

Modelling of Supercritical Water Gasification of Biomass: Development of a Mathematical Model for Yield Prediction

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ABSTRACT

One of the major advantages of supercritical water gasification (SCWG) of biomass is the possibility to process feedstock with high water content without the need of drying. Regarding the industrial application of the SCWG technology it is clear that heat-recovery and -integration will play a crucial role, as will the applied heat conversion technologies. In order to design and to assess efficient and environmentally sound SCWG processes, flow sheet simulation is an adequate tool. In order to take full advantage of the simulation tool, i.e. varying many process parameters and test different input, it is not necessary to have an exact chemical model of the SCWG process, but it must be assured that the SCWG model fulfils the mass- and energy balance and can react on different feedstock and process conditions. This paper presents the first steps of the development of a mathematical model predicting the temperature dependant product gas composition based solely on matching the molar balance between input and output. The model uses start values based on thermodynamic equilibrium calculations obtained from the literature. First calculation results are presented and compared to experimental data. The model gives feasible solutions for different feedstock and shows good accordance with experimental data for feedstock concentrations below 5 w-% but needs to be improved for higher feedstock concentrations.

INTRODUCTION

The gasification of biomass in an atmosphere of supercritical water allows the energetic valorisation of very moist feedstock yielding a product gas that can be rich in either methane or hydrogen. The product gas composition depends mainly on the feedstock composition, the reaction temperature and the solid content of the input stream. Assuming equilibrium conditions, high temperature increases the hydrogen yield high at the cost of methane production [1, 2]. Carbon monoxide and carbon dioxide production do not show a very clear trend but generally seem to increase and decrease, respectively, at elevated temperature. Further, if the solid content of the input stream is increased, methane production is favoured over hydrogen. Regarding the feedstock, it appears that different types of lignin and their depolymerisation mechanism have a great influence on the carbon conversion efficiency of the gasification process. So far, modelling of supercritical water gasification (SCWG) has been based on chemical equilibria or the minimisation of the Gibb's free energy. However, in order to analyse the potential of SCWG when applied in large-scale even less detailed models can be used as input to flow sheet based process simulation models. As the focus of such analysis is to compare different process alternatives the required model must "only" be able to react adequately on changes of the main parameters such as temperature, feedstock composition and input concentration. This paper presents the first steps of the development of a mathematical model predicting the temperature dependant product gas composition based

solely on matching the molar balance between input and output. The model uses start values based on thermodynamic equilibrium calculations obtained from references [1, 2]. First results are compared to experimental data of glucose and sucrose gasification in supercritical water, partly gained by experiments carried out by the authors.

MATERIALS AND METHODS

Description of the mathematical model

The model proposed is based on mass conversation in the reactor. The problems are solved with GAMS (General Algebraic Modeling System) using the solver CONOPT 3 (see www.gams.com). It uses specific temperature-dependant starting values for the calculation of the product gas yields. In order to match the mass balance also parameters for carbon conversion and hydrogen conversion efficiency (η_{HC}) have been adjusted. The input biomass is defined by its ultimate analysis, i.e. by its carbon, oxygen and hydrogen content. Additional elements as for example nitrogen and chloride can be added if required. At this stage, it is assumed that the feedstock will be converted to CH₄, H₂, CO and CO₂ only; carbon conversion can be incomplete and hydrogen can be also obtained from dissociation of water as present in the reactor. Other components that potentially form a part of the product gas (such as higher hydrocarbons) will be added later to the model. Firstly, the input needs to be defined by its ultimate analysis, and glucose sucrose and microalgae spirulina have been chosen as first candidates. Especially for glucose a good set of experimental data is available for model validation. The ultimate analysis of the feedstock is given in table 1. The composition of algae spirulina is taken from Phyllis2 [3] and the sulphur content has been neglected.

Table 1: Feedstock ultimate analysis in w-%

	C₆H₁₂O₆ (Glucose)	C₁₂H₂₂O₁₁ (Sucrose)	Algae spirulina
C	40.0016	42.1074	47.83
H	6.7137	6.4782	7.47
O	53.2847	51.4155	37.59
N	-	-	7.11
LHV [MJ/kg]	15.57	16.49	19.85

In order to create starting values for the temperature dependant product gas composition the yield distribution at varying temperature has been extracted from references [1] and [2]. As the goal is to provide a model that can be easily adjusted to different feedstock, the average yield at given temperature is calculated and the results are presented in Fig. 1. A linear function has been determined that allows the calculation of the yield of every product gas component. Those yields define the starting value for the actual composition calculation. Naturally, for different feedstock the values will not allow a match of the mass balance and a certain derivation around those values must be allowed. This derivation is set by the user (in this case to 35% which reflects the average derivation of the used data from the mean average). For the case of glucose and sucrose gasification full carbon conversion is assumed and for algae gasification an increase of the carbon conversion of 1%/50 °C is assumed. At 500 °C the carbon conversion efficiency (η_{CC}) is set to 92%. After that the η_{HC} as described in Eq. 1 is adjusted until a feasible solution is found. The model then solves the mass balance according to Eqs. 2-4 (n_i describes the number of moles of the component i).

$$\eta_{HC} = n_{H_2,in}/n_{H_2,out} \quad (1)$$

$$n_C = n_{C,CO} + n_{C,CO_2} + n_{C,CH_4} + n_{C,char} \quad (2)$$

$$n_H = (n_{H,H_2} + n_{H,CH_4}) \div \eta_{HC} \quad (3)$$

$$n_O = (n_{O,CO} + n_{O,CO_2}) - 0.5 \cdot n_H \cdot (\eta_{HC} - 1) \quad (4)$$

In Eqs. 3 and 4 the second term after the brackets describes the dissociation of water and its related increase of the hydrogen and oxygen yield, respectively. In Eq. 1 $n_{C,char}$ is calculated as:

$$n_{C,char} = \eta_{CC} \cdot n_C \quad (5).$$

The yields of the different product components are constrained as follows shown on the example of the component CH_4 .

$$maxCH_4(T) = n_{CH_4}(T) \cdot 1.35 \quad (6)$$

$$minCH_4(T) = n_{CH_4}(T) \cdot 0.65 \quad (7)$$

In here, the temperature dependant term describes the yield of the component based on the equations given in Fig.1.

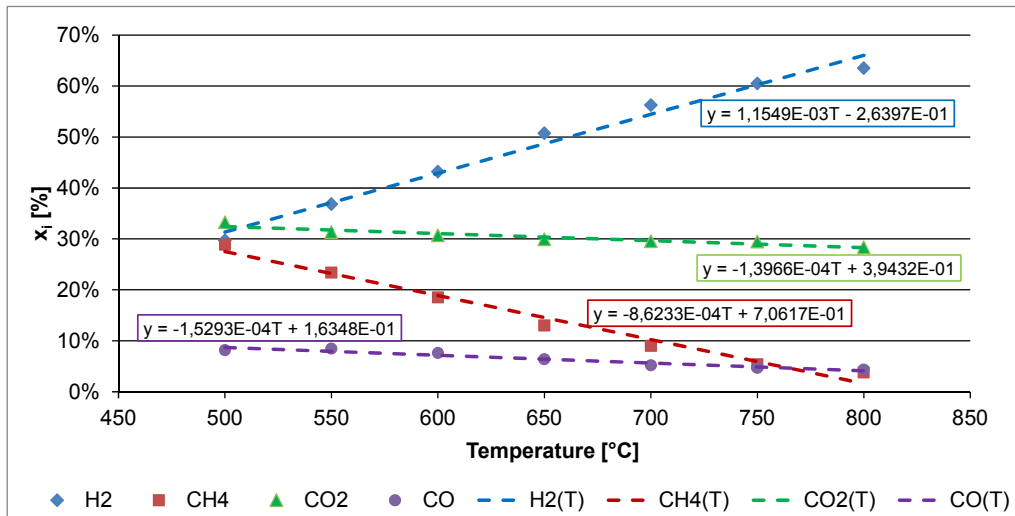


Figure 1: Yield distribution of SCWG versus reaction temperature and linear approximation equations.

Experimental setup

The experimental setting for SCWG of biomass is described in the figure below. The organic feed is introduced in suitable feed cylinders and then the sample is pumped into the reactor by means of a high pressure pump. The volumetric feed rate was also constant at a value of 3.6 ml/min. The reactor utilized for this study is a plug flow stainless steel reactor with 70% of Iron and 16% of chromium. After the reaction section, products are condensed and collected for gas and liquid analysis. Gas analysis is made by gas chromatography and the composition of the liquid products is evaluated by elemental analysis. The elemental analysis was carried

out by utilizing a CHNS analyser (Flash EA 1112 by Thermo Quest), while the gas was analysed with a gas chromatograph (Perkin Elmer Clarus 500 by Arnel). The oven has a total power of 2600W with a heating rate 140 °C/h. Three experiments were carried at constant pressure (250 bar) with temperatures and feedstock concentrations of 500 °C / 1.2 w-%, 600 °C / 2.4 w-% and 700 °C / 1.4 w-%, respectively. The product gas composition is presented in table 2.

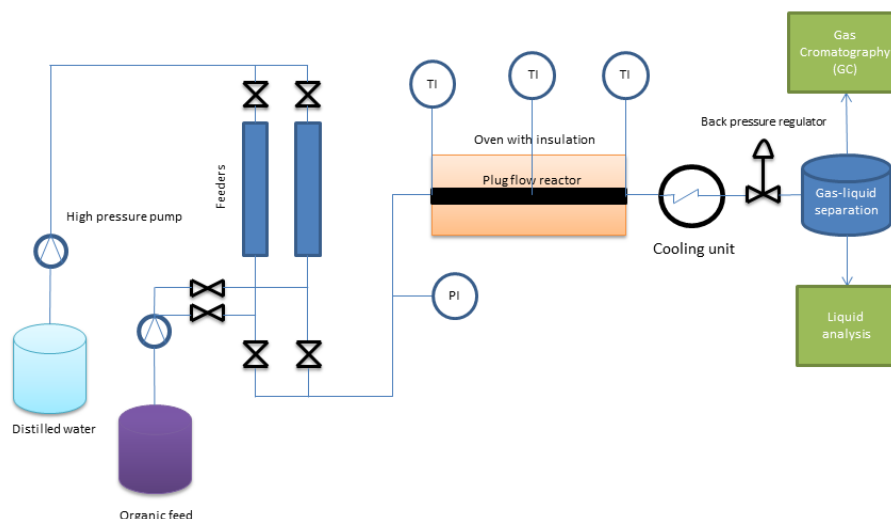


Figure 2: Experimental set-up for testing organic biomass in SCWG. The setup allows for continuous operations.

Table 2: Molar composition in mol-% of the product gas of SCWG of sucrose

Compound	500 °C	600 °C	700 °C
H ₂	13.11	20.90	35.61
CO ₂	57.62	40.90	42.69
C ₂ H ₄	0.62	1.10	0.25
C ₂ H ₆	0.78	2.57	4.80
CH ₄	3.89	15.38	15.83
CO	23.97	19.15	0.83

RESULTS

Calculated gas composition for sucrose, glucose and algae spirulina

The gas yields for H₂, CH₄, CO₂ and CO calculated for gasification of sucrose, glucose and algae spirulina in supercritical water are presented in Fig. 3. In addition also the starting values along with set boundaries are given. In general it is found that the yields calculated for different feedstock follow well the general trend that was derived from the equilibrium model. However in order to fulfil the mass balance there is a clear trend of shifting the CH₄ yields always above the starting value, whereas the H₂ yield remains below those. The same accounts for CO₂ and CO; CO is always calculated as exceeding the starting value whereas the CO₂ yield shows opposite behaviour. However, in the case of algae the CO₂ yield remains below the starting value which is likely related to the higher C/O ratio. It is less carbon required to “bind” the O₂ and hence the CO₂ generation can be smaller. Regarding the boundaries that are set by a percentage value, it can be said that the amount of freedom decreases with lower yields. In the case of CH₄ the possible derivation gets very small and for

future work a broader boundary for low starting values should be introduced to the model. Naturally the values calculated for sucrose and glucose do not vary much which stems from the very similar composition (see table 1). Summarising it can be said that the model calculates yield distribution for different feed stock that follow the trend as suggested by the equilibrium data. The model should become more reliable, once more data will be used in the calculation of the starting values.

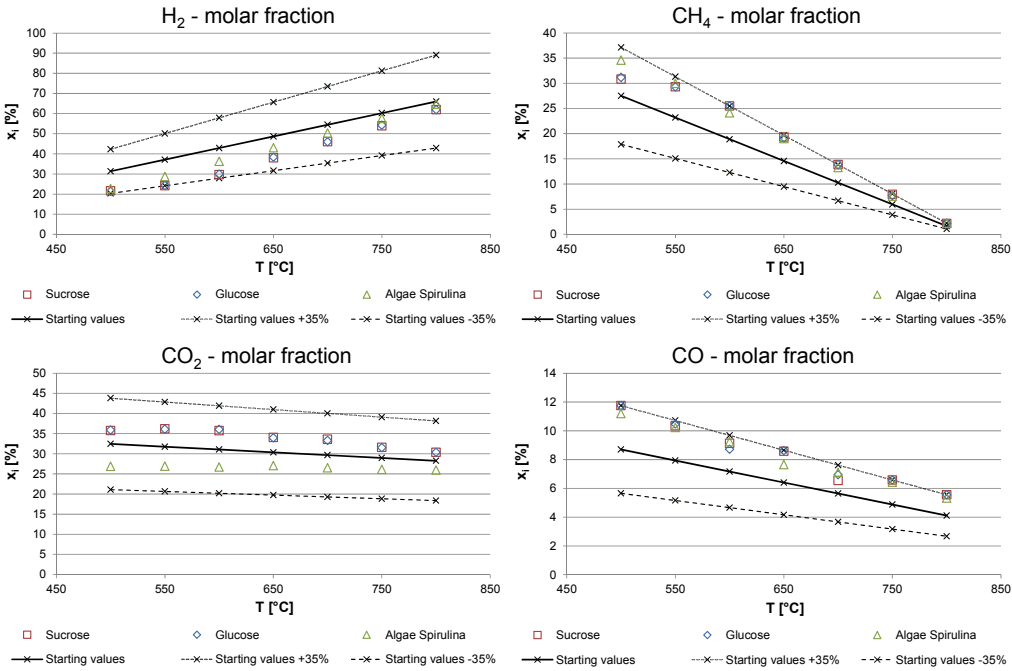


Figure 3: Calculated yield distribution of different feedstock

Fig. 3 shows the energetic conversion efficiencies along with the η_{HCS} that were adjusted in order to receive feasible results within the set boundaries. As expected the conversion efficiency (η_{conv}) increases with the temperature as a result of the higher η_{HCS} . However, it must be clear that η_{conv} just describes the ratio of the lower heating value of the product gases (CO, H₂ and CH₄) to the lower heating value of the feedstock (see table 1) and does neither consider heat that is required to keep the reactor on operation temperature nor the reaction enthalpy. Regarding the η_{HCS} , the values may appear rather high, but they are the ratio of H₂ contained in the product divided by the amount of H₂ contained in the feedstock.

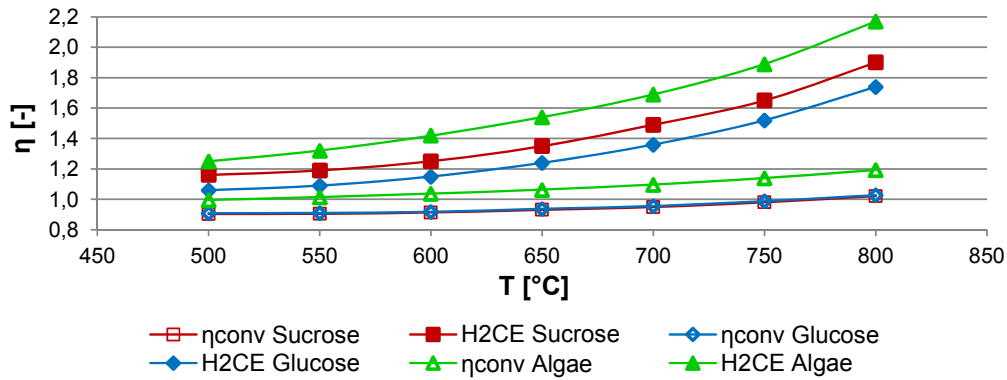


Figure 4: Energy conversion efficiency and hydrogen conversion efficiency for different feedstock

If the hydrogen generation from H_2O is related to the actual percentage of water that is dissociated during the reaction, values for algae reach 1.68 w-% to 12.61 w-% for gasification at 800 °C for feedstock concentrations of 2% and 15%, respectively. This is well in range with results presented in [4]. In contrary the same values for glucose are only in the range of 0.89 w-% to 6.66 w-% and a higher efficiencies could be obtained by allowing more water to dissociate. In the future the interdependent relation between η_{HC} , efficiency and yield distribution (affected by the boundaries set) needs to be understood better.

Comparison of calculated sucrose yields with experimental data

The data obtained from own results (see section *Experimental setup*) as well as data presented by Picou et al. [5] were used for comparison of calculated yields with experimental data. Both sets of data describe experiments carried out in non-catalysed reaction environments. The feed concentration for all cases is below 5 w-%. It can be observed from Fig. 5 that especially in the temperature range of 600 -700 °C the calculated yields are fairly close to the experimental data for all components. Also the other data points are not too far away from the calculated yields, except the CH_4 yield at 500 °C and the CO yield at 600 °C. It has to be pointed out that the increase of H_2 generation along with the temperature is well reflected by the model although the yields might be a bit overestimated. Conversely CO_2 generation seems to be slightly underestimated. Another clear weakness seems to be that the trend of CH_4 generation is poorly predicted. This needs to be improved.

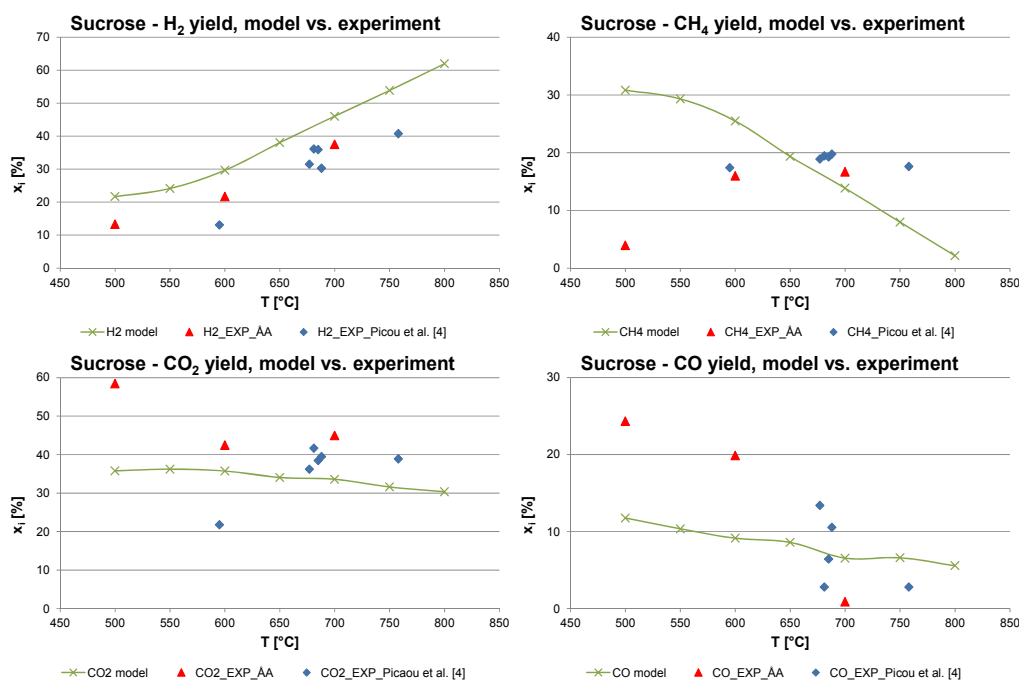


Figure 5: Comparison of calculated data with experimental results for SCWG of sucrose.

Comparison of calculated glucose yields with experimental data

As mentioned in the section *Materials and Methods* section a good set of experimental data is available from the literature for SCWG of glucose. The work used for comparison is summarised in table 3 and presents the process conditions and the feed concentration. The comparison of model results and experimental data is presented in Fig. 6. The model shows good accordance with data calculated by Voll et al. [6] who based the calculation on Gibb's free energy minimisation. The same accounts for data measured by Susanti et al. If the calculated data is compared to measurements conducted by Matsumura et al. [10] it can be concluded that the prediction is better for lower feedstock concentrations. At 700 °C Matsumura et al. measured three different feedstock concentrations of 1 w-%, 10 w-%, and 17 w-%, respectively. It can be observed that for all product gas components, except for CH₄, the data point of the test with the lowest feedstock concentration is closest to the prediction done with the mathematical model. Hendry et al. [11] used feedstock concentrations of 10 w-% and 15 w-% and varied the retention time (4 s and 6.5s). The accordance with this data is rather poor, as it is for the other references (especially for CO). The authors assume that the feedstock concentration that has not yet been implemented in the model may play an important role. In their work, Lu et al. [2] and Withag et al. [1] predicted the H₂ yield to decrease with increasing feedstock concentration, while the CH₄ yield should increase. Withag et al. predict the feedstock concentration to not influence CO and CO₂ production whereas Lu et al. predict a slight increase and decrease for CO and CO₂, respectively. Incorporating this information with the results that are gained in this work it appears that the dependency of the feedstock concentration on the yield distribution will need to be implemented to the model in order to improve accordance with experimental data. This will form the next step of our work.

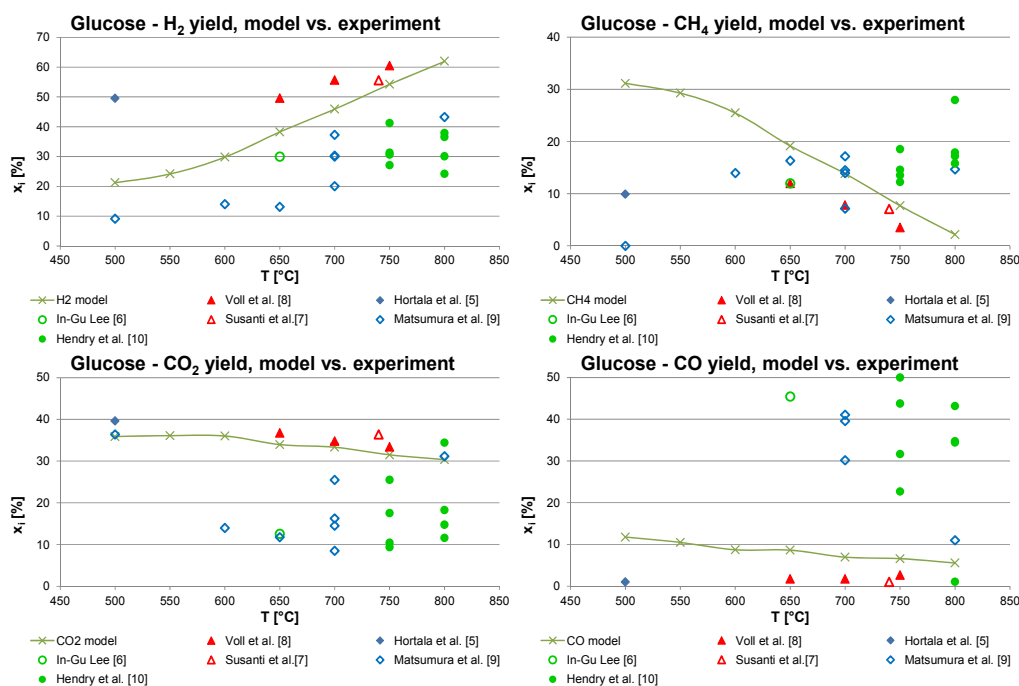


Figure 6: Comparison of calculated data with experimental results for SCWG of sucrose.

Table 3: List of references used for model validation

Reference	Pressure [bar]	Temperature [°C]	Feed conc. [w-%]
Voll et al. [6]	280	650 / 700 / 750	10.8
Hortala et al. [7]	250	500	2
In-Gu Lee [8]	280	650	10.8
Susanti et al. [9]	250	740	10
Matsumura [10]	300	500 / 600 / 650 / 700 / 800	10
		700	1 / 10 / 17
Hendry et al. [11]	220 – 330	750 / 850	10 / 15

CONCLUSION

A first mathematical model based on equilibrium data of SCWG to predict the temperature dependant product gas composition has been presented. In a blind test the model gives feasible solutions for different feedstock all representing the general yield distribution as derived from the applied equilibrium data. When the results of sucrose are compared with experiments, accordance is fairly good. However the prediction of CH₄ must be improved. The accordance of the glucose results with experimental data reveals that the model might predict well for low feedstock concentrations, but this influence must be considered in order to improve the reliability. Summarising the model developed can be easily adapted to different feedstock and will have the potential to predict product gas composition of SCWG of biomass, once the feedstock concentration is implemented. The results can then be used as input for process simulation, e.g. in order to establish mass and energy balance for varying feedstock and will form input to our upcoming energetic feasibility analysis wherein the efficiencies of different process layouts for SCWG integrated with modern power plant concepts will be analysed.

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