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Abstract:
Anaerobic digestion (AD) has become a well-established process for organic waste valorization. However, methane is a low value product that could be advantageously replaced by intermediary waste degradation products such as Volatile Fatty Acids (VFA) and alcohols. Although, potentially representing a higher value, these compounds are produced as mixtures in contact with the waste feedstock, which constitutes a major bottleneck for their recovery and further downstream processing. Recently, microbial electrochemical technologies have been identified to separate waste oxidation in an anodic compartment from the synthesis of organic molecules in a cathodic compartment. With a mass balance modeling approach, this work investigates the integration of a waste-fed microbial electrosynthesis cell within an AD facility, providing a first insight into a combined profitable environmental biorefinery.

Keywords: microbial electrosynthesis, environmental biorefinery, modeling

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Introduction

The increasing scarcity of resources and concerns about global warming are pushing our societies towards a more circular economy. Environmental biorefinery technologies offer possibilities for sustainable waste remediation by combining waste treatment with production of added value molecules (Venkata Mohan et al., 2016). Currently, anaerobic digestion (AD) is a widely used technology for organic waste valorization. However, the cost-effectiveness of this process is questionable because of the low value of its product, the biogas (Moscoviz et al., 2018). An increasing number of researches are focused on new technologies able to exploit bio-resources in a more profitable way by producing high-valued chemicals such as multi-carbon organic molecules rather than methane. With the discovery of microbial electrosynthesis (MES) (Nevin et al., 2010), a plethora of applications of environmental biorefinery emerged with the possibility of producing different organic molecules on the biocathode (Gildemyn et al., 2015). In particular, coupling a waste-oxidizing bioanode to the biocathode is an efficient way to reduce the energy consumption of MES (Desmond-Le Quéméner et al., in revision). Interestingly, AD could be combined to a waste-fed MES as a complementary process. In the combined system, biogas produced can be purified by the biocathode to remove CO_2; part of heat and electricity produced by the cogeneration could sustain the waste-fed MES to produce organic molecules. This study aims to provide a performance estimation of the integration of a waste-fed MES within a classic AD facility.

Material and Methods

The proposed biorefinery is sized for treating about 9000 t_{COD}/y of food waste. It is mainly composed of (see Figure 1):

- A batch hygienic reactor (70 °C; Hydraulic retention time (HRT) = 1 h);
- A thermophilic biological hydrolysis reactor (55 °C; HRT = 2 d; Organic loading rate (OLR) = 90 $kg_{COD}.m^{-3}.d^{-1}$);
- A mesophilic digester (37 °C; HRT = 33 d; OLR = 5 $kg_{COD}.m^{-3}.d^{-1}$) having a methane yield of 225 $Nm^3.g_{COD}^{-1}$;
- A microbial electrolysis cell (MEC) (37 °C, I = 10 $A.m^{-2}_{anode}$) composed of an anodic chamber (Electrode density of 40 $m^2.m^{-3}$; HRT = 15.3 d; OLR = 4.8 $kg_{COD}.m^{-3}.d^{-1}$; coulombic efficiency: 60%) and a cathodic chamber (Electrode density: 60 $m^2.m^{-3}$; HRT = 30 d; coulombic efficiency: 90%). The voltage of the cell (0.97 V) was modeled according to Desmond-Le Quéméner et al. (in revision).
- Two centrifuges for post-hydrolysis and post-digestion separation producing 20 %$_{DM}$ pellets. The flow of the post-hydrolysis centrifuge can be adjusted. The supernatants and pellets are fed to the anodic chamber and the digester, respectively;
- A cogeneration unit for heat (η_{heat} = 44%) and electricity (η_{elec} = 34%) from methane.

This first model considers total solids, chemical oxygen demand (COD) and CO_2 mass balances, reactors heating, thermal losses in the reactors, mixing energy, energy consumption from the centrifuges and the MEC. Labor costs are not included. All chemical prices have been retrieved from Moscoviz et al. (2018) while electricity prices for consumption and production were set at 0.08 and 0.125 €/kWh (industrial purchase price and French feed-in tariff, respectively). The polymer added during centrifugation has a price of 1.36 €.$kg_{polymer}^{-1}$.

Results and Conclusions

Anodic biofilms in MECs are efficient for converting soluble COD (*e.g.* carboxylic acids) into electricity. As such, food waste is first hydrolyzed and part of its soluble fraction is injected in the MEC after centrifugation. The part of hydrolysate injected in the centrifuge (α) can vary from 0 to 100%, resulting in a final COD recovery in the cathodic product from 0 to 14 %$_{totalCOD}$ (*i.e.* based on the COD fed in the biorefinery). At the same time both the consumption of thermal and electrical energy increases in the biorefinery (see Figure 2A-B). The increase of thermal energy consumption from 15.2 to 18.7 $MWh.d^{-1}$ is due to the heating of larger MEC as well as thermal losses during centrifugation. Electrical energy consumption increases more drastically from 4.7 to 18.3 $MWh.d^{-1}$ mainly due to the MEC itself but also because of the intensified use of the centrifuge. Meanwhile, less methane is produced in the digester as COD is diverted to the MEC (5695 and 4823 $Nm^3_{CH4}.d^{-1}$ for α = 0 and 100%, respectively), resulting in a total energy production reduction (from 24.2 to 20.5 $MWh_{thermal}.d^{-1}$ and from 18.4 to 15.6 $MWh_{electrical}.d^{-1}$ when α increases from 0 to 100%). Therefore, the biorefinery is always thermally self-sufficient while electricity must be purchased when α > 83 %.

The performance of the biorefinery depends directly on the price, COD and carbon content of the cathodic product. For instance, the potential incomes and CO_2 sequestration resulting from H_2 (market price: 200 €/t_{COD}, 0 kg_C/t_{COD}), ethanol (350 €/t_{COD}, 250 kg_C/t_{COD}), acetic acid (500 €/t_{COD}, 375 kg_C/t_{COD}) and formic acid (1800 €/t_{COD}, 750 kg_C/t_{COD}) are represented in Figure 2C-D. When α = 0 (*i.e.* no MEC), the biorefinery income of 611 k€.y^{-1} comes entirely from the sale of electricity. As α increases, the profitability drops for H_2,

ethanol and acetic acid while it goes up for formic acid. This trend is explained by the loss of revenue related to i) an increased electricity consumption; ii) a decreased methane production; and iii) larger amounts of polymer used for centrifugation which are not compensated by the income gained from selling the chemicals. In our cases, scenario including financial speculation on electricity prices (selling all electricity produced using feed-in tariff and buying electricity at market price to power MEC) have been intentionally excluded from the analysis. In this context, electricity price becomes a crucial parameter. Figure 2E reports the link between electricity prices and the additional operating costs related to the aforementioned expenditure items. For instance, as the average market price of acetic acid is 500 €/t_{COD}, the electricity price must be less than 0.095 €/kWh to increase the biorefinery profitability. Thus, with an electricity feed-in tariff of 0.125 €/KWh, molecules valued more than 650 €/t_{COD} must be produced (*e.g.* propionic acid, formic acid).

The present modeling approach provides first insights into the feasibility of an AD-MES biorefinery. Although it is based on simplifying assumptions, the model highlights first limitations related to the competition between electricity feed-in tariffs and non-subsidized chemicals. It also confirms the potential synergy between AD and MES as the biorefinery can be energy and carbon sufficient. Future model improvement and analysis capital expenditures of associated biorefinery scenario will help refining the profitability limits and choosing a consistent cathodic product.

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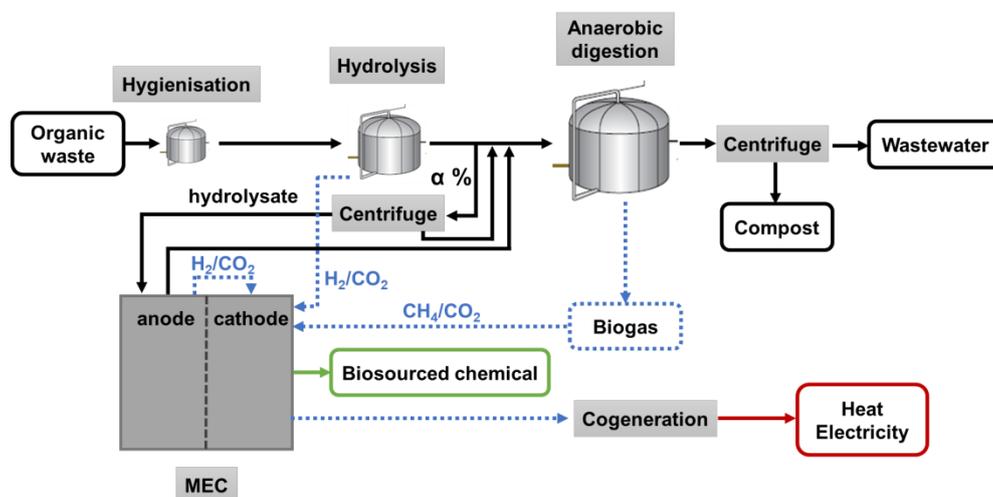
Figure 1. Waste biorefinery – Interaction between anaerobic digestion and microbial electrosynthesis
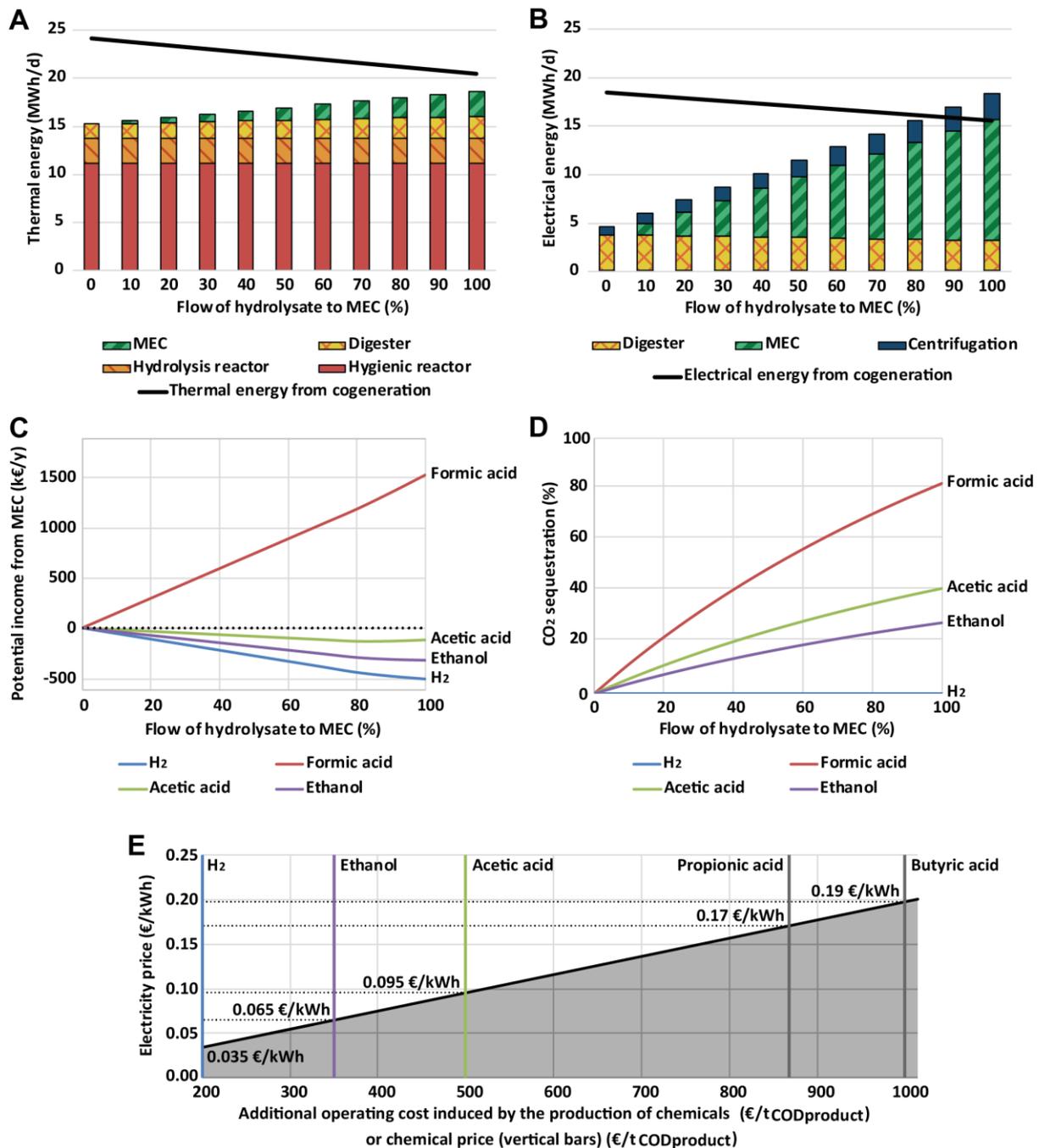
Figure 2. Global thermal (A) and electrical (B) energy balance of the biorefinery. (C) Potential annual income from MEC as function of the cathodic product. (D) CO_2 sequestration in the cathodic product normalized on the global usable CO_2 available in the biorefinery (*i.e.* without considering exhaust gases from cogeneration). (E) Additional operating costs induced by the production of chemicals as function of electricity prices.

The hygienic and hydrolysis reactors are omitted from (B) as they have a negligible electrical energy consumption. Labor and depreciation costs and are not considered in (C). The "Flow of hydrolysate to MEC" in (A-D) is equivalent to α in the text. Vertical bars in (E) represent the current average price for the corresponding chemical and the profitability area is greyed.