The investigation and improvement of hydrothermal gasification parameters on microalgal biomass

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The investigation of hydrothermal gasification (HTG) of microalgae biomass is carried out in order to produce biogas and upgrade its composition. Microalgae are suitable microbes which able to mitigate the negative environmental and social impacts of climate change, as well as capture and transform carbon dioxide into valuable compounds, such as biofuels.

In our work we investigated the role of temperature (525-575°C), pressure (250-280 bar), catalyst loading (5-15 w/w%) and ratio of homogenous catalysts (K_2CO_3/KOH) on biogas composition, gasification efficiency and total gas yield. *Chlorella vulgaris* is selected to cultivate and test as feedstock for HTG process. The biogas composition (H_2, CH_4, CO_2, CO) and the biological composition (CNHO, ash, volatile matter, fixed carbon) of the biomass arealso determined.

It is found that the application of homogenous catalyst mixture increasing significantly the biogas and hydrogen yields at elevated temperature level. The highest total gas yield is found to be 38.69 mmol g^{-1} while the H_2 yield is 24.69 mmol g^{-1} dry microalgae.

Through our work we attained high carbon gasification efficiency (>20%) and hydrogen yield in several cases. The experimental results are statistically evaluated and the main effects of influencing factors are determined.

INTRODUCTION

The application of fossil fuels affects unfavourably the environment due to the related emission of greenhouse gases such as CO_2 which contribute significantly to global climate change[1]. Moreover, the worldwide growing energy demand makes necessary the investigation of environmentally friendly, clean and sustainable processing pathways and energy sources[2]. Biomass (e.g., microalgae) is considered as a suitable substitute that provide abundant renewable energy.

Microalgae are cultivated in diluted suspension which brings difficulties at downstream processing because the evaporation of excess water requires immense energy which makes challenging economic operation[3]–[5]. Hydrothermal treatment of biomass received great attention recently because eliminates biomass drying-step and therefore contribute to more ecological processing of wet biomass[6].

Hydrothermal gasification (HTG) is a thermochemical process that produces biogas, containing mainly H_2, CH_4, CO_2 and CO where the constituent ratio can be controlled by reaction conditions. The process performed atelevated temperatures (up to 600°C)[7] and therefore the reduction of operation temperature is desirable to achieve energy efficient operation. One way to do so is applying catalysts. Homogenous catalysts such as alkali metals (K_2CO_3, KOH, Na_2CO_3, NaOH) already reported in literature in case of model compounds such as humic acids, cellulose, mannose, horse manure[8]–[13]. Catalysts can also be used for upgrading biogas improving their quality [14]. In this study we investigated the role of temperature, pressure, catalyst loading and the ratio of homogenous catalyst mixtures on biogas composition, carbon gasification efficiency and biogas yield.

MATERIALS AND METHODS

Microalgae cultivation

Chlorella vulgaris was purchased from the Mosonmagyaróvár Algal Culture Collection (Széchényi István University). BG11 medium was used for the fermentations with the following composition (in g L^{-1}): $NaNO_3$, 1.500; K_2HPO_4, 0.040; $MgSO_4 \cdot 7H_2O$, 0.075; $CaCl_2 \cdot 2H_2O$, 0.036; Citric acid, 0.006; $FeNH_4SO_4$, 0.006; $EDTANa_2$, 0.001; Na_2CO_3, 0.020 and 1 ml of trace metals solution[15].

The microalgae were cultivated in 4.25 L stirred tank reactors. Artificial irradiation was provided by an RGB-LED lighting platform (UTEX Culture Collection of Algae) where the illumination duration was set to 16:8 hours light and dark photoperiod. The light intensity was measured by a lux meter (IEC 6 LF 22, CosiluxTungram) and it was kept constant at 352 μmolphoton m^{-2} s^{-1}. The aeration was set to 1.00 vvm, where the air was filtered with a sterile filter (0.2 μm, PTFE, Sartorius Midisart 2000). An autoclave (3870ELV, Tauttnauer) was used for the sterilization of fermenter and media at 121°C for 20 minutes.

The fermentations were monitored by measuring optical density (OD) at 560 nm (Pharmacia LKB·Ultraspec Plus Spectrophotometer). Gravimetric method was applied to determine the dry weight of microalgae. 10 ml suspension was filtered through a nitrocellulose membrane (0.22 μm, MILLIPORE), and dried at 105°C for 2 hours. The dry weight was determined by Eq. 1:

$$DW = \frac{(A - B) \cdot 100}{SV} \quad (1)$$

where DW is the dry weight (g L^{-1}), A is the weight of the microalgae and the filter (g), B is the weight of filter (g), SV is the volume of algae suspension (ml).

The biomass concentration was determined with calibration based on the following equation:

$$DW = 0.3903 \cdot OD_{560} - 0.1560, R^2 = 0.9753. \quad (2)$$

The elemental composition of microalgae biomass was determined by Liebig- and Dumas-methods with LECO FP-528 analyzer. Proximate analysis was carried out based on ASTM D3172 (DENKAL 1.4/1000).

Hydrothermal gasification

The overall flowsheet of microalgae cultivation and hydrothermal gasification process performed in the experiments is shown in Figure 1. A 2 m length tubular reactor was placed in an oven where the pressure was generated and maintained with HPLC pumps (Jasco PU-980, Gilson Model 303). Throughout hydrothermal gasification the residence time and biomass concentration held constant at 120 sec and 2.6wt.%, respectively.

The composition of the produced biogas was determined by gas chromatography (HP5890A/TCD/FID, stainless steel column packed with Porapak Q 80/100 mesh, 1/8 inch OD, 1.9 m).

The carbon gasification efficiency (GE_C) was calculated by dividing the carbon content of the gas product and carbon content of the biomass (Eq. 3.).

$$GE_C(\%) = \frac{m_{C,gas}}{m_{C,feed} - m_{C,residue}}, \quad (3)$$

where $m_{C,gas}$ is the carbon contentof biogas (g min^{-1}), $m_{C,feed}$ is the carbon content of biomass, $m_{C,residue}$ is the carbon content of residue. The total carbon content of the residue was determined by Shimadzu TOC/VCSH.

The gasification yield was determined using the following equiation (Eq. 4.):

$$Y_{biogas} = \frac{n_{biogas}}{m_{biomass}}, \quad (4)$$

where Y_{biogas} is the total yield of biogas (mmol g^{-1}), n_{biogas} is the mole number of gas product (mmol), $m_{biomass}$ is the mass of dried biomass (g).

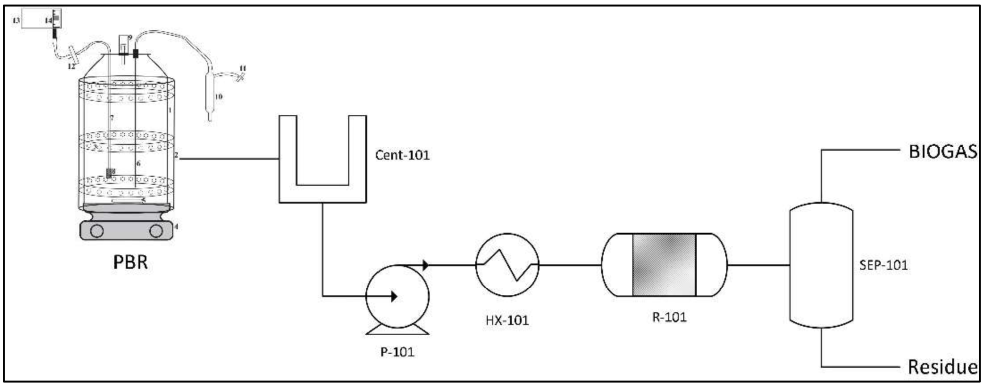

Fig. 1. Flowsheet of microalgae cultivation and hydrothermal gasification of *C. vulgaris* biomass.

Experimental design

Design of Experiments software Statistica 13.1 was used for planning the experiments andstatistical evaluation of the experimental results. $2^{(4-1)}$ fractional factorial design was applied for the investigation of factors such as temperature (525-575°C), pressure (250-280 bar), catalyst loading (5-15 wt.%) and catalysts (K_2CO_3 and KOH) ratio (2:1-1:2) on biogas composition, carbon gasification efficiency and biogas yield.

RESULTS

The proximate and ultimate analyses are presented in Table 1, the results of HTG experiments are listed in Table 2. Experiments were conducted under different temperature, pressure, catalyst loading and catalyst ratios. Non catalytic hydrothermal gasification of microalgae is also investigated for comparison purposes with catalytic HTG. It is found that applying homogenous catalyst increases hydrogen yield, while decreases CO and CO_2content of biogas which is in agreement with the findings of previous studies [9][13][16]. However, it turned out thatapplication of catalyst mixtures increase further the hydrogen yield compared to unmixedcatalysts.Applying elevated temperature and mixed homogenous catalystsraised hydrogen yield from 4.83 mmol g^{-1} to 24.69 mmol g^{-1}. The highest H_2 yield was achieved at 575°C, 280 bar, 15 wt.% catalyst loading, 2:1 catalyst ratio and it was found to be 24.69 mmol g^{-1} dry microalgae which is twice as high as reported with model compounds such as mannose [11], horse manure [10] or different heterogeneous catalysts [9].

In our findings the highest hydrogen yield paired with the highest total gas yield (38.69 mmol g^{-1}). The highest hydrogen mol fraction was 66.83 mol% at 525 °C, 250 bar, 15 wt.% catalyst loading and 2:1 catalyst ratio, though the total biogas yield was one of the lowest, only 12.55 mmol/g.

Tab.1. Proximate and elemental analysis of microalgae biomass.

Biomass	Proximate analysis (wt.%)			Ultimate analysis (wt.%)			
	Volatile matter	Fixed carbon	Ash	C	N	H	O
Chlorella vulgaris	74.20	19.43	6.37	57.65	9.73	5.30	27.32

Tab.2. $2^{(4-1)}$ fractional factorial design and the results of hydrothermal gasification.

Run	Temperature (°C)	Pressure (bar)	Cat. loading (wt.%)	K_2CO_3/ KOH ratio	H_2 (mol %)	CH_4 (mol %)	CO_2 (mol %)	CO (mol %)	GE_C (%)	Y_{biogas} (mmol/g)
0	550	250	-	-	17.83	4.11	7.54	70.52	30.49	27.14
1	525	250	5	1:2	49.73	3.31	7.42	33.59	17.23	19.58
2	575	250	5	2:1	64.39	9.24	8.68	17.54	25.95	35.78
3	525	280	5	2:1	53.58	3.48	6.87	26.26	9.60	11.47
4	575	280	5	1:2	54.13	5.51	8.66	31.35	26.35	28.12
5	525	250	15	2:1	66.83	5.06	5.92	21.53	8.54	12.55
6	575	250	15	1:2	65.68	6.45	8.56	19.31	23.43	32.44
7	525	280	15	1:2	50.03	3.17	6.36	35.31	15.85	16.03
8	575	280	15	2:1	63.81	8.12	6.44	21.33	29.07	38.69

The methane yield of biomass was increased from 1.12 mmol g^{-1} to 3.31 mmol g^{-1} algae which is almost a triple growth, while the total biogas yield was increased by 42.56% applying homogenous catalyst mixtures.

Comparing the results to the non-catalytic hydrothermal gasification, augmented hydrogen yields result in a decreasing carbon gasification efficiency. The main reason for this phenomena can be explained bythat homogenous catalysts diminish the CO content of biogas which ultimately decrease the carbon gasification efficiency.

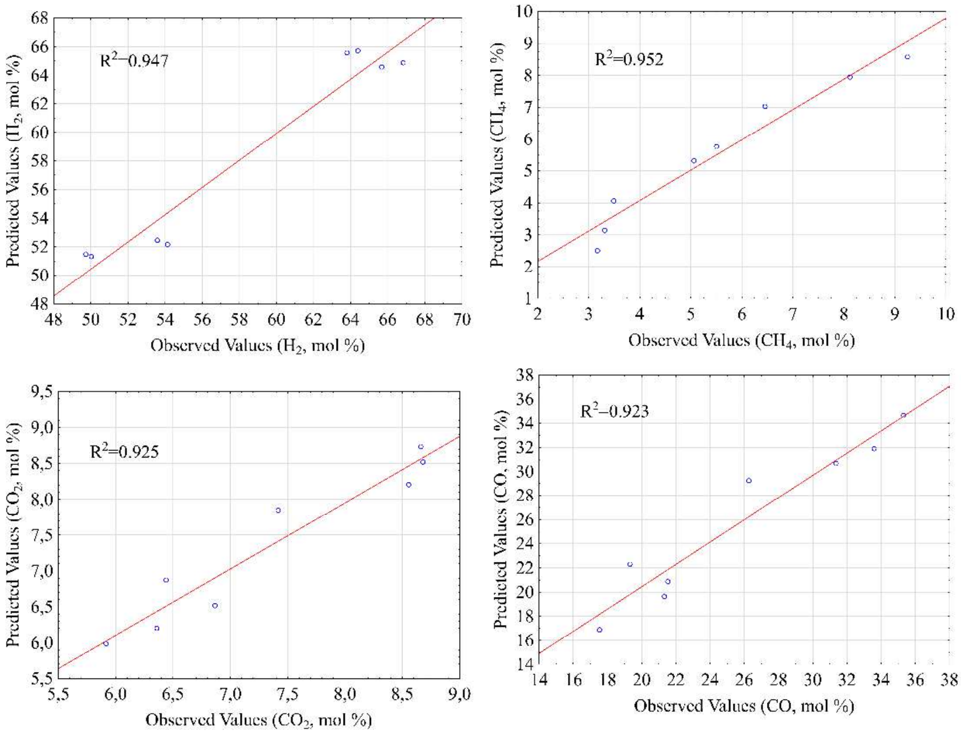

Fig. 2. Predicted and observed values from statistical model.

The statistical analysis of experimental data shows that temperature has significant effect on all independent variable (H_2, CH_4, CO_2, CO fraction, GE_C and Y_{biogas}). All dependent variables have significant effect on H_2 production (R^2=0.947). It is also turned out that both temperature and catalyst ratio are significant factors in case of CO content. The predicted and the observed values are adequate, as showed in Figure 2, and thus the experimental data fits well the applied statistical models (R^2>0.9 in all cases).

CONCLUSIONS

This study aims to explore hydrothermal gasification of microalgae biomass under different reaction parameters. *C. vulgaris* was cultured and converted into biogas, and the impact of temperature (525-575°C), pressure (250-280 bar), catalyst loading (5-15 wt.%) and catalyst ratio (K_2CO_3:KOH = 2:1;1:2)on the yield of the process was investigated based on $2^{(4-1)}$ fractional factorial experimental design.

The investigated statistical models are satisfactory and fits well experimental results.

The highest total biogas and hydrogen yield arefound to be 38.69 and 24.69mmol g^{-1}, respectively. It is demonstratedthat higher H_2 and biogas yield can be achieved by catalyst mixtures compared to single homogenous or heterogeneous catalysts. The experimental data shows thatusing different reaction conditions, in situ upgrading of biogas becomespossible due to the augmented concentration and yield of H_2 and CH_4.

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