Biogas as a Renewable Feedstock for Green Ethylene Production via Oxidative Coupling of Methane: Preliminary Feasibility Study

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A preliminary feasibility study for the use of biogas as feedstock for the oxidative coupling of methane process aiming at green ethylene production is carried out. An economic assessment is performed based on literature, market and process simulation data, with the uncertainties being considered through Monte Carlo simulations. It is shown that the proposed process is economically interesting under a wide range of scenarios. The challenges and opportunities for the implementation of the process are highlighted to guide further studies.

1. Introduction

Biogas or landfill gas are methane-rich gas mixtures also containing carbon dioxide and lesser amounts of contaminants. It is produced in the anaerobic treatment of effluents or energy crops and often combusted in biogas engines for heat and power generation after minor prior treatment. Through the removal of CO_2, biogas can alternatively be upgraded into biomethane, which can then be transported via regular natural gas pipelines after a final adjustment of the dew point and heating value and odorization (Sun et al., 2015).

The Oxidative Coupling of Methane (OCM) consists in the catalytic oxidation of methane and has been investigated since the 1980's (Keller and Bhasin, 1982) as a promising path for utilizing natural gas, and more recently shale gas, as a precursor for chemical building blocks such as ethylene. Different reaction paths have been proposed, but it is generally accepted that the desired selective oxidation path leads methane to be adsorbed in the catalyst surface and converted into the intermediary ethane (Arndt et al., 2012). Ethane reacts further, either on the catalyst surface or in the gas phase, to form the main product ethylene. The unselective oxidation of hydrocarbons into carbon monoxide and carbon dioxide, as well as the reforming and water-gas shift reactions complement the highly exothermic reaction system. Previous contributions including modelling (Esche et al., 2012) and mini-plant experiments (Godini et al., 2014) regarding the OCM reaction section have been published in related literature. The separation after the reaction consists of a compression and water removal, CO_2 removal, and distillation and it is crucial for the economic performance of the process. The CO_2 removal section have also been assessed based on optimisation studies (Esche et al., 2015), as well as through mini-plant experimentation (Stünkel et al., 2012). The process flow diagram for the OCM process is depicted in Figure 1. Herein, biogas is considered as an alternative feedstock for the OCM process.

The conversion of biogas into chemicals has not yet been extensively investigated and would enable another option for the biogas monetization and to produce fuels and chemicals through greener paths. This would allow for a distributed production of base chemicals, especially in countries with abundant biomass resources and limited fossil resources. While some research groups have already investigated the reforming of biogas to produce syngas (Chen et al., 2017), no publication is found dealing specifically with the use of biogas as a feedstock for the OCM process for ethylene production. The aim of this contribution is to assess the feasibility and potential for the utilization of biogas as a raw material for a bio-based OCM process or Bio-OCM. The scope of this study is limited to the techno-economic feasibility and other relevant aspects such as health, safety, and environment shall be addressed in the future once more detailed information is available.
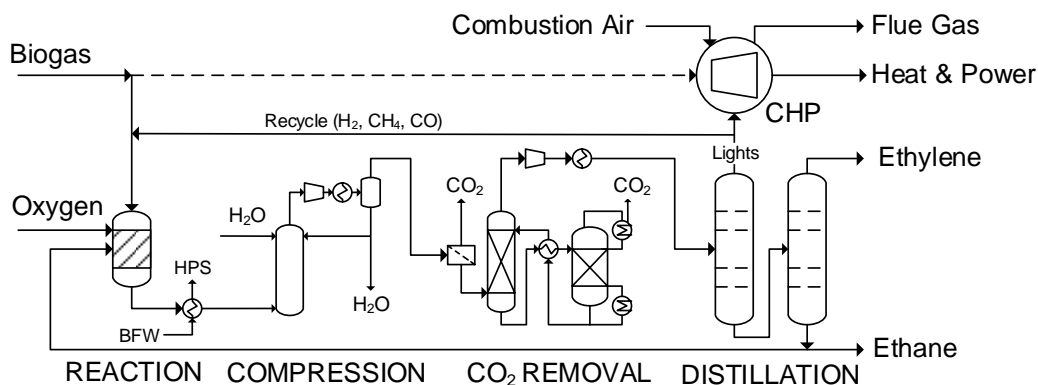
Figure 1: Process flow diagram of the OCM process

2. Methods

A biorefinery in Brazil producing 151×10^3 m³/y of anhydrous bioethanol and 1.2×10^6 m³ of vinasse, which is a liquid effluent, is taken as a base case. The vinasse is treated anaerobically in sequencing batch reactors with immobilized biomass yielding 2,200 Nm³/h of biogas with 70 mol% CH_4 and 30 mol% CO_2 (Albanez et al., 2016). Such compositions are also found in other biogas sources (Rasi et al., 2007). The OCM plant nominal capacity results in 800 t/y of ethylene, which is tiny when compared to naphtha or ethane cracking plants.

2.1 Biogas treatment

Besides methane and carbon dioxide, different contaminants in varying concentrations are expected to be present in the raw biogas. The nature and quantity of the contaminants vary significantly among literature sources, but typical compositions encountered might include up to 4,000 ppm H_2S, 15 ppm Siloxanes, 100 ppm NH_3, and chlorinated compounds (Sun et al., 2015). Other sources mention lower values for those, but also the presence of up to 287 mg/m³ of aromatics (Rasi et al., 2007). There are several different techniques that can be used to treat biogas prior to its use depending on the level and nature of contaminants, production scale, availability of utilities, and application requirements. A review of major available processes is presented in (Sun et al., 2015). The most energy intensive and costly step is often the removal of the CO_2, given its high concentration in the biogas (30-50 mol%). This step is often called "upgrade into biomethane". However, for the OCM reactor, the CO_2 contained in biogas can be used as a diluent gas, avoiding the need for introducing another diluent such as nitrogen. Therefore, the raw biogas is only treated for minor contaminants and the biogas upgrade is omitted.

A contaminant of major concern is hydrogen sulphide (H_2S), which is a toxic, malodorous, and sour gas, which causes equipment corrosion. Within the biogas industry, bio-scrubbers using Thiobacill*i* bacteria are widely used to convert H_2S into elemental sulphur and sulphate (Ramírez-Sáenz et al., 2009). This is an effective method providing low operational costs and the use of harmless educts and products in the relevant production scales. A disadvantage is the sensitivity of the microorganisms towards fluctuations in temperature and H_2S concentrations. Therefore, a constant efficient removal cannot be guaranteed (Krischan et al., 2012). An approximate cost of 0.1-0.25 EUR/kg H_2S is suggested for this method (Sun et al., 2015).

To achieve a higher H_2S removal (< 1 ppmv), adsorption on metal oxides or impregnated activated carbon is applied. This is an effective method for deep H_2S removal, but if the H_2S content in the feed gas is high, frequent replacement of adsorption material leads to high operation cost. The cost of this method is estimated to be around 3.85 €/kg H_2S (Sun et al., 2015). Physical or chemical absorption are not considered herein, as they would simultaneously remove the CO_2, increasing the energy requirement unnecessarily.

Other contaminants of concern are siloxanes. These can cause erosion and deposit of silica compounds, being a major concern for micro-turbine applications. Adsorption with activated carbon is a common method for their removal. Concentrations below 0.87 ppm can be achieved at a cost of 81-113 €/kg (Sun et al., 2015).

The selection of appropriate biogas treatment and upgrade methods should consider operational and capital investment costs as well as specific requirements for the gas application and should, therefore be done on a case by case basis. Since the specific gas quality requirements for the OCM have not yet been investigated, it is assumed that a deep removal of contaminants is required. Different biogas compositions from varied sources, e.g. livestock farms or landfill gas, are then used and the cost range of 0 to 0.028 USD/Nm³ for the treated biogas is estimated based on treatment costs collected and published by (Sun et al., 2015) for a clean and a heavily contaminated stream.

2.2 Oxidative coupling of methane process

The OCM process is assessed based on a simulation model implemented in the software Aspen Plus v9 (Aspentech, 2017). The flowsheet is developed based on previous works of the research group with the natural gas-based OCM process (Salerno et al., 2016), which have been experimentally validated in an OCM mini-plant. Other process flowsheets considering alternative separation methods, such as pressure and temperature swing adsorption, need to be considered in the future as they might bring advantages on the smaller production scales. While heat integration is performed to some extent during the synthesis of the simulation flowsheet, a more rigorous analysis needs to be performed once more flowsheet structures are available and consolidated. Two adiabatic fixed bed reactors in series are applied. The reactors are modelled as kinetic plug flow reactors, using kinetics from (Stansch et al., 1997). A dilution gas, commonly nitrogen, is applied in the reactor to deal with the reaction heat release and to avoid the formation of explosive atmospheres between oxygen and methane. The CO_2 contained in the biogas is used in this application instead. Therefore, pure oxygen (95 mol%) instead of air is fed to both reactors as the limiting reactant. The cost for the air separation unit is included in the oxygen supply price. The achieved ethane and ethylene yield is 15 %, which is lower than the current state of the art (>20 %) achieved experimentally with a more complex fixed bed membrane reactor (Godini et al., 2014). The reactors' outlet streams are used to pre-heat the feed and to generate high pressure steam.

The reactor outlet gas, containing H_2, N_2, CH_4, C_2H_4, C_2H_6, CO, CO_2, and H_2O, is quenched, compressed to 11 bar, and cooled to condense most of the water. It is then fed to the CO_2 removal section, wherein a hybrid membrane and absorption-based process (Penteado et al., 2016) is used. The bulk of the CO_2 content is removed using a cascade of polyimide membranes, while the remaining part is removed via absorption/desorption with a 30 wt% aqueous monoethanolamine solution. A CO_2 rich stream is gained as a by-product and its utilization is out of the scope of this contribution, but of significant importance given the amount that is produced. The CO_2 free gas is further compressed to 35 bar and fed to the distillation section.

The main process stream is pre-cooled in regeneration exchangers and separated in a series of two columns. The demethanizer column produces a methane-rich stream at the top. This stream is partially recycled back to the OCM reactor or used for cogeneration of heat and power. The bottom product contains ethylene and ethane, which are separated in the C2 Splitter achieving above 99.99 mol% pure ethylene and an ethane stream that is either recycled to the reaction section or sold as a by-product.

2.3 Cost estimations

Based on the simulation results, utilities' consumption and cost rates are estimated using the default utilities contained in the program's databank. For this purpose, cooling water, electricity, medium and light pressure steam, as well as refrigeration utilities are employed. The process exports electricity and heat and credit is taken for those. The default costs for the utilities in the program, which reflect U.S. Gulf Coast values, are given a range from 0.7 to 1.3 for the economic evaluation step. Similarly, the costs for the raw materials and products are given a certain price range as shown in Table 1. For simplicity and lack of information on non-commercial technologies, make-up of amine solution and cryogenic utility, and catalyst and membrane material replacement are neglected at this stage. The equipment cost is estimated using the tool Aspen Process Economic Analyzer, as well as a tool previously developed within our research group based on an industrial, pilot, and mini-plant equipment data bank (Lühe, 2012). Other plant investment costs are estimated based on the equipment cost via multiplication factors (Bejan et al., 1996), which are also given a lower and upper bound. The costs for installation, piping, automation, electric, civil, service facilities, land/terrain, engineering & procurement, construction site, contingency, maintenance are estimated this way, leading to the Fixed Capital Investment (FCI). By adding the start-up cost and the working capital, the Total Capital Investment (TCI) is calculated.

3. Economic analysis

A year-by-year cash flow analysis is then performed for the base case Bio-OCM plant. An operating-life of 30 y is assumed, which is typical for chemical plants (Bejan et al., 1996). The total capital investment is divided into 30 % for the first year (2017) and 70 % for the second. Plant operation and revenues start in January 2019. A linear depreciation until zero salvage value during the entire project duration is assumed. The assumed ranges for the main economic variables are shown in Table 1. The costs for raw material, operation & maintenance, depreciation and return to investors escalate based on the inflation rate. Due to development of alternative technologies and depletion of fossil resources, the price for the main product ethylene escalate based on the nominal escalation rate, which is slightly higher than the inflation. The break even for the project is determined based on the accumulated cash flow during the project years. The project's net present value is then calculated by Eq(1), where the NPV is the net present value, the FCI is the fixed capital investment, SU is the start-up costs, WC is the working capital, i_{eff} is the effective interest rate, z is the operation year, and NCF_z is the net cash flow on the zth year of operation. A positive NPV indicates that the project is economically feasible.

Table 1: Cost / price for utilities, raw materials, and products and main economic assumptions

Item	Price Range		Units	Item	Range	
Electricity	0.05	0.09	USD / kWh	Inflation rate (r_i)	0.02	0.09
MP Steam	1.8×10^{-6}	2.6×10^{-6}	USD / kJ	Real escalation rate (r_R)	0.03	0.06
LP Steam	1.5×10^{-6}	1.7×10^{-6}	USD / kJ	Nominal escalation rate	$(1+r_i) \cdot (1+r_R) - 1$	
Cooling Water	1.7×10^{-7}	2.54×10^{-7}	USD / kJ	Effective interest rate (i_{eff})	r_i	0.15
Refrigeration	6.0×10^{-6}	1.1×10^{-5}	USD / kJ	Total income tax	0.10	0.30
Treated biogas	0	0.028	USD / Nm³	Operation factor	0.85	0.98
Oxygen 95 %	0.050	0.074	USD / Nm³	Yearly operating hours	7,446	8,585
Ethane	46.74	96.06	USD / t	Plant operating life	30 y	
Ethylene	700	1,400	USD / t			
Carbon dioxide	3	5	USD / t			

$$NPV = 0.3 \cdot FCI + \frac{0.7FCI + SU + WC}{\left(1 + i_{eff}\right)^1} + \sum_{z=1}^{30} \frac{NCF_z}{\left(1 + i_{eff}\right)^{1+z}} \tag{1}$$

A total of 2,000 simulations are then conducted with the variables taking random values within the given ranges. For this purpose, the randomize function of Microsoft Office Excel 2016 is used. The net present value, total annualized cost, and the breakeven are recorded. The results of this Monte Carlo simulation in terms of average values and frequency distributions are presented in the results section.

4. Results and discussion

A first analysis is conducted based on the simulation results by only considering raw materials, products and utility costs. Based on the given bounds, the worst scenario occurs at the maximum biogas, oxygen, cooling water and refrigeration costs and the lowest possible ethylene, ethane, electricity, and steam prices. This results in a plant cash flow of -8.07 USD/h. The best scenario results in a plant cash flow of 181.08 USD/h. Therefore, the process can be profitable and the capital investment cost and other operation costs need to be estimated.

The total installed equipment cost is estimated at 2.1×10^6 USD. The most expensive equipment is the gas and steam turbines at the cogeneration section. The use of gas engines could provide a less capital-intensive solution at the expense of a lower efficiency. A cost estimation for a gas engine cogeneration system could not be obtained at this stage and, therefore the prices for turbines available in Aspen Plus are used. Heat exchangers represented the second most expensive equipment type, followed by membrane modules, compressors, columns, and reactors. The use of CO_2 as dilution gas also implied that the reaction and CO_2 removal are the most capital-intensive steps, while the reaction and distillation were the most capital-intensive ones while utilizing nitrogen dilution in the natural gas-based OCM (Salerno et al., 2016).

The results of the Monte Carlo simulation, namely the frequency distributions for the Net Present Value and Breakeven for the base case, are shown in Figure 2. The Net Present Value is positive in 77 % of the cases with an average value of 6.8×10^6 USD. This indicates that the process is likely to be feasible in a wide range of different scenarios regarding technological, market, and economic aspects. The standard deviation is however $\pm 9.3 \times 10^6$ USD, which is to be expected given the uncertainties assumed in the simulations. The payback period is relatively high with an average of 15 ± 4 y, since the capital expenses for the plant installation are relatively high compared to the net cash flow. This could be overcome by an increased production scale, which could help to dilute the installation costs.
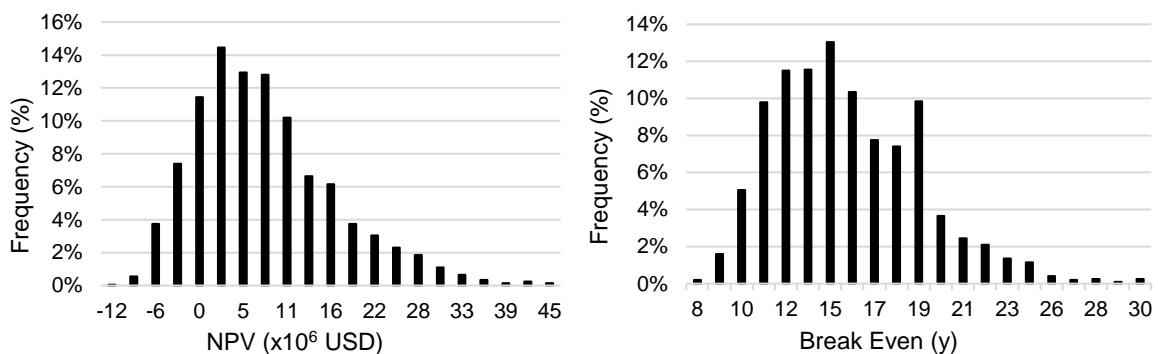

Figure 2: Frequency distribution of the Net Present Value and the Break Even for the base case

Two further studies are then conducted. The first one considers the introduction of an additional Ethane Dehydrogenation (EDH) reactor, which is placed downstream to the OCM reactor. It allows more ethane to be converted into ethylene, thus increasing the revenue. This reactor is not added to the simulation flowsheet, but a per pass ethane conversion of 60 % and a 60 % ethylene selectivity are assumed based on previous works (Salerno et al., 2016). The total raw material and utility costs are increased by 10 % and the equipment cost is assumed to be similar to the OCM reactors. The ethane recycle allows for an overall 100 % ethane conversion. This configuration greatly improves the NPV to an average of 24.6 ± 16.8 x10^6 USD, with 99.95 % of positive values, and the payback period is reduced to 10 ± 2 y.

Another study is conducted considering a higher production scale still including the EDH reactor. The scale of biogas plants is likely to grow in the future, notably in developing countries, based on modernization of agriculture, large-scale livestock farms, and urbanization. For instance, China is already experiencing a reduction in the number of household biogas plants and an increase in medium to large scale plants with a net increase in the country's biogas output (Wang et al., 2016). A very large biogas plant being commissioned in Tønder, Denmark is taken as another base point for this analysis. The plant treats liquid manure, household waste, and energy crops from 120 farmers, producing approximately 7,800 Nm³/h of biogas (Gudmundsson, 2016). Equipment cost are scaled using a simple 6/10th rule, while raw materials and utility costs as well as product revenue scale-up linearly. A further extrapolation is also performed for theoretical biogas plants producing 20,000, 50,000, and 100,000 Nm³/h of biogas. The resulting increase in the NPV is presented in Figure 3. The payback time is reduced to 8 ± 2 y at the largest scale.
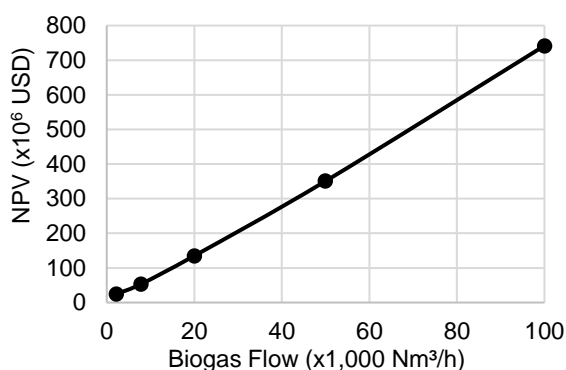

Figure 3: Sensitivity analysis for the production scale

5. Conclusions

This study is a first assessment for the potential use of biogas as a renewable feedstock for green ethylene production via Oxidative Coupling of Methane. Technical aspects are considered at a superficial level and through many assumptions to allow for a first estimation of the economic potential of this process. While the accuracy and significance of these results should not be overestimated, it can be concluded that this process is economically attractive under different conditions. The introduction of another reactor for the dehydrogenation of ethane can significantly increase ethylene production, leading to a higher revenue that increases the project's net present value and reduces the time for breakeven. Furthermore, it is also shown that the process can benefit from larger production scales, which should be a major challenge considering that biogas is produced in rather small scales when compared to natural gas or shale gas.

The proposed Bio-OCM process needs to be investigated in more detail for its further development. Experimental investigations for the operation of a mini-plant OCM reactor with biogas-like feed compositions are to be carried out. Kinetic models might need to be revised or fitted to the new operating conditions. The effect of eventual biogas contaminants, e.g. catalyst poisoning, also needs to be considered in detail, also to allow for the synthesis of a suitable biogas treatment section. The downstream separations also need to be revised, especially taking into consideration particularities of this application such as the high inlet CO_2 concentration and the reduced production scale. Energy and material integration aspects are also to be considered in the process synthesis stage, allowing, for example, for an integration with the endothermic dry reforming of methane to produce syngas. At this stage, the sustainability of the proposed process chain is also to be assessed in more detail through carbon footprint calculations and Life Cycle Analysis and compared to the equivalent fossil routes for ethylene production via naphtha or ethane cracking. From an economic standpoint, it would be reasonable to compare the performance of the Bio-OCM process with those of a standalone biogas CHP plant and with a biomethane producing plant.

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