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Biogas Plasticization Coupled Anaerobic Digestion: Continuous Flow Anaerobic Pump Test Results

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Abstract In this investigation, the Anaerobic Pump (®TAP) and a conventional continuous flow stirred tank reactor (CFSTR) were tested side by side to compare performance. TAP integrates anaerobic digestion (AD) with biogas plasticization–disruption cycle to improve mass conversion to methane. Both prototypes were fed a "real world" 50:50 mixture of waste-activated sludge (WAS) and primary sludge and operated at room temperature (20°C). The quantitative results from three steady states show TAP peaked at 97% conversion of the particulate COD in a system hydraulic residence time (HRT) of only 6 days. It achieved a methane production of 0.32 STP cubic meter CH_4 per kilogram COD fed and specific methane yield of 0.78 m^3 CH_4 per cubic meter per day. This was more than three times the CFSTR specific methane yield (0.22 m^3 CH_4 per cubic meter per day) and more than double the CFSTR methane production (0.15 m^3 CH_4 per kilogram COD fed). A comparative kinetics analysis showed the TAP peak substrate COD removal rate (R_o) was 2.24 kg COD per cubic meter per day, more than three times the CFSTR substrate removal rate of 0.67 kg COD per cubic meter per day. The three important factors contributing to the superior TAP performance were (1) effective solids capture (96%) with (2) mass recycle and (3) stage II plasticization–disruption during active AD. The Anaerobic Pump (®TAP) is a high rate, high efficiency–low temperature microbial energy engine that could be used to improve renewable energy yields from classic AD waste substrates like refuse-derived fuels, treatment plant sludges, food wastes, livestock residues, green wastes and crop residuals.

Keywords Advanced anaerobic bioconversion · Biogas · Biomass · Continuous flow · Pressure cycle · Pressure swing · Renewable energy · Waste

David R. Boone, deceased May 2005.

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Nomenclature

Biobarrier line (B_c)	A theoretical line corresponding to the maximum methane production for conventional digestion AD, generally located at the nexus of mesophilic temperature extrapolations of $(HRT)^{-1}$ vs. B to infinity (typically the $B_c \approx B$ at 60 days$\approx B_o$).
Partially fluidized suspension	A mixed slurry suspension with a fluid velocity adequate to suspend of the lighter solids fraction (heavier solids gravity separate) of the particle size and density array during active anaerobic settling tests.
Rechargeable biogas suspension	Suspension of digesting solids by natural biogas production followed by gas withdrawal (decompression or disruption) and then recharging with natural AD gas production, repeated in a continuous cycle.
MPR	Methane production rate (liters STP CH_4 per day)
GPR	Biogas production rate (liters STP CH_4 per day)
TKN	Total Kjeldahl (organic) nitrogen (grams nitrogen per liter)
OLR	Organic loading rate (kg TVS m^{-3} day^{-1} or kg COD m^{-3} day^{-1})
pCOD	Particulate chemical oxygen demand (gram particulate COD per liter)
pN	Particulate nitrogen concentration (gram particulate nitrogen per liter)
B	Methane production at a given retention time (liters STP methane per gram COD added)
B_o	Maximum methane production for retention time approaching infinity (liters STP methane per gram COD added)
R	Refractory coefficient is the decimal fraction representing the proportion of substrate COD that is non-biodegradable (refractory) at infinite digestion time.
R_o	Substrate removal rate function, either Monod or Contois (gram COD per liter day)
S_o	The initial COD concentration at time $t=0$ (gram COD per liter)
S_t	Total COD concentration at any time t (grams COD per liter)
S_{bo}	Maximum biologically available COD concentration in the feed (grams COD per liter)
S_{to}	Total chemical oxygen demand (COD) concentration in the feed (grams COD per liter)
S	Effluent COD concentration (grams COD per liter)
S_i	Concentration of particulate COD recycle + influent mixture (grams pCOD per liter)
K	Contois kinetic constant (dimensionless, gram COD substrate per gram COD organisms)
K_s	Monod substrate saturation coefficient (grams COD per liter)
Q	The flow rate into the reactor (liters/day)
Q_r	Recycle flow rate for TAP = 40 l day^{-1} for the project (all three TAP steady states)
α	$Q_r\, Q^{-1}$ = the recycle ratio
$\widehat{\mu}$	Monod and Contois maximum growth rate (day^{-1})
θ	Hydraulic retention time (days)
X	In reactor cell mass concentration (gram/liter)

Introduction

Anaerobic digestion (AD) has enormous potential for converting wet biomass to energy rich methane (CH_4), a very versatile renewable fuel. However, significant improvements in kinetic and mass conversion efficiency [1, 2] are needed to expand its use for renewable energy production. A significant proportion of biomass volatile fraction is "refractory" (R) because it resists hydrolysis by conventional AD even if held for infinite time [3]. The refractory (R) coefficient [3–5] can be related to methane production (B) by Eq. 1:

$$R = (S_T B_o / S_{To} B) - ((B_o - B)/B)) \quad (1)$$

where R represents the proportion of the substrate mass chemical oxygen demand (COD) that remains non-biodegradable at infinite time and methane production $B \neq 0$. S_{To} and S_T are the substrate input feed and reactor output COD, respectively. B and B_o are the observed methane production (liters methane per gram COD added) and the maximum methane production at infinite time, respectively. Typical refractory percentages (%R) for common AD substrates range from 28% to 70%. The maximum methane production (B_o) can be increased in direct proportion to decrease in the refractory percentage (%R) by conditioning the feed biomass. A coupled continuous AD-conditioning system that could simultaneously lower the refractory coefficient ($R \rightarrow 0$), such that biodegradable COD $S_{bo} \rightarrow S_{To}$ as $B \rightarrow B_o \rightarrow 0.35$ l STP methane (gram total COD (TCOD) fed)$^{-1}$, would greatly improve AD use for alternative energy production purposes.

Past researchers have investigated a variety of thermal, mechanical, chemical [6], and bioaugmentation pretreatment conditioning methods to improve sludge biodegradability [7]. Heating the mass with steam at 170°C, at 10 atm for 30 min [8–11] before AD can achieve approximately 10–20% improvement in hydrolysis of solid polymers to an assortment of soluble polypeptides, ammonia, volatile acids, and carbohydrates. Mechanical devices such as inline ultrasound cavitation devices [12–14] or venturi devices [15] can rupture cell walls, liberating 10–20% of the cell mass, achieving a 10–20% improvement in AD performance. These methods achieve incomplete conversion and leave considerable mass for disposal. In addition, high COD and low pH liquors (10,000–30,000 ppm COD, pH = 4–5) can be difficult to treat by physical, chemical, or microbial means [16].

Researchers have discovered that mass conversion can be improved by combining high-pressure thermal plasticization (heat) with low-pressure disruption. Contacting raw WWTP sludges with high-pressure temperature steam (196°C, 14 bar, for 5 s) followed by decompression to atmospheric pressure [17] increased soluble COD (SCOD) concentrations by 40–85%, resulting in a methane yield of approximately 0.33–0.44 m^3 CH_4 per kilogram VS. Similarly, Liu [18] subjected the primary digestate of municipal solid waste (MSW) to steam heating (250°C, 58 bar, for 5 min), increasing the overall methane yield by 40%, from 0.25 to 0.35 m^3 CH_4 per kilogram VS. However, these systems generally require significant investment in tankage, mechanicals, and energy inputs and still yield incomplete and slow bioconversion [19, 20].

The phenomenon of plasticization [21–23] is generally defined as a mechanism wherein heat or permeating gases cause a reduction in the cohesive intermolecular forces along the polymer chains, so they can move freely relative to one another, reducing polymer stiffness and cohesiveness. Lower molecular weight substances, like water (moisture), ammonia, and carbon dioxide, can move in and out of a polymer lattices over a wide spectrum of temperatures and pressures. This mechanism cannot be measured directly because direct observations of structural changes at the cellular level are simply not practical. Instead,

plasticization is usually measured indirectly by measuring polymer swelling, degree of hydrolyzation, changes in weight or glass-transition temperature (T_g), or other rheological changes [23]. For instance, wood researchers [24, 25] observed significant hydrolysis of complex wood polymers during gas plasticization experiments. Others [17, 18] found that pre-treating sludge with heat (thermal plasticization) increased volatile dissolved solids and volatile fatty acids. In experiments during active AD of sludge, biogas plasticization was capable of causing methane production (B) to increase far beyond levels explainable by ordinary substrate thickening or retention time [5, 26].

Early researchers have found that pressure significantly enhanced AD performance [27–29]. Changing the pressure in an anaerobic digester can avoid toxicity effects [26, 30, 31]. Mild pressure swings [5, 26] between 0.5 and 1.5 atmospheres have been shown to improve low temperature (20°C) AD performance during biogas plasticization batch experiments with waste-activated sludge (WAS). Batch experiments showed that a fully plasticized reactor was capable of a 43% increase in maximum methane production (B_o) to ~0.32 l methane per gram COD added and a maximum ~12× increase in COD utilization rate to 11.25 g COD per liter day [26, 32, 33]. This hybrid AD process has become known as the Anaerobic Pump [34] (®TAP).

This paper presents the analytical methods and key findings of a 1 year investigation that quantitatively compared the performance of two continuous flow AD units; a biogas plasticization–disruption unit, Anaerobic Pump (®TAP) vs. a conventional continuous flow stirred tank reactor (CFSTR). The experimental objective was to quantitatively assess the improvement plasticization–disruption had on continuous flow AD. Verification and validation of the plasticization–disruption method was a secondary objective. The investigation was independently conducted by Dr. David R. Boone (Portland State University, Oregon).

Materials and Methods

Three steady-state experiments were designed to directly compare side by side performance. TAP and CFSTR AD prototypes were juxtaposed in a 20°C temperature control room [33]. The CFSTR was the experimental control. The feed substrate was a (50:50) mixture of WAS and primary sludge, collected periodically from the Durham, Oregon municipal WWTP. Both equal volume (30 l) prototypes were fed the same substrate mixture at the same loading rates (Table 1) from the same refrigerated (4°C), mechanically mixed feed reservoir shown in Fig. 1. All environmental and operating variables are strictly controlled so that the quantitative results led to certifiably valid conclusions.

CFSTR Prototype Design

The CFSTR reactor (complete mix) with no recycle and no gas plasticization was chosen to establish the experimental (control) baseline values for the experiment. It was constructed of Plexiglas, water-jacketed with a culture volume of 30 l and headspace of 5 l. More detailed information concerning the CFSTR design, hydraulics, and operational data was described in the project's final report [33].

TAP Prototype Design

The TAP prototype (Fig. 1) stages are a completely flooded (no headspace) design with continuous recycle between stages [5, 35–38]. This maximizes culture volume and

Table 1 A 20°C experimental steady-state flow and loading plan.

Pump/ parameter	Pulse feeding frequency	Feeding rate (ml/4 min)	Nominal flow rate (liters/day)	Nominal HRT (days)	Target Organic Loading (kg TVS m^{-3} day^{-1})
Pump P-1 (ss#1)[a]	6 times/day	334	2	15	0.8
Pump P-1 (ss#2)	8 times/day	625	5	6	2.0
Pump P-1 (ss#3)	8 times/day	938	7.5	4	3.0
Pump P-2 (recycle)	continuous	–	40		
Pump P-3 (pressure)	Variable[b]				
Pump P-4 (pressure)	Variable[b]				

[a] Pump P-1 is the influent flow rate that is identical for both TAP and CFSTR

[b] TAP Stage II is pressurized or depressurized by varying pumps P-3 and P-4 rates (Fig. 1) via DOS computer control of pump variable speed heads to meet pressure set-points and durations

minimizes nonproductive space. A lithium tracer test revealed that the system was a dispersed plug flow mixing regime [5], mainly due to the high recycle rate (40 l day^{-1}). Stage I (22.6 l) was a partially fluidized suspension, and stage II (7.4 l) was a rechargeable biogas suspension. Both reactors featured an internal upflow with peripheral downflow baffles forming the submerged gas environment [5, 35–38]. Because solids' thickening via gravity in AD environments is very poor, a submerged gas volume was designed to improve solids capture. Stages I and II biogas production were independently measured with two calibrated Speece rocker-type gas totalizers [39]. A more complete presentation of TAP design details and operation are given in the author's patents [35–38] and project final report [33].

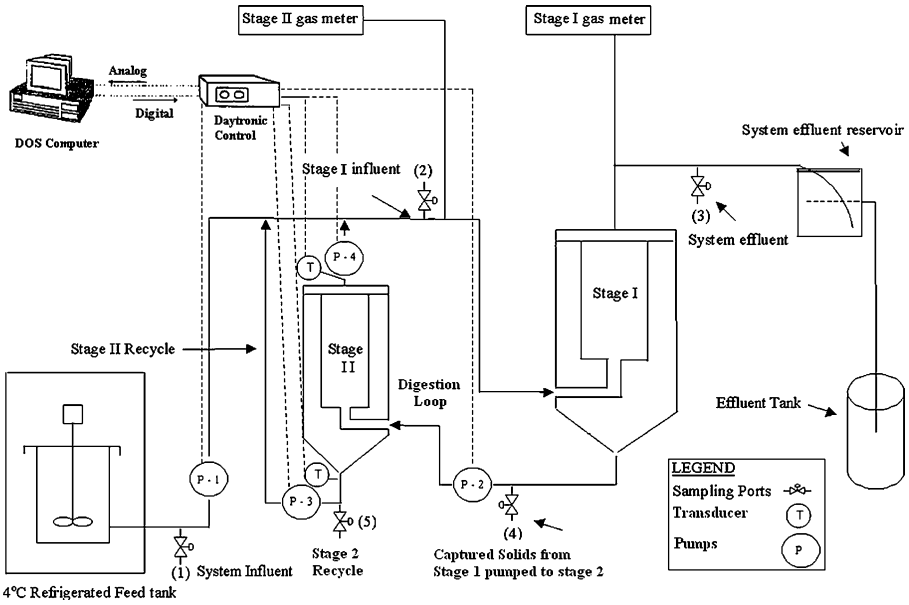

Fig. 1 Schematic diagram of Anaerobic Pump (TAP) prototype experimental setup

The design of the continuous flow stage II biogas plasticization–disruption cycle was based on results from prior batch experiments [5, 32]. The anaerobic culture autocatalytically produces biogas that recharges the suspension. A computer–pressure transducer system (Fig. 1) was used to control the continuous pressure cycle frequency (12 cycles per day). During a 1-h (1.5 atm) recharging period, pressurized biogas permeates (CO_2 and moisture) into the suspended solids, inducing chain relaxation, disentanglement, and reptation diffusion of degradable monomers outward toward well-distributed syntrophic consortia attached at digesting surfaces. During the following 1-h decompression (0.5 atm) period, the rapid gas expansion fragments the softened polymers, resulting in particle size reduction that greatly increases surface area. These solids are then recycled to stage I, exposing the new surfaces to seeding and growth. Then, as the seeded mixture passes back to stage II (P-2), maximum possible cell densities (X) are well positioned to rapidly produce more biogas by converting the plasticized reptating monomers with their very efficient catabolic systems.

Sampling and Analytical Procedures

TAP prototype schematic (Fig. 1) shows a total of eight measurement points, two standpipe-manifold assembles with Speece gas totalizers, five gravimetric and wet chemistry sampling ports, and one pressure gauge redundancy for vacuum-pressure transducer readings. The five slurry-sampling ports were sampled biweekly. The CFSTR had only three measurement points, one gas standpipe with tritube manometric gas meter and two sampling ports (influent and effluent). All slurry samples were analyzed for solids (total and volatile), TCOD, SCOD, pH, total Kjeldahl nitrogen (TKN), and free ammonia (NH_3N). Total gas production was logged daily for both prototypes. All analytical procedures were in accordance with the *Standard Methods* 20th edition [40]. All gas streams produced were analyzed by gas chromatography with He carrier gas and thermal conductivity detection [41]. All free-ammonia (NH_3N) samples were analyzed using the ammonia probe (ISE) method 4500 or the phenate method [40]. The sampling and analytical protocol was thoroughly presented in this project's final report [33].

Systems Startup

TAP stage I and CFSTR were started by charging them with a mixture of 10 l of fresh-screened mixed sludge and 25 l of anaerobic inoculum collected from a mesophilic (35°C) digester at the Durham, Oregon WWTP. The charge was followed by an initial low loading to both systems was organic loading rate (OLR) of ~0.32 kg TVS m^{-3} day^{-1}. During the startup acclimation period, stage II was charged with inoculum but kept offline (not loaded). After about three operation months, both reactors (TAP stage I and CFSTR) showed near complete acclimation with relatively steady gas production. The system feed was then increased to the first nominal steady-state loading level (Table 1). Slowly, fully acclimated and seeded mass was transferred from stages I to II via pump P-2 (Fig. 1) until stage II was full.

TAP stage II startup requires an additional startup step, the establishment of a plasticization conformation from top to bottom. The "ratchet" procedure [26, 32] was used to establish the stage II plasticization regime. For a priori design purposes, it was assumed that, as the incoming digesting mass moves through stage II, undergoing the applied pressure–decompression cycle, the mixture becomes plasticized, which increases the gas production. According to prior batch WAS plasticization experiments [32], the maximum stage II volumetric production rate is 6.11 STP liters biogas (liter/day) or the equivalent of

transferring a maximum of 11.25 g COD per liter day to the gas phase [26, 32]. Then, a 1-h plasticization half cycle should generate approximately one half the maximum specific rate or ~3.1 STP liters biogas (liter/day), transferring ~5.6 g COD per liter day to the gas phase. As the stage II biogas production rate approached this target value, computer pressure control (Table 1) was engaged.

Steady-State Operation

Both continuous flow prototypes (TAP and CFSTR) were fed the same mass loadings for each steady state shown in Table 1. A steady state was considered established when total gas production, effluent pH, and SCOD held relatively constant over at least three consecutive HRT periods. Steady states were completed in uninterrupted succession. TAP pressure cycle program controlled by the computer–pressure transducer system was set at a 2-h cycle period with 1-hour high pressure (152 kPa = 1.5 atm absolute) and 1-h at low pressure (50.7 kPa = 0.5 atm absolute). The transition between the pressure set points was accomplished using pumps P-3 and P-4 in approximately 2 min.

Data Analysis Methods

The goal of the data analysis was to quantitatively compare performance of the conventional CFSTR vs. the Anaerobic Pump (®TAP) digestion loop. The CFSTR performance establishes the baseline, the conventional biodegradability limit (biobarrier line, B_c), the refractory coefficient (R), and minimum kinetic rates for this substrate. To validate the CFSTR baseline performance, the efficiency and kinetic parameters were compared to literature values from an investigation utilizing a similar WWTP sludge substrates. The TAP analysis relied on accurate daily gas production and data from sampling ports 2 and 4 (Fig. 1) to determine the fate of carbon (COD). The loading and methane production (B, B_o) for both prototypes were used to derive the kinetic coefficients for Monod [42] and Contois [3] models. Both kinetic models were evaluated because both substrate growth limitation and high cell densities (overcrowding) limitation were possibilities in TAP's digestion loop. The TAP performance was compared to CFSTR results to show the extent to which plasticization improves bioconversion.

The three important performance parameters tracked around the TAP digestion loop are the increase in the refractory coefficient (R, Eq. 1), the percent increase particulate methane COD loss (Eq. 2), and percent increase in particulate nitrogen conversion (Eq. 3):

$$[\text{Methane produced per day}]100/0.35[\text{TCOD} - \text{SCOD fed per day}] \tag{2}$$

$$[\text{Net ammonia} - \text{N output per day}]100/[\text{TKN} - \text{NH}_3\text{N fed per day}] \tag{3}$$

Large changes of these three ratios around the digestion loop is evidence that substrate resistant fraction (R) has undergone transformation to biodegradable polymers (S_b) and biogas.

The kinetic analysis compares the data of a complete mix with no recycle kinetic model for the CFSTR steady states per Eq. 4,

$$Q(S_o - S) - R_o = 0 \tag{4}$$

and a two stage dispersed plug flow with recycle (Q_R) model for TAP Stage I per Eq. 5.

$$(1+\alpha)(S_i - S)/\theta - R_o = 0 \tag{5}$$

$$X = Y(1+\alpha)(S_i - S) \tag{6}$$

The substrate removal rate function (R_o) in Eqs. 4 and 5 can be either Monod [42, 43] or Contois [3] functions. Equations 5 and 6 contains α that is the recycle ratio (Q_R/Q). Equation 6 relates the cell mass concentration (X) with the substrate utilization and recycle ratio (α) for the Contois function. Substitute α for the ($1+\alpha$) term in Eqs. 5 and 6 when the Contois model is applied to TAP stage II. The total substrate removal for the TAP system is simply the addition of the substrate removal (R_o) for stages I and II. The linear techniques for determining the Monod and Contois kinetic constants, maximum specific growth rate ($\widehat{\mu}$) and the saturation constant (K) are similar to those used by other investigators [3, 42–44].

Results and Discussion

Feed Substrate Characterization

Table 2 shows that the feed 50:50 mixed sludge substrate volatile solids (TVS) content was about 73% (of TS). Approximately 88% of the TCOD was particulate COD (pCOD). On average, 5 wt.% of the feed solids (TS) was organic bound nitrogen. Seven weight percent of the feed volatile solids was nitrogenous material, indicating that approximately 45 wt.% of the feed volatile solid matter was proteinaceous matter. Applying Eq. 1 to the CFSTR biogas data, this substrate exhibited a relatively high resistance (R=0.65) to conventional AD when compared to compared literature value (R=0.35) [45]. The large protein fraction most likely significantly contributes to the high substrate resistant mass (R) fraction. Not shown in Table 2, this "real world" substrate contained a significant oil and grease fraction that was observed floating on the surface TAP stage I effluent reservoir (Fig. 1) during all steady states.

Table 2 Composition of the 50:50 mixed sludge substrate.

Sample parameter	Number of samples	Mean value $\overline{X}$	Standard deviation, σ
TS (wt.% of sample)	82	1.56	0.31
TVS [wt.% of sample, (% of TS)]	33	1.14 (73)	0.156
Total COD (TCOD, mg/L)	15	15,047	1240
Soluble COD (SCOD, mg/L)	9	1725	600
pH	32	6.7	0.2
TKN (mg N/l)	19	1,026	96
Free NH_3-N (mg N/l)	19	202	51
Protein content[a] (% of TVS)	19	45	3.2

Feed sludge was 50:50 mixture of primary sludge/waste-activated sludge was collected from Durham OR WWTP

[a] Average volatile (TVS) fraction protein content=(TKN-free NH_3N)×6.25 (TVS×100)$^{-1}$

Mass Balance Comparisons

For all steady-state organic loading (TAP and CFSTR), the resulting five COD and nitrogen mass balances closed within acceptable balances. During the third steady state (ss#3), CFSTR failed due to organic overload, and TAP began to show signs of organic overload (lower gas production and greater effluent solids concentrations).

Carbon (COD) Transformation Comparison

Table 3 shows the CFSTR produced an average methane production (B) of 0.15 STP liters CH_4 per gram TCOD fed during the first two steady states. Even at the longest HRT (15 days, ss#1), this unit converted less than 70% of the available biodegradable COD (S_b), resulting in a minor increase in the resistance coefficient (R) from ~0.65 (influent solids) to ~0.7 (effluent solids). Its critical OLR was 2 g TCOD per liter day at HRT=6 days. Figure 2c and d shows the CFSTR performance relative to the conventional AD biobarrier line at approximately 0.22 l STP CH_4 per gram TCOD fed and literature values [45].

Both TAP stages (Fig. 2a, b) showed the classic decrease in biogas production with increasing OLR. It demonstrated a broad operating curve (Fig. 2c, d) with a critical OLR= 3.24 g TCOD per liter day at a short 4-day HRT. TAP system ss#1 GPR was 17.8 STP liters biogas per day, nearly 50% greater than the CFSTR best GPR of 12.1 STP liters biogas per day. TAP ss#2 GPR of 39.8 STP liters biogas per day was more than three times higher than the CFSTR GPR. During ss#2, TAP system converted 97% of the influent pCOD while producing a remarkable 0.32 STP liters CH_4 per gram TCOD fed. Approximately 40% of the conversion improvement was due to solids capture plus recycle, and the remaining 60% was due to biogas plasticization–disruption conversion of the R fraction in stage II. Stage II was only one quarter of the TAP system volume, or approximately one quarter of the digestion loop residence time, yet produced 75% of the system methane. The large difference between the maximum methane production of stage I (B_o=0.081 l CH_4 per gram TCOD added) and stage II (B_o=0.241 l CH_4 per gram TCOD added), a factor of 3, is indicative of bioconversion with and without biogas plasticization–disruption. The TAP stage II volumetric biogas yield during ss#2 was approximately ten times (4.01/0.4) that of the CFSTR biogas yield (Table 3). This gas production rate has been characterized as the optimum "bubbling bed" operational mode. It was less than the 12× (6.1/0.5) obtained from WAS batch test results [26] but greater than the a priori expected value of 7.6× (3.1/0.4). The difference was most likely due to the fugitive mass losses in the TAP effluent (Fig. 1, port 3). The performance comparison is graphically depicted in Fig. 2c and d, and it shows the superior TAP methane production compared to CFSTR and literature values relative to the biobarrier line (blue line).

Further analysis of the TAP digestion loop showed that increased COD removal to the gas phase was directly proportional to the rapid improvement in substrate digestibility. Analysis showed that 75%, 89% and 49% of the TCOD concentration entering the digestion loop was converted to biogas during ss#1, ss#2, and ss#3, respectively. TAP mixture in the digestion loop (recycle) was composed of highly resistant material R→1 or R~0.96, 0.88, and 0.93 for ss#1, ss#2 and ss#3, respectively. When stage II mass (and volume it occupies) is lost by conversion to biogas in the digestion loop, it is rapidly replaced by new resistant solids from incoming recycle. During ss#2, the stage II feed solids had a C/N ratio of approximately 25 g solid COD per gram solid N and after plasticization–disruption, the mass eventually exits from sampling port 5 with only 1.7 g solid COD per gram solid N (during ss#2), a 93% reduction. The measured stage II mass

Table 3 Comparison of CFSTR and TAP performance parameters.

20°C performance	Conventional		The Anaerobic Pump								
Reactor/stage	CFSTR digester		TAP stage I			TAP stage II			System (I+II)		
Performance parameter/steady state number	ss#1	ss#2	ss#1	ss#2	ss#3	ss#1	ss#2	ss#3	ss#1	ss#2	ss#3
Methane production (STP liters per gram TVS added)	0.26	0.11	0.12	0.10	0.10	0.27	0.30	0.13	0.39	0.40	0.23
Methane production (STP liters per gram COD added)	0.19	0.11	0.08	0.08	0.07	0.18	0.23	0.10	0.26	0.31	0.17
Volumetric biogas yield (STP liters per liter day)	0.40	0.40	0.24	0.45	0.56	1.68	4.01	2.55	0.59	1.33	1.05
Volumetric CH_4 yield (γ_v) (STP liters per liter day)	0.20	0.23	0.12	0.26	0.32	0.84	2.37	1.29	0.30	0.78	0.56
Volatile solids reduction (%)	24	31	28	30	24	32	32	14	61	62	38
Solid COD removal[d] (% pCOD removed)	58	35	26	25	26	60	72	34	87	97	60
Solid nitrogen conversion[e] (% pN converted)	20	11	[a]–	–	–	[a]–	–	–	50	15	8
Expected biogas production[b]											
Expected volumetric yield (STP liters per liter day)	0.4	0.4	0.4	0.4	0.4	3.1	3.1	1.6	1.05	1.05	0.69
Expected biogas production rate (STP liters per day)	12.0	0.0	9.0	9.0	9.0	22.9	22.9	11.8	31.2	31.2	20.8
Measured biogas production and composition[c]											
Biogas production rate (STP liters per day)	12.1	11.9	5.4	10.1	12.6	12.4	29.7	18.8	17.8	39.8	31.4
Methane (% CH_4)	49.8	59.4	50.5	59.1	57.4	50.1	59.1	50.6	50.2	59.1	53.3
Nitrogen (% N_2)	3.5	4.9	4.3	2.3	3.3	4.3	2.3	5.7	4.3	2.3	4.74
Carbon dioxide (% CO_2)	46.7	35.7	45.2	38.6	39.3	45.6	38.6	43.7	45.5	38.6	41.9

[a] Nitrogen conversion to ammonia confounded by Stage TKN accumulation and low pressure ammonia carryover

[b] Based on Based on prior batch test results [19]

[c] Gas composition was measured by the gas chromatography

[d] Calculated per Eq. 2

[e] Calculated per Eq. 3

conversion rate was R_o=6.77 g COD per liter day to methane (2.37/0.35), equivalent to producing 2.37 l CH_4 per liter day (Table 3) or ~60% of the maximum plasticization rate of 11.25 g COD per liter day obtained during batch testing [26]. This was slightly higher than the a priori continuous flow design estimate of 50% of maximum plasticization production. However, this rate approaches the published glucose metabolism rate of ~7.9 g COD per liter day for anaerobic fixed bed reactors [46] as previously noted [26]. Glucose and glutamine are major substrates utilized by cells in the production of enzymes and complex proteins. These independent findings validate a priori estimates and confirm earlier batch testing results [5, 32].

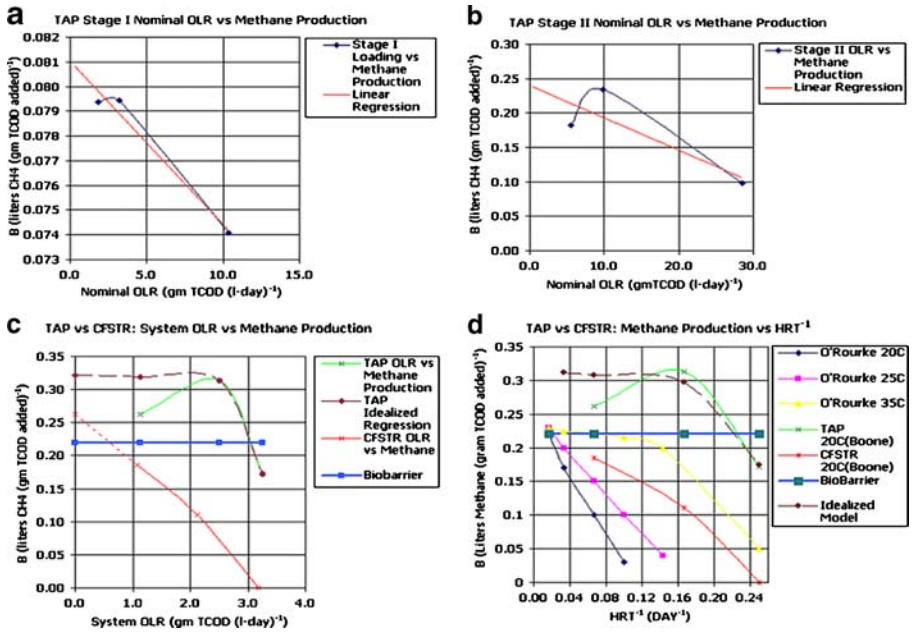

Fig. 2 **a** TAP stage I nominal OLR vs. methane production: B_o=0.08 m^3 kg $added^{-1}$; **b** TAP stage II nominal OLR vs. methane production: B_o=0.24 m^3 kg $added^{-1}$; **c** TAP vs. CFSTR: nominal OLR vs. methane production: TAP B_o=0.32 m^3 kg $added^{-1}$ and CFSTR B_o=0.22 m^3 kg $added^{-1}$; **d** TAP vs. CFSTR and literature comparison: methane production operating curves

Nitrogen (TKN) Transformation Comparison

The CFSTR converted 20% and 11% of the feed TKN to ammonia in 15 and 6 days, respectively. While better than expected, low nitrogen (protein) conversion is typical of conventional AD processes [47].

By comparison, the TAP nitrogen balance and performance (Table 3) parameter analysis showed the biogas plasticization–disruption cycle significantly advanced protein breakdown. Concurrent with increased methane production during ss#2, stage I nitrogen output increased more than 50% with a corresponding equal loss in nitrogen output (accumulation) in stage II. For the system, a simple regression analysis of particulate nitrogen conversion to soluble ammonia (Eq. 7) vs. HRT (Table 3) for all three steady state shows a linearly proportionality (r^2=0.999) according to Eq. 7.

$$[\%\ \text{Solid nitrogen converted to ammonia}] = 3.797(\text{HRT}) - 7.547 \tag{7}$$

Extrapolation of Eq. 7 predicts full conversion of particulate nitrogen to soluble ammonia in a retention time (HRT) of approximately 28 days. The combination of high biogas production with rapid TKN conversion at high R values (R~0.89–0.96) in stage II (ss#2) indicates that TAP was enabling COD conversion from resistant protein materials. This was a unique insight into the transition from predominately resistant carbohydrate (COD) conversion to resistant protein COD conversion.

Kinetics Comparison

Kinetic model coefficients were derived for both the Monod and Contois kinetic models using Eqs. 4, 5, and 6, and the results are directly compared in Table 4. Both models applied to both prototype systems fit the measured conversion data with a high correlation (r^2=0.99). Both model coefficients, $\widehat{\mu}$ and K or K_s, for the CFSTR fall within the typical range (literature values) for conventional systems digesting this substrate. TAP stage I and CFSTR Monod substrate constants (K_s) compare favorably, but the TAP growth coefficient ($\widehat{\mu}$) was much higher (3.6×). Similarly, The TAP Contois model growth constant $\widehat{\mu} = 0.34\ \text{day}^{-1}$ was 50% higher than the CFSTR $\widehat{\mu} = 0.23\ \text{day}^{-1}$ rate constant. The higher kinetic rate coefficients for TAP stage I may have been caused by increased biodegradable substrate (S_b) carry over in the recycle stream from stage II. The shift toward higher substrate coefficients was indicative of much more resistant (R) substrate in the TAP digestion loop. Both models showed that TAP steady states ss#2 and ss#3 had much higher cell yields than the CFSTR. Stage II plasticization–disruption rapidly increased the availability of easily degradable substances (S_b) and cell growth rapidly increased to consume the new S_b availability.

This both kinetic model analyses of the TAP data (Table 4) show abrupt changes in coefficients moving from stage to stage. Stage I operates at atmospheric pressure where the coefficients are reduced to more conventional values. Like the large differences in methane production, the abrupt change in kinetic parameters appears to be indicative of bioconversion with and without biogas plasticization–disruption.

Conclusions

The analytical results of this investigation, both mass conversion efficiency and kinetics, shows clear and compelling evidence that plasticization–disruption cycle (stage II) significantly improves AD process efficiency and kinetics. This phenomenon enabled TAP to operate at a peak methane production (B) of 0.32 l CH_4 per gram COD fed, well above the conventional biobarrier. Nearly all the increase in system methane production (B)

Table 4 Monod and contois 20°C kinetic and refractory coefficients.

System/ parameter, 20°C digestion temperature	Monod[a] max. specific growth rate, $\widehat{\mu}$ (day^{-1})	Monod[a] substrate constant, K_s (g pCOD l^{-1})	Monod[a] estimate refractory coefficient R (pCOD)	Contois[b] max. specific growth rate, $\widehat{\mu}$ (day^{-1})	Contois[b] substrate constant, K (TCOD)	Contois[b] estimate refractory coefficient R (TCOD)
Conventional AD range for sludge	0.1–0.4	5.0–10.0	0.3–0.7	0.1–0.3	0.2–1.1	0.3–0.7
CFSTR	0.33	6.88	0.63	0.23	0.88	0.65
TAP system	2.94	23.3	0.58	0.19	0.39	0.60
TAP stage I	1.20	6.98	0.93	0.34	1.31	0.91
TAP stage II	10.7	69.7	0.91	0.62	0.51	0.89

[a] Monod: based on pCOD concentration and cell (X) concentration estimates best fit

[b] Contois: based on TCOD concentration and cell (X) concentration estimates by Eq. 6

came from stage II that was derived from conversion of resistant mass ($R \sim 0.96$). The kinetic analysis showed similar increases, and the rapid reaction had a remarkable resemblance to sugar metabolism [26]. These independent findings constitute verification of TAP's 3× methane potential and confirm prior published mechanism descriptions and conclusions [26, 33].

Additional improvements in TAP efficiency may be realized by improving solids capture or recovery. Recycling captured solids back to TAP from an aerobic polishing (SCOD) unit is one common method. Another is improving solids COD (pCOD) containment by employing a membrane on the TAP effluent port (port 3). Future studies on (1) pathogen inactivation as compared to thermphilic AD, (2) temperature and concentration effects on plasticization efficiency, and (3) TAP performance with other resistant waste substrates could enhance the knowledge base.

Because of TAP's simplicity, only two tanks and three pumps, it is expected to be comparatively inexpensive to build, operate, and maintain [48]. The rapid mass transformation to energy over a broad operating range makes this process very desirable for renewable energy production applications. Retrofitting small, crude, or high-density AD systems with plasticization–disruption operation is promising. Hence, TAP offers many new possibilities for expanding commercial applications utilizing typical AD substrates such as MSW RDF, WWTP sludges, food wastes, animal manure, green wastes, crop residuals, and organic residues of industry. Important industrial applications are renewable energy production (space heating and distributive electrical power), nutrient-enriched irrigation water (N and P), renewable fertilizers, and protein boosted animal feeds and so on.

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