Syngas co-digestion with manure: kinetic modelling in a novel framework

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Expanding biomethane production represents a high priority of the energy transition in the perspective of net zero emissions by 2050 (International Energy Agency, 2021). In this view, the development of cost-effective processes capable to valorise recalcitrant waste streams to biomethane has the potential to expand the array of feedstocks exploitable in biomethane production and overcome some of the operational challenges related to the anaerobic digestion of hardly degradable biomass (Andreides *et al*, 2022). A promising processing line for lignocellulosic biomass consists of its thermochemical conversion to syngas (a gaseous mixture mainly composed of CO, CO_2, and H_2) coupled with downstream syngas methanation (Andreides *et al*, 2022; Grimalt-Alemany *et al*, 2018). Syngas methanation catalysed by mixed microbial consortia offers several advantages compared to thermochemical catalytic methanation, i.e., mild operating conditions, high resilience towards gas impurities, and the possibility of direct integration with anaerobic digestion of liquid organic substrates within a single reactor unit (Grimalt-Alemany *et al*, 2018; Yang *et al*, 2020). Syngas co-digestion with waste organic streams has been investigated in a variety of setups, demonstrating that mixed cultures are capable to digest the organic liquid feed and syngas at relatively high conversion efficiencies and organic load degradation rates, however at high gas retention time and achieving relatively low methane productivity (Andreides *et al*, 2022; Postacchini *et al*, 2023; Yang *et al*, 2020). The optimization of syngas co-digestion with organic waste streams thus remains an open research topic oriented towards the achievement of high technology maturity levels. Mathematical modelling could provide useful insights into the kinetics and inhibition mechanisms of the biochemical reactions involved in the process. Furthermore, the biogas output flow and composition could be systematically optimized as a function of a given set of operational parameters and variables, i.e., bioreactor configuration, liquid and gas retention time, syngas, substrate, and medium composition. Angelidaki *et al* (1999, 1993) developed the modelling framework for anaerobic digestion *Biomodel* accounting lipids, carbohydrates, and protein as substrates while hydrolysis, acidogenesis, acetogenesis, and methanogenesis were regarded as the biological processes contributing to anaerobic digestion. Ammonia concentration, pH, and volatile fatty acids (VFAs) concentration were in turn regarded as the main inhibitory and modulating factors. Recently, *Biomodel* has been expanded to include hydrogenotrophic methanogenesis and model in-situ biogas upgrading through hydrogen injection in a CSTR treating cattle manure (Lovato *et al*, 2017). On the other hand, Sun *et al* (2021) modelled syngas methanation co-digesting glucose in a bubble column reactor by modifying an analogous modelling framework (ADM1) to *Biomodel* including equations accounting for CO and H_2 metabolism as well as acidogenesis and acetogenesis inhibition terms related to the presence of syngas. This study aims in turn to model syngas co-digestion with a more complex substrate and unveil the kinetic behaviour of the underlying reaction system including inhibition mechanisms with the perspective of systematic process optimization. The specific objectives of this study include: (1) the creation of a novel and generalized framework of *Biomodel* to allow the flexible addition or removal of species mass balance equations as well as process parameters; (2) experimental determination of sensitive parameters, i.e., gas-liquid mass transfer parameters in the given reactor setup; (3) calibration and validation of the newly developed modelling framework on a continuously operated stirred tank reactor (CSTR) with co-feeding of syngas and cattle manure.

The new version of *Biomodel* was developed in Python. The model parameters were stored in an Excel database. The Python code includes commands to iterate over the parameters database and functions to define an ordinary differential equations (ODE) system as an object. The ODE system is then solved with the ODE solver implemented in the library SciPy. Besides, for the determination of calibration parameters, syngas co-digestion with manure was carried out in a 7.5 L (working volume) CSTR. The reactor was inoculated with degassed digestate originating from a manure-fed biogas plant operating at mesophilic conditions. Initially, the reactor was fed with cattle manure (with a content of volatile solids of 3 v%) as the sole substrate with hydraulic retention time of 15 days until the biogas production was stabilized. Then, syngas (45 % H_2, 30 % CO, 25 % CO_2) was fed alongside manure with an inflow rate from 1 up to 2 $mL \cdot L^{-1} \cdot min^{-1}$ syngas for the initial period (60 days) of co-feeding operation. For the whole operation period, the reactor temperature was kept at 37 °C to maintain mesophilic conditions. The gas was injected into the reactor through mass flow controllers connected to a gas sparger placed below the stirrer. The model input parameters other than input mass flows were determined with state-of-the-art protocols and consisted of the manure and inoculum content of soluble and insoluble lipids, proteins, and

carbohydrates as well as total nitrogen, VFAs, and total ammonium nitrogen. Gas samples were taken on a daily basis whereas the gas composition was determined by means of gas chromatography analysis and the gas flow was measured by displacement gas metering. VFAs concentrations were determined by means of GC-FID on daily collected samples. Kinetic parameters for stand-alone manure digestion were taken from Lovato *et al* (2017) whereas the kinetic growth parameters for hydrogenotrophic acetogenesis and methanogenesis from CO and H_2 as well as their related inhibition parameters were taken from Sun *et al* (2021). Gas-liquid transfer rates for CO and H_2, as they are regarded as the primary limiting factors and influential process parameters were determined experimentally on the given reactor setup as a function of stirring speed and gas flow rate.

The created framework of *Biomodel* allowed to flexibly add state variables, growth, and inhibition parameters in a user-friendly way directly in the Excel database and without the need to modify the code. Biomethane production during the initial stage of operation (manure feeding only) was well predicted (R^2=99%) by the model using literature kinetic parameters. The addition of syngas feed was followed by a peak of the VFA concentration, which was in turn followed by increased methane productivity, whereas the additional produced moles of methane were close to the maximum stoichiometric amount from the converted H_2 and CO moles (about 90% at the applied gas retention time). This transition was acceptably well simulated (R^2 between experimental and simulated was about 85% for all target variables, i.e., VFA concentrations, CO, H_2, CH_4, CO_2 output flows) by the developed version of *Biomodel*. After calibrating the CO inhibition parameters, the simulation accuracy was considerably improved (R^2>95%). These results imply that (1) syngas co-digestion with manure is a process concept that should be considered for scaled-up application studies; (2) the developed modelling framework is reliable on the operational configuration tested and flexible for application on a wide array of operating conditions. Ongoing work focuses on testing the process performance, stability as well as model prediction accuracy on a broad value range for the model independent variables (i.e., syngas composition, gas retention time, organic load, liquid substrate composition). In this scenario, random sampling and parameter sensitivity analysis techniques should be also applied for more accurate parameter calibration.

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