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SENSITIVITY ANALYSIS OF BIOHYDROGEN PRODUCTION FROM *IMPERATA CYLINDRICA* USING STOICHIOMETRIC EQUILIBRIUM MODEL

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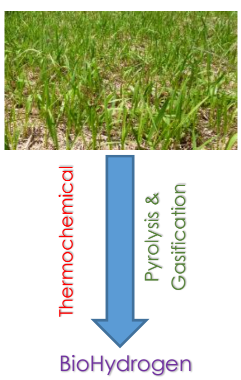
Graphical abstract



Abstract

This paper investigated the production of biohydrogen from *Imperata cylindrica*, using stoichiometric equilibrium model. The stoichiometric equilibrium model uses biomass ultimate analysis, thermodynamic equilibrium and elemental balance on biomass gasification reaction. The sensitivity analysis was studied over a wide range of operating conditions involving temperature (250 – 1500 °C), pressure (1 – 5 atm) and Steam to fuel ratio (0-5). The result shows biohydrogen and other biogas product were sensitive to temperature and steam-feed ratio, whereas effect of pressure is negligible. The operating condition for optimal biohydrogen production in moles (23%) was atmospheric pressure, temperature, 1500 °C and steam-feed ratio, 5. Biogas product mixtures are H_2, 23%, CO, 17%, CO_2, 12% CH_4, 0% and H_2O, 60%. Increase in steam-feed ratio (0, 1, 2, 3, 4 and 5) significantly increase the biohydrogen by 1381%, 90%, 46%, 31% and 24%. The stoichiometry equilibrium model could effectively be used in determining biohydrogen production and its sensitivity to temperature and steam.
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Keywords: Biomass; thermodynamics; modelling; gasification

Abstrak

Kertas kerja ini disiasat pengeluaran biohydrogen dari Imperata cylindrica, menggunakan model keseimbangan stoikiometri. Model keseimbangan stoikiometri menggunakan analisis muktamad biomass, keseimbangan termodinamik dan keseimbangan unsur reaksi biomass pengegasan. Analisis sensitiviti dikaji lebih pelbagai keadaan operasi yang melibatkan suhu (250 - 1500 ° C), tekanan (1 - 5 atm) dan wap kepada nisbah (0-5) bahan api. Hasilnya menunjukkan biohydrogen dan produk biogas lain adalah sensitif kepada suhu dan nisbah stim makanan, manakala kesan tekanan boleh diabaikan. Keadaan operasi untuk pengeluaran biohydrogen optimum dalam tahi lalat (23%) adalah atmosfera tekanan, suhu, 1500 ° C dan nisbah wap-feed, 5. Biogas campuran produk adalah H2, 23%, CO, 17%, CO2, 12% CH4, 0% dan H2O, 60%. Peningkatan dalam nisbah wap-makanan (0, 1, 2, 3, 4 dan 5) dengan ketara meningkatkan biohydrogen dengan 1381%, 90%, 46%, 31% dan 24%. Model keseimbangan stoikiometri berkesan boleh digunakan dalam menentukan pengeluaran biohydrogen dan kepekaannya kepada suhu dan wap.

Kata kunci: Biomass; termodinamik; modelling; pengegasan

1.0 INTRODUCTION

The demand for energy has been on the steady rise for more than half a century. However, in the last two decades the consumption of energy, especially in the developed countries is going astronomical and still rising [1]. In fact, the problem is meeting the ever increasing demand for energy and questioning the current major source (fossil fuel) sustainability and renewability [2]. An environmental problem such as climatic change, global warming and acid rain, resulting from burning of fossil fuel cannot be ignored anymore. Therefore, the use of biomass in the production of green and clean fuel or energy carrier such as hydrogen answers world questions on energy and environmental complications [3].

The major interest in biomass as an energy source is confirmed renewable, sustainable and more environmentally friendly unlike fossil fuel. Consequently, several kinds of biomass and agricultural products were utilized as feedstock for thermochemical conversion [4, 5]. However, food for fuel debate favors energy grasses such as Miscanthus and Switchgrass as alternative sources of biomass fuels [6-9]. Introducing a novel grass growing widely in Southeast Asia and known by many names such as *Imperata cylindrica*, Speargrass, Lalang, Japanese blood-grass, Congo-grass or Kunai. *I. cylindrica* has the ability to burn when green (wet) and difficult to eradicate on farms earning it obnoxious and farmer's nightmare weed [10, 11].

One route of converting biomass to fuel is thermochemical processes such as combustion, pyrolysis and gasification. The processes use heat in converting bulky biomass to easy and manageable energy packed biofuel. The main product of gasification is gaseous fuel (H_2, CO, CO_2 and CH_4) and occurs in the presences of a gasifying medium such as steam and/or air. [12].

This paper studies *Imperata cylindrica* as a source of biohydrogen through gasification using stoichiometric equilibrium model. Furthermore, the sensitivity analysis of the gasification biogas product mixtures to parameters such as temperature, pressure and steam to feed ratio was investigated. Using the algorithm presented and applied by many researchers in the analysis of several biomass gasification products. [2, 13-15].

2.0 EXPERIMENTAL

2.1 Experimental

Imperata cylindrica was collected from an open field in Skudai, Johor, Malaysia. The green leaves were chopped, weighed and dried at 105 oC for 36 hours in an oven. The dried leaves (brown) were milled and sieved to obtain particle size < 125 µm [16]. Consequently, the physicochemical was studied through proximate and ultimate analysis. Ultimate analysis was determined using the Vario Macro Cube CHNS elemental analyzer according to the ASTM D3179 standard. Proximate analysis was determined according to ASTM standards D3173, D3174, and D3175 for moisture, volatile matter and ash respectively and the difference gave the fixed.

2.2 Stoichiometric Equilibrium Model

The research methodology involves simulating stoichiometric elemental and equilibrium reaction balance using MATLAB R2013a. The sensitivity analysis was studied over a wide range of operating conditions involving temperature (250 – 1500 °C), pressure (1 – 5 atm) and Steam to fuel ration (0-5).

The molecular formulae of Biomass can be represented in terms of its elemental constituents as $CH_aO_bN_c$. The values of x, y and z are determined from the ratios of hydrogen (H), oxygen (O) and nitrogen (N) to Carbon (C) compositions by weight obtained through ultimate analysis. Biomass gasification reaction is summarily written as Equation (1) [13, 17]:

Biomass gasification equation:

$$CH_xO_yN_z + wH_2O + a(O_2 + 3.76N_2) \rightarrow n_1C + n_2H_2 + n_3CO + n_4CO_2 + n_5CH_4 + n_6H_2O + n_7N_2 \quad (1)$$

where $x=H/C$; $y=O/C$; $z=N/C$ in mole ratio and n_1 - n_7 are the stoichiometric coefficients of the biogas product mixture. Also *w* and *a* are the moles of steam and air supplied to the gasifier representing the independent variables.

Equations 2-5 is written by means of Elemental balance on Carbon, Hydrogen, Oxygen and Nitrogen in Equation 1.

Elemental balance:

$$C: n_1 + n_3 + n_4 + n_5 = 1 \quad (2)$$

$$H: 2n_2 + 4n_5 + 2n_6 = x + 2w \quad (3)$$

$$O: n_3 + 2n_4 + n_6 = y + w + 2x \quad (4)$$

$$N: n_7 = z + 7.52x \quad (5)$$

The Elemental balance resulted in equations with seven unknown variables (n_i). Three more equations are required from equilibrium reactions in gasification namely Bourdouard, Steam gasification, Methanation and Shift reactions (see Equations 6-9).

Equilibrium Reaction:

Bourdouard Reaction:

$$CO_2 + C \rightarrow 2CO \qquad +172 \text{ kJ/mol} \quad (6)$$

Steam gasification:
$C + H_2O \rightarrow H_2 + CO$ +131 kJ/mol (7)
Methanation:
$C + 2H_2 \rightarrow CH_4$ –75 kJ/mol (8)
Shift reaction:
$CO + H_2O \rightarrow CO_2 + H_2$ –41 kJ/mol (9)

The Shift reaction is not independent and resulted from combining Bourdouard and Steam gasification reactions. The three (3) equations selected are equations 6-8 and their equilibrium equations are Equations 10-12.

Equilibrium equation

$$K_{e1} = \frac{y_{CO}^2 \cdot P}{y_{CO_2}} \quad (10)$$

$$K_{e1} = \frac{y_{\mathrm{CO}} \cdot y_{H_2} \cdot P}{y_{H_2O}} \quad (11)$$

$$K_{e3} = \frac{y_{CH_4}}{y_{H_2O}^2 \cdot P} \quad (12)$$

where K_{ei} is the equilibrium constant, *y*- mole fraction and *P*- operating pressure.

The equilibrium constants of the reactions are dependent on change in Gibb free energy (ΔG), temperature (T) and universal gas constant (R) Equation 13. Basu[13] and Nyakuma *et al.*[12] provides the Gibbs free correlation and other necessary estimates.

$$K_e = \exp\left(-\frac{\Delta G}{RT}\right) \quad (13)$$

Furthermore, the relationship between the stoichiometric moles in the elemental balance equations 2-7 and mole fractions (*y*) in equilibrium equations 10-12 is written Equation 14.

$$y_i = \frac{n_i}{n_T} \quad (14)$$

where n_T is the total moles.

The algorithm requires the ultimate analysis and the amount of steam and air as input. The ultimate analysis values were initially used to calculate *x, y* and z. Subsequently the non-linear systems of equations 2-14 was computed in MATLAB 2013a using the *fsolve* function and the trusted region algorithm. The entire process was simulated for temperature range (250-1500 °C) and steam-feed ratio (0-5).

3.0 RESULTS AND DISCUSSION

3.1 Physicochemical Analysis

The thermogravimetric analysis, proximate and ultimate analysis of *I. cylindrica* is presented on Table 1. The results obtained from characterization are in good agreement with typical values for biomass in literature [18].

Table 1 Proximate and Ultimate Analysis of Imperata Cylindrica

	Weight (%)	Typical Biomass Literature Value [18]
Ultimate analysis (wt.% dry basis)		
C	43.19	42-71
H	5.92	3-11
N	0.59	0.1-12
O	50.16	4-36
S	0.14	0.01-2.3
Proximate analysis (dry basis)		
Moisture	7.50	3-36
Volatiles	76.58	48-86
Fixed Carbon	15.09	1-38
Ash	0.83	0.1-46

The results additional show *I. cylindrica* containing pollutant elements such as N and S in low concentration. The presences of low ash and moisture content suggest operational problems such as agglomeration, slagging and fouling are unlikely to occur during thermal conversion.

3.2 Sensitivity Analysis of Biogas Product Mixture

The biogas product mixture is essentially Hydrogen (H_2), Carbon monoxide (CO), Carbon dioxide (CO_2) and Methane (CH_4). The sensitivity of the biogas product mixture was pronounced at temperature (500-1500 °C) and steam-feed ratio (1-5). Figures 1-4 depict the profiles, temperature effect on the biogas mixture in mole fractions for steam to feed (S/F) ratio (1,2,3 and 5).

Both carbon-dioxide and methane decline with increase in temperature for all S/F. However, methane was completely consumed at temperature 1500 °C, 1370 °C, 1280 °C and 1160 °C for S/F 1, 2, 3, and 5 respectively. Furthermore, temperature increase favors syngas composition (H_2 + CO) with the composition of hydrogen steadily increasing with increase in steam. Vagia and Lemonidou[19], Nyakuma *et al.*[20] reported similar results. All the profiles show a good relationship between methane conversion and syngas production.

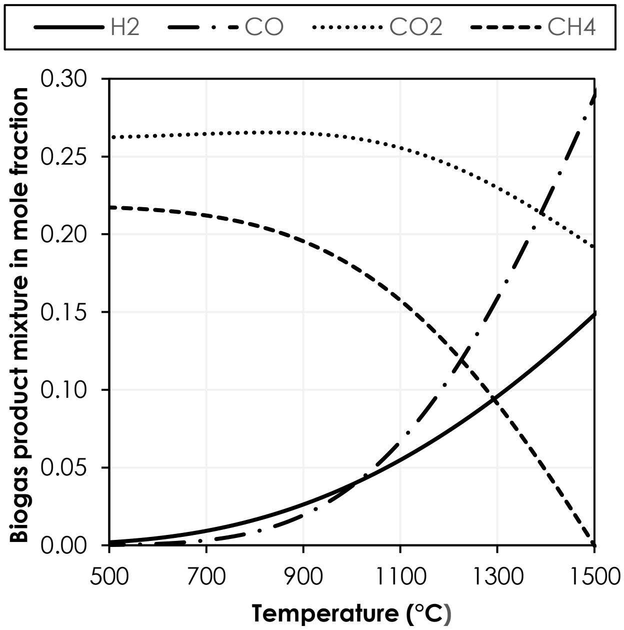

Figure 1: Effect of Temperature on Biogas mixture product and S/F=1

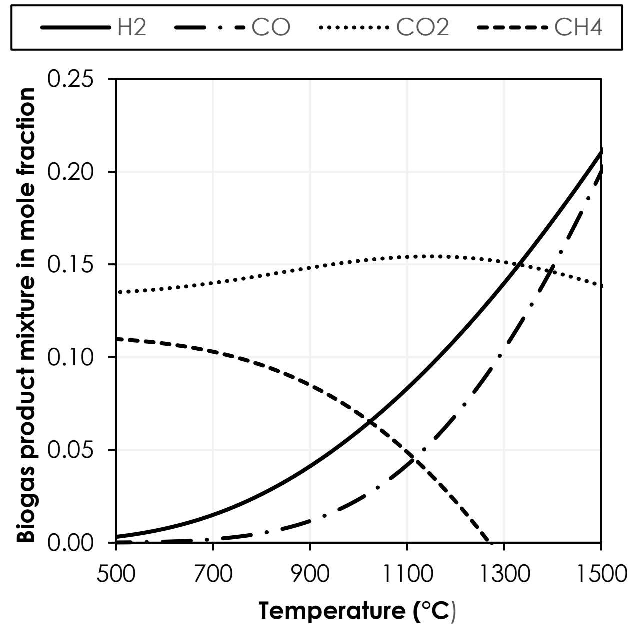

Figure 3 Effect of Temperature on Biogas mixture product and S/F=3

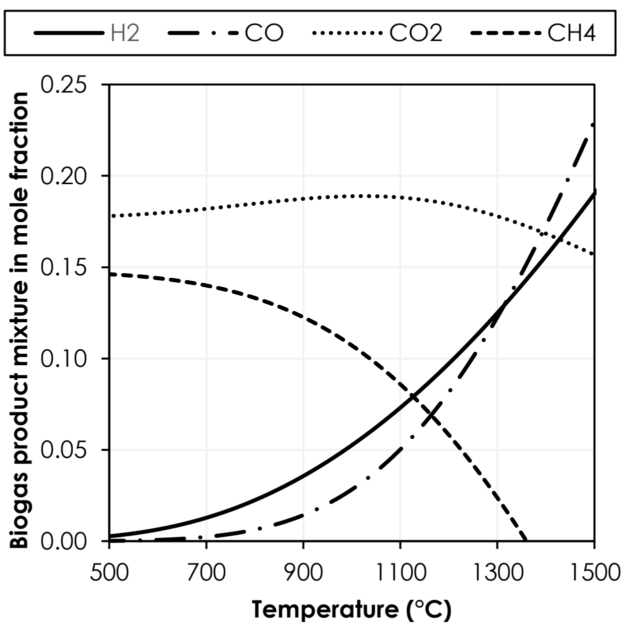

Figure 2 Effect of Temperature on Biogas mixture product and S/F=2

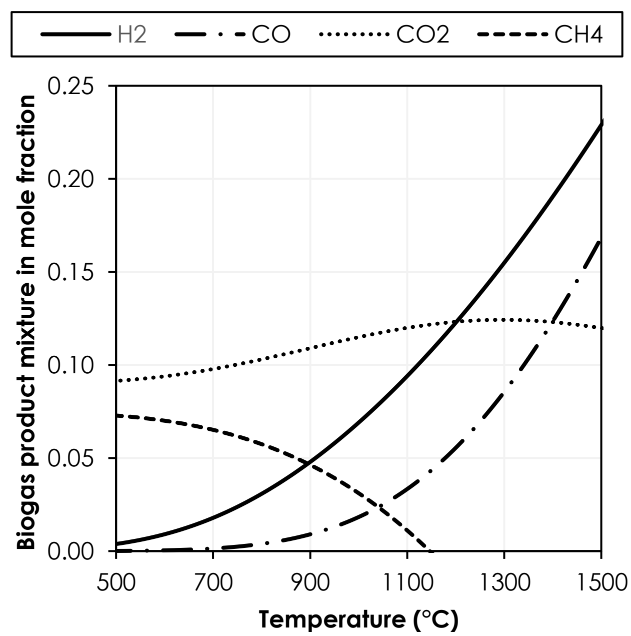

Figure 4 Effect of Temperature on Biogas mixture product and S/F=5

Figure 1, represent equal amount of steam and feed shows mole fractions of hydrogen increase from 0.01 at 500 °C to maximum of 0.15 at 1500 °C. Similarly, minimum and maximum compositions in mole fraction for CO are 0-0.29 at 500-1500 °C. CO_2 and CH_4 maximum compositions are 0.27 and 0.22 at temperatures 750 and 500 °C respectively.

Doubling S/F gave an appreciable increase in hydrogen production relative to other gas products with maximum mole fraction of 0.19 (1500 °C) representing an increase of 27%. The maximum compositions and corresponding temperatures of CO, CO_2 and CH_4 are 0.23 (1500 °C), 0.19 (1050 °C) and 0.15 (500 °C) respectively see Figure 2.

The profile for S/F equal 3, shows syngas components (H_2 + CO) reached a significant 0.01 mole fraction at different temperatures 560 °C and 800 °C for H_2 and CO respectively. Consequently, low temperatures favors hydrogen production. The presence of excess steam favors hydrogen as well for all temperatures considered (see Figure 3). Comparing the maximum compositions of the biogas product mixture H_2, CO, CO_2 and CH_4 are 0.21 (1500 °C), 0.20 (1500 °C), 0.15 (1160 °C) and 0.11 (500 °C) respectively.

Figure 4 depicts the combine effect of steam (5 times) ratio biomass feedstock and temperature of the biogas product mixture. The temperature when hydrogen attained 0.01 mole fraction was considerably reduced to 530 °C and maximum value of 0.23 mole fraction at 1500 °C. Furthermore, CO production was significantly delayed till 830 °C and steadily increase to 0.17 at 1500 °C. The maximum mole fractions of CH_4 and CO_2 are 0.07 (500 °C) and 0.12 (1310 °C) respectively. The comparable trend for syngas are reported in literatures [21-23].

3.3 Effect of Steam to Feed Ratio on Biohydrogen

Steam to Feed ratio (S/F) significantly impacted the production of biohydrogen from biomass gasification. The effect of steam to feed ratio is further influenced with temperature and depicted in Figure 5.

Figure 5 profiles biohydrogen moles dependent on temperature for steam to feed ratios (0-5) for *I. cylindrica* reforming reaction. All simulations show biohydrogen production is not favored by temperatures below 500 °C. The absence of steam (S/F=0) resulted in negligible biohydrogen production despite an increase in temperature.

However, with a steady increase in steam to feed ratio (S/F =1-5) there are positive differences in moles of biohydrogen. The biohydrogen increase is more significant at high temperatures and maximum on 1500 °C. The percent increase for steam to feed ratio S/F= 1, S/F= 2, S/F= 3, S/F= 4 and S/F= 5 are 1381%., 90%, 46%, 31% and 24% respectively at 1500 °C. Therefore, effect of S/F on biohydrogen production diminishes with further increase and finding the optimal S/F is beyond the scope of the study [24].

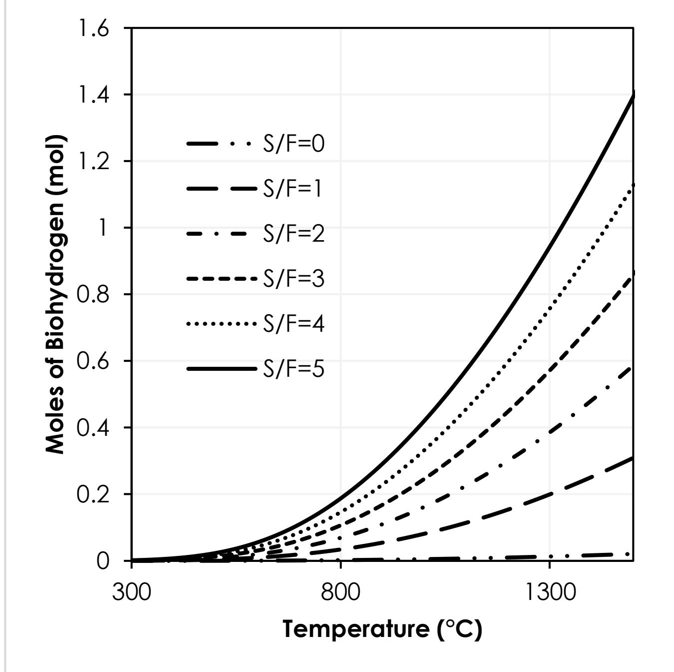

Figure 5 Biohydrogen production for S/F (0-5) at varying temperatures

4.0 CONCLUSION

The stoichiometric and thermodynamic analysis were successfully carried out in MATLAB. The biomass is gasifier at 530 °C forming hydrogen, carbon monoxide, carbon dioxide and methane. The sensitivity analysis parameters are temperature and steam to feed ratio, which affected considerably the biogas product mixtures.

The study shows biomass gasification for the production of biohydrogen depend considerably on steam to feed ratio and reactor temperature. For every increase in steam-feed ratio there is a corresponding increase in biohydrogen at temperatures above 500 °C. The optimal operating conditions were 1 atm, temperature 1500 °C and steam-feed ratio (S/F = 5) for the biohydrogen production.

Since the rate of biohydrogen diminishes at the same temperature with increase in steam-feed ratio. There is need for process optimization considering variables such as steam cost, gasifier energy consumption and the presence of other desired gas products.

Acknowledgement

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