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Conceptual Design of Digital Twin for Bio-Methanol Production from Microalgae

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In the last decades, microalgae have gained a lot of interest in the energy and chemical industry thanks to their higher biofuel productivity potential rather than other land plants. To better exploit their green nature and renewable power, anaerobic digestion (AD) fits perfectly for the scope. AD is a metabolic process that generates a methane-rich gas, the biogas, which can then be used for clean electricity and chemicals production. High interest has arisen in the field of AD in industrial practice, and a lot of experiments were done to produce biogas from different types of feedstocks. In this manner, microalgae represent a promising opportunity to produce biogas from renewable and self-sustainable organisms. Biogas is mostly used to produce electrical energy and heat through cogeneration cycles or is upgraded to biomethane through the removal of CO2 and impurities, reaching a CH4 purity above 95-97% vol. On the other hand, an interesting perspective of biogas exploitation is its conversion in biofuels such as methanol or dimethyl-ether. This new concept of bio-refining lays the ground for two aspects: The economical valorisation of the biomass with a more valuable product as bio-methanol and the conversion of biogas to biofuel to fix part of the carbon in a chemical molecule, avoiding the re-emission in the atmosphere of CO2. The scope of this work is to present and technically analyse a conceptual design of a circular bio-refinery based on microalgae biomass feedstock with the final output of methanol production. Biogas production from microalgae is modelled with PythonTM (v3.9) while process simulations are computed using state of the art industrial simulation packages like Aspen HYSIS® v11. Interesting factors to analyse are carbon emission, the field of use for functional production, the global process yield and preliminary feasibility analysis.

* 1. Introduction

Because of the continued impoverishment of fossil resources for combustibles production, a huge effort is put to find renewables and affordable alternatives for the next future. Microalgae, thanks to their high productivity and biofuel yield (Wang et al., 2013), have gained a lot of attention. They are photosynthetic prokaryotic or eukaryotic microorganisms capable of growing rapidly and living in harsh conditions thanks to their simple single-cell or multicellular structure and can be found in both marine and freshwater environments. To optimally exploit these characteristics anaerobic digestion (AD) as the first step for biofuel production represents a good alternative (Sialve et al., 2009), since the direct extrapolation of methane from microalgae allows the use of standard and more efficient processes for fuel production and, together with the incentives earnable from the exploitation of green energy production processes as AD, it drastically reducing the total cost of the plant. A prospective way to valorise the biomasses as biogas feedstock is the chemical conversion in high-added valuable chemicals as bio-methanol. Methanol is the raw chemical to produce formaldehyde, methyl-tert-butyl ether (MTBE), acetic acid and dimethyl-ether (DME) (Olah, 2005). Furthermore, in the last years, this molecule is increasingly considered as H2 storage: CH3OH-H2O mixtures can be converted back to H2 with a reforming process (Andersson et al., 2020). Methanol fuel is potentially important but today is negligible, about 2% (Althaus et al., 2007).According to Zhen et al., the use of methanol as fuels with an adaptive engine with a compression ratio of 10:1; CO, CO2, and NOx emissions were reduced by about 37%, 30%, and 22% respectively compared to standard fuel (Zhen and Wang, 2015). Plants that produce methanol from microalgae do not exist today. However, because this technology is always evolving, the goal of this work is to give a conceptual examination of this process that demonstrates its potential and trustworthiness on an industrial scale.

* 1. Materials and methods
		1. Biogas production model

The anaerobic digestion of microalgae involves their degradation by microorganisms in the absence of molecular oxygen to give a wide range of products, by-products, and reaction intermediates. The process is divided into four reactive stages (Hydrolysis, Acidogenesis, Acetogenesis and Methanogenesis) through which the raw material undergoes breakdown producing liquid intermediates (e.g., ammonia, potassium and phosphorous) and the biogas.

From a global point of view, biogas is mainly composed of methane (45-70%v/v), carbon dioxide (25-45%v/v), hydrogen (<2%v/v) and hydrogen sulphide (<3.5%v/v). The semi-liquid product, known as digestate, is obtained at the end of digestion and, after separation from digestive sludge and various bacterial residues, is ideal for the cultivation of microalgal species, as it is rich in nutrients and micronutrients. The biomethane potential of microalgae is much higher than terrestrial plants, reaching values of 360 mL CH4 g-1 VS (Ayala-Parra et al., 2017), and the total methane yield oscillates between 200 mL CH4 g-1 COD to over 500 mL CH4 g-1 COD (Ward et al., 2014).

To understand the potential and feasibility of the process under study, a first numerical analysis is done to properly simulate microalgae AD. Nowadays, to decrease expenditures for biogas upgrading processes (i.e., H2S removal), in-situ biological treatments are used, exploiting sulfur oxidant bacteria, known as SOB, which reduce the acid gas rising the reactor headspace with a little amount of oxygen. To correctly simulate all the reactive environments in the system, the ADE model is used, which includes both hydrogen sulfide production and breakdown (Moretta et al., 2021). Influent substrate characterization was taken from the work of Mairet et al. (2011), and information about the sulfur content is taken from the work of Bi and He (2013), which have estimated that microalgae contain about 1% (dry basis) of sulfur compounds. So, to treat H2S properly, with the aim to lowering its content as much as possible without inhibition the methane production, about 0.027 kg/m3 of O2 were inserted in the headspace it should be mentioned that pure oxygen is considered for the simulation since the micro aeration procedure which concern this treatment makes it rather affordable from an economical point of view. Influent characteristics are reported in Table 1.

Table 1: Influent values used in the model for the simulation

|  |  |  |  |
| --- | --- | --- | --- |
| Name | Value | UOM | Meaning |
| $$W\_{ch}^{in}$$ | 3.0 | kg/m3 | Influent concentration of carbohydrates |
| $$W\_{xc}^{in}$$ | 27.0 | kg/m3 | Influent concentration of particulate matter |
| $$S\_{SO\_{4}^{2-} }^{in}$$ | 2.7 x 10-3 | kg/m3 | Initial concentration of sulfur in the feedstock |
| $$S\_{O\_{2}}^{in}$$ | 0.027 | kg/m3 | Initial concentration of oxygen injected injected in the reactor. |

From the results obtained (reported in Table 2) it is possible to see that, for a medium-large plant of 7000 m3, the rate of production of methane is quite high, with a total methane flowrate of 26.11 m3/d (Biogas flowrate equal to 37.06 m3/d) reaching a total methane yield of 1840 mL CH4 g-1COD (the dilution rate of the process is equal to 0.06).

Table 2: Gas composition from simulation results

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Species | Methane | Carbon Dioxide | Oxygen | Hydrogen Sulfide | Hydrogen |
| Gas Composition | 70  | 25 | 4 | 1 | ~1.5 |
| UOM | %v/v | %v/v | %v/v | %v/v | ppm |

The methane composition in the gas flow is confirmed in the literature and represent a key factor for the feasibility of the process. On the other hand, the total amount of acid gases (H2S and CO2) in the stream forces the insertion of a guard before entering the next units to avoid structural damages and corrosion problems. The amount of oxygen and hydrogen present in the stream can be considered negligible, being in the order of ppm.

* + 1. Biogas to Bio-methanol

Once biogas production is modelled, there is the implementation of the biorefinery section, from biogas feedstock to the conversion in methanol.

The entire process simulation is computed with Aspen HYSIS® v11 implementing SRK thermodynamic model.

The Soave–Redlich–Kwong (SRK) equation-of-state is implemented to improve phase equilibrium calculations in water–hydrocarbon systems and equation based calculations by using composition independent fugacity (Kontogeorgis and Folas, 2009). Methane reforming (MR) reactor and furnace models are simulated with a Gibbs Reactor avoiding the implementation of complete kinetic schemes and PFR reactors. This simplification is possible because the simulation concerns the steady-state case and in this condition, both reactions are close to the thermodynamic equilibrium (Entesari et al., 2020).

The reactions involved in reforming sections are:

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| --- | --- | --- |
| Steam Reforming | CH4 + H2O ↔ CO + 3H2 | (1) |
| Dry Reforming | CH4 + CO2 ↔ 2CO + 2H2 | (2) |
| WGS | CO + H2O ↔ CO2 + H2 | (3) |

Due to diversity of operating conditions between industrial production and biorefinery, the model for methanol reactor is computed with refitted Graaf kinetics (Graaf et al., 1988) which are more suitable in mild conditions, typical of biogas plants (Bisotti et al., 2021).This kinetic model is added in Aspen HYSYS® v11 plug flow reactor. Side-reaction involved in the formation of higher alcohols and side-products are not investigated. The focus is the study of the chemical behavior of the process and the evaluation of the sensible parameters, the final purification of chemicals is not involved. Methanol synthesis passes through these reactions:

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| --- | --- | --- |
| CO hydrogenation | CO + 2H2 ↔ CH3OH | (4) |
| CO2 hydrogenation | CO2 + 3H2 ↔ CH3OH + H2O | (5) |
| WGS | CO + H2O ↔ CO2 + H2 | (6) |

For the sake of simplicity and clarity, Figure 1 is shown the basic flowsheet of the process instead of Aspen HYSIS® layout.



Figure 1: Conceptual flowsheet of DME synthesis plant

Biogas feedstock rich in H2S requires the abatement in Biogas Filters to avoid corrosion of unit and degradation of catalyst (Nguyen and Zondervan, 2019) and enters in the compressor K1 with outlet pressure of 13 bara. It passes in a feed-effluent heat exchanger (E1) which allows the heating of the reagents with the enthalpy of the hot syngas exiting the reforming unit. Pressurized water (@13 bara) contacts the hot biogas in the mixer before the reactions. The MR chemical conversion happens at 850-950 °C and pressure of 13 bara, the outlet products (humid syngas and traces of unconverted CH4 and CO2) pass through E1 unit to preheat the compressed biogas. Despite heat recovery, hot syngas needs to be further cooled in E2 before entering in dewatering separator V1. This condensing unit recovers water sending back in the recycle loop of the MR reagents, since parts of it are converted through reactions (1) an external integration is mandatory to ensure the optimal C/steam ratio. The gas-phase exiting V1 is anhydrous syngas, it passes in compressor two-stages compressor to reach the desired pressure of 60 bara. After this operation, hot syngas is heated up in E3 to 250 °C before entering the Methanol Reactor, modelled with kinetic equations, where take place the methanol conversion. The Gas Hourly Space Velocity (GHSV) has values between 10,000-20,000 h-1 according to typical space velocity of methanol converter as Lurgi, ICI, Haldor-Topsoe configurations (Matthey et al., 2017) and depending on the recycle ratio implemented in the mixer of the recycling loop. Exiting the isothermal fixed bed reactors, the mix of products (methanol, water, and unconverted syngas) contact the cooler E4 before the raw separation in the separator V2 which allows the separation of light gases from the liquid phase rich in MeOH and H2O. The incondensable are recycled back to the reactor after heating and compression in K3 and E5 units, parts of them depending on the chosen ratio will be purged and sent to the furnace. The heat generated by the furnace from the combustion, partly satisfies the required duty for the reforming reactor, the difference of heat will be provided by the combustion of raw biogas or natural gas. This partial heat recovery, depicted in Figure 1 as a red dashed line, allows lowering the net CO2 emissions making the process self-sustaining since combustion of external utilities will increase the carbon footprint of the plant. Table 3 highlight the main operating conditions and parameters of the process.

Table 3: Operating conditions of biogas to biomethanol process

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Parameters | Biogas Flowrate | Reforming Temperature | Reforming Pressure | Methanol Temperature | Methanol Pressure | GHSVMethanol Reactor |
| Value | 40 | 850 | 13 | 250 | 60 | 16,000 |
| UOM | Nm3/h | ˚C | bara | ˚C | bara | h-1 |

Relating to the economic feasibility of the process, the analysis was approached with Guthrie’s formula (Seider et al., 2018) with the evaluation of fixed cost, operative cost, revenues, and raw materials. The result will be shown in the next section.

* 1. Results and discussions
		1. Technical analysis

Regarding technical analysis, some important parameters are analysed and reported in Table 4 to highlight the performance of the process.

Table 4: Key indicators of the process

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Parameters | Methane Conversion | Stoichiometric Number | Global CO2 Conversion | Methanol Production | Global Massive Yield |
| Value | 95 | 1.85 | 43.41 | 42.88 | 99.5 |
| UOM | % | - | % | kg/h | % |

Due to reactions of steam methane reforming and dry reforming, result of CH4 conversion is about 95%, this led to low value of methane slip which avoid bigger dimension of the methanol converted in design phase. This is a beneficial key point for the recycle loop. Stoichiometric number (SN), represents the quality of produced syngas is defined as:

|  |  |
| --- | --- |
| $$SN=\frac{Mole\_{H\_{2}}-Mole\_{CO\_{2}}}{Mole\_{CO\_{2}}+Mole\_{CO}}$$ | Eq(1) |

For methanol production, SN of value near 2 corresponds to ideal conditions, values lower than 2 indicate H2 deficiency while values larger than 2 mean an excess of it (Ott et al., 2012). In this case, the value is lower than ideal conditions, but this is acceptable considering as feedstock biogas which has lower methane content than conventional natural gas. An optimal key performance indicator of the process is represented by CO2 global conversion which takes in account the inlet and outlet value of carbon dioxide in system boundaries; 43.41% highlights that nearly half of this greenhouse gas (GHG) is chemically converted in the process to high added valuable chemicals as methanol.

Regarding chemical production, the simulation results show 42.88 kg/h of massive methanol production, assessing a global massive yield, computed as ratio of methanol production and biogas utilization, near to the unit.

* + 1. Preliminary economic analysis

A preliminary economic analysis is carried to evaluate the effort of investment to produce bio-methanol via micro-algae biogas. Table 5 shows the main economics as CAPEX, OPEX, evaluated with Guthrie’s formula (Bailie and Whiting, 1998)and expected revenues coinciding with the selling of the dimethyl ether. In the analysis is not included the human resource voice of cost, the CAPEX/OPEX associated with final product purification, and the government incentives. Analyst data for the price of methanol is taken from a specific website (“Methanex,” 2019). Raw materials include the cost of the catalysts, coolants, and natural gas. Revenues are computed with the actual price of methanol based on the relative production.

The performance feasibility indicator used to assess the profitability of the plant is payback time (PBT), it correlates OPEX and CAPEX according with the following equation (Eq.2):

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| --- | --- | --- |
| $$Payback Time=\frac{CAPEX}{REVENUES-OPEX}$$ |  | Eq(2) |

PBT (Payback time) is defined as the time required after the plant start-up to recover the fixed capital investment costs. Short PBTs is reflected in more profitable project.

From the economic assessment of Table 5, the payback time computed is 5.82 years. This value is aligned with other literature sources proving that microalgae-based biogas chemical conversion is generally economically feasible with payback period in the range of 4-8 years (Zhao et al., 2020).

Table 5: Results of preliminary economic analysis

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Parameters | CAPEX | OPEX | Raw Materials | Revenues | PBT |
| Value | 900.000 | 51.320 | 23.27 | 206.052 | 5.82 |
| UOM | kUSD | kUSD/years | kUSD | kUSD/years | Years |

Conclusions

Microalgae can represent a potential raw material to produce methanol. The algae digestion shows a promising CH4/CO2 ratio of 3, which is higher than many sludge-based AD, and the H2S impact in the system is rather low and treatable from a simple dedicated and green guard unit, based. Finally, the methanol production process showed to have a great environmental footprint, and the feasibility of the plant is rather high thanks to both the high revenues from the methanol selling in the market, which makes a lower PBT with respect to other similar plants, and the statal incentives earnable from the green processes involved in the system. In fact, both AD and methanol production process from bio-sources are new and attractive technologies in the energy and chemical market, and have the potential, put together, to heavily influence positively the biorefinery feasibility. The global carbon dioxide emission balance is negative with partial chemical conversion in high added valuable chemicals and has a synergic effect with the metabolic activity of microalgae, which grows also in water environment adsorbing CO2 as principal nutrient, so hugely reducing potential emissions for the planet.

The analysis of the process is still at preliminary level, no optimization is done based on the micro-algae cultivation and the following digestion for biogas production. Also, methanol synthesis from biogas feedstock is currently on experimental level, however with promising results. Future works will be focused on more detailed engineering analysis and optimization for the process.

References

Althaus, H., Chudacoff, M., Hischier, R., Jungbluth, N., Osses, M., Primas, A., Hellweg, S., 2007. Life cycle inventories of chemicals. ecoinvent report No.8, v2.0. Final Rep. ecoinvent data … 1–957.

Andersson, J., Krüger, A., Grönkvist, S., 2020. Methanol as a carrier of hydrogen and carbon in fossil-free production of direct reduced iron. Energy Convers. Manag. X 7, 100051. https://doi.org/10.1016/j.ecmx.2020.100051

Ayala-Parra, P., Liu, Y., Field, J.A., Sierra-Alvarez, R., 2017. Nutrient recovery and biogas generation from the anaerobic digestion of waste biomass from algal biofuel production. Renew. Energy 108, 410–416. https://doi.org/10.1016/j.renene.2017.02.085

Bailie, R.C., Whiting, W.B., 1998. Analysis, synthesis, and design of chemical processes, Choice Reviews Online. https://doi.org/10.5860/choice.36-0974

Bi, Z., He, B.B., 2013. CHARACTERIZATION OF MICROALGAE FOR THE PURPOSE OF BIOFUEL PRODUCTION. Trans. ASABE 56, 1529–1539.

Bisotti, F., Fedeli, M., Prifti, K., Galeazzi, A., Dell’Angelo, A., Barbieri, M., Pirola, C., Bozzano, G., Manenti, F., 2021. Century of Technology Trends in Methanol Synthesis: Any Need for Kinetics Refitting? Ind. Eng. Chem. Res. 60, 16032–16053. https://doi.org/10.1021/acs.iecr.1c02877

Bruno Sialve; Nicolas Bernet; Olivier Bernard, 2009. Anaerobic digestion of microalgae as a necessary step to make microalgal biodiesel sustainable. Biotechnol. Adv. 27, 490–416.

Entesari, N., Goeppert, A., Prakash, G.K.S., 2020. Renewable Methanol Synthesis through Single Step Bi-reforming of Biogas. Ind. Eng. Chem. Res. 59, 10542–10551. https://doi.org/10.1021/acs.iecr.0c00755

Graaf, G.H., Stamhuis, E.J., Beenackers, A.A.C.M., 1988. Kinetics of low-pressure methanol synthesis. Chem. Eng. Sci. 43, 3185–3195. https://doi.org/10.1016/0009-2509(88)85127-3

Kontogeorgis, G.M., Folas, G.K., 2009. Thermodynamic Models for Industrial Applications: From Classical and Advanced Mixing Rules to Association Theories, Thermodynamic Models for Industrial Applications: From Classical and Advanced Mixing Rules to Association Theories. https://doi.org/10.1002/9780470747537

Mairet, F., Bernard, O., Ras, M., Lardon, L., Steyer, J.P., 2011. Modeling anaerobic digestion of microalgae using ADM1. Bioresour. Technol. 102, 6823–6829. https://doi.org/10.1016/j.biortech.2011.04.015

Matthey, J., Box, P.O., Avenue, B., 2017. Methanol Production – A Technical History 172–182.

Methanex [WWW Document], 2019. URL https://www.methanex.com/news/methanex-reports-stronger-fourth-quarter-2019-results-and-full-year-record-production-volume

Moretta, F., Rizzo, E., Manenti, F., Bozzano, G., 2021. Enhancement of anaerobic digestion digital twin through aerobic simulation and kinetic optimization for co-digestion scenarios. Bioresour. Technol. 341. https://doi.org/10.1016/j.biortech.2021.125845

Nguyen, T.B.H., Zondervan, E., 2019. Methanol production from captured CO2 using hydrogenation and reforming technologies- environmental and economic evaluation. J. CO2 Util. 34, 1–11. https://doi.org/10.1016/j.jcou.2019.05.033

Olah, G.A., 2005. Beyond oil and gas: The methanol economy. Angew. Chemie - Int. Ed. 44, 2636–2639. https://doi.org/10.1002/anie.200462121

Ott, J., Gronemann, V., Pontzen, F., Fiedler, E., Grossman, G., Burkhard Kersebohm, K., Weiss, G., Witte, C., 2012. Methanol - An Industrial Review by Lurgi GmbH, Air Liquide GmbH and BASF AG. Ullmann’s Encycl. Ind. Chem.

Seider, W.D., Seader, J.D., Lewin, D.R., 2018. Product and Process Design Principles: Synthesis, Analysis and Design. Prod. Process Des. Princ. Synth. Anal. Des.

Wang, M., Sahu, A.K., Rusten, B., Park, C., 2013. Anaerobic co-digestion of microalgae Chlorella sp. and waste activated sludge. Bioresour. Technol. 142, 585–590. https://doi.org/10.1016/j.biortech.2013.05.096

Ward, A.J., Lewis, D.M., Green, F.B., 2014. Anaerobic digestion of algae biomass: A review. Algal Res. https://doi.org/10.1016/j.algal.2014.02.001

Zhao, X., Joseph, B., Kuhn, J., Ozcan, S., 2020. Biogas Reforming to Syngas: A Review. iScience 23, 101082. https://doi.org/10.1016/j.isci.2020.101082

Zhen, X., Wang, Y., 2015. An overview of methanol as an internal combustion engine fuel. Renew. Sustain. Energy Rev. 52, 477–493. https://doi.org/10.1016/j.rser.2015.07.083

**APPENDIX**

*Table 6. Graaf's kinetic parameters for low pressure methanol synthesis*

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| --- | --- | --- |
| $$Reactions$$ | $$Rates of Reactions$$ | $$Kinetic Parameters$$ |
| $$CO\_{2}+3H\_{2}\rightarrow CH\_{3}OH+H\_{2}O$$ | $$r\_{CO\_{2}/MeOH }= \frac{k\_{1}K\_{CO\_{2}}\left(f\_{CO\_{2}}f\_{H\_{2}}^{\frac{3}{2}} -\frac{f\_{MeOH }f\_{H\_{2}O}}{f\_{H\_{2}}^{\frac{3}{2}}K\_{eqCO\_{2}}}\right)}{DEN}$$ | $$k\_{1}=1.09∙10^{5} e^{- \frac{87500}{RT}}$$ |
| $$CO\_{2}+H\_{2}\rightarrow CO+H\_{2}O$$ | $$r\_{RWGS }=\frac{k\_{2}K\_{CO\_{2}}\left(f\_{CO\_{2}}f\_{H\_{2}} -\frac{f\_{H\_{2}O}f\_{CO}}{K\_{eqRWGS}}\right)}{DEN}$$ | $$k\_{2}=9.64∙10^{11} e^{- \frac{152900}{RT}}$$ |
| $$CO+2H\_{2}\rightarrow CH\_{3}OH$$ | $$r\_{CO/MeOH }=\frac{k\_{3}K\_{CO}\left(f\_{CO}f\_{H\_{2}}^{\frac{3}{2}} -\frac{f\_{MeOH}}{f\_{H\_{2}}^{\frac{1}{2}}K\_{eqCO}}\right)}{DEN}$$ | $$k\_{3}=4.89∙10^{7} e^{- \frac{113000}{RT}}$$ |