**Supplementary Material**

**Thermodynamic model**

**Air Gasification**

The moisture content per mole of biomass is calculated from the following equation:

|  |  |
| --- | --- |
|  |  (A1)  |

where *MWbiomass* and *MWw* demonstrate the biomass and water molecular weights, respectively. *MC* is the moisture content of biomass.

 The element balances of carbon, hydrogen and oxygen for the global reaction are as below:

Carbon balance:

|  |  |
| --- | --- |
|  | (A2) |

Hydrogen balance:

|  |  |
| --- | --- |
|  | (A3) |

Oxygen balance:

|  |  |
| --- | --- |
|  | (A4) |

Nitrogen balance:

|  |  |
| --- | --- |
|  | (A5) |

The chemical reactions occurring in the gasification process in the presence of air are given by:

|  |  |
| --- | --- |
|   | (A6) |
|  | (A7) |

The equilibrium constant (*Ki*) can be expressed based on the participating species in stoichiometric coefficient as below:

|  |  |
| --- | --- |
| (A8) |  |
| (A9) |  |

where *nt* is the total number of produced gas.

On the other hand, the equilibrium constants as a function of temperature are expressed as follows:

|  |  |
| --- | --- |
|  | (A10) |
|  | (A11) |

The energy balance is the last necessary equation for the model, which can be written as below:

|  |  |
| --- | --- |
|  | (A12) |

where *h* is enthalpy of components given by the following equation.

|  |  |
| --- | --- |
|  | (A13) |

Now there are six unknowns namely *nH2*, *nCO*, *nCO2*, *nH2O*, and *nCH4* as the molar flow rate of the species in the product from the global reaction and gasification temperature (*T*) from the energy balance. Therefore, six equations are required to find the unknowns, gained from the three element balances of carbon, hydrogen and oxygen, two equilibrium constant equations, and an energy balance for the whole system.

**Steam Gasification**

Element balances for carbon, hydrogen and oxygen are described as follow:

Carbon balance:

|  |  |
| --- | --- |
|  | (A14) |

Hydrogen balance:

|  |  |
| --- | --- |
|  | (A15) |

Oxygen balance:

|  |  |
| --- | --- |
|  | (A16) |

The chemical reactions occurring in the steam gasification process are:

*Methane decomposition reaction:*

|  |  |
| --- | --- |
|   | (A17) |

*Water gas shift reaction:*

|  |  |
| --- | --- |
|   | (A18) |

*Solid carbon reaction:*

|  |  |
| --- | --- |
|   | (A19) |

The equilibrium constants of the above equations are expressed as below:

|  |  |
| --- | --- |
|  (A20)  |  |
| (A21) |  |
| (A22) |  |

The equilibrium constants in terms of temperature are as below:

|  |  |
| --- | --- |
|  | (A23) |
|  | (A24) |
|  | (A25) |

The energy balance can be defined as below:

|  |  |
| --- | --- |
|  | (A26) |

**Air/Steam Gasification**

Element balances are:

Carbon balance:

|  |  |
| --- | --- |
|  | (A27) |

Hydrogen balance:

|  |  |
| --- | --- |
|  | (A28) |

Oxygen balance:

|  |  |
| --- | --- |
|  | (A29) |

Nitrogen balance:

|  |  |
| --- | --- |
|  | (A30) |

The chemical reactions occurring in the presence of air/steam are as below:

*Methane generation reaction:*

|  |  |
| --- | --- |
|   | (A31) |

*Water gas shift reaction:*

|  |  |
| --- | --- |
|   | (A32) |

 *Methane decomposition reaction:*

|  |  |
| --- | --- |
|   | (A33) |

The equilibrium constant in terms of temperature represented as:

|  |  |
| --- | --- |
|  | (A34) |
|  | (A35) |
|  | (A36) |

The energy balance is given by:

|  |  |
| --- | --- |
|  | (A37) |

**Figures:**



**S1 (a)**



**S1 (b)**



**S1 (c)**

**Figure S1**: Producer gas compositions as a function of gasification temperature for (a) air, (b) steam, and (c) air/steam gasification process

**Nomenclatures**

|  |  |
| --- | --- |
|  | Isobaric heat capacity (kJ mol-1 K-1) |
|  | Activation energy of reaction i (J mol-1 K-1) |
|  | Gibbs function (kJ kmol-1) |
|  | Enthalpy change (kJ kmol-1) |
| *ki* | Rate constant of reaction i (s-1) |
|  | Lower heating value (kJ kg-1) |
|  | Molecular weight (g mol-1) |
|  | Oxygen to biomass molar ratio (mole) |
|  | Pressure (Pa) |
|  | Universal gas constant (J mol-1 K-1) |
|  | Temperature (K) |
| *w* | Moisture content per mole of biomass |
|  | Mole fraction  |
| **Subscripts and superscripts** |
| *ch* | Chemical |
| *eq* | Equilibrium |
| *f* | Formation |
| *g* | Gas |
| *i* | i-th reaction |
| *j* | j-th component |
| *ph* | Physical |
| *t* | Total |
| *w* | Water  |
| *ͦ* | Standard |