Integrating anaerobic digestion and gasification to biomethane

Guiot, Serge; Cimpoia, Ruxandra; Dubé, Charles-David

Integrating anaerobic digestion and gasification to biomethane.

Serge R. Guiot[1], Ruxandra Cimpoia[1] and Charles-David Dubé[1]

[1] Energy, Mining & Environment, National Research Council of Canada (NRC), Montreal, H4P 2R2 CANADA

1. Introduction

Anaerobic digestion (AD) is an effective way of recycling waste and biomass. However, AD still hardly competes with landfilling or composting. One of the reasons put forward is that the revenue generated from the biogas utilization does not compensate the cost for AD infrastructure and operation. Hence AD needs incentives such as governments grant premiums for green power initiatives, long-term feed-in tariff (FIT) mechanisms, CO_2 credits to trade in on carbon markets, banning organics from landfill.

The natural gas (NG) market might also become a strong driver, even though the NG prices are low in North America, due to the surge in supply of NG from shale gas. Lower NG costs translate to more NG vehicles and a bigger market for renewable natural gas (RNG), as there is a demand for adding RNG or biomethane in the NG grids, which is growing. For instance, Canada's natural gas utilities have set a target of 5% RNG-blended natural gas in the pipeline distribution system by 2025 and 10% by 2030 [1]. Nationally, the increased RNG content would result in 14 Mt of greenhouse gas (GHG) emission reductions per year by 2030. This growing demand is expected to prompt a higher price for RNG, up to three times as compared to the actual market price of NG.

The theoretical methane yield of biomass, based on average elemental composition and stoichiometry of the net reaction, is 0.48 Nm^3 CH_4/kg volatile solids (VS) [2]. However, for most of wastes, current CH_4 yield hardly exceeds 0.3 Nm^3/kg VS added, or an anaerobic degradation efficiency of 60% [3], because they contain compounds which are hardly or not biodegradable (e.g. lignin, peptidoglycan, cell membrane proteins), or the solubilization of which might be limited by an hydrolytic deficiency of the actual populations (lignocellulose, cellulose, hemicellulose, proteins). If AD would be processed with a conversion efficiency of over 80%, the revenue would increase accordingly (but as well the capital and operation costs, due to the addition of a pre-treatment stage).

2. Biomethanation of syngas

When the organic residue is relatively dry (e.g. woodchips) or non-biodegradable (bark, plastics, rubber), AD is ruled out to the advantage of thermo-chemical conversion techniques such as gasification, which transforms biomass at high temperature (500-1500°C) and pressure (1-80 atm) with limited amounts of water and oxygen into a synthesis gas (or syngas) mainly composed of carbon monoxide (CO), CO_2 and hydrogen. Syngas is also of interest with respect to the RNG market. The chemically catalyzed methanation of syngas usually involves high pressure and temperature, and the catalyst can be poisoned by impurities and tends to have low product specificity [4]. To circumvent these disadvantages, anaerobic consortia could be harnessed to

biochemically convert the syngas compounds into biogas, at ambient temperature and pressure.

We previously showed that AD sludge had a non-negligible carboxydotrophic (i.e. CO-consuming) methanogenic potential, without a particular adaptation was required [5]. With such a mixed anaerobic consortium, other indirect reactions also occur, for instance: CO-hydrogenogenesis followed by the methanogenic reduction of CO_2 or CO; homoacetogenesis followed by acetoclastic methanogenesis [6].

Regardless of the specific reaction, the methane yield is 0.25 mol CH_4 per mol CO, plus 0.25 mol of CH_4 per mol of H_2. Based on the range of CO and H_2 typically contained in syngas, this is equivalent to about 0.2 to 0.4 Nm^3 CH_4/kg dry solid gasified, depending on the syngas composition (i.e. CO between 30 and 60 % (vol./vol.), H_2 between 60 and 25%, and CO_2 between 35 and 3%), and when the syngas is efficiently introduced and dissolved in the anaerobic mixed liquor.

We also showed that industrial anaerobic sludge presented some tolerance to impurities commonly found in the syngas (HCN; NH_3; H_2S; aromatic hydrocarbons), based on the culture bioactivity response to the compounds dosage in comparison with the control (i.e. CO alone). There was no significant impact at low concentrations (≤ 500 ppm for NH_3, ≤ 1 ppm for aromatic hydrocarbons and ≤ 50 ppm for H_2S and ≤ 15 ppm for HCN). Nevertheless it is likely that syngas will have to be at least partially cleaned before to be bioprocessed.

3. Advanced reactors for bioprocessing the syngas

Various types of reactor systems have been investigated for their CO conversion and gas-liquid mass transfer performances: a completely stirred tank reactor (CSTR), a closed-loop gas-lift reactor (GLR), a bubble column reactor (BCR), and a trickling-bed reactor (TBR). In biotic conditions (mixed culture), the GLR and BCR systems showed a volumetric gas-to-liquid mass transfer rate (k_La) ranging between 1 and 6 h^{-1}, while the TBR's k_La had a median value of 10 h^{-1} under optimal conditions, and the CSTR, around 20 h^{-1}.

The BCR reactor, inoculated with anaerobic granular sludge, was operated over a 189 days period with a CO flow rate > 7L/d and a gas recirculation rate > 1200L/d. Maximum volumetric activity (62±4 mmol CO per liter of reactor (RXR) and per day, corresponding to 10 mmol CO/g volatile suspended solid (VSS)·d) was achieved at gas loads (100% CO, 1.62 atm) of 22±0.8 L/d (101 mmol CO/L_{RXR}·d, 13.4 mmol CO/g VSS·d), with a 85% efficiency of CO transformation for a gas retention of 1 day, and an average methane yield of 26±2 % (mol CH_4/mol CO). For similar mass transfer conditions and methane yields, the CO-consuming volumetric activity of BCR was twice that of GLR (also inoculated with anaerobic granules, and with comparable specific activities in the range of 9-10 mmol CO/g VSS·d). At similar volumetric load (15-20 mmol CO/L_{RXR}.d), the CSTR was more limited, despite higher specific activity of the culture (65 mmol CO/g VSS.d), presumably because of lower tolerance to CO of the culture in fine suspension in CSTR, as opposed to granular biofilms in BCR.

The TBR (V_{RXR} = 30 L) was packed with a random carrier material [12x12 mm borosilicate Raschig rings] to which microbial biomass attached (biofilm). The 13 L packing bed volume (V_{PB}) had a void volume (V_{EB}) of 7.5 L. The TBR has been inoculated with industrial anaerobic sludge (15 g VSS/L_{PB}). During the first phase (358 days), the TBR, fed at the bottom with CO only, added with various levels of N_2, was operated at 35°C and

neutral pH, while continuously supplied with a mineral and nutrient buffered solution (hydraulic retention time, 31 days), constantly recycled downward over the packed bed at countercurrent of the gas phase. At a load of 0.7 L_{STP} CO/L_{RXR}.d, (i.e. 30 mmol CO/L_{RXR}.d, i.e. 68 mmol/L_{PB}.d, or 117 mmol CO/L_{EB}.d), and a gas retention time through the void volume (EBRT) of 0.06 d, the reactor remained stable with a CO removal efficiency of 82-87%. The volumetric CO-consuming activity was at 24-26 mmol/L_{RXR}.d (56-61 mmolCO/L_{PB}.d or 100-108 mmol CO/L_{EB}.d) and almost all the substrate was transformed into methane (96% of the stoichiometric yield). No residual dissolved CO was detected in the liquid. At the end of this phase, the CO-consuming activity of the acclimated biofilm was 9 times higher than that of the inoculum; and the hydrogenotrophic activity, 2.5 times higher. This is presumably explained by an important metabolic shift, due to an augmentation of the populations of acetate-oxidizing syntrophs and hydrogenotrophic methanogens.

Afterwards, the TBR was fed a synthetic syngas (20% CO, 20% H_2, 10% CO_2 and 50% N_2). At a CO + H_2 load of 44-64 mmol/L_{RXR}.d and an EBRT of 0.11 d, 92% of the gaseous organics (CO + H_2) were degraded (versus 82-87% obtained with CO only), with as a result, a methane productivity of 0.7 L_{STP} CH_4/L_{PB}.d and a methane yield of 31 % (vol. CH_4/vol CO + H_2) (i.e. 380-410 mL_{STP} CH_4/g COD-equivalent consumed, i.e. 100% of the theoretical yield). The presence of H_2 in the gas mix doubled the reducing power of the organic load as compared to previous phase with CO only, and accordingly, the methane production.

From this comparison exercise the TBR may be considered as a reference system. The carboxydotrophic specific activity and volumetric mass transfer coefficient of TBR were higher than with other reactors. Effective acclimation of anaerobic sludge to CO/syngas allowed higher carboxydotrophic methanogenic activity and opens interesting perspectives at large scale.

4. Biogas upgrading

To be compatible with natural gas, biogas needs to be properly upgraded, namely the CO_2 content to be reduced at 2.5%. Methods for biogas or syngas upgrading are mainly based on the removal of CO_2 accompanied with a little CH_4 loss (e.g. adsorption, absorption and membrane separation techniques). Alternatively, biological processes can be used to upgrade the biogas by converting CO_2 into additional CH_4, either *in situ* or *ex situ*: injection of exogenous H_2 into the AD system, bioprocessing of the biogas into an external hydrogenotrophic methanogenic reactor or a microbial electrolysis cell (MEC) reactor, integration of bio-electrochemical functionalities within the AD system [7-9].

Hydrogen to be injected in a bioreactor to upgrade biogas, can be produced in an external commercial electrolyzer, using for instance electricity during the off-peak hours. To upgrade the biogas produced from syngas by the TBR in this study, the additional hydrogen was co-injected to the TBR directly with the syngas. When the volume of H_2 added reached a ratio of 5 volumes per volume of CO, we were able to achieve a near 100% removal of CO_2 with little residual H_2 (6%) in the off-gas. The percentage of methane was 90%, the balance being made of H_2, CO, N_2 and water vapour.

5. Conclusions

The organic fraction of municipal solid waste (OMSW) that could be digested represents 30% at the most. If AD could be complemented by gasification of the non-digestible fraction of OMSW and

biomethanation of the syngas produced, at a conservative yield of 0.3 Nm^3 CH_4/kg solid gasified, the overall CH_4 production would be several times the production by AD alone (Figure 1).

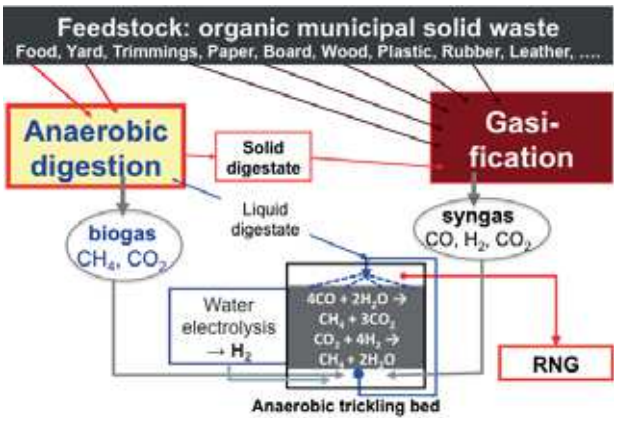

Figure 1. Waste-to-RNG platform. The integration of AD and gasification allows for a simplified processing chain, still able to cover a wide range of organic waste, with a minimum of residue.

More importantly, pairing AD and gasification within an integrated processing facility, with RNG as the only and ultimate target, would result in additional gains in capital and operational cost. For instance, by keeping AD for only the easy fraction of OMSW, a pre-treatment unit could be avoided, since gasification could handle the dry and poorly biodegradable materials that otherwise would have required intensive hydrolysis before AD. The solid digestate, when it cannot be traded as a soil amendment, could also be processed in the gasifier, and its residual energy, extracted and converted into additional methane, instead of being disposed off, at a cost. Furthermore, the use of an AD system for upgrading the synthesis gas into CH_4 would favorably make it possible not to use catalytic reforming.

6. References

[1] Canadian Gas Association. Renewable natural gas technology roadmap for Canada. http://www.cga.ca/wp-content/uploads/2015/04/The-Renewable-Natural-Gas-Technology-Roadmap.pdf [Online] (2014).

[2] Braun, R. Anaerobic digestion : a multi-facetted process for energy, environmental management and rural development, p. 335-416. *In* R. Paolo (ed.), Improvement of crop plants for industrial uses. Springer, Dordrecht, Netherland (2007).

[3] Moletta, R. La méthanisation. Lavoisier, Editions Tec & Doc, Paris (2008).

[4] Gallei, E. and Schwab, E. Development of technical catalysts. Catalysis Today 51:535-546 (1999).

[5] Guiot, S.R. et al. Potential of wastewater-treating anaerobic granules for biomethanation of synthesis gas. Environ. Sci. Technol. 45:2006–2012 (2011).

[6] Sancho Navarro, S. et al. Biomethanation of syngas using anaerobic sludge: Shift in the catabolic routes with the CO partial pressure increase. Front. Microbiol. 7:1-13 (2016).

[7] Tartakovsky, B. et al. Electrolysis-enhanced anaerobic digestion of wastewater. Biores. Technol. 102:5685-5691 (2011).

[8] Luo, G. and Angelidaki, I. Hollow fiber membrane based H_2 diffusion for efficient in situ biogas upgrading in an anaerobic reactor. Appl. Microbiol. Biotechnol. 97:3739–3744 (2013).

[9] Bo, T. et al. A new upgraded biogas production process: Coupling microbial electrolysis cell and anaerobic digestion in single-chamber, barrel-shape stainless steel reactor. Electrochem. Comm. 45:67-70 (2014).