

## Bioenergy with carbon emissions capture and utilisation towards GHG neutrality: Power-to-Gas storage via hydrothermal gasification

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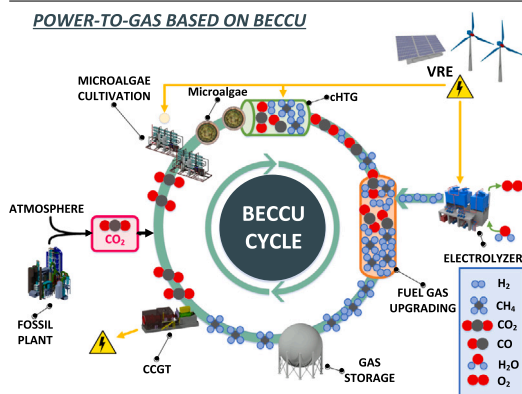
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### GRAPHICAL ABSTRACT



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### ABSTRACT

The low efficiency of renewable electricity storage has been considered as a bottleneck of the scalable and low-carbon Power-to-Gas energy transformation concept. This paper investigates the combination of CO<sub>2</sub> biofixation using *Spirulina platensis* microalgae and catalytic hydrothermal gasification of wet organic feedstock for the storage of fluctuating electricity and direct utilisation of waste CO<sub>2</sub>. The presented method enables wet microalgae biomass conversion into H<sub>2</sub> and C<sub>1</sub>-C<sub>2</sub> rich fuel gas stream using hydrothermal conversion that is valorised further to methane. For bridging the gap between theoretical investigations and the application of this approach, experiments were carried out at elevated temperatures (632.9–717.0 °C) based on a central composite design of the experiment. Biogas upgrading was evaluated by ASPEN Plus flowsheeting software. The results show that the proposed storage cycle outperforms the state-of-the-art biological and chemical-based Sabatier methanations with an overall round-trip efficiency of 42.3%. The optimised thermo-chemical process enables to achieve simultaneously high H<sub>2</sub> (9.05 mol kg<sup>-1</sup>) and CH<sub>4</sub> (7.91 mol kg<sup>-1</sup>) yields with an enhanced 71.23% carbon conversion ratio. Moreover, the environmental and cost evaluations of the currently proposed bio-synthetic process indicate low associated CO<sub>2</sub> equivalent emission (99.4 ± 12.6 g CO<sub>2,eq</sub> kWh<sup>-1</sup>) with 144.9 €/MWh<sup>-1</sup> normalised total annual natural gas production cost. Ideally the proposed storage cycle requires less H<sub>2</sub> from external sources, effective CO<sub>2</sub> utilisation becomes available through the biofixation and hydrothermal conversion of the wet organic feedstock and closed carbon emission cycle can be accomplished.

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## 1. Introduction

Global warming and security of energy supply urge the spread of sustainable solutions that advance the climate-neutral transition of energy sector [1]. The European Commission outlines that an all-round shift towards decarbonisation and net-zero GHG emissions should be based on the utilisations of renewables and diversified electricity sources [2]. Limiting global warming demands effective carbon dioxide removal (CDR) technologies and large-scale application of renewable energy sources (RES) [3]. Synthetic fuels (e.g., hydrogen, methane, methanol, ammonia, diesel) generated from renewable electricity via Power-to-X (P2X) processes are regarded as green and low-carbon energy vectors that support to reach ambitious energy storage and emission mitigation targets [4]. Schnuelle et al. [5] discussed that the integration of P2X alternatives to the energy system could become a feasible solution, and it strengthens the flexibility of energy supply. A conceptual design of a P2X process was already demonstrated [6] for the production of liquid and solid hydrocarbons using solar energy, water and the CO<sub>2</sub> content of air, while Götz et al. [7] evaluated chemical and biological Power-to-Gas (P2G) storage alternatives.

Variable renewable energy (VRE) sources (e.g., wind and photovoltaic) provide abundant surplus clean energy; however, the integration of these technologies into the existing grid system is a challenging task [8], as they are intermittent and the VRE storage efficiency is low in comparison to conventional technologies. The variability in electricity production and consumption can be balanced if the produced VREs are efficiently stored. The P2G is a promising method that implements the production of heat, synthetic materials and fuels [9] and it can enhance the resilient operation of thermal power plants [10]. The Power-to-Methane (P2M) concept involves the (1) utilisation of excess electricity for the production of H<sub>2</sub> by water electrolysis and (2) the methanation of carbon oxides (CO, CO<sub>2</sub>) to produce methane. Unlike H<sub>2</sub>, methane (CH<sub>4</sub>) is characterised by 4 to 5-times lower storage volume, and it can be injected to the available natural gas grid [11]. The technological readiness of the P2G methodology is still in its early stage and limited by low efficiencies (water electrolysis (with alkaline and polymer electrolyte membrane): 47.2–82.3% [12]; catalytic methanation: up to 85% [13]; biological methanation: 77%–80% [14]; combined cycle gas turbine (CCGT): 50%–65% [15]). It is estimated that the round-trip efficiency of the Power-to-Methane conversion route including electricity production is about 36% [16] implying that only the third of the produced variable renewable electricity can be recovered after the storage. Bareschino et al. [17] investigated a P2M alternative that was coupled with solid fuel chemical looping combustion (CLC). It was obtained that a near-zero carbon emission can be reached with this combination, but the electric efficiency was found to be low (around 16%) due to high input energy requirement of the CLC process. A microbial electromethanogenesis was analysed for CO<sub>2</sub> valorisation by Ceballos-Escalera et al. [18]. The bioelectrochemical system was characterised by high electricity storage efficiency (>40%), but the microbial dynamic was reported to be slow, limiting the power peak balancing capability of the process. Another technological bottleneck is paired with the purity of the input CO<sub>2</sub> stream. Impurities and toxic compounds deactivate the catalysts used in catalytic chemical methanations [19] and have a detrimental effect on methanogen bacteria in biological methanations [20]. This limitation makes necessary the prior separation of CO<sub>2</sub> from industrial flue gas sources or from the air that results in increased energy demand (4–5 GJ (t CO<sub>2</sub>)<sup>-1</sup> using monoethanolamine based absorption [21] or up to 8.1 GJ (t CO<sub>2</sub>)<sup>-1</sup> with the application of direct air capture technology [22].) Numerous forecasts of energy sector predict that the share of fluctuating renewable energy sources in the electricity mix is going to increase immensely until 2050 due to the electrification of transportation [23], deployment of RES [24] and to reach decarbonisation emission targets [25]. These trends give rise to a strong technological need to improve the overall

process efficiency, operational costs and to remove bottlenecks that prevent the long-term storage of VRE.

Bioenergy with carbon capture and utilisation (BECCU) offers a natural way to (1) neutralise CO<sub>2</sub> emissions and to (2) convert this waste and hazardous platform molecule into value-added synthetic materials and fuels. Zhang et al. [26] investigated the utilisation of CO<sub>2</sub> captured from biomass combustion and concluded that biogenic CO<sub>2</sub> sources contribute to obtaining a higher degree of GHG emission reduction compared to non-biogenic feedstocks. Blanco et al. [27] expressed that CO<sub>2</sub> could be supplied from the air or via biofixation for the P2M process, but the cumulated GHG footprint of such systems should be below 123–181 g CO<sub>2,eq</sub> kWh<sup>-1</sup> to be able to outperform the environmental effects of conventional natural gas utilisation.

BECCU organisms are capable of absorbing CO<sub>2</sub> and transforming them into value-added metabolic products. Methanogen microorganisms produce methane in hypoxic conditions [28] while microalgae biomass uses carbon dioxide as a substrate for photosynthesis [29]. Microalgae, as a fast reproducing BECCU feedstock is characterised by high biomass productivity [30] and excellent CO<sub>2</sub> biofixation rate up to approximately the twice of the produced weight of biomass [31]. Despite its advantageous properties, the downstream processing of algae is limited due to the extremely dilute feedstock (0.5–4 g L<sup>-1</sup>) that is harvested from cultivation systems. Atmospheric thermochemical processes (e.g., torrefaction, pyrolysis, gasification) necessitate the drying of aquatic feedstocks that decreases the energy return of investment to unsatisfactory levels [32]. On the other hand, the thermal disintegration of wet biomass in sub-, or supercritical water (a.k.a. hydrothermal conversion) make the pre-drying process dispensable, enabling high energy saving potentials [33]. Wet microalgae suspension can be converted directly into combustible green fuel gas with a high calorific value above the supercritical point of water (374 °C and 22.1 MPa) via hydrothermal gasification (HTG) [34]. Various homogeneous (alkali hydroxides and -carbonates [35]) and heterogeneous catalysts (activated carbon, transition metals, oxides [36]) can be used in the hydrothermal process to improve the biogas quality (heating value, gas composition), product selectivity, carbon conversion ratio and to decrease reaction temperature and pressure levels. Up to now, there have been many efforts to convert high moisture containing biomass into viable fuels since bio-based energy carriers are regarded as sustainable and renewable. Advancements were already achieved in the fields of genetically engineered strains [37], eco-friendly biofuel production [38] and the utilisation of solar energy to upgrade biomass and fuels [39]. However, conventional downstream conversion technologies have been limited by inadequate energy balances. In our study, bypassing this weak point, (1) catalytic hydrothermal gasification of wet biomass is investigated at elevated temperature levels to boost the conversion efficiency and (2) bio-based fuel gas is examined as an intermediate energy vector for intermittent renewable electricity storage.

In the current work, a Power-to-Gas configuration is demonstrated, based on a BECCU cycle that offers an efficient and low-carbon solution for the storage of fluctuating renewable electricity. The introduced bio-synthetic Power-to-Methane approach is an effective CO<sub>2</sub> valorisation method that enables low-carbon operation in conjunction with elevated round-trip efficiency compared to the available biological and chemical methanations. In our approach, microalgae biomass is selected as a BECCU feedstock over methanogens bacteria since it has excellent photosynthetic efficiency, biomass productivity and capability to capture anthropogenic CO<sub>2</sub> from the air and industrial flue gas sources. Catalytic hydrothermal gasification is applied for the conversion of high moisture containing biomass and integrated to the Power-to-Gas CO<sub>2</sub> utilisation concept. It is already reported that homogeneous alkali catalysts boost the H<sub>2</sub> evolving rate at moderate hydrothermal reaction conditions (T<sub>HTG</sub> < 600 °C) [40]. For this reason, alkali catalyst (NaOH) is selected in our investigation to raise the yields of hydrothermal conversion. As there is a lack of data in the literature performing cHTG at increased temperature levels, experiments were

carried out between 632.9 and 717.0 °C to improve the performance of hydrothermal gasification. The results show that catalytic hydrothermal gasification is a suitable process to convert organic feedstocks with high moisture content into methane and hydrogen-rich fuel gas mixture. The conversion of *Spirulina platensis* microalgae strain is carried out with high carbon conversion ratio (CCR: 71.2%) and elevated total gas yield ( $Y_{GAS}$ : 35.4 mol kg<sup>-1</sup>) when the operation is optimised to gain increased methane yield. The H<sub>2</sub>, CO<sub>2</sub> and CO content of the cHTG gas mixture is upgraded further to a methane-rich fuel gas stream that can be suitably stored and distributed via the natural gas grid infrastructure. It is found that the microalgae-based bio-synthetic P2M system outperforms chemical storage (Synthetic Power-to-Methane, Power-to-Methanol) alternatives regarding energy and environmental aspects as a consequence of

- (i) the sequential biofixation and valorisation of CO<sub>2</sub>,
- (ii) high cHTG fuel gas yields, and
- (iii) enhanced energy recovery.

## 2. Materials and methods

### 2.1. Bio power-to-methane-to-power scenario description

BECCU technologies that involve the transformation of high moisture containing feedstocks (e.g., microalgae) can become competitive only if biomass drying energy can be avoided. Since hydrothermal conversion methods do not require dried feedstock, a significant amount of energy can be saved during the conversion of wet biomass. Water electrolysis offers an opportunity to produce H<sub>2</sub> and store renewable electricity in the form of synthetic fuels. In the investigated process scenario, the hydrogen is regarded as the main connection point between VRE storage and biomass conversion, as it is presented in Fig. 1. Additionally, in our approach, VREs are used for the cultivation of microalgae biomass and to provide the required utility for cHTG process and biogas upgrading. It is assumed that anthropogenic CO<sub>2</sub> is captured by microalgae biomass during the metabolism and propagation of cells in a controlled photobioreactor cultivation system. Then, the produced biomass suspension is transferred to a downstream facility.

The BECCU based Power-to-Methane process is separated into two main downstream conversion stages and an auxiliary energy recovery system as it is detailed in Fig. S1. In the first stage, the fermented and pre-concentrated wet microalgae feedstock is compressed up to 22.0–34.4 MPa and converted into H<sub>2</sub>, CH<sub>4</sub>, CO<sub>2</sub>, CO, C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> containing fuel gas mixture via catalytic hydrothermal gasification. The applied temperature profile ranges between 632.9–717.0 °C to enhance the gasification performance in the supercritical region of water solvent. Surplus hydrogen – which is produced through water electrolysis – is added to the biogas mixture according to the syngas modular (Eq. (5)) to produce methane via catalytic methanation and to meet the purity specification of natural gas. The high-quality methane-rich gas stream is compressed up to 10.0 MPa and injected into the natural gas grid. The methane is stored in already existing natural gas storage infrastructure, and it is combusted in Combined Cycle Gas Turbines (CCGT) to satisfy the energy demands of consumers. Following the combustion process, the co-produced CO<sub>2</sub> platform molecule is re-used in microalgae cultivation closing the carbon emission cycle.

### 2.2. Hydrothermal gasification

The catalytic hydrothermal gasification of microalgae biomass (*Spirulina platensis*) was carried out in a plug flow tubular reactor system (2 m length, 3.175 mm outer diameter, stainless steel 316). The HTG reactor was placed into an electric furnace (DENKAL LTP-F) to provide the required temperature for the process. The temperature was monitored at the beginning and at the end of the high-pressure plug flow reactor. The inlet fluid was transferred and pressurised by

a Perkin Elmer SERIES 200 Micro Pump. The inlet feedstock flow rate was held at 2.5 mL min<sup>-1</sup>. A phase separator was installed after the HTG reactor system to separate the produced process water and fuel gas products. The gas-phase was collected in a calibrated gas burette which was washed with argon before the measurements. The gas-phase was sampled with a sampling septum attachment placed on the top of the gas burette. The biogas and its composition were analysed by an HP5890SIIA/TCD/FID gas chromatograph. A packed column with 3.175 mm OD and 190 cm length was used with Porapak Q polymer beds (80/100 mesh). The argon carrier gas was entered to the column with a column head pressure of 150 kPa. The initial oven temperature was set to 50 °C, and it was held for 0.5 min. 20 °C min<sup>-1</sup> heating rate was applied to reach the final temperature (150 °C) that was held for 2 min. The injection temperature was 130 °C.

The gas yield related to the input mass of feedstock was determined by Eq. (1):

$$Y_{GAS} \text{ (mol kg}^{-1}\text{)} = \frac{\sum(n_{GAS,k})}{m_{algae}} \quad k = \text{H}_2, \text{CH}_4, \text{CO}_2, \text{CO}, \text{C}_2\text{H}_4, \text{C}_2\text{H}_6, \quad (1)$$

where  $Y_{GAS}$  is the total gas yield (mol kg<sup>-1</sup>),  $n_{GAS,k}$  is mole number of the kth biogas component, while  $m_{algae}$  is the mass of the feed (kg). The HTG conversion efficiency was evaluated calculating the carbon conversion ratio (CCR) (Eq. (2)):

$$CCR \text{ (\%)} = \frac{\sum(m_{GAS,i} \cdot \frac{MW_C}{MW_{GAS,i}})}{m_{algae} \cdot \frac{w_{C,algae}}{MW_C}} \cdot 100 \quad i = \text{CH}_4, \text{CO}_2, \text{CO}, \text{C}_2\text{H}_6, \text{C}_2\text{H}_4 \quad (2)$$

where CCR is the carbon conversion ratio (%),  $m_{GAS,i}$  is the mass of the ith gas component (kg),  $MW_C$  is the molar weight of carbon (kg kmol<sup>-1</sup>),  $MW_{GAS,i}$  is the molar weight of the ith gas component (kg kmol<sup>-1</sup>),  $m_{algae}$  is the mass of algae (kg),  $w_{C,algae}$  is the carbon content of algae biomass (-).

Central Composite Design (CCD) of the experiment was employed for the evaluation of impacts of process parameters. The statistical effects of 4 factors were investigated on 5 levels, namely: (X<sub>1</sub>) Temperature: 632.9–717.0 °C, (X<sub>2</sub>) Pressure: 22.6–34.4 MPa, (X<sub>3</sub>) Biomass dry weight (DW): 4.1–20.9 wt% and (X<sub>4</sub>) Concentration of NaOH catalyst (c<sub>NaOH</sub>): 0.48–5.52 wt%. The dependent variables were ( $\hat{Y}_1$ ) H<sub>2</sub> mol%, ( $\hat{Y}_2$ ) CH<sub>4</sub> mol%, ( $\hat{Y}_3$ ) CO<sub>2</sub> mol%, ( $\hat{Y}_4$ ) CO (mol%), ( $\hat{Y}_5$ ) C<sub>2</sub>H<sub>4</sub> (mol%), ( $\hat{Y}_6$ ) C<sub>2</sub>H<sub>6</sub> (mol%), and ( $\hat{Y}_7$ ) biogas yield (mol kg<sup>-1</sup>). The experimental data were evaluated with the Response Surface Methodology (RSM), where the polynomial quadratic response model was described by Eq. (3):

$$\hat{Y}_z = \beta_0 + \sum_{i=1}^k \beta_i X_i + \sum_{i=1}^k \beta_{ii} X_i^2 + \sum_{i=1}^k \sum_{j=1}^k \beta_{ij} X_i X_j + \varepsilon, \quad (3)$$

where  $\hat{Y}_z$  is the predicted response variable (z: H<sub>2</sub> (mol%), CH<sub>4</sub> (mol%), CO<sub>2</sub> (mol%), CO (mol%), C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub> (mol%),  $Y_{GAS}$  (mol kg<sup>-1</sup>)),  $X_i$  is the independent variable (HTG temperature (°C), pressure (MPa), biomass dry weight (wt.%), NaOH concentration (wt.%)),  $\beta_0$ ,  $\beta_i$ ,  $\beta_{ii}$ ,  $\beta_{ij}$  are regression coefficients and  $\varepsilon$  is the random error.

The desirability function approach was applied for the optimisation of cHTG process. The methane yields were transformed into desirability values (d<sub>i</sub>) ranging from 0 to 1 as unacceptable and more desirable cases. For larger-the-better response, the desirability is defined by Eq. (4):

$$d_i = \begin{cases} \left( \frac{y - LSL}{USL - LSL} \right)^s & LSL \leq y \leq USL \\ 0, & y < LSL \\ 1, & y > USL, \end{cases} \quad (4)$$

where USL and LSL are upper and lower restricts,  $s$  is a shape constant.

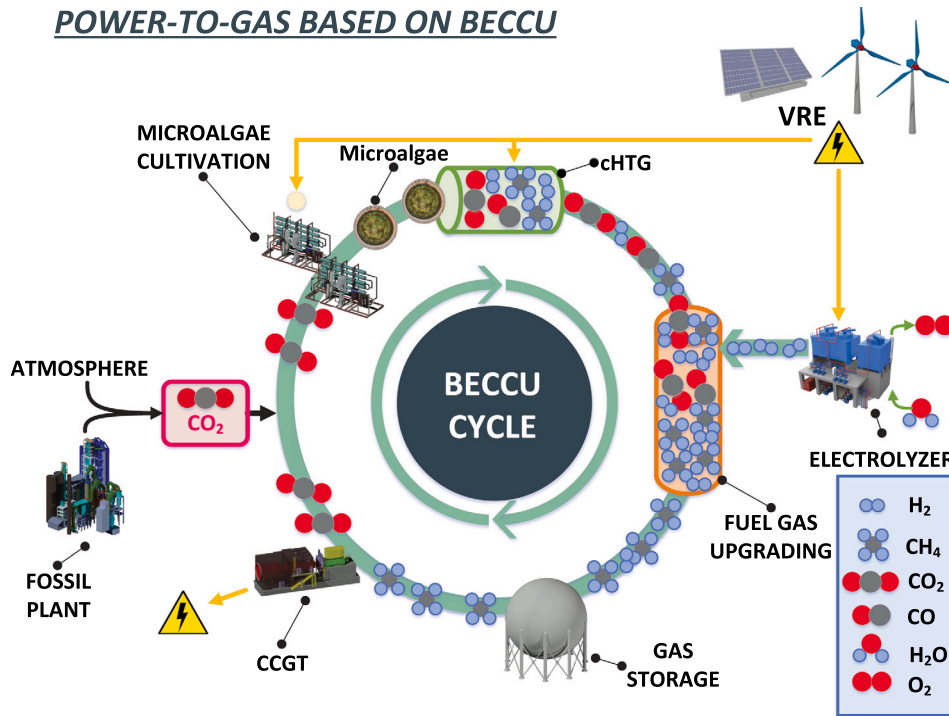


Fig. 1. CO<sub>2</sub> utilisation pathway via the combination of Power-to-Power round-trip and Bioenergy with Carbon Capture and Utilisation cycle. cHTG: catalytic hydrothermal gasification, VRE: variable renewable electricity, CCGT: combined cycle gas turbine.

### 2.3. Biogas upgrading and energy analysis

The flowsheeting and energy analysis were performed with ASPEN Plus V10.0 software [41]. Microalgae biomass was defined as a non-conventional solid; component attributes were specified based on proximate analysis and elemental composition. Proximate analysis of biomass feedstock was performed by burning samples according to the standards of the American Society for Testing Materials (ASTM): D3172 (fixed carbon), D3174 (ash) and D3175 (volatile matter content). The results of the proximate analysis are presented in Table S1. Predictive Soave–Redlich–Kwong (PSRK) property method was selected for the calculation of phase equilibria because the water was involved in the flowsheeting procedure above its supercritical point. The cHTG process was modelled based on the determined quadratic polynomial equations derived from the results of the RSM method. Energy recovery was examined by using the high-temperature cHTG product stream to evaporate working fluids in Rankine- (RC), and Organic Rankine Cycles (ORC). Energy losses were considered during the operation, assuming isentropic expansion in RC and ORC turbines with an efficiency of 0.8 [42]. The Langmuir–Hinshelwood–Hougen–Watson (LHHW) kinetic approach was used for the simulation of carbon oxides reduction. The catalytic methanation reactions were considered to be (1) CO hydrogenation, Eq. S1; (2) Water–gas shift reaction Eq. S6 [43]; and (3) Sabatier-reaction, Eq. S13 [44]. The applied kinetic equations and constants (Eq. S1–Eq. S18) are listed in Table S2.

The required amount of hydrogen for the methanation of carbon oxides was determined by calculating the syngas modular (Eq. (5)) [45]:

$$M(\text{H}_2)(-) = \frac{Z_{\text{H}_2} - Z_{\text{CO}_2}}{Z_{\text{CO}} + Z_{\text{CO}_2}} \quad (5)$$

where  $M(\text{H}_2)(-)$  is the syngas modular,  $Z_{\text{H}_2}$ ,  $Z_{\text{CO}_2}$ ,  $Z_{\text{CO}}$  stand for the molar fraction of hydrogen, carbon dioxide and carbon monoxide (-). The corrected syngas modular ( $M'(\text{H}_2 - \text{H}_{2,HTG})(-)$ ) was calculated based on Eq. (6):

$$M'(\text{H}_2 - \text{H}_{2,HTG})(-) = \frac{Z_{\text{H}_2} - Z_{\text{H}_{2,HTG}} - Z_{\text{CO}_2}}{Z_{\text{CO}} + Z_{\text{CO}_2}} \quad (6)$$

where  $Z_{\text{H}_{2,HTG}}$  is the H<sub>2</sub> molar fraction of the biogas (-).

The energy input for water electrolysis was determined by Eq. (7):

$$E_{\text{H}_2} (\text{kWh}) = [M(\text{H}_2)(Z_{\text{CO}} + Z_{\text{CO}_2}) + Z_{\text{CO}_2}] \cdot m_{\text{GAS}} \cdot E_{\text{AEL}}, \quad (7)$$

where  $E_{\text{H}_2}$  is the required energy for hydrogen production (kWh),  $M(\text{H}_2)$  is the syngas modular (-),  $Z_{\text{CO}}$  and  $Z_{\text{CO}_2}$  are the molar fractions of CO and CO<sub>2</sub> (-),  $m_{\text{GAS}}$  is the total weight of the gas stream (kg),  $E_{\text{AEL}}$  is the energy consumption of the alkaline electrolysis (AEL) technology (kWh) which is estimated to be 3.5 kWh Nm<sup>-3</sup> H<sub>2</sub> in the case of part-load operation [46].

The power requirement of the circulation in the microalgae cultivation system was estimated based on Eq. (8) [47]:

$$E_{tPBR} (\text{W}) = (v\pi r^2) \Delta P \cdot \left( \frac{k_{\beta} a}{\sqrt{f_m d^{-1}}} \cdot D + l \right), \quad (8)$$

where  $\Delta P$  is the pressure drop (Pa m<sup>-1</sup>) that was considered to be 58.6 Pa m<sup>-1</sup> for straight tubes,  $r$  is the radius of the tube (m),  $v$  is the velocity of the media (m s<sup>-1</sup>),  $D$  is the pipe diameter (m),  $f$  is the Blasius friction factor (-),  $k_{\beta}$  is a correction factor that is determined by the elbow's degree,  $a$  is the roughness and  $l$  is the length of the tubular PBR (m). In the case of 90° the value of  $k_{\beta}$  is equal to 1.

The energy gain burning the produced biogas was determined by Eq. (9):

$$E_{\text{biogas}} (\text{kWh}) = \sum (m_i \cdot \frac{LHV_i}{3.6}), \quad (9)$$

where  $E_{\text{biogas}}$  is the retrieved energy by burning biogas (kWh),  $m_i$  is the weight of the gas components (kg),  $LHV_i$  is the lower heating value of the gas components (CH<sub>4</sub>=50.0 MJ kg<sup>-1</sup>, C<sub>2</sub>H<sub>4</sub>=47.195 MJ kg<sup>-1</sup>, C<sub>2</sub>H<sub>6</sub>=47.622 MJ kg<sup>-1</sup> and H<sub>2</sub>=119.96 MJ kg<sup>-1</sup>).

The net energy ratio (NER, -) was calculated based on Eq. (10):

$$NER (-) = \frac{\sum E_{\text{out},i}}{\sum E_{\text{in},j}}, \quad (10)$$

where  $\sum E_{\text{out},i}$  is the total energy gained during the conversion (kWh),  $\sum E_{\text{in},j}$  is the total energy invested into the storage chain (kWh).



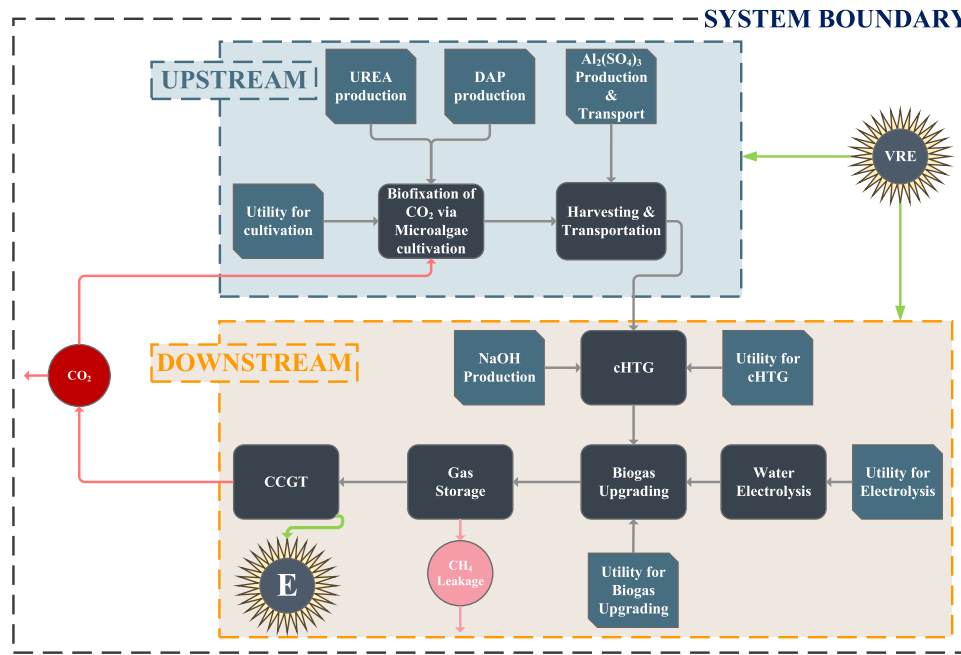


Fig. 2. Life cycle system boundary of the Power-to-Power round trip based on bioenergy with carbon capture and utilisation. VRE: variable renewable electricity, E: Electricity.

The overall-round-trip-efficiency of the Power-to-Power storage chain was determined by Eq. (11):

$$\eta_{BECCU} (-) = \frac{E_{CCGT} \cdot \eta_{CCGT} + E_{TURB}}{\sum E_{in,j}}, \quad (11)$$

where  $\eta_{BECCU} (-)$  represents the overall efficiency of the proposed Power-to-Gas energy storage chain based on bioenergy with carbon capture and utilisation,  $E_{CCGT}$  is the produced energy by burning fuel gas in combined cycled gas turbine (kWh),  $\eta_{CCGT}$  is the efficiency of the combined cycle gas turbine (CCGT) (-),  $E_{TURB}$  is the generated electricity in the Rankine and Organic Rankine cycles (kWh). The efficiency of the CCGT was estimated to be 64% [15].

Hot and cold utilities were considered in the energy analysis. Electrical heating was assumed for hot utilities. In the case of cold utility, cooling water was used from river or lake, and the availability was estimated unlimited at 20 °C [48]. Cooling utilities were calculated and incorporated in the overall round-trip efficiency under 20 °C.

#### 2.4. Cost estimation

ASPEN Process Economic Analyzer v10 was applied for the estimation of equipment cost. Table 1 shows the cost evaluation specifications for the bio-synthetic BECCU plant. The annualised capital expenditure ( $C_{CAPEX}$ ) was determined by Eq. (12):

$$C_{CAPEX} (\text{€}) = TPC \cdot CRF(N, R_i), \quad (12)$$

where TPC is the Total Plant Cost (€),  $CRF(N, R_i)$  is the Capital Recovery Factor (-). CRF was calculated based on Eq. (13):

$$CRF(N, R_i)(-) = \frac{R_i \cdot (1 + R_i)^N}{(1 + R_i)^N - 1}, \quad (13)$$

where N is the estimated lifetime of the BECCU plant (y),  $R_i$  is the rate of interest. The Total Annual Cost (TAC) was determined by Eq. (14):

$$TAC (\text{€y}^{-1}) = C_{CAPEX} + C_{OPEX}, \quad (14)$$

where  $C_{OPEX}$  is the operation and maintenance expenditure for one year ( $\text{€y}^{-1}$ ).

Table 1

Input data for total annual cost evaluation of Power-to-synthetic natural gas conversion pathway using catalytic hydrothermal gasification for biomass valorisation. TPC: Total Plant Cost (€).

Element	Value	Unit	Source
Estimated plant lifetime (N)	25	y	Current estimation
Working hours in a year	8000	h	Current estimation
Rate of Interest ( $R_i$ )	5	%	Current estimation
Installation Cost	15	% of TPC (€)	[49]
Maintenance and chemicals	1.5	% of TPC (€)	[50]
General expense	0.5	% of TPC (€)	[50]
Ordinary and extraordinary expense	1.5	% of TPC (€)	[50]
Cost of microalgae cultivation	440	$\text{\$ t}_{biomass}^{-1}$	[51]
CAPEX of a 10 MW $\text{H}_2\text{O}$ electrolyser	650	$\text{€ kW}^{-1}$	[52]
$\text{CO}_2$ tax	30	$\text{\$ t}_{\text{CO}_2}^{-1}$	[53]
USD/EUR exchange rate	0.85	-	Current estimation

#### 2.5. Environmental analysis

Early-stage sustainability analysis of BECCU cycle was carried out to quantify GHG footprint [54] and additional mid-, and endpoint environmental impacts. Life cycle assessment was performed using SimaPro v8.5.2. Life Cycle Inventory (LCI) was composed based on the Ecoinvent V3.4 database, experimental and simulation data. The life cycle boundary is illustrated in Fig. 2. The results of the LCI was collected in Table 2. The impact assessment was performed by the multi-purpose IMPACT 2002+ V2.14 method to evaluate mid-, and endpoint impacts. The uncertainty of input and output data was examined by Monte Carlo analysis with 10,000 number of runs using a 95% confidence interval.

### 3. Results

#### 3.1. Hydrothermal valorisation of wet biomass

Following the biofixation of  $\text{CO}_2$  and the cultivation of biomass, the wet microalgae are decomposed in hot compressed water into small gaseous molecules – fuel gas – via catalytic hydrothermal gasification. The cHTG gas mixture contains several compounds ranging from  $\text{H}_2$

**Table 2**

Summarising life cycle inventory of the Power-to-Gas-to-Power storage cycle based on Bioenergy with Carbon Capture and Utilisation. Data refer to 1 t of algae suspension with 12.5 wt% dry weight content.

Process	Value	Unit	Source
Microalgae suspension (DW = 12.5%)	1.000E+03	kg	Current estimation
Biofixation of CO <sub>2</sub>	2.034E+02	kg	Current estimation
Make-up CO <sub>2</sub>	3.320E+01	kg	Current calculation
Circulation in tPBR	1.935E+01	kWh	[47,55]
UREA production	8.688E+00	kg	[56]
UREA production	2.398E+01	kWh	Ecoinvent V3.4 database
DAP production	5.969E+00	kg	[56]
DAP production	2.132E+01	kWh	Ecoinvent V3.4 database
Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> for harvesting	4.220E-02	kg	[57]
Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> production	1.536E-01	kWh	Ecoinvent V3.4 database
Transportation of Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	1.000E+02	tkm	Ecoinvent V3.4 database
Transportation of algae suspension	1.000E+02	tkm	Ecoinvent V3.4 database
cHTG energy input (reactor+pump+RC)	8.979E+02	kWh	Current simulation
Required NaOH catalyst	3.300E+01	kg	Current estimation
NaOH production	3.847E+01	kWh	Ecoinvent V3.4 database
Energy gain through RCs	1.486E+02	kWh	Current simulation
Biogas upgrading utility	1.221E+02	kWh	Current simulation
H <sub>2</sub> production	4.830E+02	kWh	Current estimation
H <sub>2</sub> from external sources	1.117E+01	kg	Current estimation
Methane transmission & leakage from storage	1.100E+0	%	[58]
Gas turbine, 10MW	8.531E-07	pt	Ecoinvent V3.4 database
Emitted CO <sub>2</sub> due to Fuel Gas combustion	1.702E+02	kg	Current estimation
Assumed Wind/PV ratio	0.745:0.255	-	Current estimation

**Table 3**

The applied Central Composite Design (CCD) of the experiment (4 factors in 5 levels) and experimental results (fuel gas composition, total gas yield and carbon conversion ratio) of the catalytic hydrothermal gasification process.

Temperature (° C)	Pressure (MPa)	DW <sub>algae</sub> (wt.%)	C <sub>NaOH</sub> (wt.%)	H <sub>2</sub> (mol%)	CH <sub>4</sub> (mol%)	CO <sub>2</sub> (mol%)	CO (mol%)	C <sub>2</sub> H <sub>4</sub> (mol%)	C <sub>2</sub> H <sub>6</sub> (mol%)	Y <sub>GAS</sub> (mol kg <sup>-1</sup> )	CCR (%)
675.0	28.5	12.5	3	34.5356	14.7560	40.4286	2.8623	0.7697	6.6478	27.16	46.33
700.0	32.0	17.5	1.5	31.1290	11.0177	45.9269	3.9433	0.5734	7.4096	21.46	39.42
717.0	28.5	12.5	3	26.9428	20.2153	40.1761	5.1040	0.4192	7.1428	38.79	75.56
675.0	28.5	12.5	5.52	43.6131	16.7371	24.9183	1.7281	2.6459	10.3575	20.97	31.53
700.0	32.0	7.5	1.5	34.9599	12.7186	40.2784	3.1930	1.8110	7.0390	34.06	59.09
675.0	28.5	12.5	0.48	34.5366	11.5893	43.3699	3.2444	0.7561	6.5037	22.22	38.80
675.0	28.5	12.5	3	32.0493	15.3224	43.4457	2.9875	0.6234	5.5718	24.74	44.88
675.0	28.5	4.09	3	55.0620	11.4546	22.7543	4.4372	0.6117	5.6802	47.05	56.38
675.0	28.5	20.91	3	39.8922	10.9016	38.2006	4.0221	0.7906	6.1929	11.57	18.54
675.0	22.6	12.5	3	39.2971	10.5808	40.7066	2.1041	0.8178	6.4937	29.35	47.51
700.0	25.0	7.5	4.5	52.8598	9.0896	29.6545	2.6561	0.5924	5.1475	34.50	43.37
700.0	25.0	17.5	4.5	42.6712	8.3478	39.4362	3.3685	0.5593	5.6170	17.59	26.90
650.0	25.0	17.5	1.5	31.2901	12.8931	47.3807	2.3757	0.8404	5.2200	17.18	31.48
650.0	32.0	17.5	4.5	40.1217	8.2645	43.6689	2.3531	0.4822	5.1096	23.98	38.29
675.0	34.4	12.5	3	38.0896	11.2575	42.0606	1.3290	0.5417	6.7216	34.05	56.21
650.0	32.0	7.5	4.5	53.1096	13.2217	23.5116	2.2119	0.7675	7.1777	39.19	49.01
650.0	25.0	7.5	1.5	46.9333	11.4601	31.1824	3.0431	0.9276	6.4536	21.80	30.85
632.9	28.5	12.5	3	33.9309	15.5986	43.0118	1.9989	0.7742	4.6856	22.17	39.05

to C<sub>1</sub>-C<sub>2</sub> components depending on the reaction conditions (as it is detailed in Table 3 along with the employed design of experiment).

The gas composition and yields can be controlled and influenced in the process, and this flexibility in the operation enhances the applicability of HTG through the production of biomethane, ethane and hydrogen. Natural gas consists of mainly methane and thus integration of hydrothermal gasification to the currently existing gas infrastructure demands high feedstock conversion selectivity towards CH<sub>4</sub>. Consequently, the key objectives of the cHTG process are to obtain high methane yield along with enhanced carbon conversion ratio. In order to achieve these goals, the mathematical correlation between the gas components and reaction parameters was examined and determined. Quadratic polynomial statistical models and analysis of variance were applied to evaluate the effects and statistical significance of reaction conditions and to determine how the quality of fuel gas mixture can be increased. The ANOVA table and model's regression coefficients are presented in case of all dependent variables in Table 4 and Table S3.

The statistical analysis shows that cHTG temperature (L) is a significant factor ( $p < 0.05$ ) that is characterised by high Fischer's variance ratio [59] with low probability in the cases of H<sub>2</sub> (F = 14.902, p

= 0.031), CO (F = 60.919, p = 0.004) mole fractions and carbon conversion ratio (F = 11.914, p = 0.041).

It is found that the system pressure (Q) has significant effect on the H<sub>2</sub> (F = 34.062, p = 0.010), CH<sub>4</sub> (F = 14.444, p = 0.032) and CO (F = 32.302, p = 0.011) mol%. It is determined that the biomass-to-water ratio has decisive effect on H<sub>2</sub> (L: F = 239.499, p = 0.001; Q: F = 162.195, p = 0.001), CH<sub>4</sub> (Q: F = 13.188, p = 0.036), CO<sub>2</sub> (L: F = 78.709, p = 0.003; Q: F = 14.952, p = 0.031), CO (Q: F = 26.510, p = 0.014) mole fractions, on total gas yield (L: F = 30.313, p = 0.012) and CCR (L: F = 15.799, p = 0.028).

The statistical analysis demonstrates that the catalyst-to-suspension ratio influences significantly the H<sub>2</sub> (L: F = 25.139, p = 0.015; Q: F = 38.410, p = 0.008), CO<sub>2</sub> (L: F = 26.685, p = 0.014), CO (L: F = 14.528, p = 0.032) and C<sub>2</sub>H<sub>4</sub> (L: F = 17.115, p = 0.026) mole fractions.

The acceptability of statistical models was screened by lack-of-fit tests and graphical methods. The lack-of-fit test were found to be insignificant ( $p > 0.05$ ) in all cases (H<sub>2</sub> (mol%): F = 0.2952, p = 0.7929; CH<sub>4</sub> (mol%): F = 31.7813, p = 0.1245; CO<sub>2</sub> (mol%): F = 1.6024, p = 0.4877; CO (mol%): F = 14.6613, p = 0.1816; C<sub>2</sub>H<sub>4</sub> (mol%): F = 14.1317, p = 0.1849; C<sub>2</sub>H<sub>6</sub> (mol%): F = 1.8944, p = 0.4570, Y<sub>GAS</sub> (mol kg<sup>-1</sup>): F = 14.2720, p = 0.1840; CCR: F = 79.3944, p = 0.0791)

**Table 4**

Analysis of variance (ANOVA) table for the high temperature catalytic hydrothermal gasification of *Spirulina plantensis*. A *p*-value less than 0.05 indicates significant factor effects. df = degree of freedom, SS = Sum of Squares.

Source	df	H <sub>2</sub> (mol%)			CH <sub>4</sub> (mol%)			CO <sub>2</sub> (mol%)			CO (mol%)		
		SS	F-value	p-value	SS	F-value	p-value	SS	F-value	p-value	SS	F-value	p-value
<b>Linear (L)</b>													
X <sub>1</sub> : Temperature (° C)	1	24.417	14.902	0.031	10.657	3.087	0.177	4.021	0.630	0.485	4.821	60.919	0.004
X <sub>2</sub> : Pressure (MPa)	1	0.729	0.445	0.552	0.229	0.066	0.813	0.917	0.144	0.730	0.300	3.796	0.147
X <sub>3</sub> : DW <sub>algae</sub> (wt.%)	1	392.440	239.499	0.001	3.483	1.009	0.389	170.232	78.709	0.003	0.004	0.053	0.833
X <sub>4</sub> : c <sub>NaOH</sub> (wt.%)	1	41.192	25.139	0.015	13.250	3.838	0.145	502.113	26.685	0.014	1.150	14.528	0.032
<b>Quadratic (Q)</b>													
X <sub>1</sub> <sup>2</sup>	1	6.453	3.938	0.141	1.992	0.577	0.503	3.585	0.562	0.508	0.392	4.952	0.112
X <sub>2</sub> <sup>2</sup>	1	55.813	34.062	0.010	49.863	14.444	0.032	2.685	0.421	0.563	2.556	32.302	0.011
X <sub>3</sub> <sup>2</sup>	1	265.771	162.195	0.001	45.527	13.188	0.036	95.387	14.952	0.031	2.098	26.510	0.014
X <sub>4</sub> <sup>2</sup>	1	62.939	38.410	0.008	9.783	2.834	0.191	50.973	7.990	0.066	0.443	5.597	0.099
<b>Interaction</b>													
X <sub>1</sub> by X <sub>2</sub>	1	27.063	16.516	0.027	23.733	6.875	0.079	12.261	1.922	0.260	0.139	1.762	0.276
X <sub>1</sub> by X <sub>3</sub>	1	26.687	16.287	0.027	0.146	0.042	0.850	54.735	8.580	0.061	0.494	6.248	0.088
X <sub>1</sub> by X <sub>4</sub>	1	6.922	4.224	0.132	0.172	0.050	0.838	0.327	0.051	0.836	0.229	2.889	0.188
X <sub>2</sub> by X <sub>3</sub>	1	10.154	6.197	0.089	6.751	1.956	0.256	0.004	0.001	0.982	0.090	1.132	0.365
X <sub>2</sub> by X <sub>4</sub>	1	2.384	1.455	0.314	12.675	3.672	0.151	13.752	2.156	0.238	0.917	11.586	0.042
X <sub>3</sub> by X <sub>4</sub>	1	1.714	1.046	0.382	3.687	1.068	0.377	8.186	1.283	0.340	0.074	0.938	0.404
Error	3	4.916			10.356			19.138			0.237		
Total SS	17	1148.418			160.642			1048.085			16.383		
R <sup>2</sup>			0.99572			0.93553			0.98174			0.98551	
Source	df	C <sub>2</sub> H <sub>4</sub> (mol%)			C <sub>2</sub> H <sub>6</sub> (mol%)			Y <sub>GAS</sub> (mol kg <sup>-1</sup> )			CCR (%)		
		SS	F-value	p-value	SS	F-value	p-value	SS	F-value	p-value	SS	F-value	p-value
<b>Linear (L)</b>													
X <sub>1</sub> : Temperature (° C)	1	0.063	0.604	0.494	3.019	3.267	0.168	138.158	4.813	0.116	666.618	11.914	0.041
X <sub>2</sub> : Pressure (MPa)	1	0.038	0.365	0.588	0.026	0.028	0.878	11.023	0.384	0.579	37.834	0.676	0.471
X <sub>3</sub> : DW <sub>algae</sub> (wt.%)	1	0.132	1.265	0.343	0.187	0.203	0.683	870.159	30.313	0.012	883.938	15.799	0.028
X <sub>4</sub> : c <sub>NaOH</sub> (wt.%)	1	1.786	17.115	0.026	7.426	8.035	0.066	0.788	0.027	0.879	26.367	0.471	0.542
<b>Quadratic (Q)</b>													
X <sub>1</sub> <sup>2</sup>	1	0.100	0.956	0.400	1.155	1.250	0.345	5.998	0.209	0.679	73.199	1.308	0.336
X <sub>2</sub> <sup>2</sup>	1	0.046	0.444	0.553	0.055	0.059	0.823	15.440	0.538	0.516	3.787	0.068	0.812
X <sub>3</sub> <sup>2</sup>	1	0.036	0.343	0.599	1.098	1.188	0.356	1.058	0.037	0.860	240.702	4.302	0.130
X <sub>4</sub> <sup>2</sup>	1	1.047	10.032	0.051	3.906	4.226	0.132	69.202	2.411	0.218	334.674	5.982	0.092
<b>Interaction</b>													
X <sub>1</sub> by X <sub>2</sub>	1	2.020	19.359	0.022	7.752	8.388	0.063	29.192	1.017	0.388	10.145	0.181	0.699
X <sub>1</sub> by X <sub>3</sub>	1	0.101	0.967	0.398	2.144	2.320	0.225	11.687	0.407	0.569	84.814	1.516	0.306
X <sub>1</sub> by X <sub>4</sub>	1	0.097	0.933	0.405	0.730	0.790	0.440	14.020	0.488	0.535	54.750	0.979	0.395
X <sub>2</sub> by X <sub>3</sub>	1	0.246	2.357	0.222	0.109	0.118	0.754	4.932	0.172	0.706	26.408	0.472	0.541
X <sub>2</sub> by X <sub>4</sub>	1	0.096	0.922	0.408	1.092	1.181	0.357	60.092	2.093	0.244	237.272	4.241	0.132
X <sub>3</sub> by X <sub>4</sub>	1	0.127	1.213	0.351	0.068	0.073	0.804	27.734	0.966	0.398	8.287	0.148	0.726
Error	3	0.313			2.773			86.117			167.851		
Total SS	17	4.939			27.859			1428.154			3081.549		
R <sup>2</sup>			0.93662			0.90048			0.93970			0.94553	

proving that the applied models fit well on the experimental data. The R<sup>2</sup> of polynomial equations is found to be higher than 0.9 (as it is showed in Table 4). Moreover, model accuracy, normal distribution and homogeneity of variance were confirmed based on graphical evaluation in case of each dependent variable (as it is presented in Figures S2–S8).

Repeated cHTG measurements were carried out at random levels to verify RSM models. It is obtained that predicted values describe well experimental data affirming the applicability and robustness of statistical models (Fig. S9–S10).

The interaction between the effects of factor levels was investigated on 3D response surfaces (Fig. 3 and Fig. S11–S17). It is found that raised H<sub>2</sub> mole fraction (>41.5%) can be achieved either by applying high-temperature level (720 °C) with low system pressure (24.0 MPa) or

lower temperature with high pressure (640 °C, 34.0 MPa) at constant 12.5 wt% DW<sub>algae</sub> and 3 wt% NaOH concentration (Fig. 3(a)). Chen et al. [60] reported high H<sub>2</sub> yield (15.49 mol kg<sup>-1</sup>) at 540 °C using KOH catalyst. In our investigation, it is found that the hydrogen evolving rate can be boosted up to 25.91 mol kg<sup>-1</sup> with a maximum H<sub>2</sub> molar fraction of 55.06% at 675 °C using dilute algae suspension (4.09 wt%) in the process. It is determined that high temperature and pressure levels are favourable to achieve elevated methane (20.22%), ethane (10.36%) mole fractions and total gas yield (47.05 mol kg<sup>-1</sup>) (Figs. 3(b), S16 and 3(c)). High temperature, algae dry weight and catalyst-to-suspension ratio increase the carbon dioxide content of fuel gas even up to 45.93 mol% (Figure S13) elevating the required amount of hydrogen in the following methanation section. The experiments demonstrate that the

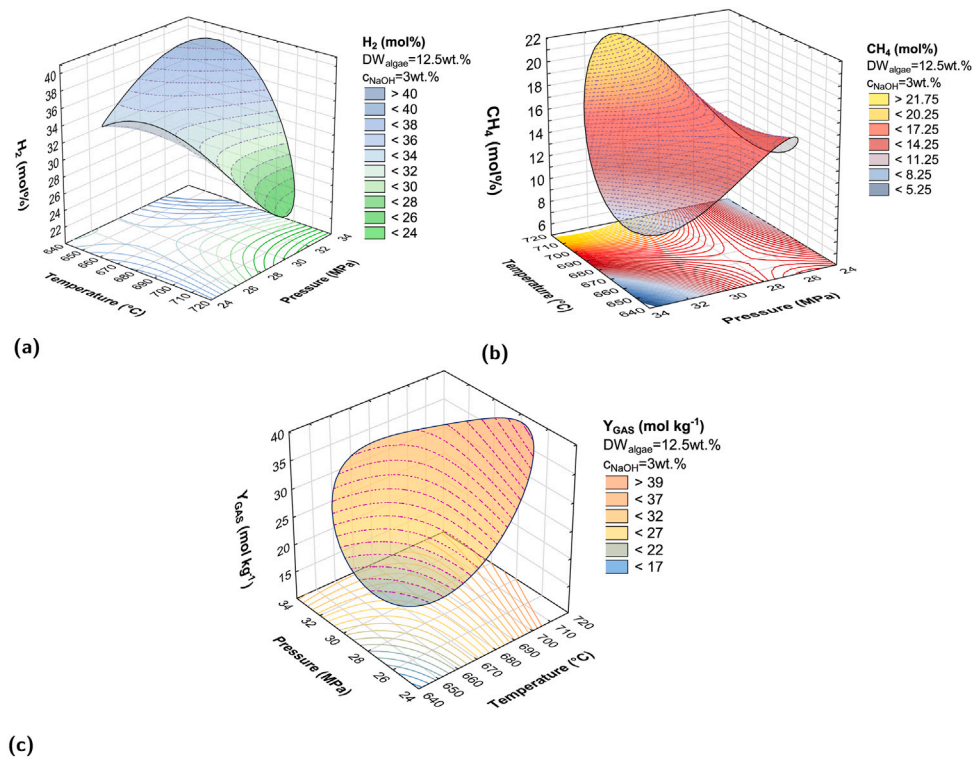


Fig. 3. Response surfaces fitted to the results of catalytic hydrothermal gasification (cHTG) in the case of (a) H<sub>2</sub> molar %, (b) CH<sub>4</sub> molar % and (c) Total Gas Yield (mol kg<sup>-1</sup>) to investigate interactions between the levels of reaction variables.

concentration of CO can be suppressed down below 5.10 mol% at elevated temperature and low NaOH concentration levels (Fig. S14).

The experimental results show that using elevated temperature regime during hydrothermal gasification is beneficial to boost component yields. The efficient operation of the Power-to-Methane chain demands high CH<sub>4</sub> yield that is coupled with an increased carbon conversion ratio. It was discussed by previous works that microalgae biomass could be converted into a multi-component gas product with various composition via HTG. Sztancs et al. [61] reported that the H<sub>2</sub>/CO molar ratio could be adjusted by process parameters. Okolie et al. [62] obtained 2.26 mol kg<sup>-1</sup> hydrogen yield at 500 °C gasifying biomass compounds and indicated that temperature settings have high a effect on the expected gas yield. Macr et al. [63] performed hydrothermal gasification on microalgae biomass and found that the transformation of high moisture containing feedstock improves energy performances. In order to achieve high VRE storage efficiency in line with low GHG emission rates, the targeted production of biogas should be prioritised. cHTG process optimisation was carried out to determine the highest achievable methane yield during operation. The result of desirability approach method indicates that the highest methane yield (8.97 mol kg<sup>-1</sup>) can be obtained at elevated temperature, pressure and catalyst-to-suspension ratio levels (as it is presented in Table 5). However, it is found that high CH<sub>4</sub> and H<sub>2</sub> yields are not coupled with increased carbon conversion ratio. Maintaining high CCR is inevitable to prevent carbon loss in the process. A sensitivity study was performed to investigate the relationship between the catalyst-to-suspension ratio and CCR. Fig. 4 shows that the methane yield grows monotonically by increasing the catalyst concentration. On the other hand, the CO<sub>2</sub> yield is declining by raising the level of catalyst. For these reasons, CCR can be described with a curve having a maximum point at 3.25 wt% NaOH concentration.

The application of homogeneous alkali catalyst enhances the evolution rate of H<sub>2</sub> (Fig. S11) which is preferable because *in-situ* formed cHTG hydrogen can be utilised in the second stage downstream conversion, i.e., biogas upgrading. The optimisation of cHTG process improves

the gas quality, but biogas upgrading is necessary for the production of high purity gaseous hydrocarbon stream that can be injected to the conventional natural gas grid.

### 3.2. Fuel gas upgrading via methanation

The CO<sub>2</sub> and CO content of fuel gas was upgraded to CH<sub>4</sub> using hydrogenation reactions to meet natural gas specifications (87.0 mol% < CH<sub>4</sub> < 96.0 mol%; CO<sub>2</sub> < 1.0 mol%) and to increase the heating value up to the range of 42–55 MJ kg<sup>-1</sup>. The results of LHHW kinetic simulation are presented in Fig. 5.

The methanation of carbon oxides was carried out in two steps as it is presented in Fig. S1. Sensitivity analyses were performed to determine ideal reaction conditions that ensure to (1) reach the required biogas quality and to (2) limit the utilisation of H<sub>2</sub> from external sources. Fig. 5(a) shows that cHTG biogas can be upgraded to a methane-rich stream (CH<sub>4</sub> mole fraction > 0.9) using temperature and pressure settings ranging from 260 to 340 °C and from 2 to 3 MPa.

The benefit of hydrothermal valorisation of wet biomass is that hydrogen evolving in the process as a co-product that can be used for methanation. The HTG process does not provide enough H<sub>2</sub> for the total conversion of carbon oxides. Therefore, in our investigation, the feed gas composition was enriched with additional hydrogen. It is assumed that H<sub>2</sub> is supplied from water electrolysis which is the crucial connection point that enables the combination of bioenergy with carbon emissions capture and utilisation and Power-to-Gas storage technologies. The amount of H<sub>2</sub> and the feed gas composition for methanation was determined based on the syngas modular.

Figs. 5(b) and 5(c) show that there is an interaction between the temperature and pressure process parameters and the syngas modular. It is found that the methane content of the final gas product can be increased from 22.4 mol% up to 95.8 mol% following the methanation of carbon oxides and the separation of ethane, ethylene and water. The highest methane mole fraction was achieved at 280 °C, 2.5 MPa applying a syngas modular of 2.31 (Fig. 5(b)). Within these conditions,



**Table 5**

Desirability approach based optimisation and subsequent sensitivity analysis of cHTG process to obtain the highest methane yield and to the increase carbon conversion ratio.

Objective	d (-)	Optimised value (mol kg <sup>-1</sup> )	Temperature (° C)	Pressure (MPa)	DW <sub>algae</sub> (wt.%)	c <sub>NaOH</sub> (wt.%)	
CH <sub>4</sub> (mol kg <sup>-1</sup> ) maximum	1.000	Y <sub>CH<sub>4</sub></sub> = 8.97	717.04	34.4	12.5	5.52	
The values of dependent variables at optimised levels							
H <sub>2</sub> (mol%)	CH <sub>4</sub> (mol%)	CO <sub>2</sub> (mol%)	CO (mol%)	C <sub>2</sub> H <sub>4</sub> (mol%)	C <sub>2</sub> H <sub>6</sub> (mol%)	Y <sub>GAS</sub> (mol kg <sup>-1</sup> )	CCR (%)
37.54	26.40	15.88	2.20	3.06	14.92	33.56	56.57
The values of dependent variables at 717 °C, 34.4 MPa, 12.5 wt% DW <sub>algae</sub> , 3.3 wt% NaOH							
H <sub>2</sub> (mol%)	CH <sub>4</sub> (mol%)	CO <sub>2</sub> (mol%)	CO (mol%)	C <sub>2</sub> H <sub>4</sub> (mol%)	C <sub>2</sub> H <sub>6</sub> (mol%)	Y <sub>GAS</sub> (mol kg <sup>-1</sup> )	CCR (%)
25.58	22.37	35.69	2.78	2.23	11.33	35.38	71.23

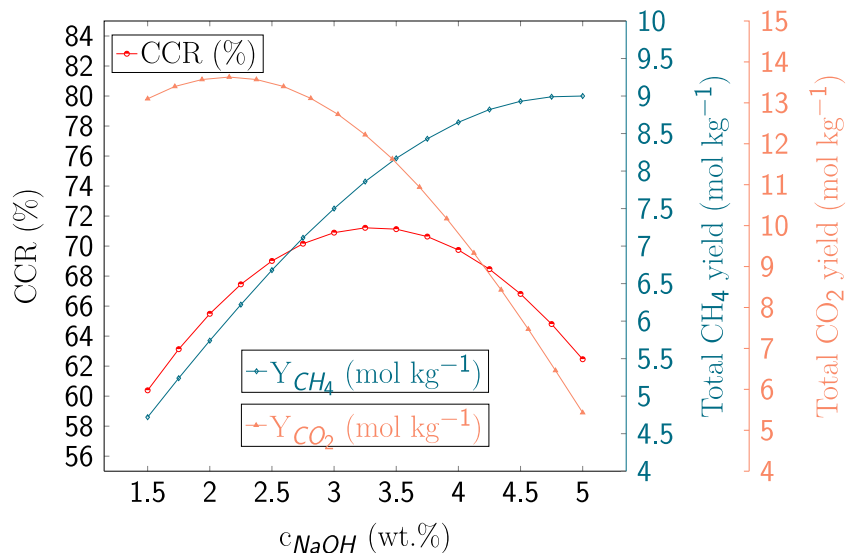


Fig. 4. Carbon Conversion Ratio, methane and carbon dioxide yields in the function of catalyst-to-suspension ratio at 717 °C, 34.4 MPa and 12.5 wt% DW<sub>algae</sub>.

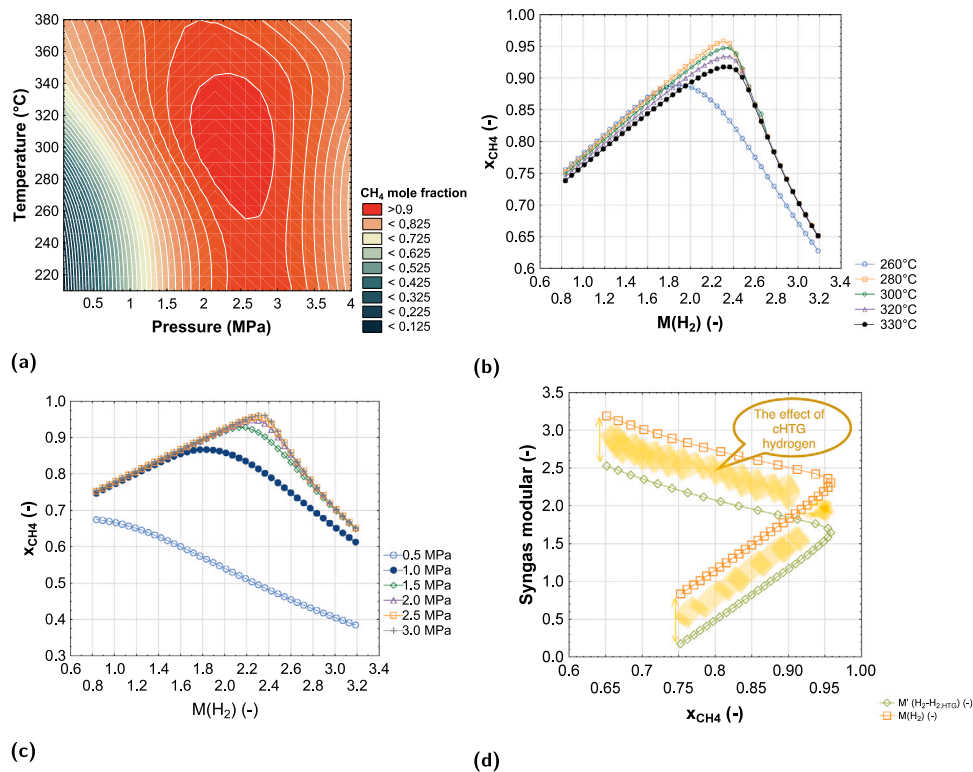


Fig. 5. The effects of independent variables on cHTG fuel gas upgrading. (a) Effects of methanation reaction parameters (temperature and pressure) on CH<sub>4</sub> molar fraction, (b) Effects of syngas modular and methanation temperature on CH<sub>4</sub> molar fraction at 2.5 MPa, (c) Effects of syngas modular and system pressure on CH<sub>4</sub> molar fraction at 280 °C, (d) The difference between syngas-, and corrected syngas modular.

**Table 6**

Summary of economic results. Data referred to the production and conversion of 1 t h<sup>-1</sup> microalgae suspension (DW: 12.5 wt%).

Element	Cost of SNG
<b>Cost of CO<sub>2</sub> biofixation</b>	55.5 €MWh <sup>-1</sup>
<b>Normalised CAPEX of 1st stage conversion: cHTG</b>	
Reactor	2.0 €MWh <sup>-1</sup>
High pressure pumping	33.6 €MWh <sup>-1</sup>
<b>Normalised CAPEX of 2nd stage conversion: Biogas upgrading</b>	
Reactors	0.7 €MWh <sup>-1</sup>
Heat exchangers	0.3 €MWh <sup>-1</sup>
Separators	1.6 €MWh <sup>-1</sup>
Compressor	11.0 €MWh <sup>-1</sup>
<b>Normalised CAPEX of energy recovery: RCs &amp; ORCs</b>	
Heat exchangers	1.4 €MWh <sup>-1</sup>
Pumps	2.6 €MWh <sup>-1</sup>
Turbines	5.6 €MWh <sup>-1</sup>
<b>Normalised CAPEX of water electrolyser</b>	3.9 €MWh <sup>-1</sup>
<b>Normalised OPEX</b>	26.7 €MWh <sup>-1</sup>
<b>Normalised total annual cost</b>	144.9 €MWh <sup>-1</sup>

the CO<sub>2</sub> concentration remains below 1 mol% (with an actual value of 0.987 mol%) while CO is present only in traces (<0.01 mol%) in the mixture. The syngas modular is corrected (Eq. (6)) based on the cHTG H<sub>2</sub> evolving rate to be able to determine the amount of hydrogen that is required from external sources. Fig. 5(d) shows that maintaining high H<sub>2</sub> yield in cHTG process decreases the H<sub>2</sub> supply ratio from external sources, and consequently, it has a positive effect on the Power-to-Methane energy transformation efficiency.

### 3.3. The energy performance of bio power-to-methane-to-power cycle

The biomass-based P2G technology can become viable only if the net energy ratio of wet biomass conversion is sufficiently high. The overall round-trip efficiency of the Power-to-Methane-to-Power process based on BECCU is determined by evaluating the energy flow of catalytic hydrothermal gasification, cHTG biogas upgrading and electricity production using combined cycle gas turbine. It is found that the two-stage downstream conversion of the wet organic feedstock and intermediate cHTG gas mixture offers good opportunities to lower intake energy demands and utilities by (1) increasing synergies between conversion stages and (2) applying energy recovery system.

As it is highlighted in Section 3.1, the elevated operational temperature has to be maintained during hydrothermal conversion to obtain increased total biogas yield with high methane content. In order to achieve high degrees of energy saving, the cHTG product stream (T<sub>S-105</sub> = 717 °C; P<sub>S-105</sub> = 34.4 MPa) is used to evaporate working fluids in Rankine cycles (RC) (Fig. S1). Additionally, Organic Rankine cycles (ORC) with propene, R-124 and n-pentane working fluids were applied

to recover waste heat in RCs and to increase overall P2G efficiency. The results show that Rankine cycles contribute significantly to the VRE storage efficiency with an electricity production share of 22.0%.

Upgrading biogas mixture involves the utilisation of exothermic methanation process that generates heat during operation. The reaction heat of methanation was used to superheat SORC-204 and SORC-205 streams after the HX-203 evaporator to increase electricity production and thus energy recovery. Heat integration is also applied between HX-204 and HX-304 to support the condensation of working fluid in the second RC.

The energy requirements and gains are listed for each operational unit in Table S4, while the energy flow is illustrated in a Sankey diagram (Fig. 6). The highest overall efficiency of the investigated bio-synthetic Power-to-Methane process including electricity production ( $\eta_{BECCU}$ ) is found to be 42.3%, and the alternative is outperforming pure chemical and biological P2M methods (as it is shown in Table 8). The elevated efficiency is obtained as a result of increased product yields of cHTG, moderate external H<sub>2</sub> supply ratio, enhanced synergies between the conversion stages and utilisation of RCs and ORCs. As it is presented in Fig. 6, the highest amount of energy is invested into the cHTG process (56.1%) which is followed by Water electrolysis (30.2%), Biogas Upgrading (7.6%) and Upstream section (6.1%). The energy analysis shows that fertiliser production (urea and diammonium phosphate (DAP)) takes the most significant part in the Upstream section with a share of 45.6%. The circulation in the photobioreactor cultivation system represents 19.6% energy requirement, while the transportation of aquatic biomass through pipeline and harvesting account to 22.7 and 12.1%, respectively. In the case of Biogas Upgrading, the 69.1% of energy requirement is paired with the methanation process, 19.1% is used for biogas pre-treatment while 11.8% for biogas purification and injection to the gas grid. Regarding the cHTG process, the highest energy demand (92.9%) is associated with the hydrothermal transformation, 4.3% is accounted for the production of NaOH homogeneous catalyst, and 2.8% is used for the operation of Rankine and Organic Rankine cycles.

### 3.4. Cost estimation of synthetic natural gas production via P2G based on BECCU

The economic evaluation of the bio-synthetic P2M is summarised in Table 6 and Fig. 7. The results show that the biofixation of CO<sub>2</sub> has the highest share of total annual cost with a value of 38.3%. The hydrothermal gasification of biomass takes the second place (24.6%) that is followed by the biogas upgrading (9.3%) and energy recovery processes (6.7%). The share of water electrolysis is found to be 2.7%. The low cost of electrolysis highlights the importance to boost the *in-situ* H<sub>2</sub> formation in the cHTG process. The normalised total annual cost of SNG production via bioenergy with carbon capture and CO<sub>2</sub> valorisation is amounted to 144.9 € MWh<sup>-1</sup>. Gorre et al. [52] reported SNG

**Table 7**

Multi-perspective environmental impact assessment of the Power-to-Gas-to-Power process based on BECCU using IMPACT2002+ V2.14 method. Functional Unit (FU) = 1 kWh retrieved electricity from storage. SD: standard deviation.

Impact category	Value	SD	Unit	IMPACT2002+ $\mu$ Pt kWh <sup>-1</sup>	Share (%)
Aquatic acidification	8.36E-04	7.57E-05	kg SO <sub>2,eq</sub>	-	-
Aquatic ecotoxicity	1.22E+01	3.12E+00	kg TEG water	4.44E-02	0.1
Aquatic eutrophication	6.33E-05	5.54E-05	kg PO <sub>4</sub> P-lim	-	-
Carcinogens	2.36E-03	3.78E-04	kg C <sub>2</sub> H <sub>3</sub> Cl <sub>eq</sub>	9.32E-01	1.9
Global warming	9.94E-02	1.26E-02	kg CO <sub>2,eq</sub>	1.00E+01	20.4
Ionising radiation	1.45E+00	9.23E-01	Bq C-14 eq	4.26E-02	0.1
Land occupation	2.14E-02	6.90E-03	m <sup>2</sup> org.arable	1.72E+00	3.5
Mineral extraction	1.78E-02	2.64E-03	MJ surplus	1.17E-01	0.2
Non-carcinogens	3.70E-03	1.19E-03	kg C <sub>2</sub> H <sub>3</sub> Cl <sub>eq</sub>	1.46E+00	3.0
Non-renewable energy	2.37E+00	2.36E-01	MJ primary	1.55E+01	31.6
Ozone layer depletion	1.87E-08	3.20E-09	kg CFC-11 eq	2.77E-03	0.0
Respiratory inorganics	1.77E-04	1.88E-05	kg PM <sub>2.5,eq</sub>	1.75E+01	35.6
Respiratory organics	6.14E-05	8.60E-06	kg C <sub>2</sub> H <sub>4,eq</sub>	1.84E-02	0.0
Terrestrial acid/nutri	2.82E-03	2.63E-04	kg SO <sub>2,eq</sub>	2.14E-01	0.4
Terrestrial ecotoxicity	2.73E+00	5.68E-01	kg TEG soil	1.57E+00	3.2

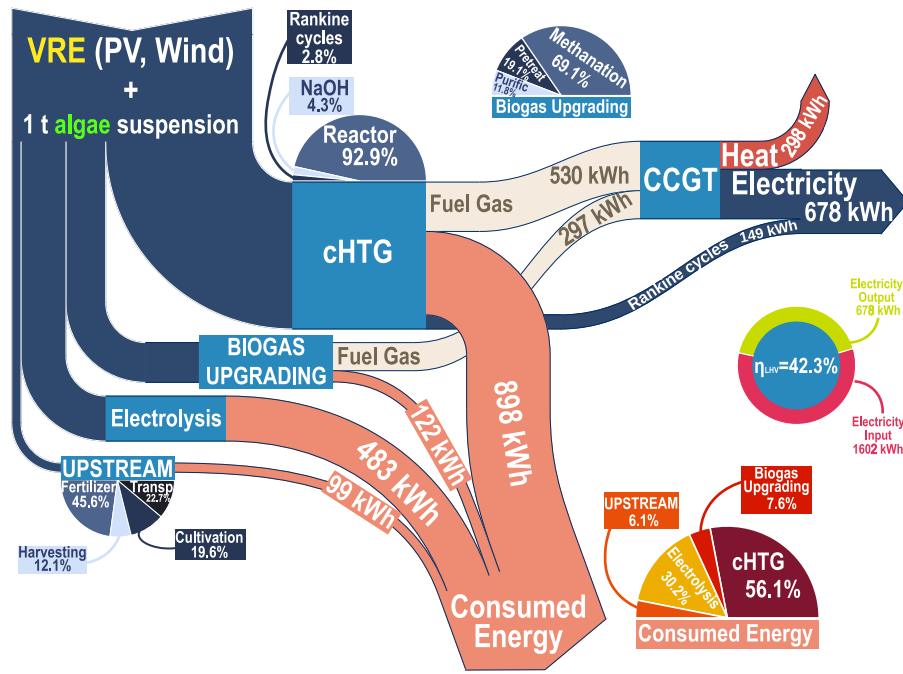


Fig. 6. Sankey diagram of the Power-to-Power round-trip storage chain based on BECCU, LHV: Lower Heating Value, VRE: Variable Renewable Energy, PV: photovoltaic, cHTG: catalytic Hydrothermal gasification, Pretreat: Biogas pretreatment, Purific: Gas purification, Transp: Transportation of feedstock.

Table 8

Comparing the greenhouse gas footprint and the efficiency of conventional and Power-to-X-to-Power electricity-producing technologies. BECCU: bioenergy with carbon capture and utilisation.

Technology	g CO <sub>2,eq</sub> kWh <sup>-1</sup>	η <sub>electricity</sub> (%)	Source(s)
Utilisation of brown coal	1,183	37.9	[64]
Utilisation of hard coal	1,142	36.7	[64]
Utilisation of natural gas	490–572	44.4	[64,65]
Power generation with biomass	130–420	–	[65]
Chemical Power-to-Methanol	150	–	[66]
Chemical Power-to-Methane	104 <sup>a</sup> , 191 <sup>b</sup> , 406, 562	18.2–36.6	[11,16,67–71]
Power-to-Methane based on BECCU	99.4 ± 12.6	42.3	Current research

<sup>a</sup>PtG wind.

<sup>b</sup>PtG PV.

production cost via P2M between 128 and 210 € MWh<sup>-1</sup>. Michailos et al. [72] investigated four P2G concepts based on biomethanation and atmospheric gasification and determined that the selling price of biomethane is in the range of 135–183 £MWh<sup>-1</sup>. These data show that the cost of Power-to-Methane production based on BECCU is in the similar range compared to other chemical and biological P2G alternatives. The high share of CO<sub>2</sub> biofixation indicates that cost reduction of microalgae cultivation could have positive effects on the normalised cost of P2G method. The same tendency can be expected in the case of catalytic hydrothermal gasification, where homogeneous and heterogeneous catalysts development could ensure to decrease further the cost of synthetic natural gas production.

### 3.5. Environmental evaluation of BECCU emission cycle

The environmental aspects of the bio-synthetic P2G technology are evaluated conducting a cradle-to-grave Life Cycle Analysis (LCA). The results of the impact assessment are summarised in Fig. 8 and Table 7. The mean GHG emission of the P2G based on BECCU is estimated to be only 0.0994 ± 0.0126 kg CO<sub>2,eq</sub> kWh<sup>-1</sup>. This low emission value outranks those Power-to-Gas alternatives that do not involve the biofixation of CO<sub>2</sub> (related data are collected in Table 8). Fig. 8(a) presents the GHG footprint distribution by processes. It is found that the highest carbon dioxide equivalent emission is paired with the combustion of produced fuel gas in CCGT (62.7%). The combustion of fuel gas is

identified as an environmental hot spot. The advantage of this emission element is that it can be described as a point CO<sub>2</sub> emission source. Conventional retrofit post-combustion capture technologies could be used to neutralise it.

The emission contribution of catalytic hydrothermal gasification is 11.0% that comes from utilities and the utilisation of VRE. The production of nitrogen fertiliser is found to be the third-largest emitter with a GWP share of 10.2%. Fertiliser production is generally characterised by significant CO<sub>2</sub> emissions [73]. The future development of sustainable fertiliser production technologies using PV and wind power (i.e., Power-to-Ammonia [74] and Power-to-Fertiliser [75]) could influence positively the environmental effects of P2G storage based on BECCU. The H<sub>2</sub> and NaOH production account to the 5.9 and 3.3% of the total GHG emission. These values highlight the importance of investigating various homogeneous and heterogeneous catalysts that can promote further *in-situ* H<sub>2</sub> formation in the cHTG process and decrease cumulative emission rates. The methane leakage from the long-term storage is estimated to correspond to 1.3% of the total emitted GHGs.

Monte Carlo analysis was performed to examine the uncertainty of inventory data. The analysis does not indicate serious outliers and demonstrates that random predicted trial values have amounted to the mean GWP value (Fig. 8(b)).

Multi-perspective impact assessment is also analysed using IMPACT 2002+ V2.14 LCIA method. The mid-, and endpoint LCA results are illustrated in Fig. 8(c). The endpoint impacts show that 41.0% of the

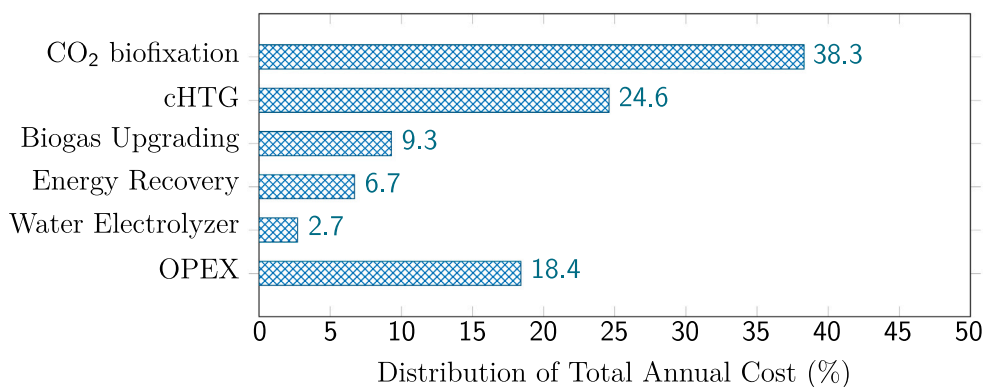


Fig. 7. Total annual cost distribution of Power-to-Methane conversion incorporating biological CO<sub>2</sub> mitigation via the cultivation of microalgae biomass and catalytic hydrothermal gasification for the valorisation of high moisture containing organic feedstock.

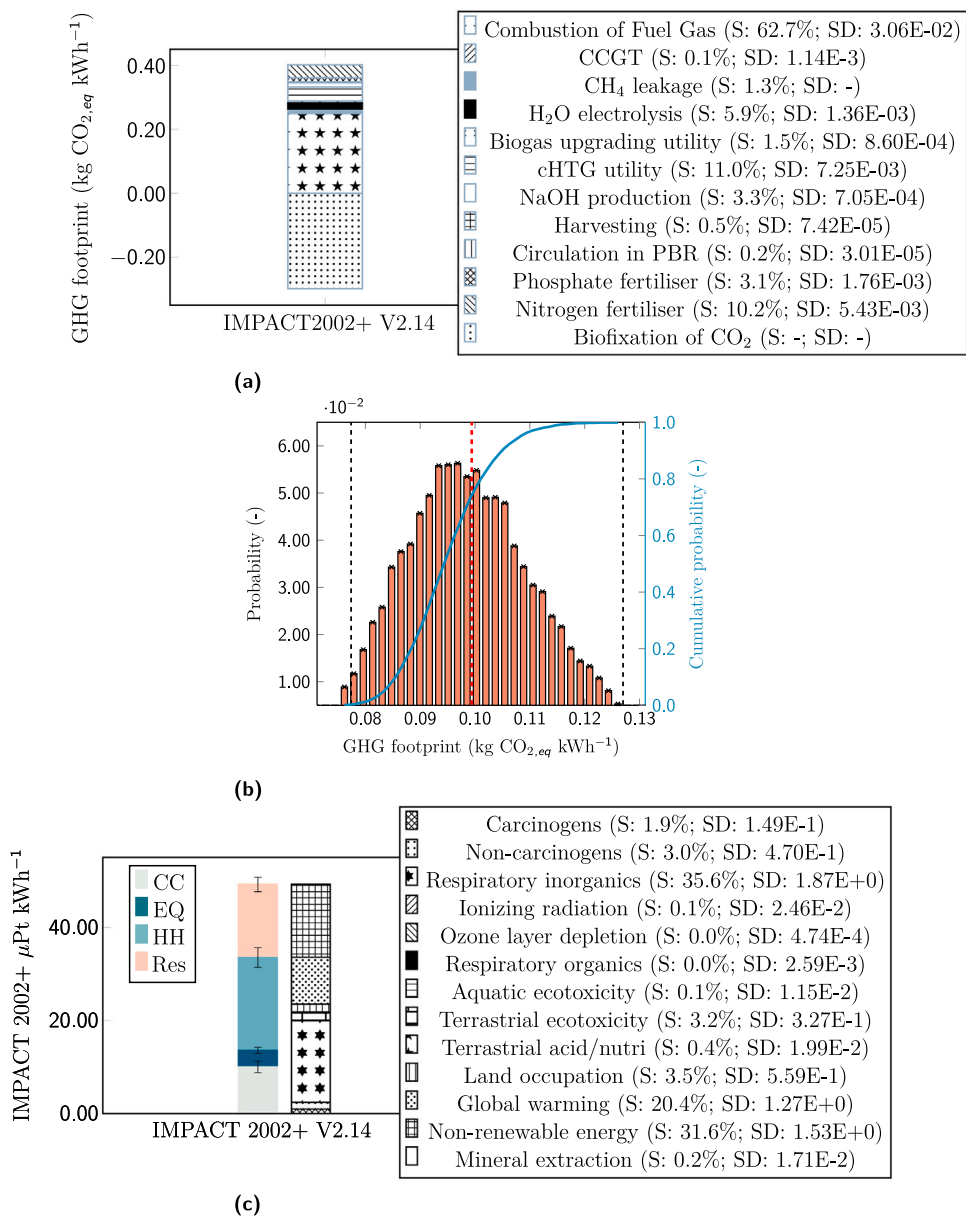


Fig. 8. Result of the LCA. (a) GHG footprint distribution by sub-processes, S: Share; SD: Standard Deviation (kg CO<sub>2,eq</sub> kWh<sup>-1</sup>) (b) Monte Carlo analysis of GHG footprint, black dashed lines indicate 95% confidence interval, red dashed line shows mean value, (c) Multi-perspective impact assessment using IMPACT2002+ V2.14 method indicating mid-, and endpoint LCA results. CC: Climate Change; EQ: Ecosystem quality; HH: Human Health; Res: Resources; S: Share; SD: Standard Deviation (μPt kWh<sup>-1</sup>).



total environmental damages are associated with human health due to the high emission of respiratory inorganics (Table 7). The Resources category takes second place with 31.2%, which is followed by Climate change (19.5%) and Ecosystem quality (7.3%) categories. The mid-point analysis shows that the most serious environmental damages are coupled with the emission of respiratory inorganics (36.0%) and the application of non-renewable energy sources (31.9%) that related to the production of fertilisers and NaOH catalyst. The multi-perspective environmental impact examination confirms that greener fertiliser production and the replacement of fossil energy carriers could potentially decrease further the environmental impacts of the P2G technology combined with BECCU.

#### 4. Discussion

Comparing the biomass-based P2G conversion pathway to conventional ones shows that the application of bioenergy with carbon capture and utilisation is an effective CO<sub>2</sub> valorisation method and a more favourable option regarding environmental impacts and VRE storage potentials. The obtained results indicate that 11.9-times less amount of CO<sub>2</sub> equivalent emission can be expected during the operation of the bio-synthetic P2G methodology in contrast to the utilisation of brown coal. At the same time, this value is 4.9 in the case of natural gas (Table 8). The P2G storage is already demonstrated using methanogens bacteria for the production of methane, but the technology is limited by the requirement of pure CO<sub>2</sub> feedstock substrate stream since these organisms cannot tolerate the presence of oxygen and toxic compounds of flue gas (NO<sub>x</sub>, SO<sub>x</sub>, heavy metals in traces). On the other hand, microalgae biomass can be utilised to capture CO<sub>2</sub> directly from the air or from flue gas. In this way, energy-intensive chemical-based carbon capture can be excluded from Power-to-X process configurations. Decentralised CO<sub>2</sub> recycling via photosynthesis offers large scale anthropogenic carbon sequestration capacities. The integration of high moisture containing biomass conversion and fuel gas upgrading to the Power-to-Methane process is an important stage of development towards energy system transition. This combination could be expanded to the application of organic carbon-rich waste feedstocks as potential CO<sub>2</sub> sources. The BECCU based Power-to-Gas alternative meets the low carbon emission target and outperforms the pure chemical and biological methanations with less than 100 g CO<sub>2,eq</sub> kWh<sup>-1</sup> GWP emission and with high round-trip efficiency (42.3%). The highest GHG emission of the BECCU P2G chain can be expected during energy retrieving where CO<sub>2</sub> is produced as a consequence of methane combustion. The neutralisation of this point source emission by available CDR technologies could lead to complete climate-neutral operation because the carbon dioxide equivalent emission contribution of this sub-process is higher than the expected overall emission rate of the BECCU cycle. The moderate cumulated CO<sub>2,eq</sub> value confirms that bioenergy with carbon capture should be considered in all kinds of energy-related applications that involve either the production of energy carriers or the storage of fluctuating renewable electricity because it contributes to achieving the transformation of energy industry towards a carbon emissions neutral operation. Combining the Power-to-Gas VRE storage system and bioenergy with carbon emission capture and utilisation (BECCU) offers several advantages over the chemical-based Power-to-Gas buffer chains:

- (i) Using biofixation for carbon dioxide removal (CDR) provides an effective method with low energy requirements compared to chemical-based carbon capture (e.g., absorption with amines, direct air capture) that improves overall VRE storage efficiency.
- (ii) It closes the carbon emission cycle which enables low-carbon emission operation.
- (iii) The reduction of carbon oxides requires less H<sub>2</sub> from external sources (i.e., water electrolysis) due to the high inner H<sub>2</sub> evolving rate in the cHTG process resulting in lower energy consumption and higher P2G operational efficiency.

- (iv) CO<sub>2</sub> utilisation becomes available directly from the air or through the injection of industrial flue gas sources to the microalgae culture broth.
- (v) It corrects the uncertainty paired with the fluctuating behaviour of renewable energy production and offers an efficient and clean path for a steady supply of renewable electricity.

#### 5. Conclusions

The widespread use of variable renewable electricity is limited by the fluctuation in their production, which has a different cycle than that of the consumption. In this work, we propose a novel Power-to-Gas energy storage method based on bioenergy with carbon capture and utilisation (BECCU) that serves as a buffer cycle to minimise the level of uncertainty in renewable energy production and offers an effective way for CO<sub>2</sub> utilisation. Presented electricity storage approach is characterised by low greenhouse gas footprint ( $99.4 \pm 12.6$  g CO<sub>2,eq</sub> kWh<sup>-1</sup>) that outperforms pure biological and chemical storage alternatives and prognosticates an essential future role in the transformation of the energy sector towards carbon neutrality. Simultaneously, it has been reported on superior energy storage round-trip efficiency compared to the currently available Power-to-Methane-to-Power methods. The achieved high electric efficiency is a consequence of (i) the utilisation of microalgae biomass for CO<sub>2</sub> removal, (ii) the effective transformation of wet organic feedstock with increased methane yield and carbon conversion ratio via catalytic hydrothermal gasification and (iii) the enhanced energy recovery and synergies between conversion stages.

#### CRedit authorship contribution statement

**Dániel Fózser:** Investigation, Conceptualization, Formal analysis, Visualization, Writing - original draft. **Mirco Volanti:** Resources. **Fabrizio Passarini:** Data curation. **Petar Sabev Varbanov:** Funding acquisition, Writing - review & editing. **Jiří Jaromír Klemeš:** Funding acquisition, Writing - review & editing. **Péter Mizsey:** Funding acquisition, Methodology, Writing - review & editing.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Acronyms	
ANOVA	Analysis of Variance
BECCU	Bioenergy with Carbon Capture and Utilisation
CAPEX	Capital Expenditure
CC	Climate Change
CCGT	Combined Cycle Gas Turbine
CCD	Central Composite Design
CCR	Carbon Conversion Ratio (%)
CDR	CO <sub>2</sub> removal
cHTG	Catalytic hydrothermal gasification
CRF	Capital Recovery Factor (-)
DAP	Diammonium phosphate
df	Degree of freedom
DW	Dry Weight (wt.%)
FU	Functional Unit
GHG	Greenhouse Gas
GWP	Global Warming Potential (kg CO <sub>2,eq</sub> )
HH	Human Health
HX	Heat exchanger
LCI	Life cycle inventory
LCIA	Life cycle impact assessment
LHHW	Langmuir–Hinshelwood–Hougen–Watson
LHV	Lower Heating Value (MJ kg <sup>-1</sup> )
LSL	Lower restrict value (-)
NER	Net Energy Ratio (-)
OPEX	Operation and maintenance expenditure for one year
ORC	Organic Rankine Cycle
P2G	Power-to-Gas
P2X	Power-to-X
P2M	Power-to-Methane
PV	Photovoltaic
RC	Rankine Cycle
RES	Renewable Energy Sources
Res	Resources
RSM	Response Surface Methodology
SNG	Synthetic Natural Gas
SORC	Input/Output stream of organic rankine cycle
SS	Sum of Squares
tPBR	Tubular photobioreactor
TAC	Total Annual Cost (€)
TPC	Total Plant Cost (€)
USL	Upper restrict value (-)
VRE	Variable Renewable Energy
Latin letters	
a	Roughness (-)
d <sub>i</sub>	Desirability value (-)
D	Diameter of pipe (m)
E <sub>H<sub>2</sub></sub>	Required energy for H <sub>2</sub> production (kWh)
EQ	Ecosystem Quality
E <sub>tPBR</sub>	Power requirement of tubular photobioreactor circulation (W)
f	Blasius friction factor (-)
F	Fischer's variance ratio (-)
k <sub>β</sub>	Correction factor related to the tubes elbow's degree (-)
l	Length of the tubular photobioreactor (m)
L	Linear
m <sub>algae</sub>	Mass of microalgae feedstock (kg)
M <sub>H<sub>2</sub></sub>	Syngas modular (-)
M'(H <sub>2</sub> – H <sub>2,HTG</sub> )	Corrected syngas modular (-)
m <sub>GAS,i</sub>	Mass of the ith gas component (kg)
MW <sub>C</sub>	Molar weight of carbon (kg kmol <sup>-1</sup> )
MW <sub>GAS,i</sub>	Molar weight of the ith gas component (kg kmol <sup>-1</sup> )

N	Estimated plant lifetime (years)
n <sub>GAS,k</sub>	Mole number of the kth biogas component (mol)
p	Probability (-)
ΔP	Pressure drop (Pa m <sup>-1</sup> )
Q	Quadratic
r	Radius of tube (m)
R <sub>i</sub>	Rate of interest (%)
S	Share
s	Shape constant (-)
v	Velocity of media (m s <sup>-1</sup> )
w <sub>C,algae</sub>	Carbon mass fraction of algae biomass (-)
x <sub>CH<sub>4</sub></sub>	Methane molar fraction (-)
Y <sub>GAS</sub>	Total gas yield (mol kg <sup>-1</sup> )
Ŷ <sub>z</sub>	Predicted response variable
Z <sub>H<sub>2</sub></sub> , Z <sub>CO<sub>2</sub></sub> , Z <sub>CO</sub>	Molar fraction of H <sub>2</sub> , CO <sub>2</sub> and CO (-)
Greek letters	
β <sub>0</sub> , β <sub>i</sub> , β <sub>ii</sub> , β <sub>ij</sub>	Regression coefficients of statistical models (-)
ε	Random error
η <sub>BECCU</sub>	Round-trip efficiency of BECCU (-)

## Appendix A. Supplementary data

Supplementary material related to this article can be found online at <https://doi.org/10.1016/j.apenergy.2020.115923>.

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