# Methodology for Selecting Appropriate Feedstock Material for Biomass Gasification in Supercritical Water by Means of Process Modelling

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## ABSTRACT

The theoretical effect of the elemental composition of biomass materials considered as possible feedstock for supercritical water gasification (SCWG) on performance indicators such the total and individual gas yields, calorific value of product gas (HHV), cold gas efficiency (CGE) and the heat required for the endothermic SCWG reactions ($\Delta H_R$) were investigated. A typical SCWG process model was simulated in Aspen Plus®. The results for the performance indicators in terms of the $C_{mass\%}:H_{mass\%}$ ratio and oxygen content (wt.%) of the biomass feedstock materials were presented on generalised contour plots at various operating temperatures (600, 650, 700, 750 and 800°C), biomass feed concentrations (2.5, 5, 10, 15, 20 and 25 wt.%) and a constant operating pressure (250 bar). Maximum $H_2$ yields can be achieved when biomass with low C:H ratios and low oxygen are gasified at high temperatures (> 700°C) and low biomass feed concentrations (< 5 wt.%). Conversely, maximum $CH_4$ yields can be achieved when biomass with low C:H ratios and low oxygen content are gasified at low temperatures (< 650°C) and high biomass concentrations (> 15 wt.%). The contour plots generated can aid in the selection of appropriate biomass materials for SCWG prior to conducting experimental work or for the use in mass and energy balance calculations in determining the thermal efficiency of SCWG for a specific feedstock.

## INTRODUCTION

An increase in the global energy demand, together with stricter regulations on the emission of greenhouse gases have led to an increased effort in the development of sustainable, renewable energy conversion processes using biomass as source. Additionally, high volumes of aqueous organic waste materials are generated from various industries (such as food processing plants, agricultural activities, wastewater treatment plants), which need to be treated or disposed of in an environmentally friendly manner. The high organic content of these waste streams makes it a potential fuel source, which could be harnessed through the application of biomass conversion processes. However, the high moisture content in these waste streams (80-99 wt.%) limits it’s use for pyrolysis, thermal gasification and direct combustion due to the high energy required for drying [1].

SCWG, a process in which large biomass molecules are broken down into smaller molecules such as $H_2$, $CH_4$, CO and $CO_2$ in the presence of water at supercritical conditions, is a promising option for gasification of organic waste streams with high moisture content. The major advantage of SCWG is that, if carried out correctly, the formation of char during the process can be minimal, no drying of the sludge is necessary prior to the SCWG process and $CO_2$ can easily be separated from the rest of the gaseous product due to its high solubility in water. The process is very versatile and wide variety of feedstock materials can be gasified. A wide range of model compounds (such as glucose [2], glycerol [3], ethanol [4], methanol [5] and cellulose [6]) and real biomass materials (such as micro algae [7], corn starch and sawdust mixtures [8], sewage sludge [9], pulp/paper-mill-sludge [10]) have been used as feedstock material in SCWG experimental studies for the formation of $H_2$, $CH_4$, CO and $CO_2$.

Thermodynamic modelling is a very useful tool which can be used to predict the theoretical product yields of a process. This is especially useful for the selection of appropriate biomass materials for SCWG prior to conducting expensive and time consuming experimental work. Various studies have focussed on the thermodynamic modelling of SCWG for the prediction of product gas yields for specific feed stock materials [11–15]. Most of these studies only focussed on the effect of operating conditions (temperature, pressure and biomass concentration) on the product gas yields, and did not investigate the effect of the composition of the biomass on the product yields. Knowing the effect of biomass composition on the product gas yields, a methodology can be developed to aid in determining whether a specific biomass material is suitable as feedstock for SCWG prior to conducting experimental work.

Hence, the aim of this study was to develop a methodology to determine whether a specific biomass material is suitable as feedstock for SCWG based on the elemental composition of the biomass material at various operating conditions. This was done by simulating a typical SCWG process in Aspen Plus® and varying the elemental composition of the feedstock, temperature and water-to-biomass ratio (*i.e.* biomass concentration of the feed). The total and individual gas yields, calorific value of product gas (HHV), cold gas efficiency (CGE) and the heat required for the endothermic SCWG reactions ($\Delta H_R$) were used as performance indicators. Generalised contour plots for these performance indicators in terms of the carbon-to-hydrogen ratio ($C_{mass\%}$:$H_{mass\%}$) of the biomass (on a dry, ash-free basis) and the oxygen content (wt.%) were generated. These contour plots can then be used to predict the range of each performance indicator for any biomass material if the C:H ratio and the oxygen content on a dry, ash-free basis is known.

## MATERIALS AND METHODS

### *Process Description*

A typical flow diagram used in various SCWG experimental studies [4,9,10] was simulated in this study using Aspen Plus® (see Figure 1). Biomass (on a dry, ash-free basis) is mixed with water (MIXER), pressurised to the reactor operating pressure using a high-pressure pump (PUMP) and heated to the reactor operating temperature in a heat exchanger (HEATER) before it is gasified in the SCWG reactor (RYIELD + RGIBBS). The product stream is then cooled in a heat exchanger (COOLER) and expanded in a relief valve (VALVE), after which the liquid (LIQUID) and gas (SYNGAS) products are separated in a gas-liquid separator (GL-SEP). Biomass is defined as a non-conventional component in Aspen Plus®. The ultimate and proximate analysis as well as the HHV of biomass must therefore be specified. Non-conventional components must first be decomposed into its elemental components (C, $H_2$, $O_2$, $N_2$, Cl and S) using the RYIELD reactor block, before it can be processed by chemical and phase equilibrium models in Aspen Plus®. Once the biomass is decomposed, Gibbs-free energy minimisation is applied (RGIBBS) to calculate the chemical equilibrium composition at the specified reactor temperature and pressure.

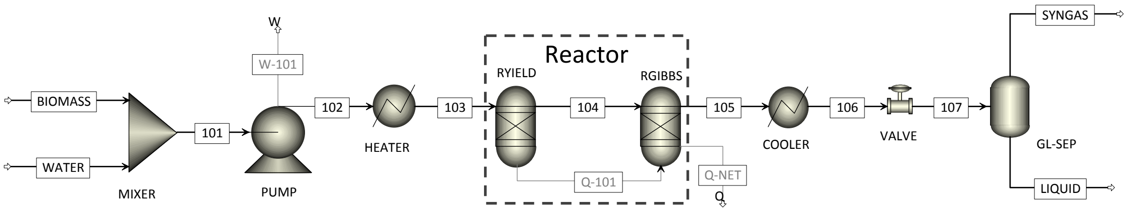

**Figure 1: Schematic flow sheet for SCWG process used in Aspen Plus® simulation**

The following additional assumptions were made:

- The Peng-Robinson equation of state with Boston-Mathias modifications (PR-BM) was used as property method;
- The product stream for RGIBBS consists of only $H_2O$, $H_2$, CO, $CO_2$, $CH_4$, $C_2H_6$, $N_2$, $N_2O$, $NO_2$, NO, $NH_3$, $SO_2$, $SO_3$, HCl, $Cl_2$, $O_2$, and $C_{(s)}$;
- No tar is formed and char consists of only solid carbon ($C_{(s)}$);
- RYIELD and RGIBBS are both isothermal and isobaric;

*Biomass Properties*

The elemental composition (in terms of ultimate analysis and proximate analysis) of 49 organic waste materials and 5 model compounds (glycerol, ethanol, glucose, cellulose and methanol) were obtained from the Phyllis database [16]. The organic waste materials included (amongst others) spent coffee, crude glycerine from biodiesel production, leather waste, olive mill effluent, manure from various livestock, char from sugarcane bagasse, sewage sludge, black liquor and sludge from pulp/paper mill. The range of the ultimate and proximate analysis as well as the HHV on a dry, ash free (daf) basis, of the biomass materials are shown in Table 1.

**Table 1: Range for properties of 54 biomass materials considered**

| **Biomass Properties** | **Min** | **Max** | **Ave ± Std Dev** |
|---|---|---|---|
| *Ultimate Analysis (daf)* | | | |
| C | 34.17 | 86.24 | 51.19 ± 8.87 |
| H | 3.28 | 13.13 | 6.83 ± 1.77 |
| O | 9.63 | 60.59 | 38.74 ± 9.42 |
| N | 0.00 | 13.99 | 2.32 ± 3.17 |
| S | 0.00 | 7.02 | 0.53 ± 1.05 |
| *Proximate analysis (daf)* | | | |
| Fix carbon | 0.36 | 89.70 | 21.29 ± 19.01 |
| Volatile matter | 10.30 | 99.64 | 78.28 ± 18.95 |
| C/H | 3.00 | 26.29 | 8.03 ± 3.31 |
| $HHV_{Milne}$ [MJ/kg] | 10.02 | 32.91 | 21.57 ± 4.28 |

A dry, ash-free basis was used in order to get comparable results only in terms of the elemental composition. The correlation by Milne [16] was used to determine the HHV of the biomass materials as it was the most accurate when compared to other correlations ($R^2 = 0.94$ and RMSE = 1.81 MJ/kg):

$$HHV_{Milne} = 0.341C + 1.322H - 0.12O - 0.12N + 0.0686S - 0.0153Ash \tag{1}$$

### *Implementation of Process Model*

The C:H ratio and oxygen content of the biomass feed stream (BIOMASS) were varied between the maximum and minimum values of the 54 biomass materials considered in this study. Constant values for the minor components of biomass, nitrogen (N), sulphur (S) and chlorine (Cl), were assumed as the average values of the 54 biomass materials (see Table 1). The operating temperature and biomass feed concentration were varied for each C:H and oxygen content combination between 600, 650, 700, 750 and 800 °C and 2.5, 5, 10, 15, 20 and 25 wt.%, respectively, while the operating pressure was kept constant at 250 bar.

The results were evaluated in terms of the total and individual gas yields ($Y_{Total}$ and $Y_i$), the higher heating value of the product gas ($HHV_{gas}$), the cold gas efficiency (CGE), as well as the heat required for the endothermic reactions ($\Delta H_R$). The CGE is the percentage of the heat of combustion (in terms of LHV) of the biomass available in the cooled product gas. The equations used to calculate each of these performance indicators can be seen in equations (2)-(6).

$$Y_{Total} = \frac{\dot{m}_{total,gas}}{\dot{m}_{dry,ash-free,biomass}} \tag{2}$$

$$Y_i = \frac{\dot{m}_i}{\dot{m}_{dry,ash-free,biomass}} \tag{3}$$

$$HHV_{gas} = x_{H_2} HHV_{H_2} + x_{CH_4} HHV_{CH_4} + x_{CO} HHV_{CO} \tag{4}$$

$$CGE = \frac{\dot{m}_{total,gas} LHV_{gas}}{\dot{m}_{dry,ash-free,biomass} LHV_{dry,ash-free,biomass}} \tag{5}$$

$$\Delta H_R = \frac{\sum H_{i,out} - \sum H_{i.in}}{\dot{m}_{dry,ash-free,biomass} + \dot{m}_{water}} \tag{6}$$

### *Process Model Validation*

The process model was validated by comparing the predicted values to experimental results obtained from SCWG of corn starch and sawdust mixtures [8]. The Pearson's correlation coefficient ($R^2$) and the root mean square error (RMSE) for the prediction of dry mole fraction of $H_2$, $CH_4$, CO and $CO_2$ in the product gas are shown in Table 2. The predicted mole fractions are in good agreement with the experimental values and the process model can therefore be used for the modelling of SCWG of other biomass materials.

**Table 2: Model validation for SCWG of corn starch (CS), and sawdust (SD) at 240 bar.**

| Component | | $H_2$ | | $CH_4$ | | CO | | $CO_2$ | |
|---|---|---|---|---|---|---|---|---|---|
| Feed wt.% | T [°C] | Ex | Model | Ex | Model | Ex | Model | Ex | Model |
| | | Dry mole fraction | | | | | | | |
| 10.4% CS[a] | 650 | 0.47 | 0.48 | 0.15 | 0.13 | 0.02 | 0.01 | 0.37 | 0.38 |
| 13.7% CS | 715 | 0.55 | 0.51 | 0.06 | 0.11 | 0.03 | 0.03 | 0.34 | 0.36 |
| 10.72% SD[b] + 4.01% CS | 685 | 0.43 | 0.43 | 0.17 | 0.19 | 0.03 | 0.03 | 0.38 | 0.37 |
| | RMSE | 0.024 | | 0.006 | | 0.011 | | 0.030 | |
| | $R^2$ | 0.94 | | 0.87 | | 0.99 | | 0.89 | |

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[a] Ultimate analysis of CS: C = 42.7 %, H = 6.2 %, O = 50.9%, N = 0.1%, S = 0.1%, ash = 0.1%

[b] Ultimate analysis of SD: C = 49.4%, H = 6.0 %, O = 45.`%, N = 0.1%, S = 0%, ash = 0.2%

## RESULTS

Contour plots showing the predictions of the total gas yield, individual gas yields, HHV of product gas, CGE and $\Delta H_R$ in terms of the C:H ratio and oxygen content of biomass for SCWG of biomass at 700°C, 250 bar and biomass concentration of 5 wt.% are shown in Figure 2(a)-2(h).

Maximum total gas yield (2.6-2.8 $kg/kg_{biomass}$), $CO_2$ yield (2.0-2.4 $kg/kg_{biomass}$) and CO yield (0.075-0.10 $kg/kg_{biomass}$) are achieved when biomass with typically low oxygen content (< 12 wt.%) and high C:H ratios (> 12) are used as feedstock. Maximum $H_2$ yield (0.24-0.26 $kg/kg_{biomass}$) and $CH_4$ yield (0.45-0.50 $kg/kg_{biomass}$) are achieved when biomass with low C:H ratios (< 6) and low oxygen content (< 20 wt.%) are gasified. Biomass with relatively low C:H ratios and low oxygen content will typically have a higher hydrogen content and lower carbon and oxygen content than biomass with relatively high C:H ratios and low oxygen content. Hence, when biomass with lower C:H ratios and low oxygen content are gasified, more hydrogen will be available for the formation of $H_2$ and $CH_4$ than at higher C:H ratios. Therefore, when selecting a biomass material for the formation of $H_2$ and $CH_4$, both the C:H ratio and the oxygen content should be as low as possible. This will also result in a product gas with a maximum HHV (26-32 MJ/kg), as $H_2$ and $CH_4$ both have high calorific values (141.8 MJ/kg and 55.5 MJ/kg, respectively), compared to that of CO (10.10 MJ/kg) and are therefore are the main contributors to the HHV of the product gas. However, the heat needed for the endothermic reactions to occur isothermally is unfortunately at its maximum (3.5-4.5 $MJ/kg_{total\ feed}$) when biomass which will yield maximum amounts of $H_2$ and $CH_4$ are gasified. The CGE was typically greater than 100% for the whole range of biomass compositions. The maximum CGE (111-112%) was achieved when biomass with relatively high C:H ratios (> 12) and oxygen content between 20 and 55 wt.% were gasified. Interestingly, at C:H ratios less than 6, the effect of C:H ratio is more predominant on the gas yields, HHV and $\Delta H_R$, while at C:H ratios higher than 6, the effect of the oxygen content becomes more predominant.

Similar contour plots to those presented in Figure 2 for all the other combinations of operating temperatures (600, 650, 750 and 800°C) and biomass feed concentrations (2.5, 10, 15, 20 and 25 wt.%) were generated. Although the maximum and minimum values differed for the various operating conditions, the trends were the same as in the case of 5 wt.% and 700°C.

Figure 3(a)-3(f) shows the combined effect of biomass concentration and operating temperature of the SCWG of biomass with a C:H ratio of 14 and oxygen content of 35 wt.% on the total yield, $H_2$, $CH_4$ and CO yields, HHV, CGE and $\Delta H_R$. The maximum total gas yield (2.2-2.3 $kg/kg_{biomass}$), $H_2$ yield (0.15-0.17 $kg/kg_{biomass}$) and CGE (114-116%) are achieved when operating at high temperatures (> 700°C) and low biomass feed concentration (< 7.5 wt.%). However, the maximum $CH_4$ yield and HHV is achieved when operating at low temperatures (< 650°C) and high biomass concentrations (> 15 wt.%). The heat required for the endothermic reactions is mostly influenced by the biomass concentration and is more or less independent of the operating temperature. The least heat (1.0-1.5 MJ/kg) is required at low biomass feed concentrations (< 5 wt.%). The results show that the gas yields, HHV of product gas, CGE and $\Delta H_R$ are influenced by both the elemental composition of the biomass and the operating conditions.

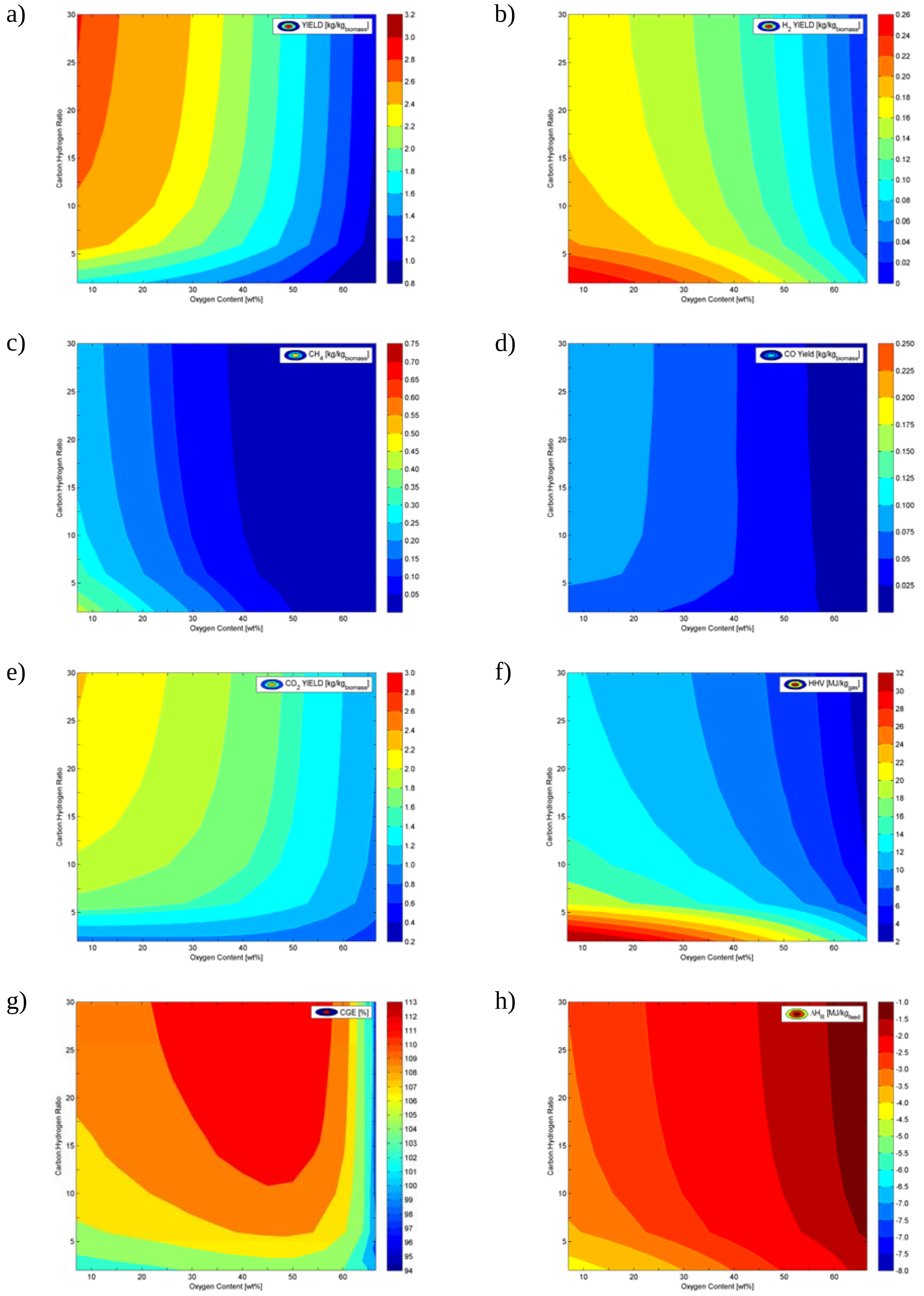

**Figure 2: Results showing the effect of C:H ratio and oxygen content on $Y_{Total}$ (a), $Y_{H_2}$ (b), $Y_{CH_4}$ (c), $Y_{CO}$ (d), $Y_{CO_2}$ (e), $HHV_{gas}$ (f), CGE (g) and $\Delta H_R$ (h) for SCWG at 700°C, 250 bar and biomass concentration of 5 wt.%**

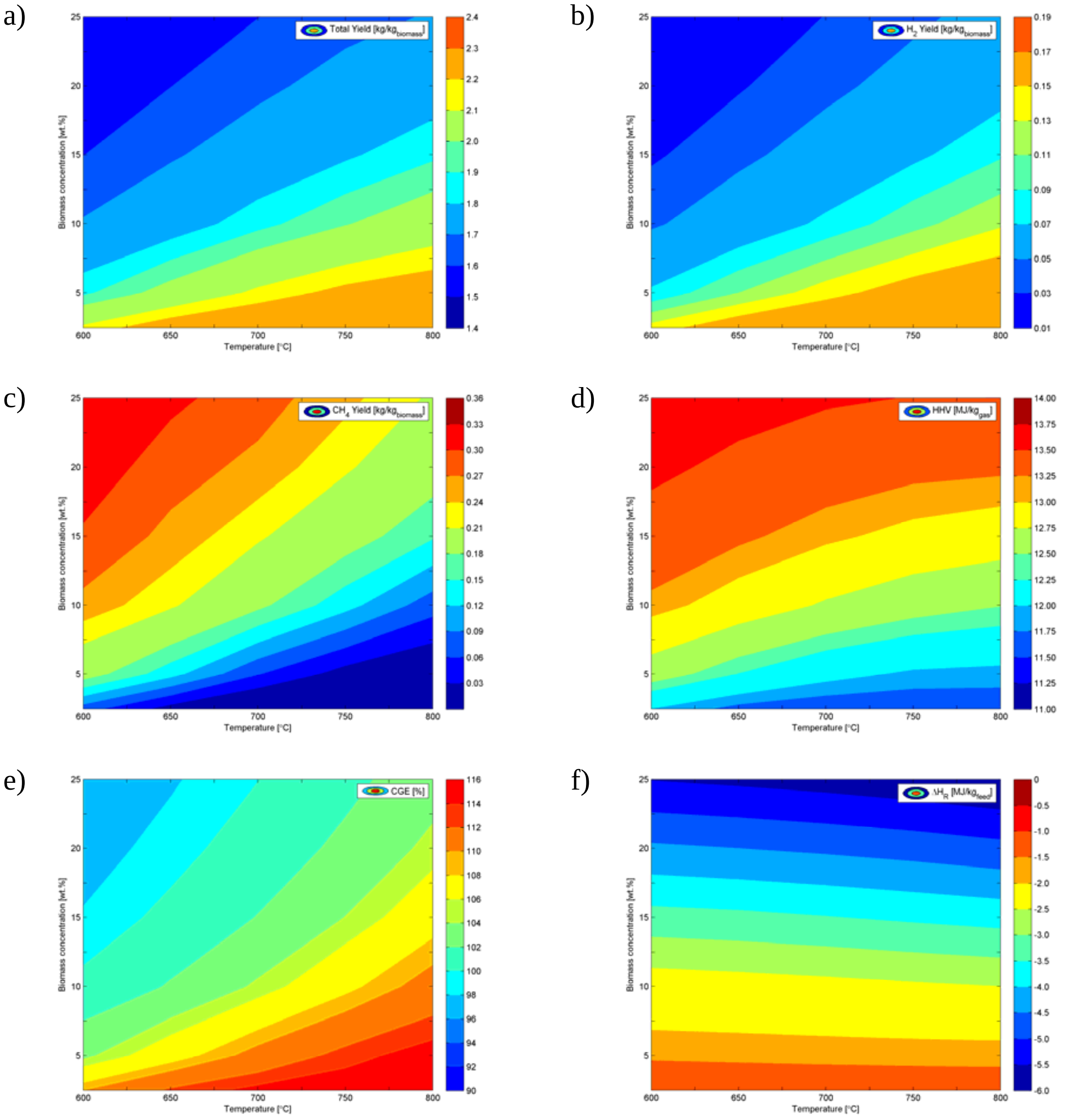

**Figure 3: Results showing the effect of temperature and biomass concentration on $Y_{Total}$ (a), $Y_{H_2}$ (b), $Y_{CH_4}$ (c), $HHV_{gas}$ (d), CGE (e) and $\Delta H_R$ (f) for SCWG of biomass with C:H ratio of 14 and oxygen content of 35 wt.%**

Hence, when considering a wide variety of biomass materials as possible feedstock for SCWG, both of the elemental composition and the effect of operating conditions should be taken into account.

The contour plots generated in this study can aid in the selection of biomass materials prior to conducting experimental work. Once the ultimate analysis of a certain biomass material is known on a dry, ash-free basis, these contour plots can be used to determine the expected range for each performance indicated at different operating conditions by simply locating the C:H ratio and the oxygen content of the biomass on each contour plot. These plots can aid in the selection of appropriate biomass materials for SCWG as well as the selection of operating conditions prior to conducting experimental work. It can also be used for mass and energy calculations in order to determine the thermal efficiency of the process at various operating conditions.

## CONCLUSION

The generalised contour plots generated in this study for the performance indicators for SCWG (total and individual gas yields, $HHV_{gas}$, CGE and $\Delta H_R$) can aid in identifying appropriate biomass materials for SCWG prior to conducting experimental work. The oxygen content has a greater effect on the performance indicators at C:H ratios greater than 6, while the effect of the C:H ratio is more predominant at C:H ratios lower than 6. For maximum $H_2$ and $CH_4$ yields, biomass materials with a relatively low oxygen content and low C:H ratio will be most appropriate. Maximum $H_2$ yields will be achieved when operating at temperatures greater than 700°C and biomass concentrations lower than 5 wt.%, while maximum $CH_4$ yields will be achieved when operating at temperatures lower than 650°C and biomass concentrations greater than 15 wt.%.

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