	0.04	0.07	0.11	-	0.13	0.02	0.11
b(xi)	-	0.11	0.11	0.14	0.19	0.26	0.39	0.09	0.18	0.02	0.11	-	0.11	0.18
b(xii)	-	0.04	0.04	0.01	0.05	0.11	0.27	0.06	0.05	0.13	0.02	0.15	-	0.11

Manure and cheese waste. Control and experimental CSTRs with (also tested briefly with second stage, not shown here)

The performance of Equation A is patchy, with poor agreement in phases III and VI. Use of Equation B improves this considerably, but still gives poor agreement in some cases, especially in phase III for the experimental reactor. Phase III lasted only 7 days, and was the only phase where the stirring speed was increased from 80 to 140 rpm in both the control and the experimental reactor. There are also some differences in pH in the control reactor under the same conditions e.g. cases (i) and (xi) in phases I and V.

As expected, regression analysis across all phases showed poor agreement for Equation A with R^2 ranging from 0.17-0.45 and no cases significant at the 5% level, although RMSE values were below 0.1. Use of Equation B improved R^2 slightly with values from 0.48-0.73, RMSE < 0.04 and significance at the 5% level in all cases, but slope and intercept values (not shown) were poor for both equations in all cases. Multiple variable parameters in different phases may also mean this type of analysis is unsuitable for the experimental design used.

Table S34

Tao, B., Alessi, A.M., Zhang, Y., Chong, J.P., Heaven, S. and Banks, C.J., 2019. Simultaneous biomethanisation of endogenous and imported CO2 in organically loaded anaerobic digesters. Applied Energy, 247, pp.670-681.

CSTRs operated in duplicate, 37 °C, 0.5 L working vol, synthetic feed, H_2 addition by bubbling with gas recirculation, varied OLR and H_2. At OLR 2 and 3 g VS L_{-1} day_{-1} also provided additional exogenous CO_2 and H_2.

OLR 2	Phase	(i) 1 No H_2	(ii) No H_2	(iii) 2 With H_2	(iv) With H_2	(v) 3 H_2+CO_2	(vi) H_2+CO_2	RMSD	R^2	RMSE	Sig
Temp	°C	37	37	37	37	37	37	-	-	-	-
OLR	g VS L^{-1} day^{-1}	2	2	2	2	2	2	-	-	-	-
HRT	days	15	15	15	15	15	15	-	-	-	-
H_2 input	L L^{-1} day^{-1}	0.0	0.0	2.1	2.1	5.4	6.2	-	-	-	-
SMP_{tot}	L CH_4 g^{-1} VS	0.288	0.289	0.534	0.531	0.891	0.971	-	-	-	-
CH_4	%	49.8	50.0	91.2	93.7	90.9	94.6	-	-	-	-
TAN	mM	52.0	49.4	35.2	34.9	36.9	36.5	-	-	-	-
VFA	mM	0.7	0.2	0.8	1.1	14.2	9.3	-	-	-	-
pH	-	7.14	7.14	7.80	7.94	7.75	7.88	-	-	-	-
pCO_2	-	0.472	0.474	0.047	0.037	0.041	0.035	-	-	-	-
a x 10^8	-	15.19	15.12	30.92	28.32	40.79	34.45	-	-	-	-
b x 10^8	-	0.78	0.74	1.06	0.96	0.88	0.90	-	-	-	-
Difference between experimental and predicted pH based on Eqn A with coefficient *a*(x)											
a(i)	-	-	0.00	0.28	0.24	0.39	0.32	0.28	0.969	0.07	*
a(ii)	-	0.00	-	0.28	0.24	0.39	0.32	0.28	0.969	0.07	*
a(iii)	-	0.31	0.31	-	0.03	0.11	0.04	0.20	0.980	0.07	*
a(iv)	-	0.27	0.27	0.04	-	0.15	0.08	0.19	0.990	0.05	*
a(v)	-	0.42	0.43	0.11	0.15	-	0.07	0.28	0.995	0.04	*
a(vi)	-	0.35	0.35	0.04	0.08	0.07	-	0.23	0.978	0.07	*
Difference between experimental and predicted pH based on Eqn B with coefficient *b*(x)											
b(i)	-	-	0.02	0.12	0.08	0.05	0.06	0.07	0.993	0.03	*
b(ii)	-	0.02	-	0.14	0.10	0.07	0.08	0.09	0.993	0.03	*
b(iii)	-	0.13	0.15	-	0.04	0.07	0.06	0.10	1.000	0.01	*
b(iv)	-	0.09	0.11	0.04	-	0.03	0.02	0.07	0.995	0.03	*
b(v)	-	0.05	0.07	0.07	0.03	-	0.01	0.05	0.996	0.03	*
b(vi)	-	0.06	0.08	0.06	0.02	0.01	-	0.06	0.996	0.02	*
Difference between experimental and predicted pH for Eqn A with *a*(x) and phosphate adjustment											
Period (i)	-	-	0.02	0.06	0.01	0.18	0.10	0.10	0.962	0.06	*
Period (ii)	-	0.02	-	0.08	0.03	0.20	0.12	0.11	0.962	0.06	*
Period (iii)	-	0.06	0.08	-	0.05	0.12	0.04	0.08	0.976	0.06	*
Period (iv)	-	0.01	0.03	0.04	-	0.17	0.09	0.09	0.987	0.04	*
Period (v)	-	0.20	0.22	0.13	0.17	-	0.08	0.17	0.993	0.03	*
Period (vi)	-	0.11	0.13	0.05	0.10	0.08	-	0.10	0.974	0.06	*

CSTR, 37 °C, duplicate control and experimental reactors. Synthetic organic feedstock with varied organic loading rates and with / without H_2 addition.

At OLR 2 g VS L^{-1} day^{-1} Equation A gave good or reasonable agreement between duplicates in phase 1 and between all digesters in phases 2 and 3, but agreement between phase 1 and the following phases was poor. Equation B gave a considerable improvement in correlation coefficient and RMSD in comparison with Equation A. The phosphate adjustment also improved agreement but could not fully eliminate the effect of some VFA in phase 3.

Table S34 ctd

OLR 3	Phase	(i) 1 No H_2	(ii) No H_2	(iii) 2 With H_2	(iv) With H_2	(v) 3 H_2+CO_2	(vi) H_2+CO_2	RMSD	R^2	RMSE	Sig
Temp	°C	37	37	37	37	37	37	-	-	-	-
OLR	g VS L^{-1} day^{-1}	3	3	3	3	3	3	-	-	-	-
HRT	days	15	15	15	15	15	15	-	-	-	-
H_2 input	L L^{-1} day^{-1}	0.0	0.0	2.9	2.9	2.9	7.4	-	-	-	-
SMP_{tot}	L CH_4 g^{-1} VS	0.287	0.289	0.496	0.490	0.452	0.804	-	-	-	-
CH_4	%	50.0	50.1	93.7	90.9	75.0	76.6	-	-	-	-
TAN	mM	75.0	73.8	45.4	45.2	49.4	44.3	-	-	-	-
VFA	mM	0.2	0.3	1.5	1.6	7.2	6.4	-	-	-	-
pH	-	7.34	7.35	8.00	7.93	7.82	7.81	-	-	-	-
pCO_2	-	0.474	0.473	0.040	0.046	0.071	0.077	-	-	-	-
$a \times 10^8$	-	9.29	9.23	22.08	23.03	19.45	18.67	-	-	-	-
$b \times 10^8$	-	0.69	0.68	0.97	1.00	0.81	0.70	-	-	-	-
Difference between experimental and predicted pH based on Eqn A with coefficient *a*(x)											
a(i)	-	-	0.00	0.32	0.35	0.29	0.27	0.28	0.995	0.02	*
a(ii)	-	0.00	-	0.33	0.35	0.29	0.28	0.28	0.996	0.02	*
a(iii)	-	0.37	0.37	-	0.02	0.05	0.07	0.24	1.000	0.00	*
a(iv)	-	0.39	0.39	0.02	-	0.07	0.09	0.25	0.998	0.02	*
a(v)	-	0.31	0.32	0.05	0.07	-	0.02	0.20	0.998	0.02	*
a(vi)	-	0.30	0.30	0.06	0.08	0.02	-	0.19	0.998	0.02	*
Difference between experimental and predicted pH based on Eqn B with coefficient *b*(x)											
b(i)	-	-	0.01	0.13	0.14	0.06	0.00	0.09	0.980	0.04	*
b(ii)	-	0.01	-	0.14	0.15	0.07	0.01	0.10	0.979	0.04	*
b(iii)	-	0.14	0.15	-	0.01	0.07	0.13	0.11	0.983	0.04	*
b(iv)	-	0.16	0.17	0.01	-	0.09	0.15	0.13	0.990	0.03	*
b(v)	-	0.06	0.07	0.07	0.08	-	0.06	0.07	0.987	0.04	*
b(vi)	-	0.00	0.01	0.13	0.14	0.06	-	0.09	0.997	0.02	*
Difference between experimental and predicted pH for Eqn A with *a*(x) and phosphate adjustment											
Period (i)	-	-	0.01	0.05	0.07	0.06	0.01	0.05	0.993	0.02	*
Period (ii)	-	0.01	-	0.06	0.08	0.07	0.01	0.06	0.993	0.02	*
Period (iii)	-	0.06	0.07	-	0.01	0.00	0.05	0.05	0.995	0.02	*
Period (iv)	-	0.09	0.10	0.03	-	0.02	0.07	0.07	0.996	0.02	*
Period (v)	-	0.07	0.08	0.01	0.01	-	0.06	0.06	0.997	0.02	*
Period (vi)	-	0.01	0.02	0.04	0.06	0.05	-	0.04	0.999	0.01	*

At OLR 3 g VS L^{-1} day^{-1} Equation A gave good agreement between duplicates in phase 1 and between all digesters in phases 2 and 3 but agreement between phase 1 and the following phases was poor. Equation B slightly reduced the correlation coefficient in some cases, but considerably improved agreement for individual points and RMSD in comparison with Equation A. The phosphate adjustment maintained a high correlation coefficient and improved RMSD.

Note: Much of the information in this table is given in Table 3 in the main text, but is also included here for completeness and ease of reference.

Table S34 ctd

OLR 4	Phase	(i) 1 No H_2	(ii) No H_2	(iii) 2 With H_2	(iv) With H_2	RMSD	R^2	RMSE	Sig
Temp	°C	37	37	37	37	-	-	-	-
OLR	g VS L^{-1} day^{-1}	4	4	4	4	-	-	-	-
HRT	days	15	15	15	15	-	-	-	-
H_2 input	L L^{-1} day^{-1}	0	0	4.43	3.8	-	-	-	-
SMP_{tot}	L CH_4 g^{-1} VS	0.291	0.290	0.562	0.524	-	-	-	-
CH_4	%	49.9	49.8	91.4	90.1	-	-	-	-
TAN	mM	86.1	84.5	66.5	56.5	-	-	-	-
VFA	mM	0.8	0.8	8.1	1.9	-	-	-	-
pH	-	7.39	7.39	8.16	8.09	-	-	-	-
pCO_2	-	0.476	0.478	0.055	0.057	-	-	-	-
$a \times 10^8$	-	8.28	8.24	10.53	12.16	-	-	-	-
$b \times 10^8$	-	0.71	0.69	0.60	0.66	-	-	-	-
Difference between experimental and predicted pH based on Eqn A with coefficient *a*(x)									
a(i)	-	-	0.00	0.09	0.14	0.10	0.996	0.00	*
a(ii)	-	0.00	-	0.09	0.15	0.10	0.996	0.00	*
a(iii)	-	0.10	0.10	-	0.05	0.09	1.000	0.00	*
a(iv)	-	0.16	0.16	0.05	-	0.14	1.000	0.00	*
Difference between experimental and predicted pH based on Eqn B with coefficient *b*(x)									
b(i)	-	-	0.01	0.06	0.03	0.04	0.998	0.00	*
b(ii)	-	0.01	-	0.05	0.02	0.03	0.998	0.00	*
b(iii)	-	0.07	0.06	-	0.04	0.06	1.000	0.00	*
b(iv)	-	0.03	0.02	0.04	-	0.03	1.000	0.00	*
Difference between experimental and predicted pH for Eqn A with *a*(x) and phosphate adjustment									
Period (i)	-	-	0.01	0.09	0.10	0.08	0.999	0.00	*
Period (ii)	-	0.01	-	0.08	0.09	0.07	0.999	0.00	*
Period (iii)	-	0.09	0.08	-	0.02	0.07	1.000	0.00	*
Period (iv)	-	0.10	0.09	0.01	-	0.08	1.000	0.00	*

At OLR 4 g VS L^{-1} day^{-1} Equation A gave good or reasonable agreement between all cases. Both Equation B and the phosphate adjustment were able to improve this slightly.

Table S34 ctd

OLR 5	Phase	(i) 1 No H_2	(ii) No H_2	(iii) 2 With H_2	(iv) With H_2	RMSD	R^2	RMSE	Sig
Temp	°C	37	37	37	37	-	-	-	-
OLR	g VS L^{-1} day^{-1}	5	5	5	5	-	-	-	-
HRT	days	15	15	15	15	-	-	-	-
H_2 input	L L^{-1} day^{-1}	0	0	4.2	4.2	-	-	-	-
SMP_{tot}	L CH_4 g^{-1} VS	0.278	0.278	0.452	0.451	-	-	-	-
CH_4	%	48.6	48.7	71.9	72.2	-	-	-	-
TAN	mM	78.5	78.2	77.9	100.6	-	-	-	-
VFA	mM	1.7	0.9	0.6	1.0	-	-	-	-
pH	-	7.37	7.38	7.71	7.83	-	-	-	-
pCO_2	-	0.489	0.488	0.154	0.152	-	-	-	-
a x 10^8	-	8.37	8.33	11.93	8.86	-	-	-	-
b x 10^8	-	0.64	0.64	0.92	0.88	-	-	-	-
Difference between experimental and predicted pH based on Eqn A with coefficient a(x)									
a(i)	-	-	0.00	0.14	0.02	0.08	0.934	0.00	no
a(ii)	-	0.00	-	0.15	0.02	0.09	0.935	0.00	no
a(iii)	-	0.15	0.15	-	0.12	0.14	1.000	0.00	*
a(iv)	-	0.02	0.03	0.12	-	0.07	1.000	0.00	*
Difference between experimental and predicted pH based on Eqn B with coefficient b(x)									
b(i)	-	-	0.00	0.15	0.13	0.11	0.991	0.00	no
b(ii)	-	0.00	-	0.14	0.13	0.11	0.991	0.00	no
b(iii)	-	0.15	0.15	-	0.02	0.12	1.000	0.00	*
b(iv)	-	0.13	0.13	0.02	-	0.11	1.000	0.00	*
Difference between experimental and predicted pH for Eqn A with a(x) and phosphate adjustment									
Period (i)	-	-	0.00	0.08	0.06	0.06	0.996	0.00	*
Period (ii)	-	0.00	-	0.08	0.07	0.06	0.996	0.00	*
Period (iii)	-	0.08	0.09	-	0.02	0.07	1.000	0.00	*
Period (iv)	-	0.06	0.07	0.01	-	0.05	1.000	0.00	*

At OLR 5 g VS L^{-1} day^{-1} Equation A gave good or reasonable agreement between all cases. Equation B did not improve individual values significantly but gave an increase in R^2. The phosphate adjustment was able to produce good agreement throughout. Results of regression analysis for Equation A and B were not significant, probably due to slightly unstable operation at the higher OLR as well as the small number of cases considered. All regression results were significant at the 5% level with the phosphate adjustment.

Overall comments:

In addition to minor variations in VFA concentration some changes in TAN concentration were seen during this study, both between different OLR and over time during the experimental period: both Equation B and the phosphate adjustment performed well in these cases.

Figures S2-S5 show values for data series corresponding to the average values given in Table 34 for the full dataset of values with TAN and VFA data. Figure S3b and b present similar information to Figure 2a and b in the main text but are included here for completeness and ease of reference: small differences are due to the use of a slightly smaller dataset in Figure 2a and b where the phosphate adjustment is also shown.

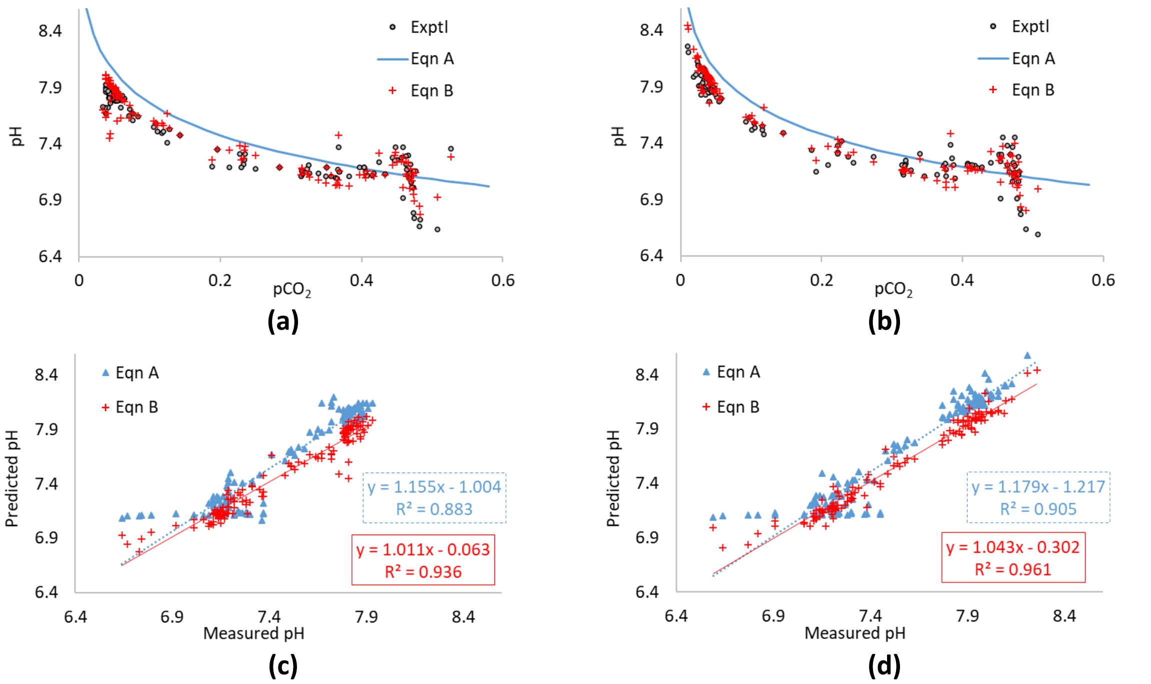

Figure S2 Measured pCO_2 and measured and predicted pH values ((a) and (b)) and predicted pH values from Equations A and B ((c) and (d)) for duplicate reactors during mesophilic CO_2 biomethanisation of phosphate-containing synthetic feed at OLR 2 g COD L^{-1} day^{-1} from Tao et al. (2019) for data points with measured VFA and measured or interpolated TAN.

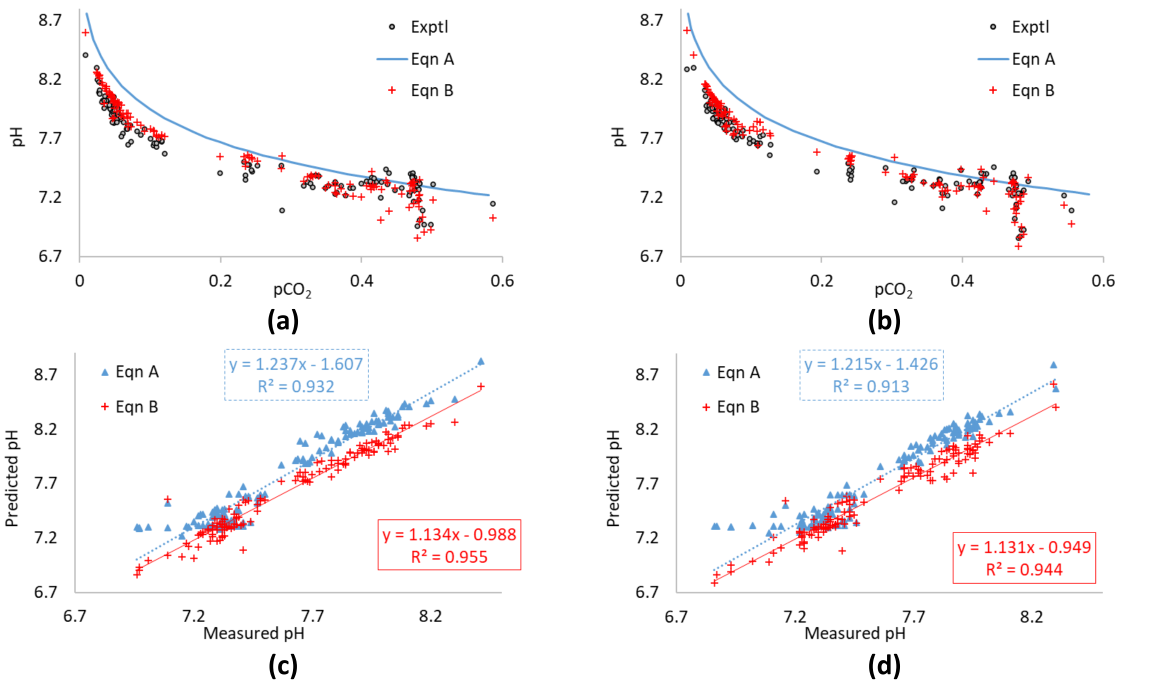

Figure S3 Measured pCO_2 and measured and predicted pH values ((a) and (b)) and predicted pH values from Equations A and B ((c) and (d)) for duplicate reactors during mesophilic CO_2 biomethanisation of phosphate-containing synthetic feed at OLR 3 g COD L^{-1} day^{-1} from Tao et al. (2019) for data points with measured VFA and measured or interpolated TAN.

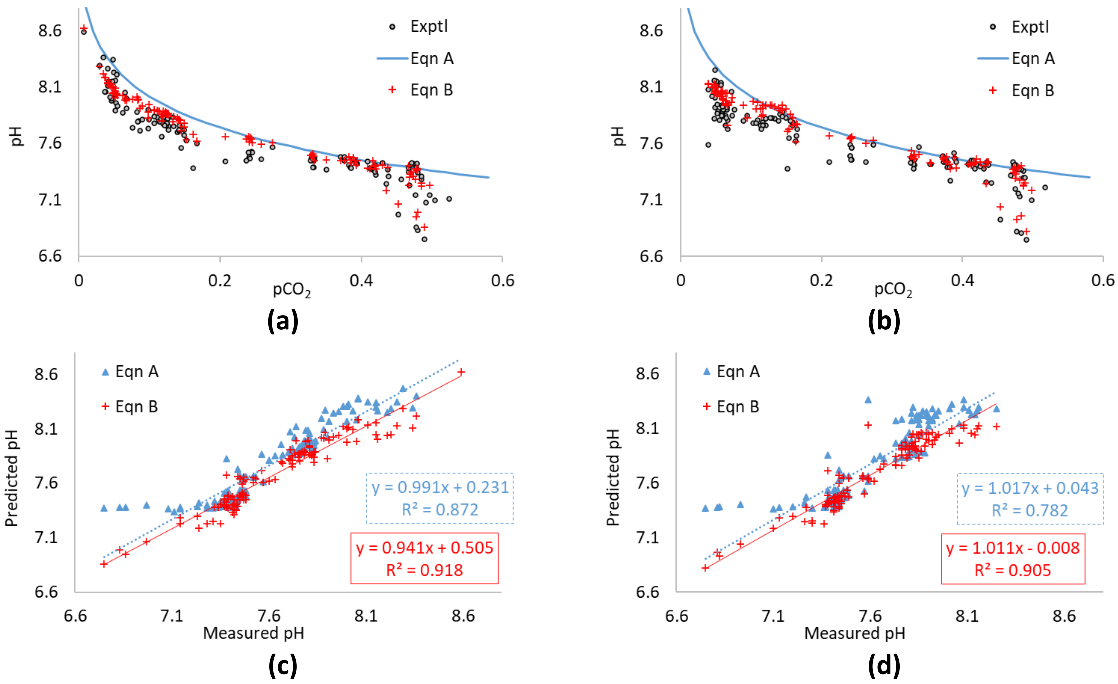

Figure S4 Measured pCO_2 and measured and predicted pH values ((a) and (b)) and predicted pH values from Equations A and B ((c) and (d)) for duplicate reactors during mesophilic CO_2 biomethanisation of phosphate-containing synthetic feed at OLR 4 g COD L^{-1} day^{-1} from Tao et al. (2019) for data points with measured VFA and measured or interpolated TAN.

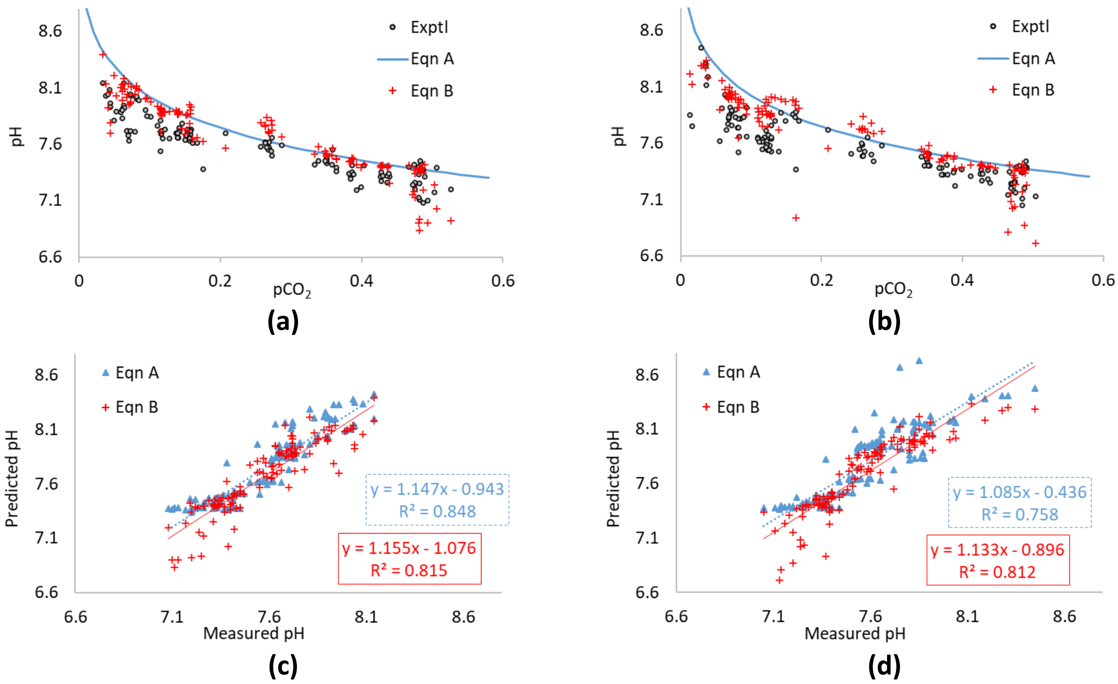

Figure S5 Measured pCO_2 and measured and predicted pH values ((a) and (b)) and predicted pH values from Equations A and B ((c) and (d)) for duplicate reactors during mesophilic CO_2 biomethanisation of phosphate-containing synthetic feed at OLR 5 g COD L^{-1} day^{-1} from Tao et al. (2019) for data points with measured VFA and measured or interpolated TAN.

Table S35

Tao, B., Zhang, Y., Heaven, S. and Banks, C.J., 2020. Predicting pH rise as a control measure for integration of CO2 biomethanisation with anaerobic digestion. *Applied Energy*, *277*, p.115535.

TAN 2 g N L^{-1}		(i)	(ii)	(iii)	(iv)	(v)	(vi)	(i)	(ii)	(iii)	(iv)	(v)	(vi)	RMSD
Days		123-132		251-259		332-340		123-132		274-283		332-340		
Replicate no.		1	2	1	2	1	2	3	4	3	4	3	4	
		No H_2	No H_2	With H_2	With H_2	No H_2	No H_2	No H_2	No H_2	No H_2	No H_2	With H_2	With H_2	
Temp	°C	37	37	37	37	37	37	37	37	37	37	37	37	-
OLR	g VS L^{-1} day^{-1}	3	3	3	3	3	3	3	3	3	3	3	3	-
HRT	days	15	15	15	15	15	15	15	15	15	15	15	15	-
H_2 input	L L^{-1} day^{-1}	0	0	2	2	0	0	0	0	0	0	2.4	2.4	-
SMP_{tot}	L CH_4 g^{-1} VS	0.272	0.274	0.385	0.420	0.283	0.294	0.264	0.269	0.292	0.298	0.481	0.442	-
CH_4	%	53.9	53.5	85.5	84.4	51.8	53.4	54.3	53.9	54.2	54.5	88.6	88.5	-
VFA	mM	24.7	19.6	15.4	24.6	n/a	n/a	59.3	73.3	4.9	2.8	n/a	n/a	-
pH	-	7.67	7.69	8.03	7.90	7.59	7.59	7.61	7.53	7.67	7.66	8.22	8.23	-
pCO_2	-	0.458	0.458	0.123	0.146	0.473	0.461	0.454	0.453	0.455	0.451	0.111	0.104	-
$a \times 10^8$	-	4.44	4.17	6.70	7.84	5.22	5.26	5.16	6.25	4.42	4.57	4.47	4.61	-
Difference between experimental and predicted pH based on Eqn A with coefficient *a*(x)														
a(i)	-	-	0.03	0.05	0.08	0.07	0.07	-	0.08	0.06	0.05	0.05	0.04	0.06
a(ii)	-	0.03	-	0.07	0.10	0.09	0.10	0.08	-	0.14	0.13	0.13	0.11	0.10
a(iii)	-	0.06	0.09	-	0.02	0.01	0.01	0.06	0.14	-	0.01	0.00	0.01	0.06
a(iv)	-	0.09	0.11	0.02	-	0.02	0.02	0.05	0.13	0.01	-	0.01	0.00	0.06
a(v)	-	0.07	0.09	0.01	0.02	-	0.00	0.06	0.14	0.00	0.01	-	0.01	0.06
a(vi)	-	0.07	0.10	0.01	0.02	0.00	-	0.05	0.13	0.02	0.00	0.01	-	0.06

CSTR, 37 °C, duplicate pairs operated as control and experimental reactors over different periods. Synthetic organic feedstock with controlled TAN concentrations.

Equation A generally showed good agreement, apart from in replicate 4 without H_2 addition during a brief increase in VFA (days 123-132) when agreement was reasonable. Regression analysis was not carried out but the RSMD was ≤ 0.1 for all cases.

Table S35 ctd

TAN 3 g N L^{-1}		(i)	(ii)	(iii)	(iv)	(v)	(vi)	(i)	(ii)	(iii)	(iv)	(v)	(vi)	RMSD
Days		123-132		230-239		312-325		123-132		230-239		312-325		
Replicate no.		5	6	5	6	5	6	7	8	7	8	7	8	
		No H_2	No H_2	With H_2	With H_2	With H_2	With H_2	No H_2	No H_2	No H_2	No H_2	No H_2	No H_2	
Temp	°C	37	37	37	37	37	37	37	37	37	37	37	37	-
OLR	g VS L^{-1} day^{-1}	3	3	3	3	3	3	3	3	3	3	3	3	-
HRT	days	15	15	15	15	15	15	15	15	15	15	15	15	-
H_2 input	L L^{-1} day^{-1}	0	0	1.6	1.6	1.6	1.6	0	0	0	0	0	0	-
SMP_{tot}	L CH_4 g^{-1} VS	0.239	0.246	0.416	0.380	0.367	0.381	0.251	0.235	0.227	0.238	0.268	0.257	-
CH_4	%	54.2	54.9	81.7	80.9	80.8	80.3	54.3	53.0	53.0	53.5	55.5	55.2	-
VFA	mM	32.6	15.5	8.9	10.6	n/a	n/a	23.1	13.6	34.1	31.2	n/a	n/a	-
pH	-	7.80	7.82	8.11	8.11	8.18	8.16	7.79	7.77	7.71	7.70	7.87	7.86	-
pCO_2	-	0.454	0.448	0.178	0.182	0.185	0.187	0.455	0.465	0.468	0.472	0.442	0.440	-
$a \times 10^8$	-	3.20	3.11	3.71	3.65	3.00	3.10	3.29	3.40	3.89	4.02	2.81	2.91	-
Difference between experimental and predicted pH based on Eqn A with coefficient a(x)														
a(i)	-	-	0.01	0.06	0.05	0.02	0.01	-	0.01	0.07	0.08	0.06	0.05	0.05
a(ii)	-	0.01	-	0.07	0.06	0.01	0.00	0.01	-	0.05	0.07	0.08	0.06	0.05
a(iii)	-	0.06	0.07	-	0.01	0.08	0.07	0.07	0.05	-	0.01	0.13	0.12	0.08
a(iv)	-	0.05	0.06	0.01	-	0.07	0.06	0.08	0.07	0.01	-	0.14	0.13	0.08
a(v)	-	0.03	0.02	0.08	0.07	-	0.01	0.06	0.08	0.13	0.14	-	0.01	0.08
a(vi)	-	0.01	0.00	0.07	0.06	0.01	-	0.05	0.06	0.12	0.13	0.01	-	0.07

Equation A showed good agreement apart from briefly for replicates 7&8 without H_2 addition towards the end of the trial when there was a brief increase in VFA.

These operating periods were based on those designated as representative in Bywater et al. (2022), but in several cases there were insufficient values for VFA and TAN to allow use of Equation B.

Figures S6-S9 show values for data series corresponding to the average values given in Table 35. Note that data in Figure S8b and D is also shown in Figure 2 c and D in the main text but is included here for completeness and ease of reference.

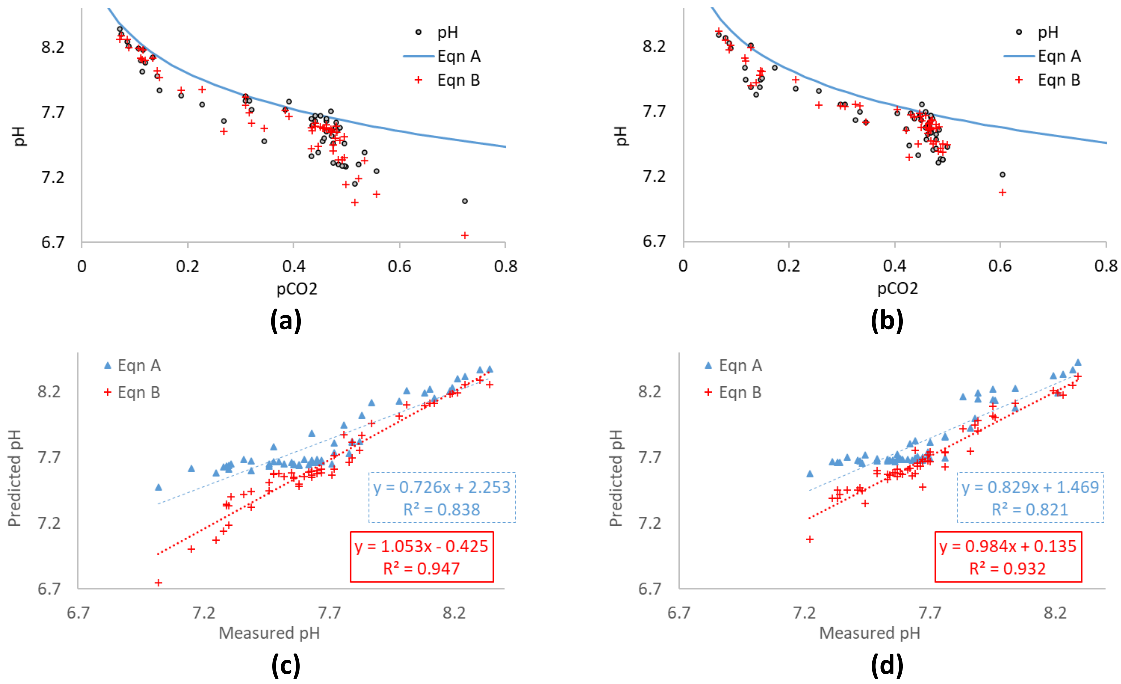

Figure S6 Measured pCO_2 and measured and predicted pH values ((a) and (b)) and predicted pH values from Equations A and B ((c) and (d)) for first set of duplicate reactors during mesophilic CO_2 biomethanisation of phosphate-containing synthetic feed at 2 g N L^{-1} from Tao et al. (2020) for data points with measured VFA and measured or interpolated TAN.

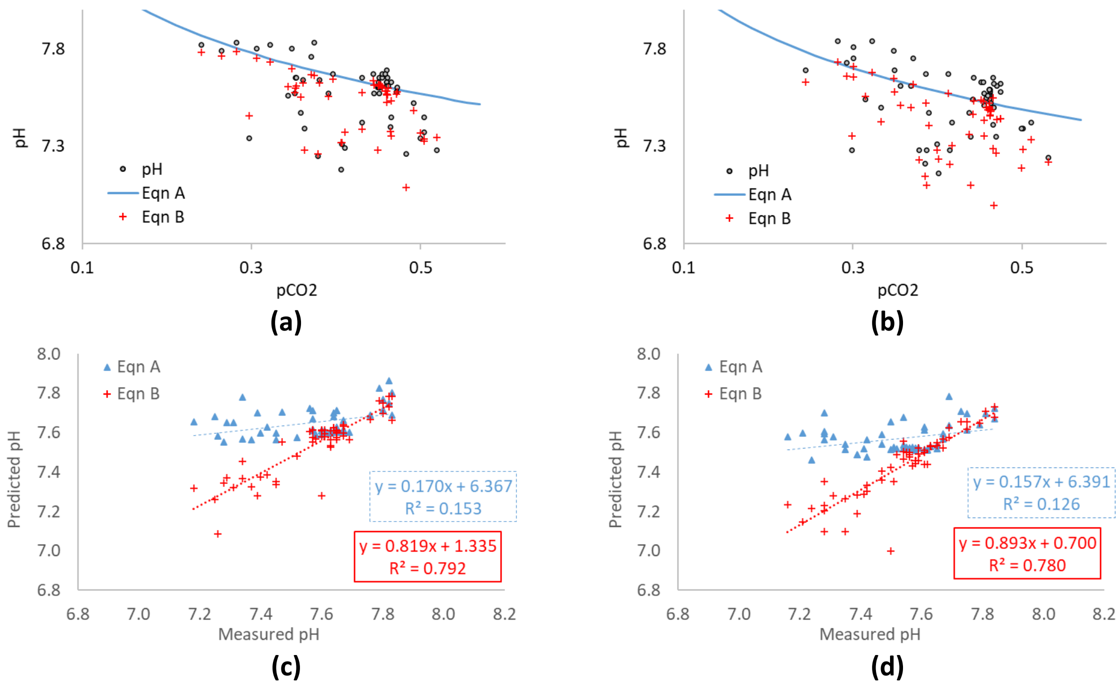

Figure S7 Measured pCO_2 and measured and predicted pH values ((a) and (b)) and predicted pH values from Equations A and B ((c) and (d)) for second set of duplicate reactors during mesophilic CO_2 biomethanisation of phosphate-containing synthetic feed at 2 g N L^{-1} from Tao et al. (2020) for data points with measured VFA and measured or interpolated TAN.

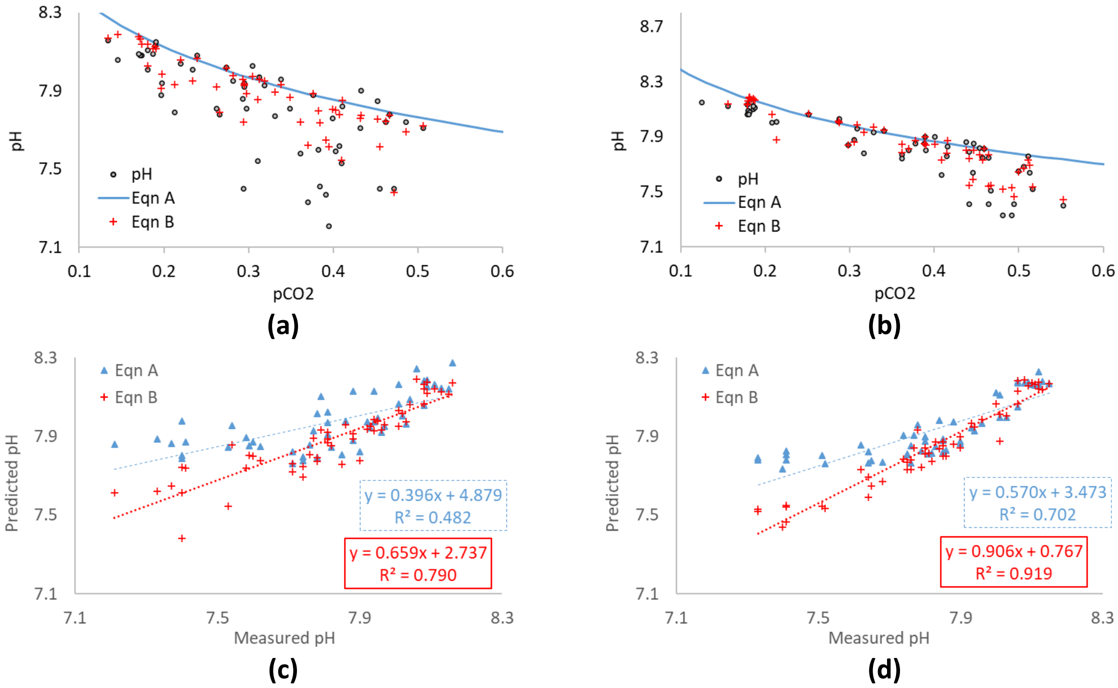

Figure S8 Measured pCO_2 and measured and predicted pH values ((a) and (b)) and predicted pH values from Equations A and B ((c) and (d)) for first set of duplicate reactors during mesophilic CO_2 biomethanisation of phosphate-containing synthetic feed at 3 g N L^{-1} from Tao et al. (2020) for data points with measured VFA and measured or interpolated TAN.

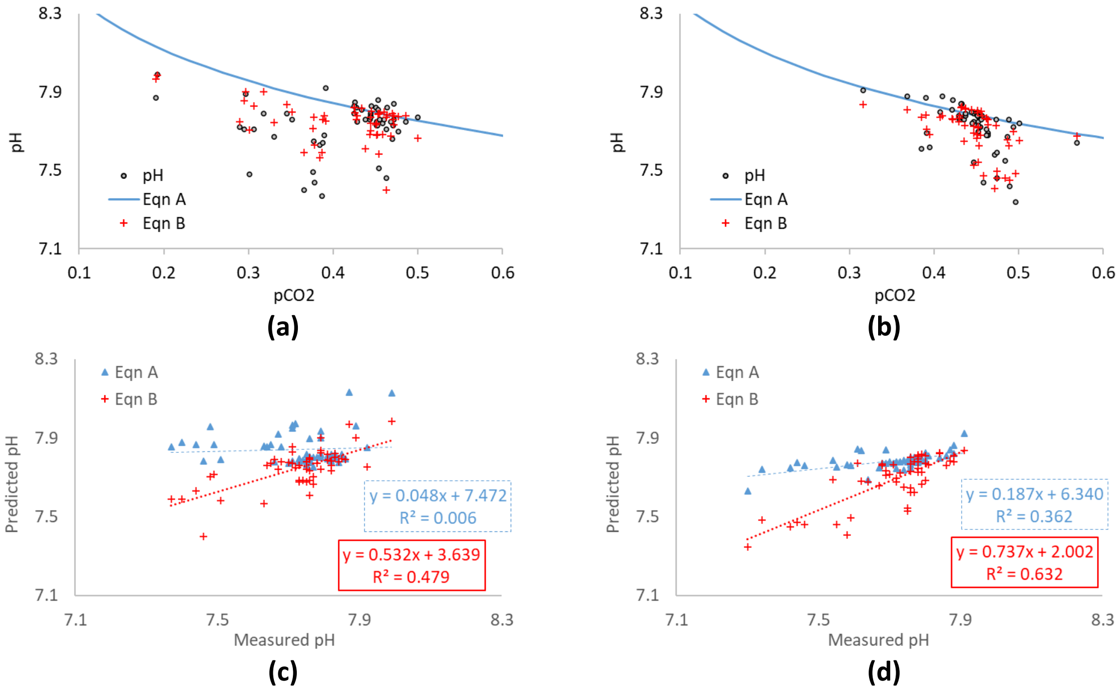

Figure S9 Measured pCO_2 and measured and predicted pH values ((a) and (b)) and predicted pH values from Equations A and B ((c) and (d)) for second set of duplicate reactors during mesophilic CO_2 biomethanisation of phosphate-containing synthetic feed at 3 g N L^{-1} from Tao et al. (2020) for data points with measured VFA and measured or interpolated TAN.

Table S36

Andreides, D., Pokorna, D. and Zabranska, J., 2022. Assessing the syngas biomethanation in anaerobic sludge digestion under different syngas loading rates and homogenisation. Fuel, 320, p.123929.

		(i)	(ii)	(iii)	(iv)	(v)	(vi)	(vii)	(viii)	(ix)	(x)	(xi)	(xii)
	Phase	Control period		1		2		3		4		5	
		No gas	No gas	No gas	Gas	No gas	Gas	No gas	Gas	No gas	Gas	No gas	Gas
Temp	°C	55	55	55	55	55	55	55	55	55	55	55	55
OLR	g VS L^{-1} day^{-1}	1.9	1.9	2.3	2.3	2.0	2.0	1.9	1.9	1.8	1.8	1.9	1.9
HRT	days	21	21	21	21	21	21	21	21	21	21	21	21
Syngas input	L L^{-1} day^{-1}	0	0	0	0.3	0	0.7	0	1	0	1.5	0	1.5
SMP_{tot}	L CH_4 g^{-1} VS	0.37	0.38	0.39	0.46	0.41	0.53	0.38	0.63	0.37	0.55	0.38	0.36
CH_4	%	65.0	64.8	65.7	59.1	64.8	49.7	64.9	43.1	65.1	34.8	64.6	50.3
TAN	mM	n/r	n/r	n/r	n/r	n/r	n/r	n/r	n/r	n/r	n/r	n/r	n/r
TVFA	g L^{-1}	0.25	0.26	0.30	0.33	0.30	0.22	0.26	0.16	0.18	0.15	0.21	8.02
pH	-	7.60	7.61	7.62	7.65	7.61	7.86	7.62	8.01	7.63	8.10	7.60	8.60
pCO_2	-	0.349	0.351	0.343	0.335	0.352	0.289	0.351	0.257	0.350	0.219	0.354	0.237
$a \times 10^8$		6.23	6.04	6.02	5.69	6.02	3.72	5.88	2.72	5.74	2.43	6.14	0.42
Difference between experimental and predicted pH based on Eqn A with coefficient *a*(x)													
a(i)	-	-	0.01	0.01	0.03	0.01	0.19	0.02	0.29	0.03	0.33	0.01	0.85
a(ii)	-	0.01	-	0.00	0.02	0.00	0.18	0.01	0.28	0.02	0.31	0.01	0.84
a(iii)	-	0.01	0.00	-	0.02	0.00	0.18	0.01	0.28	0.02	0.31	0.01	0.84
a(iv)	-	0.03	0.02	0.02	-	0.02	0.15	0.01	0.26	0.00	0.29	0.03	0.82
a(v)	-	0.01	0.00	0.00	0.02	-	0.18	0.01	0.28	0.02	0.31	0.01	0.84
a(vi)	-	0.19	0.18	0.18	0.16	0.18	-	0.17	0.11	0.16	0.14	0.19	0.67
a(vii)	-	0.02	0.01	0.01	0.01	0.01	0.17	-	0.27	0.01	0.30	0.02	0.83
a(viii)	-	0.30	0.29	0.29	0.27	0.29	0.11	0.28	-	0.27	0.04	0.30	0.56
a(ix)	-	0.03	0.02	0.02	0.00	0.02	0.16	0.01	0.26	-	0.30	0.03	0.82
a(x)	-	0.34	0.33	0.33	0.31	0.33	0.15	0.32	0.04	0.31	-	0.34	0.53
a(xi)	-	0.01	0.01	0.01	0.03	0.01	0.18	0.02	0.29	0.03	0.32	-	0.85
a(xii)	-	0.89	0.88	0.88	0.85	0.88	0.69	0.87	0.57	0.86	0.52	0.89	-

55 °C CSTR fed on sewage sludge with added syngas (H_2:CO 55:45% v/v). Varied mixing (mechanical phase 1-4, gas phase 5) and syngas loading.

Agreement in control period and periods 1 & 2 good or reasonable. Thereafter agreement in control reactor remains good but experimental reactor with increasing syngas addition is poor. Very high VFA in period 5, no TAN data.