Modelling of a solar-powered supercritical water biomass gasifier

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1. Abstract

This paper presents the results of a rigorous modelling exercise to design a solar supercritical water gasification (SCWG) reactor. A formative reactor concept model has been developed. This model incorporates a solar receiver/reactor operating at conditions of 28 MPa and 873 – 973 K. An initial heat exchange unit is incorporated to preheat the biomass, using the waste heat (steam) of a downstream Fischer-Tropsch process. An intermediate heat exchange unit is incorporated that recovers the waste heat proceeding biomass gasification. Under the ideal assumptions applied, the predicted thermal energy efficiency of the reactor is 53%.

Keywords: Biomass, gasification, supercritical water, reactor modelling.

2. Introduction

Gasification describes the endothermic reaction between a hydrogen lean feedstock (such as coal or biomass) and steam, with substantial heat input and potentially also oxygen, to produce synthesis gas (CO, H₂, CH₄, CO₂). If oxygen is supplied to the gasification reactor, a portion of the feedstock undergoes combustion to supply the heat requirement; otherwise an external heat exchange mechanism must be employed. Synthetic chemicals and fuels derived from the conversion of a synthesis gas, via the Fischer-Tropsch (FT) reaction as a syncrude, represent an attractive replacement to fossilized crude oil [1]. The FT reaction involves the conversion of CO and H₂ to a hydrocarbon mixture (C₅H₇) and byproduct gases CO₂ and/or H₂O, with associated heat rejection. The ability to efficiently gasify biomass would offer one potential source of sustainable hydrocarbons and deliver desirable environmental outcomes.

The industrial focus on gasification to date has predominantly centred on the conversion of fossilised feedstocks (particularly natural gas) to produce synthesis gas for subsequent FT liquids conversion. There are three key reasons for the lack of industrial interest in biomass gasification. Firstly, biomass is a hydrogen lean feedstock and has a lower specific energy content than CH₄. Accordingly more external heating must be supplied to drive the gasification reaction. Secondly, existing gasification processes result in the adverse formation of char and tar by-products. These by-products represent inherent carbon inefficiency and rapidly foul process equipment. Thirdly, conventional gasification reactors require low moisture content feedstock. This either eliminates numerous biomass sources, or undesirably, involves pre-heating the feedstock to reduce the moisture content.

Gasification of biomass by means of supercritical water gasification (SCWG) presents a promising avenue for utilisation of wet and/or woody biomass that is not so attractive for other methods of gasification, and an exciting option for production of solar-boosted hydrocarbon fuels at moderate scales [2][3]. It has been found that when biomass gasification is completed in a supercritical water medium (T ≥ 647.1 K, P ≥ 22.09 MPa), gasification proceeds rapidly and cleanly (char free) yielding a gas rich in H₂, CH₄, CO and CO₂ [3][4]. Moreover, as a ‘wet-process’, SCWG process efficiency is invariant of moisture content of the biomass [5]. Literature reports on lab-scale SCWG reactors however identify a number of technical issues pertinent to an industrial-scale SCWG reactor. These include reactor plugging/fouling, heat transfer rates, high hoop stress, and ensuring complete feedstock conversion. To date SCWG reactor modelling remains undeveloped, although there is an emerging body of work regarding experimental and thermodynamic SCWG process analyses. In this study, a reactor model is developed for investigating industrial-scale SCWG.
3. System description

Our concept for an industrial scale SCWG reactor incorporates the integration of three heat-exchange/reactor units (Figure 1). This sequence of units is integrated into the overall Biomass-to-Liquids process plant. This integration is realised in the production of an unprocessed synthesis gas, and the exchange of heat with a downstream FT reactor. In the current case a low-temperature FT slurry bubble column reactor (LTFT-SBCR) was selected. The SBCR has found extensive use in industry for FT. Modelling of SBCR operation has been well documented in literature [6][7][8][9], and is continued as part of the current work [10]. For the current model, the LTFT-SBCR operating conditions were selected, which in turn determined the FT waste heat flows associated with the coolant; saturated steam at 510 K. Regenerating this coolant fluid as saturated water at 510 K and recovering energy, for continuous FT cooling and maximizing thermal efficiency, are key process requirements. In commercial applications this is ordinarily achieved by passing the coolant through a medium pressure turbine [11], thereby recovering some work from the waste heat. In the current context of wet biomass gasification, and given the low exergy of the steam, it was felt that this heat source was more valuable for use in preheat treatment.

Accordingly, the first unit of the SCWG reactor is a preheat unit. Preheating of biomass, also known as hydrothermal pulping, causes the structural decomposition of cellulosic material [12]. Experiments conducted by Kato et al. reveal that preceding liquidation treatment at 423 K promoted subsequent gasification of biomass in supercritical water [12].

The second unit in the unit sequence is a secondary heat exchanger to recover the waste heat of gasification, and to further heat the biomass slurry. In the context of reactor design, Matsumura et al. [3] suggested the biomass slurry should be pre-heated to a temperature of ≥ 723 K prior to entering a gasification reactor, to mitigate the risk of fouling the reactor surface. The rate of heat transfer should also be high to avoid fouling of the heat exchange surfaces. Matsumura et al. [3] suggested a heating rate of ~300 K min⁻¹ was required to prevent fouling of the reactor surfaces. Heat recovery is also identified in the literature as an issue of importance for thermally efficient process design [3][13]. With the biomass slurry requiring a large excess of water, as the gasification temperature is increased the SCWG thermal efficiency falls. The heat recovery performed by this heat exchange unit is necessary to maximize process thermal efficiency.

The third unit is the gasification reactor. This unit raises the fluid temperature up to the required 873 – 973 K to allow gasification to proceed rapidly, and provides sufficient residence time for this reaction to proceed to completion. The gasification reactor is formed of an arrangement of numerous vertical tubes, which in parallel conducts the preheated biomass slurry flow, and which are directly heated by concentrated solar irradiance. The design assumes a high-temperature solar heat input from a heliostat field or dish collector (Figure 2). These solar thermal concentrators operate over suitable temperature range (773 – 1073 K and 773 – 1473 K respectively) [14] for high-temperature supercritical gasification. Solar driven supercritical gasification of biomass has been demonstrated at a small scale (16 kW thermal input to the SCWG stage)[15][16].

This ‘heated tube’ gasification reactor concept was chosen for two key reasons. Firstly, Matsumura et al. [13] identified that direct heating of the biomass slurry medium had higher thermal efficiency, as compared to mixing biomass slurry with an excess of supercritical water. Secondly, as a tubular design limits the maximum hoop stress it reduces the required tube thickness, and therefore presents a more materially efficiency reactor design.
A supercritical water reactor is inevitably impacted by the confluence of high pressures and high temperatures in the context of fundamental material constraints. The corrosive environment constituted by water in the supercritical state further limits the material choices. The alloy used in this reactor model (Inconel 625®) begins to rapidly lose mechanical integrity above 973 K. Accordingly the design substituted an increased reactor length and more tubes for a more moderate internal diameter, to both reduce the hoop stress and increase residence time. Reducing the tube thickness, in the context of poor heat conduction of Inconel 625®, is of critical importance for the maximizing the rate of heat exchange. These concepts in tube sizing were applied in the design across all three units. For the purposes of simulating the SCWG reactor model, the set of un-optimised reactor geometric parameters listed in Table 1 were used.

Table 1: SCWG Reactor Geometric Parameters (10 kg s⁻¹ flow; 1.6% mol C₆H₁₂O₆)

<table>
<thead>
<tr>
<th>Component</th>
<th>Inner Radius (m)</th>
<th>Outer Radius (m)</th>
<th>Stress (MPa)</th>
<th>FOS</th>
<th>Length (m)</th>
<th>Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Preheat Vessel</td>
<td>0.275</td>
<td>0.30</td>
<td>385</td>
<td>2</td>
<td>10</td>
<td>1</td>
</tr>
<tr>
<td>Preheat Tubes</td>
<td>0.005</td>
<td>0.00625</td>
<td>100</td>
<td>6.6</td>
<td>10</td>
<td>1200</td>
</tr>
<tr>
<td>Recycle Vessel</td>
<td>0.275</td>
<td>0.30</td>
<td>320</td>
<td>2</td>
<td>10</td>
<td>1</td>
</tr>
<tr>
<td>Recycle Tubes</td>
<td>0.005</td>
<td>0.006</td>
<td>-</td>
<td>-</td>
<td>10</td>
<td>1500</td>
</tr>
<tr>
<td>Gasifier Tubes</td>
<td>0.0125</td>
<td>0.0136</td>
<td>320</td>
<td>2</td>
<td>10</td>
<td>1000</td>
</tr>
</tbody>
</table>

*1: Factor of safety (FOS) based on maximum temperature attained of 500 K. (σₘ = 660 MPa at 500 K).
*2: Factor of safety (FOS) based on maximum temperature of 973 K (σₘ = 640 MPa at 973 K).
*3: Reactor modelled as isobaric, hoop stress should be negligible across tube-side.
*4: Gasifier tube has a 5 m-heated length (at 973 K), the remaining 5 m is perfectly insulated.

4. Model description

The reactor model implements a one-dimensional non-isothermal plug flow reactor (PFR) representation. This simplified reactor representation allows for change in concentration of flow constituents by either reaction or change in fluid density. In this case mass transfer is by advective means only, and the model makes no admission for mass flow by axial mixing (driven by concentration gradients). This simple model description has been previously applied for supercritical reactor modelling by Cocero et al. [17]. Cocero published a simple supercritical water oxidation reactor (SCWO) model for the destruction of pollutant species (acetic acid or DMSO (dimethyl sulfoxide)). The differential equation for mass balance as presented by Cocero et al. [17] is shown below. The concentration of the i-th component (Cᵢ) is recovered from the molar flux rate (Fᵢ), using the continuity of mass and the calculation of fluid density.

\[
\frac{dF_i}{dx} = Ar_i
\]

\[
C_i = \frac{F_i}{ym/p} \left( \sum F_iMW_i \right) / \left( p(F_1,F_2,...,F_n,P,H) \right)
\]

\[
\frac{dH}{dx} = \frac{U\rho(T_1 - T_2) - r_i\Delta h_iA}{m}
\]

Whereas Cocero et al. used a temperature explicit form for energy balance, the current model is explicit in specific enthalpy (H) for energy balance. It was found that the enthalpy explicit form was more numerically
tractable in the current case. The above differential equations require a mathematical description of five key aspects of reactor behaviour. These are the heat transfer behaviour, gasification kinetic behaviour, thermodynamic properties, reaction thermodynamics, and transport properties. The proceeding sections briefly outline the theoretical basis for these sub-models and there numerical incorporation into the overall SCWG reactor model.

4.1 Reactor Heat Transfer

A description of heat transfer requires the elucidation of three heat transfer terms. These are the radial conduction and the inner and outer convective heat transfer terms. The radial conduction term is assumed constant over the axial dimension \( (k_r = 9.8 \text{ W m}^{-1}\text{K}^{-1}) \). However, given the dramatic change in fluid properties (temperature and composition) and flow properties (velocity and viscosity) both the convective heat transfer term must be evaluated locally \((h_i\) and \(h_o\)). Once these terms have been elucidated, these are reduced to the single local heat transfer constant \((U_o)\) as defined over the outer exchange surface \((A_o)\).

\[
U_o = \left( \frac{1}{h_o} - \frac{r_p \ln(r_c/r_t)}{k_x} - \frac{r}{r_i h_i} \right)^{-1}
\]

For modelling the tube-side FT-steam at the pre-heat unit the model assumes that the convective heat transfer behaviour is well modelled by boiling heat transfer correlation presented in [18]. This necessitates the solving for an unknown inner-wall temperature \((T_{wall,i})\) iteratively along the axial dimension. This was implemented in simulation using a direct root solving method.

\[
h_i = 2.54 \left( T_{wall,i} - T_{sat} \right)^3 \exp \left( \frac{P_{sat}}{1.551 \times 10^5} \right)
\]

For modelling the convective heat transfer over the remaining four transfer surfaces, the model implements a set of empirical relations for forced-convection heat transfer [18]. This set of relations covers all physical contingencies (Reynolds number). The correlations implemented are the Eckert Drake relation and Churchill-Bernstein relations. Where \( d \) is the characteristic length over which transfer occurs, and having determined the conductivity of the fluid (see transport properties sub-model), the convective heat transfer can be determined from the definition of Nusselt number.

\[
Nu = \frac{h_d d}{k} = \begin{cases} 
0.43 + 0.50 \text{Re}^{0.65} & \text{Pr}^{0.5} \frac{Pr}{Pr_c} & 1 < \text{Re}_d < 10^3 \\
0.3 + 0.62 \text{Re}^{0.5} \text{Pr}^{1/3} \left[ 1 + \left( \frac{0.4}{\text{Pr}} \right)^{2/3} \right]^{0.3} & \left( \frac{\text{Re}}{282 \times 10^4} \right)^{1/5} & 10^3 < \text{Re}_d < 10^7 \\
0.3 + 0.62 \text{Re}^{0.5} \text{Pr}^{1/3} \left[ 1 + \left( \frac{0.4}{\text{Pr}} \right)^{2/3} \right]^{0.5} & \left( \frac{\text{Re}}{282 \times 10^4} \right)^{0.5} & 2 \times 10^7 < \text{Re}_d < 4 \times 10^7 
\end{cases}
\]

4.2 Gasification Kinetic Behaviour

For the design of a reactor, the rate laws and associated kinetic parameters are essential elements of modelling. Unfortunately there are only a few rate laws for biomass gasification under supercritical conditions. As biomass covers all manner of carbonaceous feedstock, these are limited in literature to key ‘model’ compounds. After an extensive literature search these were found to include only cellulose and lignin [19], xyllose [20], glycerol [21] and glucose [22]. Of these however only the kinetics for glucose are immediately useful.

The first-order rate law of Lee et al. [22] for glucose gasification embodies the complete reaction network, from glucose input through intermediates to product gases. Glucose as the monomer of cellulose and primary constituent of hemi-cellulose is highly plentiful source biomass and thus an attractive biomass model.

\[
r_{\text{GLU}} = \left( 0.03^{0.89} \text{exp} \left( \frac{-67.6 \times 10^3}{RT} \right) \right) C_{\text{GLU}} \text{J} 28 \text{ MPa}, \text{ 753 – 1023K}
\]
The envisaged gasification reaction represents two consecutive reactions, an initial glucose reforming reaction that is instantly followed by the water gas shift reaction (WGSR). The succeeding WGSR recognises that this reaction is rapid and that the equilibrium position inherently favours the formation of H₂ and CO₂. However, being a reversible reaction, the gaseous product balance may later changing under altered reactor conditions, and accordingly this and other gas-phase chemistry should be accounted for.

\[
\begin{align*}
\text{C}_6\text{H}_{12}\text{O}_6 + 6\text{H}_2\text{O} & \rightarrow 6\text{CO}_2 + 12\text{H}_2 & \Delta_h^0 = -125\text{kJ/mol} \\
\text{CO} + \text{H}_2\text{O} & \leftrightarrow \text{CO}_2 + \text{H}_2 & \Delta_h^0 = -\Delta\text{kJ/mol} \\
\text{CO} + 3\text{H}_2 & \leftrightarrow \text{CH}_4 + \text{H}_2\text{O} & \Delta_h^0 = -206\text{kJ/mol}
\end{align*}
\]

In addition to the WGSR, the most other relevant gas product reaction is the methanation reaction. Much like the gasification chemistry however, there are few rate relationships available for describing the kinetics of gaseous products under supercritical conditions. To our current knowledge there are no published methanation reaction rate laws covering supercritical conditions. WGSR rate laws under supercritical conditions are also limited to first-order CO relationships as reviewed by Sato et al. [23]. None of these published rate laws were immediately useful for modelling the reversible reaction. Under a set of assumptions outlined in our original work [10], the following reversible rate law was used for modelling.

\[
r_{\text{e}} = (793)\exp\left[-\frac{1.45\times10^3}{RT}\left(C_{(\text{H}_2\text{O})}^{(793)}\right)\exp\left[-\frac{1.45\times10^3}{RT}\left(C_{(\text{H}_2\text{O})}^{(793)}\right)\right]
\]

The rate of the methanation reaction is more reliably assumed as zero as evidenced by the reactor experiments of Taylor et al. [24]. Taylor reported on experiments on methanol reforming in supercritical water at 823 – 973 K under 27.6 MPa in a tubular Inconel-625 reactor. Taylor reported that the production of methane was suppressed, and the WGSR was accelerated. It was concluded that Inconel-625 kinetically inhibits the formation of methane from achieving thermodynamic equilibrium. Discounting the possibility that the glucose precursor undergoes hydrogasification to produce methane directly, this eliminates the methane component from further analysis.

The reaction equilibrium position under isothermal and isobaric assumptions is required to account for the reversibility of the WGSR (K_{eq}). This is calculated from the ideal gas mixture Gibbs free energy and the non-ideal contribution to the Gibbs free energy. This is calculated using NASA polynomials [25], and the residual Gibbs free energy of reaction (see reaction thermodynamics sub-model).

\[
K_i = \left[\frac{\partial G}{\partial \tau}\right]_{p,T} = \exp\left[-\frac{\Delta_g G}{RT}\right]
\]

### 4.3 Thermodynamic Property Model

The model implements the Peng-Robinson Equation-of-State (PR-EoS) fluid model [26] to predict the thermodynamic properties of the mixture properties. The \(p-V-T\) relationship is characterised by the cubic equation with the equation parameters \(a\) (temperature dependent attraction parameter) and \(b\) (temperature independent repulsion parameter). The definition of these parameters is given in terms of the mixture components critical properties \((T_{ci}, P_{ci}, \omega_i)\) is left to reference [27]. The model applies Van der Waals one-fluid theory classical mixing rules, with binary interaction parameters calculated according to the method of Praustnitz and Cheu [28]. The critical properties were taken from Reid et al. [29].

\[
p = \frac{RT}{(v-b)} - \frac{a}{v(v+b)+b(v-b)}
\]

By taking the partial thermodynamic derivatives of the PR-EoS, provides the means to evaluate the remaining thermodynamic properties of interest \((U, S, H, G, C_v, C_p)\). The residual quantity of any thermodynamic property describes difference between that of the real fluid mixture and the ideal gas mixture, and is described by the departure functions of the applied equation of state. Melham et al. [30]
provides a full derivation of the required analytical thermodynamic derivatives of the PR-EoS, which were implemented in this model. The ideal thermodynamic quantities of an ideal gas mixture were established using NASA polynomials assuming a linear mixture model. The fluid enthalpy at $T$ is referenced to a common enthalpy datum at the reference condition (298.15 K, 1 bar).

$$h = \sum_i x_i h_i^0 + \sum_i \int_{T_{ref}}^T c_p^0 \, dT + \left( \frac{RT(Z-1)}{b^2/2} - a \right) \ln \left[ \frac{Z + (\frac{1}{2})B}{Z + (\frac{1}{2})B} \right]$$

The molar entropy, internal energy and Gibbs free energy (and the specific equivalents; $U, S, G$) each have forms similar of that given above for molar enthalpy. The molar heat capacities $c_v$ and $c_p$ (and their specific equivalents) can be obtained directly by differentiation of $u$ and $h$ respectively. Lastly, as the energy balance is given in terms of specific enthalpy ($H$) the model must at each spatial location determine the fluid temperature for the given composition and pressure. This temperature is found by solving the non-linear equation posed by the residual equation form of the above enthalpy equation (in specific form). A Brent solver method was implemented.

### 4.4 Reaction Thermodynamic Model

The enthalpy changes resulting from chemical reactions (the breaking and formation of chemical bonds) are calculated using Hess’s Law. In this model, this process shall be considered as both isothermal and isobaric. The ideal component of the heat of reaction (ideal-gas to ideal-gas enthalpy of reaction; $\Delta h^\beta$) is calculated using NASA polynomials and a referenced enthalpy datum (298.15 K, 1 bar).

To observe energy balance during the chemical reaction at conditions other than ideal gas conditions, the reaction enthalpy must also include the enthalpy change resulting from the reaction of real compounds at high pressure. This can include the enthalpy difference resulting of any phase changes. This enthalpy difference is the residual enthalpy of reaction. Applying the same summation under Hess’s law, this can be evaluated from the component residual partial molar enthalpies. Partial molar enthalpies were calculated using the Peng-Robinson equation of reaction (PR-EoR) presented by Marroqui de la Rosa et al. [31].

$$\Delta_h = \sum_i v_i \left( \Delta_j h_{ref}^0 + \int_{T_{ref}}^T c_p^0 \, dT - \frac{\partial (g_i^G - g_i^R)}{\partial T} \right)_{T,p,s,m}$$

The spontaneity and directionality of a chemical reaction can be ascertained by evaluating the Gibbs free energy of reaction. The ideal Gibbs free energy is conveniently evaluated from NASA polynomials referenced to the Gibbs free energy datum of each species. The residual contribution to the Gibbs free energy is determined from the respective partial molar Gibbs free energy of each component. A key thermodynamic requirement is realized in the Second Law of Thermodynamics, which dictates that, under isothermal and isobaric conditions, only a reaction with free energy change $\Delta G < 0$ is spontaneous. The model calculates the respective values for $\Delta G_{gasify}$ and $\Delta G_{pyro}$ to zero out the gasification reaction rate (if the reaction is entropically prohibited) and to determine the equilibrium constant (directionality) of the WGSR.

$$\Delta_{g} = \sum_i v_i \left( \Delta_j g_{ref}^0 + \int_{T_{ref}}^T c_p^0 \, dT - \int_{T_{ref}}^T \frac{c_p^0}{T} \, dT - R \ln \frac{p}{p_o} - \frac{\partial (g_i^G - g_i^R)}{\partial T} \right)_{T,p,s,m}$$

### 4.5 Transport Property Model

Transport properties such as viscosity ($\mu$) and conductivity ($\lambda$) exhibit strong composition, temperature and pressure dependency. Whilst an isobaric assumption is made, the fluid experiences wide temperature variation (298 – 973 K), and radical fluid composition variance, such that the transport properties shall vary significantly. A flexible transport property model was required to calculate fluid transport properties.
The pure component viscosities and conductivities are determined using the method of Chung et al. [32]. The method of Chung is valid for the calculation of high-pressure, high-density gases. This is achieved by a corresponding states method to correlate the change in transport properties according to the change in PVT properties. The method also accounts for molecular properties; including molecular weight, dipole moment and association factor to characterize molecular effects upon transport properties.

The method first establishes the low-pressure gas transport property value ($\mu$, $\lambda$). Further given relations map the component low-pressure transport property to the high-pressure region ($\mu$, $\lambda$). Mixture viscosity and conductivity are determined using the mixing rule methods of Wilke (for $\mu$) and Wassiljewa (for $\lambda$) as reported by Reid et al. [29]. These methods are applicable for dense gas mixtures and report good results for polar-polar mixtures.

5. Results

The ordinary differential equations for mass and energy balance for each reactor unit were solved simultaneously using MATLAB (2009). Initial value problems (preheat and gasifier units) were solved using the ode15s routine. The two-point boundary value problem posed by the heat recovery exchanger unit was solved using BVP5c routine. The issue presented by the unknown right-side boundary condition was resolved by applying a tearing process across the gasifier outlet stream and the heated tube-side heat recovery unit. A maximum absolute deviation between these streams, in any component or stream enthalpy, of $\varepsilon = 1 \times 10^{-4}$ % was allowed. The system rapidly converged upon the final solution after several iterations.

The SCWG reactor was simulated under 10 kg s$^{-1}$ mass flow rate with a 60:1 H$_2$O:glucose molar excess. Departure functions of PR-EoS for enthalpy were adapted to model the required pumping work required to compress the inlet mixture from ambient pressure to 28 MPa at room temperature (298 K). Subsequent performance analysis of SCWG reactor was based on three metric categories. These are biomass conversion, the heating effects, and SCWG energy efficiency.

The conversion of biomass ($X$) is defined as the percentage of biomass input having undergone gasification. Attaining near complete gasification should clearly be a key process goal so as to minimize the complexity of the downstream processing operations for the reactor liquid effluent stream. The current SCWG reactor configuration indicates that 97% of the glucose shall gasify. This would suggest that the residence time, and by consequence the scale of the reactor tube units, are close to ideal under the simulated mass flow.

The heating metrics utilised are the pre-gasification temperature and the heating rate. The mean heating rate over the heat recovery exchange unit was calculated from the temperature lift and residence time. The simulated design fails to lift the fluid temperature to the suggested pre-gasification temperature of 723 K suggested by Matsumura et al. [3] (modelled to reach 703 K). However, the recycle heat exchange surface is predicted to provide the required rapid heating rate in excess of 300 K min$^{-1}$ (simulated to proceed at 310 K min$^{-1}$). While this goes some way to alleviate the aforementioned plugging issues, optimisation should be completed to enhance the heating rate and boost the temperature lift achieved by the heating transfer surface.

<table>
<thead>
<tr>
<th>Energy Flow</th>
<th>Power (MW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_6H_{12}O_6$ LHV</td>
<td>21.3</td>
</tr>
<tr>
<td>$W_{comp}$</td>
<td>0.25</td>
</tr>
<tr>
<td>$Q_{FT}$</td>
<td>7.1</td>
</tr>
<tr>
<td>$Q_{vol}$</td>
<td>13.5</td>
</tr>
<tr>
<td>CO Fuel LHV</td>
<td>0.0015</td>
</tr>
<tr>
<td>$H_2$ Fuel LHV</td>
<td>22.3</td>
</tr>
</tbody>
</table>

Figure 3: Heat recovery and gasifier units temperature profile
The energy efficiency ($\eta$) has been defined analogously to that of Calzavara et al. [33]. This relates the thermomechanical energy inputs (compression work, preheating, solar heating) and chemical energy (heating value of glucose) and relates this to the recovered thermomechanical energy (expansion work and heat recovery) and chemical energy (heating value of CO and H$_2$). The current study makes no consideration of the potential thermomechanical energy recoveries from the reactor effluent. These energy flows are presented in Table 2, and give an overall energy efficiency of 53% (subsequent to further energy recovery).

$$
\eta = \frac{F_{CO}^{out} LHV_{CO} + F_{H_2}^{out} LHV_{H_2}}{X \cdot F_{Glu}^{in} LHV_{Glu} + Q_{in} + Q_{PT} + W_{comp} - W_{receiver} - Q_{receiver}}
$$

The reactor energy efficiency was compared to the 28 MPa SCWG model of Calzavara et al. (Table 3). The current model presents an intermediate energy efficiency between the two ideal zero-dimensional models of Calzavara et al. in which energy is not recovered (33%) and in which energy recovery is performed (76%). A key difference is the lower required external heat per unit biomass input (50% less) as driven by the internal heat recovery. The means to derive additional efficiencies can only be realised by considering subsequent heat and work recovery. The extent to which the water effluent (which retains the bulk of the waste heat) could be directed towards useful heating purposes, such as a heat source to drive the water gas shift reaction in the post-processing of the generated syngas, is an avenue of potential further investigation.

<table>
<thead>
<tr>
<th>Experimental [33]</th>
<th>Thermodynamic [33]</th>
<th>This Model</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biomass</td>
<td>$C_6H_{10}O_5$</td>
<td>$C_6H_{12}O_6$</td>
<td></td>
</tr>
<tr>
<td>$C_6H_{10}O_5$</td>
<td>0.12</td>
<td>1.43</td>
<td>kg/s</td>
</tr>
<tr>
<td>$H_2O:C_6H_10O_5$</td>
<td>60:1</td>
<td>60:1</td>
<td>mol/mol</td>
</tr>
<tr>
<td>$\chi$</td>
<td>100</td>
<td>97</td>
<td>% Conv</td>
</tr>
<tr>
<td>$Energy Input$</td>
<td>29.31</td>
<td>27.65</td>
<td>MJ/kg $C_6H_{10}O_5$</td>
</tr>
<tr>
<td>$\eta$ (no recovery)</td>
<td>33</td>
<td>36</td>
<td>%</td>
</tr>
<tr>
<td>$\eta$ (recovery)</td>
<td>76</td>
<td>93</td>
<td>%</td>
</tr>
</tbody>
</table>

6. Conclusions

A solar powered FT-SCWG integrated process presents a potentially attractive option for the sustainable production of hydrocarbon chemicals and solar boosted fuels. SCWG has been demonstrated as a viable means for the conversion of a woody biomass resource to an industrially useful synthesis gas in laboratory reactor scale experiments. This work describes modelling of a new solar reactor based upon reported laboratory scale experimental data and empirical relations.

A one-dimensional non-isothermal plug-flow reactor model was developed for the purpose of investigating SCWG reactor behavior, and provides an initial basis for designing a SCWG reactor. Specific model attributes included accounting for gasification kinetics, heat transfer, and a broad range of thermo-physical properties. The work also addresses many issues identified in the literature, including high hoop stress, high-temperatures, the effects of a corrosive water medium, achieving high heat transfer rates, mitigating reactor plugging/fouling, and ensuring near complete biomass gasification. Further optimization of the SCWG reactor design and integration with a solar field has yet to be completed.

The energy efficiency of the SCWG reactor, before additional energy recovery, was 53%. The majority of the unrecovered waste heat, that embodied of the reactor effluent stream, is associated with the water fraction due to its large excess in the biomass slurry. In a combined FT-SCWG system it is quite possible that this waste heat resource can be applied to a downstream process, which would in turn drive enhanced process
efficiency. It should also be noted that this efficiency figure ignores the additional inefficiency due to the thermal and optical losses associated with a solar receiver and heliostat system. As such, the overall process efficiency would be lower than in this ideal model.

References