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COMPARED PERFORMANCE OF TRICKLE-BED AND FLUIDIZED BED BIOREACTORS FOR SYNGAS BIO-UPGRADING INTO RNG

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ABSTRACT: The present study investigates, optimizes and compares the conversion of carbon monoxide (CO) and syngas ($CO/H_2/CO_2$, 40/40/20, and 20/20/10, v/v) to renewable natural gas (RNG) in two types of reactors, trickle-bed reactor (TBR) and fluidized bed reactor (FBR), highlighting their respective advantages and disadvantages. The comparison considered various aspects of reactor operation efficiency with regards to the specific roles of the different microbial trophic groups forRNG production. Overall, TBR results indicate good conversionefficiencies (up to 97%) and a relatively constant stoichiometry-based CH_4 yield (88-100%), for CO partial pressures lower than 0.5atm. regardless of the operational condition tested. Once the biofilm was sufficiently developed, a maximum CO conversion activity of 37 $mmolCO.g^{-1}$ volatile suspended solid (VSS). $d^{-1}$was achieved. In FBR, restricted mass transfer and absence of attached biomass growth limited the overall reactor efficiency. Only 10% of initial biomass concentration was recovered at the end of the test. The reactor was operativeat higher CO partial pressure with non-diluted syngas but the maximum efficiency obtained under stable operating conditions was barely 82-85%. During thereactoroperation, methanogenic, hydrogenophilic, acetoclastic and carboxydotrophic specific activities variedin function of substrate composition, biofilm type and structure.
Keywords: bioenergy, renewablenatural gas (RNG), syngas, anaerobic process, fixed bed, circular economy

1 INTRODUCTION

Renewable natural gas (RNG) plays a central part in the future energy system as a sustainable fuel that can be used with high efficiency and ultralow emissions. There are a number of conversion routes for the production of RNG. Anaerobic digestion (AD) is the main conversion path for methane production. Likewise anaerobic microorganisms that fix carbon dioxide (CO_2) and carbon monoxide (CO) are capable of converting gaseous carbon in RNG. To overcome AD limitations and optimize the carbon recovery the thermochemical conversion path such as gasification of lignocellulosic feedstock and organic wastes followed by syngas methanation made good progress in the last decade. The later technology can utilize syngas from a wide range of feedstock including organic matter of any sort (e.g., municipal solid waste, industrial waste, biomass, and agricultural waste residues) or industrial off-gases (e.g., from steel mills or processing plants). In addition, there is more and more interest into the power-to-gas concept, where surplus, intermittent or stranded electricity is used to produce hydrogen, which in turn can be used to reduce carbon dioxide and/or carbon monoxide to methane. Therefore, several synergies between these technologies are in development.

Biomass gasification to RNG process is studied in projects like GoBiGas in Sweden, Güssing Gasifier (Repotech), Austria, ECN, Netherlands, Gaya, France and at Paul Scherrer Institute, Switzerland. The composition of syngas may vary depending upon type and quality of feedstock, operating conditions in the gasifier and overall steps conducted for the gasification process. Presently the complexity of the process (operational steps) is a barrier in technology development, despite the significant demand of gas utilities for RNG. Also, given the distributed nature of biomass resulting in high transportation costs, conventional approaches to biomass gasification/synthesis is also limited in scale. As a result, "economies of scale" will not be available and hence, reducing theprocess complexity is necessary to be cost-effective at smaller scale. As result, conventional approaches to biomass gasification/synthesis seem to be slowed down.

The present project addressesthe RNG production from syngas aiming atreducing theoverall process complexity, by using small-scale biomethanation processes, adapted from reactor technologies already used in other industrial applications.

Biomethanation offers a simple and flexible pathway for producing RNG at relatively small scale. The biological process simplifies the approach for production of RNG and maximizes the energy potential of residuals - avoiding the use of catalysts, circumventing thermochemical side reactions, minimizing the cost related to gas mix pre-treatment and reduce the number of process steps (unit operations) required.

A complete assessment of the two reactor types (i.e., the trickling bed reactor (TBR), and the fluidized bed reactor (FBR)) is proposed to be completed in the present work at a laboratory-scale (35L). The suitability of a bioreactor system for gas to liquid mass transfer applications is basedon its capability to correlate with the reaction kinetics.

2 MATERIALS AND METHODS

2.1 Reactor design and set-up

Both reactors have been operated at 35°C and neutral pH. Their performance wasmonitored in relation witha variety of parameters including: flow rates, gas pressure and composition, dissolved CO, volatile fatty acids (VFAs).

2.1.1 Trickling-bed reactor (TBR)

A trickle-bed reactor (TBR) is a reactor that uses the downward movement of liquid and gas over a packed bed of solid particles. It is considered to be the simplest reactor type for performing three-phase reactions, where a gas and liquid (normally both reagents) are present in the reactor. Accordingly it is extensively used in processing plants. Although the reactor design is relatively simple, the hydrodynamics in the reactor is extremely complex and itsunderstanding is still limited.

Despite numerous advantages in using TBR compared

to other multiphase reactors, such higher values of effective interfacial areas and low operating cost, undesired mass gradients may exist, as well as poor temperature control, channeling and scale-upuncertainty.

The 35L double-jacketed stainless steel reactor (internal diameter 0.2 m; height 1.13 m) was packed randomly with 12x12mm borosilicate Raschigrings (Willmad Lab Glass, NJ, USA) and inoculated with an with industrial anaerobic sludge (Lassonde, Rougemont, Qc.) for a relative concentration of 7 gVSS/L of reactor working volume (L_{RXR})corresponding to 15.3gVSS/Lof packed bed (PB). The packed bed volume and the empty bed (EB) volume were 13L and 7.6L, respectively. Internals specifications of the column are presented in Table I.

Table I: Column internal specifications (TBR)

Specifications	
Mass (kg)	3.7
Total Volume (L)	13
Column Height (m)	0.41
Packing weight (kg/m^3)	308
Void fraction (m^3/m^3)	58
Specific surface area (m^2/m^3)	2000

The reactor temperature was controlled by two probes (DP-41, Omega Engineering Inc, Stamford, CT) placed in the upper and lower levels and maintained at 35°C using a hot water jacket connected to a thermostatic bath (RA8; MGW Lauda, Konigshofen, Germany) through a custom-made controller. The pH was measured (electrode 405-DPAS-SC-K8S, Mettler Toledo GmbH, Urdorf, CH; controller PHP-194, Omega Engineering Inc, Stamford, CT) and controlled manually between 6.5 and 7.1 using 1 M NaOH or 1 M HCl.

The reactor was continuously fed (HRT 175 days) with a mineral and nutrient buffered solution which is constantly recycled with a magnetic drive gear pump (PN L20297 0715 MOD GC-M25, Micropump Inc., Vancouver, WA., USA) into the reactor via nozzles located above the packed bed, downward at countercurrent of the gas phase. This provides large specific gas–liquid interfacial areas. The gaseous substrate was introduced at the bottom of the reactor and, after transformation, vented towards agasmeter (model L1, Wohlgroth SA, Schwerzenbach, CH).

2.1.2 Fluidized bed reactor (FBR)

A second series of experiments were carried in a 35L upflow double-jacketed stainless steel reactor (internal diameter 0.2 m; height 1.13 m; working liquid volume 30 L) equipped with same auxiliaries, such thermocouples, pH probes and thermostatic bath, as described above. The reactor has been inoculated with industrial anaerobic sludge (Lassonde, Rougemont, Qc.) at 10 g VSS/L_{RXR}. The reactor was continuously fedwith a mineral and nutrient buffered solution (average HRT 55 days). The gaseous substrate (CO, H_2, CO_2 (Praxair Canada Inc, Mississauga, ON, CA) was introduced into the reactor via the gas recirculation line, at the bottom of the reactor, nominally at 25-250 sccm (mL/min), and diluted in N_2 during the acclimation phase. The gas flow rates were measured and controlled by thermal mass flow meters (MC-XXXSCCM-D, XXX = 50, 100, 200 or 500, Alicat Scientific Inc., Tucson, AZ,). The gas exits the reactor through a pressure valve (TM Swagelok, Solon, OH) to maintain the reactor headspace at 1.5 atm (manometer 0-20PSI, US Gauge, Ira Township, MI). The gas phase was recycled with a vacuum Pump (UN726.1.2 FTP, KNF Neuberger Inc., Trenton, NJ) at 0.5 to 1.5 L/min and exhausted towards a gasmeter (model L1, Wohlgroth SA, Schwerzenbach, CH).

2.2 Anaerobic activity tests

The specific substrate activities were determined in 60 mL serum bottletests by measuring the depletion of a non-limiting concentration of asingle substrate and the methane production over time. The activities were measuredonthe initial inoculum and on sludge aliquotsintermittently sampled from the reactor. The specific activity is used as an indicatorof the relative content of target trophic groups within the biomass. Thetarget trophic group is defined by the substrate used in the test and methane yield. Moredetails can be found elsewhere [1].

2.3 Analytical methods

The suspended solids (SS), volatile suspended solids (VSS), and chemical oxygen demand (COD) were determined according to Standard Methods [2].

Measurement of volatile fatty acids (VFA) wasmade on an Agilent 6890 gas chromatograph (Wilminton, DE, USA) equipped with a flame ionization detector (FID). Nine hundredμL of filtered sample were mixed with 100 μL of internal standard (2-ethylbutyric in 25% formic acid). Oneμl of sample was automatically injected into a Nukol capillary column (30m x 0.25 mm x 0.25 μm; Supelco, Bellefonte, PA., USA). The column temperature program starts at 80°C for 0.5 minutes up to 200°C with a rate of 10°C/min. Total run time is 13 minutes. Helium was the carrier gas at a velocity of 30 cm/sec. The injector uses a split ratio of 10:1 at 200°C and the detector temperature was 250°C. Calibration curve was made by injecting a mixture of eight volatile fatty acids diluted in deionized water and mixed with the internal standard.

The gas composition (H_2, N_2, O_2, CO, CH_4 and CO_2) was measured by injecting 300 μL of gas (model 1750 gas-tight syringe, Hamilton, Reno, NV) into a GC Agilent 7820A gas chromatograph (Agilent technologies, Wilmington, DE) equipped with a ShinCarbon ST packed column (Restek Corporation, Bellefonte, PA, USA) coupled to a thermal conductivity detector with argon as the carrier gas. The column was heated at 40 °C for 5 min then the temperature was raised to 200 °C at a rate of 20 °C/min and maintained for 2 min. The injector and detector were maintained at 125 °C and 250 °C. The dissolved CO concentration (dCO) of liquid was estimated from the CO partial pressure in the headspace of the liquid sample-containing vial after equilibrium was reached at 100°C, as described previously [3]

3 RESULTS

The TBR and FBR operations have begun by an acclimatization phase, wherethe reactors have been feed with CO alone, after which the reactors were assessedby being fed with artificial synthesis gas, for different compositions and loads. When appropriate, the biogas upgrading to RNG process has been performed using exogenous hydrogen (e.g. electrolytic hydrogen, e.g. using off-peak electricity, asan opportunity for electricity storage together with CO_2 sequestration). Operational parameters and main results are presented in Tables II and

IV.

Table II: Performance of the Fluidized Bed Reactor and Trickle Bed Reactor, as a function of operational conditions when fed with carbon monoxide. Unit of measurement: Q_{CO} : [$L_{STP}CO/d$], C_{CO} : [%], E_{COD} : [%], YCH4 : [$mL_{stp}CH_4/gCOD_{cons.}$], kCO : [$mmol_{CO}/gVSS.d$], dCO : [$\mu mol/L$]

Q_{CO}	Rx	C_{CO}	E_{COD}	Y_{CH4}	k_{CO}	d_{CO}
14.4	TBR	20	85	308	3.0	13
		40	91	224	3.5	12
	FBR	-	-	-	-	-
21.6	TBR	20	84	434	5.1	6
	FBR	100	84	410	4.3	0.0
28.8	TBR	20	81	406	8.3	10
	FBR	100	80	336	4.6	0.0
36.0	TBR	20	65	490 (182)	9.2	110 (110)
	FBR	100	65	301	5.0	0.0
43.2	TBR	-	-	-	-	-
	FBR	100	48	367	6.8	0.0
57.6	TBR	-	-	-	-	-
	FBR	100	59	297	11.8	0.0
72.0	TBR	-	-	-	-	-
	FBR	100	63 (28)	248 (70)	14.8	20
28.8	TBR	20	66	392	8.2	90 (80)
	FBR	100	89	276	9.3	0.0
21.6	TBR	20	82	336	8.2	0.0
	FBR	-	-	-	-	-

3.1 Carbon monoxide

The TBR reactor was started up at low CO inflow, using a gas mix containing CO and nitrogen for the feeding. The CO was removed at 100% with a methane production at 89% of the stoichiometric yield. After the acclimatizing step, the first experimental phase (Q_{CO} 14.4 L/d, OLR 20mmolCO/L_{RXR}.d, empty bed retention time (EBRT) 0.09d, and CO partial pressure at the entry, 0.46atm) was completed successfully. The substrate was degraded at 85%and the methane reached 88% of the stoichiometric yield. Increasing the CO content ofthe inflow gas mix from 20% to 40% raisedthe COpartial pressure to0.64atmpushing CH_4yields downto 64%. In both conditions, the carboxydotrophic volumetric activity remainedconstant at 17-18 mmol CO/L_{RXR} (40-41 mmolCO/L_{PB}.d or 0.07mol/L_{EB}.d) and the CO removal efficiency reached 91%.

To restore optimal methanogenic conditions the inflowpartial pressure was setataround 0.4atm (20%CO in inflowgas mix) for all future experiments. Subsequent increase of the CO loadto 30 and 40mmol/L_{RXR}.drestored completely the CH_4yield at its maximum and the CO removal efficiency returnedto the 81-84% level. In this phase the average volumetric removal rate attained 120mmolCO/L_{EB}.d. Similar volumetric specific activities were obtained after a further increase of the CO load (36 L/d or 50mmolCO/L_{RXR}.d corresponding to an EBRT of 0.035 d), but the removal efficiencydropped to 65±5%, thedissolved CO in the liquid attainedvalues around 0.1mM and the reactor is not stable anymore. The average CH_4yield at 140± 52% of the stoichiometric maximum, suggests that biomass was stressed and decayed, providing a supplementary source of substrate for methane production. In this phase a certain limitation in CO_2 (only 7% in the off-gas) followed by an increase of the H_2 concentration suggests that the system could have reached its maximum capacity.

From this point the reactor was operated at lower OLR, to validate on the long term the performance results obtained before. After 358 days of operation itcan be confirmed that the reactor was stable and performedwith an82-87%removal efficiencyfor a CO loadof 21.6 L/d (30mmolCO/L_{RXR}.d, 68mmol/L_{PB}.dor 117mmolCO/L_{EB}.d) and a 0.06 d EBRT. The volumetric carboxydotrophic activity rate was 24-26mmol CO/L_{RXR}.d (56-61mmolCO/L_{PB}.d or 100-108mmolCO/L_{EB}.d) and almost all the substrate was transformed in methane (i.e. yield at96% of the stoichiometric maximum). Residual dissolved CO was not detected anymore in the liquid.

The FBR reactor was started up at a CO loading rate of 32mmolCO/L_{RXR}.dwith a relatively low CO content in the mix gas feeding (51-68 %). The CO removal increased from 49 to 68% with a CH_4 yield up to 99% of the stoichiometric maximum. This translated into a productivity of 0.5-0.7 mmol CH_4/g VSS.d or 0.2 L_{STP} CH_4/ L_{RXR}.d (data not shown). Subsequent increase of the CO content in the feeding gas (up to 100%) had no effect on the methanogenic activity of biomass (80% CO removal with a CH_4 yield at 96% of the stoichiometric maximum). A slight decrease of methaneyields (84-88 %) were observed when the organic loading ratewas augmented to 36, 43.2 and 57.6 L_{STP}/d (53, 64 and 86 mmolCO/L_{RXR}.d, respectively). Despite the continuous increase of carboxydotrophic specific activity (from 2.4 to 11.8 mmolCO/gVSS.d), the efficacy of the reactor to consume CO decreasedfrom 80% to 48%. The reactor performance waschallenged by the process kinetics and limited by low bacterial growth and mass transfer. The subsequentorganic load increase (72L_{STP} CO/d or 107 mmolCO/L_{RXR}.d) had a deleterious effect on the methanogenic activity of biomass (63 ± 28 % CO removal with a CH_4 yield at 71 ± 20%, and probably changed the metabolic pathways. Under those conditions, dissolved CO was detected in the liquid. Upon re-establishing former conditions (load at 1.3 mol CO/d or 1 L_{STP} CO/ L_{RXR}.d), the reactor did recover completely its former CO conversion capacity (89%) but the methane yield remained low (79%), regardless of the methanogenic specific activity increase from 0.8 to 1.8 mmolCH_4/gVSS.d. Finally, optimal results were obtained at an OLR of 43 mmolCO/L_{RXR}.d. The CO removal efficiency of the reactor stabilized at 89%, and the CH4 yield was at 70% of the stoichiometric maximum. The specific caboxydotrophic activity of thereactor biomass was at9.3mmol CO/gVSS.d. These results were better, or at least comparable, to the results obtained with the TBR, when CO was the only substrate. It is also important to notice that the biofilm consumed alwaysall the substrate available dissolved in the liquid, except during the phase where the OLR was at 107 mmol CO/L_{RXR}.d.

The biomass present in the reactors has been characterizedat the end of each feeding phase (Table III).

Table III: Specific activity as a function of reactor type and operational conditions (standard deviation value in parentheses, if larger than 10% of the average value)

Substrate	TBR		FBR	
	Sp. activity	CH_4 Yield	Sp. activity	CH_4 Yield
	mmol/ gVSSd	%	mmol/ gVSSd	%
Inoculum				
CO	1.3	76	1.3	79
H_2/CO_2	57.5	59	204	45
Acetate	4.2	118	3.4	126
End CO				
CO	11.4	80	25.2	115
H_2/CO_2	140	83	$182_{(41)}$	119
Acetate	7	51	2.9	73
End syngas				
CO	37.1	58	21.6	52
H_2/CO_2	314	111	65-432	$62_{(28)}$
Acetate	nd	nd	1.9	119
End syngas and H_2 (biofilm)				
CO	32.6	89	na	na
H_2/CO_2	340	95	na	na
Acetate	11.5	136	na	na
End syngas and H_2 (planktonic)				
CO	66.4	65	na	na
H_2/CO_2	519	80	na	na
Acetate	1.8	119	na	na

The TBR reactor VSS profile revealed that 88.21gVSS of biomass were attached on Raschig rings, with an average of 23mgVSS/ring. The microbial populations maintained in their original granular form accounted for 54% and 44gVSS were attached on rings as new biofilm.

As presented in Table III, the relative content of all trophic microbial groups studied augmented, and in some cases, the gain was remarkable. Extrapolating these results to TBR, the reactor maximum carboxydotrophicconversion capacitycould reach 77mmolCO/L_{PB}.d, as validated at an OLR of 50mmolCO/L_{RXR}.dand an EBRT of 0.035 d. The instability of the reactor under specifically those conditionswas probably due to the heterogeneity of the system (i.e. undesired thermal/mass gradients, channeling, and pressure drop). The concentration of the limiting substrate, in both the liquid and gas phases, and the distribution of the reactant and products between the gas and liquid phases may vary as a function of theconversion efficiency and regulate the reaction kinetic. For instance, the pressure drop between the bottom and the top of the reactor was roughly 0.7atm and the CO partial pressure gradient, 0.38atm. Therefore the reactor design is probably accountable for the fact that, in optimum conditions (87% CO removal) the reactor activity represented 72% of itsmaximum capacity.

Likewise, the low methaneyield observed in the acetoclasticactivity microcosms (51%, representing a drop of 57% compared tovalues obtained oninoculum) and the increased methaneyield observed in hydrogenophilicactivity microcosms (83%, representing a risingof 41% compared tovalues obtained oninoculums) suggests an important metabolic shift (i.e. enrichment insyntrophic acetate oxidizing (SAO)and hydrogenotrophic methanogenic microorganisms), which confirm previous hypotheses [4].

On the other hand, in the FBR reactoroperated under CO-feedingconditions, the biomass washout rangedfrom 0.1 to 0.6gVSS/d. After 91 days of operation, the reactor biomass density decreased from 10.1 to 4.1gVSS/ $L_{RXR}$and the ratio of planktonic to granulated biomass increased from 1% to 10%. These results are quite comparable to the results obtained with the TBR, when fed with CO as the only substrate. However, the evaluation of specific activities revealed some discrepancies. For instance, the carboxydotrophicspecific activity was two times higher than in the TBR and might explain the capability of the reactor to work at relative high CO concentration and to consume all the substrate dissolved in the liquid. Meanwhile, the hydrogenophilicspecific activity kept relatively constant on average compared to that of the inoculum but with a high variability. Nevertheless, the most significant change was observed for the acetoclasticpopulations: their specific activity decreased at the end of experiment and, most importantly, the acetate oxidizing and hydrogenotrophic methanogenic populationsdid not seem to be well established in the reactor. This weaknesswill constitute a major challenge for the next stages of the experiment.

3.2 Syngas

At that point the flow-thru experiment was resumed, and the reactors restarted with a synthetic (artificial) syngas (40% CO, 40% H_2 and 20% CO_2).

The TBR was first fedat low inflow rate (0.024 mol CO+H_2/L_{RXR}.d). The CO removal efficiencywas as high as 97±1%, however, the reactor medium suffered an acidification (pH drop), resulting into a lower methane yield, probably caused by the relative high CO partial pressure (i.e. 0.63 atm). This necessitated a downward changeof the loading conditions (20% CO, 10% CO_2 and 20% H_2 concentration in the feeding gas, added with 50% N_2) and an upgrade ofthe buffer formulation. The TBR operation was then resumed at a syngas load of75mmol/L_{RXR}.d and an EBRT of 0.11 d. The presence of H_2 in the gas mix doubled the reducing power of the organic load as comparedto previous phases with CO only, and accordingly, the methane production. At those conditions, 92% of the gaseous organics were degraded (versus 82-87% obtained with CO only), with as a result, a methane productivity of 0.7 L_{STP} CH4/L_{PB}.d and a methane yield of 359mL_{STP} CH4/g COD-equivalent consumed, i.e. 100% of the theoretical yield.Subsequent increases in load (data presented in Table IV) demonstrate that the capacity of the reactor is limited to a load of 126L_{syngas}/d and a CO partial pressure lower than 0.4atm.In spite of the averaged specific activities in the reactor higher than 20 mmolCO/ gVSS.d., residual dissolved CO waspresentin the liquid and the efficiency of the reactor has been reduced by 80%.

By comparison with the results obtained in the TBRpresented above, the FBR tolerateda syngas feeding athigher concentration in CO (40%) without negative effects on the methane yield. The CO feeding conditions were reset to the same ones as in the previous phase. The CO conversion efficiency values obtained were significantly lower whereas the specific activity values for CO consumption increased compared to the results obtained previously under similar conditions. The saturation curve for hydrogenotrophic activity, showing the relation between the substrate concentration and the volumetric reaction rate, reach lineally a maximum of 1L_{STP} H_2/L_{RXR}.

Table IV: Performance of the Fluidized Bed Reactor and Trickle Bed Reactor, as a function of operational conditions when fed with synthetic syngas. Unit of measurement: Q_{CO}: [$L_{STP}CO/d$], C_{CO}: [%], E_{COD} : [%], Y_{CH4} : [$mL_{stp}CH_4/gCOD_{cons.}$], k_{CO} : [mmolCO/gVSS.d], dCO : [μmol/L]

Q_{CO}	Rx	C_{CO}	E_{COD}	Y_{CH4}	k_{CO}	d_{CO}
7.2	TBR	20	97	339	3.8	0.0
	FBR	-	-	-	-	-
14.4	TBR	20	92	359	7.7	0.0
	FBR	40	81	319	13.2	0.0
28.8	TBR	-	-	-	-	-
	FBR	40	69	331	9	0.0
36.0	TBR	20	86	375	17.9	0.0
	FBR	-	-	-	-	-
43.2	TBR	20	84	385	20.9	2.0
	FBR	40	62	315	15.3	0.0
50.4	TBR	20	79	396	22.6	2.0
	FBR	-	-	-	-	-
57.6	TBR	-	-	-	-	-
	FBR	40	43	309	16.4	0.0

On the other hand, in spite of the relatively high partial pressure of CO, the mass transfer was limited in the reactor; reactor design and the low cell density might being the most apparent causes. The absence of significant growth and the biomass washout (0.6gVSS/d) led to the reactor failure due to the low biomass density; at the end of operations, only 10% of the initial quantity of biomass was still present in the reactor. Consequently, the efficiency of the reactor never exceeded 81% and the specific activity of thein-reactor biomass was limited to 16.4 mmolCO gVSS.d.

In order to conclude the tests in the FBR reactor, potential toxicity of CO on biomass activity was documented at the end of experiment. Accordingly, the presence of carbon monoxide in the reactor was reduced by 50% and, ultimately, eluded. The reduction of CO to 50% of initial concentration had no impact on microbial activity. In absence of CO, the hydrogenotrophic methanogenesis specific activity was evaluated at 32.1 mmol H_2/g.VSS.d, almost 3 times more than in the control test, but the methane yield declined by 7%. That observationspecifically reflects the time effect on the hydrogenotrophic populations present in the reactor. It also shows that the reactor fluid hydrodynamics did not allow for favorable microbial growth conditions and that the hydrogenotrophic methanogenic populations outcompeted the homoacetogenic populations.

Encouraging results were obtained when carbon dioxide was completely removed from the feeding gas. Under these experimental conditions, a significant increase in the carboxydotrophic activity and the methanogenic yield led to an overall additional increase in methane production by approximately 20%.

Finally, the biomass present in the reactors has beencharacterizedat the end of the experiments and the results obtained from microcosm tests are presented in Table III.

While in microcosm testswith the TBR biomass, the acetoclastic activity remained undetectable, asignificantproliferationofthe hydrogenotrophic methanogenicpopulations were observed. Under such circumstances, the low methaneyield obtained in the carboxydotrophicactivity tests wasremarkable; the addition of H_2/CO_2 in the system divertedthe methanation process fromthe carbon monoxide.

As for the FBR reactor, the carboxydotrophicactivity kept constant after the syngas phase and presented the same metabolic shift. The methane yield decreased to as low as 52% of the theoretical yield.

It is interesting to note that in the FBR, the average carboxydotrophicspecific activity reached78% of the maximum activitywhile in the TBR it was solely at 61%, probably because of the reactor limitations linked to the plug flow regime. Remarkably, the acetoclastic methanogenic populations remained activein FBR.Simultaneously with the stagnation of carboxydotrophic activity in FBR, the biomass presents a high variability by regards todepletion rate of H_2/CO_2 substrateand corresponding methanogenic yield.

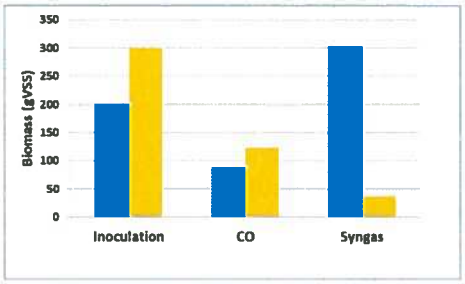

Figure 1: Biomass evolution in TBR (yellow) and FBR (blue) as a function of operational phases.

Important dissimilarities were also observed with respect to the biomass density. If the carboxydotrophic substrate decreased the biomass density in a similar way for both reactor designs the addition of H_2/CO_2had a different effect for each of the reactors (Fig. 1). The packed bed of TBR avoided the biomass loss by shear stress and facilitated the development of an adapted biofilm, particularly when operated with syngas.

3.3 Biogas upgrading to RNG

The biogas upgrading to RNG process has been performed using exogenous hydrogen only in the TBR reactor.

Subsequent increasing of H_2 concentration from 20% to 77% (data no shown) allowed for reachinga humid off-gas containing 89 % CH_4 and 6% H_2while the reactor efficiency at 98%. The optimal H_2/CO ratio is 1/5 (v/v).

As reported previously, in the FBR, the hydrogen is not completely consumed; between 17 and 34% of residual hydrogen persistedin the off-gasof the reactorfedwith syngas. Consequently, the enrichment of syngas using exogenous hydrogen was not applied to FBR reactor. Instead, the FBR reactor was integrated into a two-stage reactor system, with syngas upgrade in an anaerobic reactor followed by biogas polishing in a bioelectrochemical reactor (bioelectrochemical filter, eBF). In this two-step configuration, the resulting biogas containing residual CO and H_2 was fed to a cathode compartment of theeBF. Preliminary results are encouraging. In addition to CO_2 conversion to CH4, the eBF provided at least partial

conversion of CO to CH_4. At an influent CO concentration of 10-15%, almost half of CO was microbiologically converted to CH_4. Overall, the eBF achieved a near complete CO_2 removal/transformation and an at least partial transformation of CO. As a result, in the two-stage syngas treatment system the off-gas only contained methane (up to 81%) and hydrogen gases.

4 CONCLUSION

The present results confirmsthat mixed populations from anaerobic digestersare effectively acclimated to CO/syngas allowing for a significant carboxydotrophic (CO-consuming) methanogenic activity and opens interesting perspectives at large scale.

The ideal reactor design is to provide a high mass transfer and a high cell concentration under no substrate limiting and inhibitory conditions. In the present study the TBR reactor seems to allow a better mass transfer butthe plug flow regime limits reaction kinetics, due tovariability of the reactants and products distribution between the gas and liquid phases. In the TBR, biomass experience simultaneously, in different parts of the reactor, substrate limitation and inhibitory conditions.

An optimal reactor design must also avoidbiomass loss by shear stress and facilitate the development of an adapted biofilm, as materialized in TBR.For this particular reactor design, the methanogenic yield reaches the maximum stoichiometric valuefor substrate partial pressures lower than 0.4atm. Moreover, the TBR efficiency, when operated in optimal conditionsand fed with CO only, couldreach 87% conversion efficiency, comparatively to82% in the FBR and a bubble column reactor (BCR), and 75% in a gas lift reactor (GLR). The TBR efficiency fed with synthetic syngas variedbetween 92 and 97 % and the actual methanogenic yield was nearthe maximum stoichiometric value. It was confirmed that the acetate oxidation route was the main metabolic pathway that madepossible these methane-producing activities from CO.

The FBR design had similarconversion efficiency to the TBR with a comparable biomass density, when loaded with CO. Effective adaptation of anaerobic sludge to CO was confirmed. Overall, the syngas conversion performance of the FBR design was limited by a low cell density, especially for reactor designs requiring high velocity conditions and having an effect on shear-sensitive microorganisms. This limitation was found to be the most restrictive factor for higher CO loading rates, affecting the stability of the reactor and the methanogenic yield.

Overall this experimental study demonstrated the feasibility of syngas fermentationand bio-upgrading into RNG and quantified key parameters which characterize the process, such as product yields, biomass growth and decay rates, biomass accumulation capacity, and bioconversion specific rates. Such data are instrumental for process optimization and upscale assessment.

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