

Modelling of Two Stage Gasification of Waste Biomass

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In this work, a two-stage gasification process enabling low tar content of gas was studied by experimental investigation and mathematical modelling. A computer model capable of predicting mass and energy balances of both steps, producer gas composition, and kinetics of thermal decomposition was developed. As input data, the characteristics of raw material estimated in the laboratory were used. Kinetic and heat transfer data were derived from literature. A mixture of different types of ligno-cellulosic waste biomass was assumed to be gasified in an industrial scale pyrolysis/gasification system with a pyrolysis reactor, a char gasification reactor and a catalytic volatile gasification reactor. Gasification of a mixture of wheat straw, corn stalks, corn leaves, barley straw and wooden chips was modelled under various conditions. Temperature in the pyrolysis reactor was 550 °C and that in the catalytic volatile gasification reactor at optimal air to biomass mass ratio was 850 °C. As the gasification agent, air, oxygen enriched air and pure oxygen were used. The amount and composition of producer gas were determined. All types of waste biomass were studied also by thermogravimetric (TGA) analysis, differential scanning calorimetry (DSC), elemental analysis and bomb calorimetry. Elemental composition of pyrolysis char and solid fraction and also the composition of gases from the pyrolysis stage were measured experimentally. Optimal oxidising medium to biomass mass ratio was estimated to be 1.5 for air, 0.45 for oxygen rich air (70 % oxygen), and 0.35 for technically pure oxygen (99 %). Lower heating value (LHV) of gas from the gasification stage calculated based on its composition was 6.6 MJ/Nm³, 10.3 MJ/Nm³ and 11.0 MJ/Nm³ for air, oxygen rich air and pure oxygen.

1. Introduction

From the view point of energy application, two types of biomass are distinguished; the first type is the biomass grown for this purpose, and the second type is the waste biomass. Waste biomass includes wood and wood waste from forestry and wood processing industry, waste from agriculture and landscape maintenance, waste from livestock and organic waste from food industry. The two first mentioned types of waste biomass are formed mainly of lignocellulosic materials; the major components of their structure are cellulose, hemi-cellulose and lignin. These groups of waste biomass represent a huge potential of renewable energy, however, their degradation by biological methods is very slow and therefore suitable for thermal processing. Thermal methods allow the decomposition of lignocellulosic biomass in a short period of time.

In general, gasification is a more efficient and eco-friendly method of biomass conversion to energy compared to incineration. In addition, gasification enables the recovery of material products, such as syngas, hydrogen, and methanol (Higman and Van der Burgt, 2008). A design of production fuel gas from barley straw is presented in Sun et al. (2014).

Until now, various gasification technologies particularly for coal and biomass gasification, have been developed (Sansaniwal et.al., 2017). Also, co-gasification of biomass and coal was tested by McIlveen-Wright et al. (2006). Gasification of biomass and solid waste has been studied by many authors in the last two decades; a review on biomass gasification for electricity generation has been provided by Ruiza et al. (2013). Gas obtained by the gasification process is usually incinerated to produce electricity. In order to use this gas in internal combustion engines or turbines, it has to meet quite strict requirements for the tar content. Gas produced by conventional gasification techniques usually contains a significant amount of tar and cannot be directly combusted in internal combustion engines or turbines. Although much attention has been devoted to gasification in recent years, tar

free gasification is still a challenge. In order to reduce the tar content in the product gas, the so called two-stage gasification has been developed, where the solid material is subjected to a pyrolysis process in the first step and the products of pyrolysis are subjected to a gasification process. From the published works in this area results that using this method can significantly reduce the tar content in the product gas (Henriksen et al., 2006). Except for the downdraft two stage gasification process developed by authors from the Technical University of Denmark, the two stage pyrolysis/gasification practically has not been the subject of other research. The concept used in our previous works (Haydary et al., 2013) and also by other authors (Kosov and Zaichenko, 2016), deals with only cracking of volatile fraction in the second stage. This work deals with a different configuration of the two-stage gasification process than presented in Henriksen et al. (2006) and different than two stage gasification set-up presented by Hamel et al. (2007). A pyrolysis reactor is combined with a char gasification reactor and a catalytic volatile gasification reactor.

Modelling of gasification and pyrolysis processes has been the subject of different research works. A review of gasification models can be found in the work published by Puig-Arnavat et al. (2010); another review work published by Di Blasi (2007) describes different models of biomass pyrolysis. However, research works on modelling of a two stage pyrolysis/gasification process are very scarce. This work deals with computer design and simulation of two stage pyrolysis/gasification of biomass with the configuration presented in Figure 1. The proposed model is capable of predicting mass and energy balances of both steps, producer gas composition, and kinetics of thermal decomposition. The considered feed (waste biomass) was studied by thermogravimetric (TGA) analysis, differential scanning calorimetry (DSC), elemental analysis and bomb calorimetry and the data obtained were used in the model.

2. Materials and methods

A mixture of lingo-cellulosic waste biomass consisting of 25 mass% of wheat straw, 25 mass% of corn stalks and leaves, 25 mass% of barley straw and 25 mass% of wooden chips was ground to particles with the equivalent diameter of less than 1 mm. Thermogravimetric (TG) and differential scanning calorimetric (DSC) analysis were provided by a simultaneous TG/DSC analyser (Netzsch STA 409 PC Luxx, selb, Germany). Samples of around 20 mg were used in the TG/DSC measurements.

Dry basis elemental composition of biomass was estimated by a Vario Macro Cube ELEMENTAR elemental analyser. A CHNS (C, H₂, N₂, S) module with the combustion tube temperature of 1,150 °C and the reduction tube temperature of 850 °C was used. The module did not enable the determination of the chlorine content. The mass of the samples for elemental analysis was around 1 g.

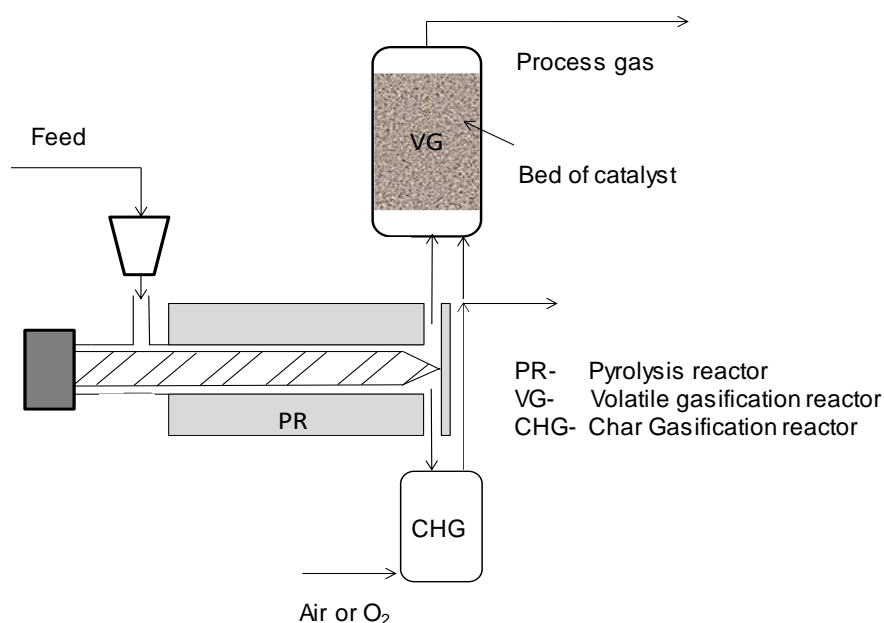


Figure 1: Concept of the studied two stage pyrolysis/gasification process

Results of both proximate and elemental analyses are given in Table 1. The symbol (*) indicates moisture free based. The content of oxygen was calculated by the difference up to 100 %. Thermal decomposition heat of

reaction estimated by DSC measurement was 390 kJ/kg. Higher heating value (HHV) of waste biomass was measured using an FTT isoperibolic calorimetric bomb, Fire Testing Technology Limited. Combustion of the sample took place in a calorimetric bomb under oxygen atmosphere at 30 bars.

Table 1: Proximate and elemental composition of used waste biomass mixture (mass %)

Moisture	Volatiles*	Fixed* C	Ash*	C*	H*	N*	S*	O*
10.00	83.18	13.11	3.71	49.02	5.74	0.71	0.22	40.60

The sample mass was around 1 g. Benzoic acid was used as a standard material. To eliminate the effect of sample heterogeneity, more samples of biomass were taken for this measurement; in addition, each measurement was repeated at least three times, the allowed variation between the measurements was 0.2 MJ/kg, average HHV was 18 MJ/kg.

The feed biomass enters a screw type reactor (PR) working in the temperature range from 500 to 600 °C. The volatile fraction from the pyrolysis reactor enters the catalytic vapour gasification reactor (VG) and the solid fraction enters the char gasification reactor (CHG). The producer gas from the CHG can be also led to the catalytic vapour gasification reactor. This configuration of two stage gasification can ensure very low concentration of tar.

3. Mathematical model

3.1 Model of pyrolysis stage

For modelling the pyrolysis stage, one of the most used reaction schemes in literature, shown in Figure 2, was applied by Di Blasi (2007) and more recently by Park et al. (2010).

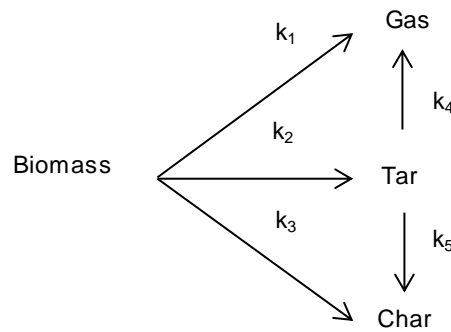


Figure 2: Reaction scheme of the pyrolysis stage (Park et al., 2010)

$$\frac{\partial \rho_B}{\partial t} = -(k_1 + k_2 + k_3)\rho_B \quad (1)$$

$$\frac{\partial \rho_C}{\partial t} = k_3\rho_B + k_5\rho_T \quad (2)$$

$$\frac{\partial \varepsilon \rho_T}{\partial t} = k_2\rho_B - (k_5 + k_4)\rho_T \quad (3)$$

$$\frac{\partial \varepsilon \rho_G}{\partial t} = k_1\rho_B + k_4\rho_T \quad (4)$$

$$k_i = A_i e^{\left(\frac{-E_i}{RT}\right)} \quad (5)$$

Where Eq(1) represents the rate of biomass consumption, Eq(2), Eq(3) and Eq(4) describe the rate of char, tar and gas formation, ρ_B , ρ_C , ρ_T and ρ_G are mass concentration of biomass, char, tar and gas, respectively, k_i is the rate constant of reaction pathway i calculated by Arrhenius equation Eq(5), A is the pre-exponential factor, E the activation energy, R the gas constant, T is temperature in K and ε is the porosity of biomass which is calculated as:

$$\varepsilon = 1 - \frac{\rho_s}{\rho_B} (1 - \varepsilon_B) \quad (6)$$

In Eq(6), ε_B is the initial porosity of biomass, which is considered to be 0.4, ρ_s and ρ_B are mass concentrations of solid phase and virgin biomass. Energy conservation in a volume element of particles is given by the equation:

$$(C_B \rho_B + C_C \rho_C + \varepsilon C_T \rho_T + \varepsilon C_G \rho_G) \frac{\partial T}{\partial t} = \frac{1}{r^2} \frac{\partial T}{\partial r} \left(r^2 \lambda \frac{\partial T}{\partial r} \right) + Q \quad (7)$$

Heat transfer to the particle surface is given by the boundary condition:

$$\frac{\partial T}{\partial r} = h(T_G - T) + \delta e_s (T_s^4 - T^4) \quad (8)$$

Where C_B , C_C , C_T , and C_G are heat capacities of biomass, char, tar and gas, respectively, r is the particle diameter, λ is the effective thermal conductivity calculated based on thermal conductivities of all components and heat radiation through pores, Q is the heat released or consumed by the reaction, h is the convective heat transfer coefficient, δ , is the Stephan-Boltzman constant, e_s the surface emissivity and t is time. For more details on the pyrolysis model, see literature review works such as Di Blasi (2007).

3.2 Model of gasification stage

The process configuration shown in Figure 1 enables considering that in the gasification step, the chemical equilibrium is approached and equilibrium constant can be calculated based on the standard Gibbs free energy. The change of the Gibbs free energy for a reaction system are given by:

$$\Delta_r G = \Delta_r G^o + RT \ln \prod_i a_i^{v_i} \quad (9)$$

Where $\Delta_r G^o$ is the standard (reference) Gibbs free energy, a_i is the activity of component i , and R is the gas constant. At an equilibrium state, $\Delta_r G = 0$ and from Eq(9) it follows:

$$\Delta_r G^o = -RT \ln K_e \quad (10)$$

$$K_e = \prod_i a_i^{v_i} \quad (11)$$

is the equilibrium constant of the chemical reaction. Standard Gibbs free energy can be calculated from standard Gibbs free energies of formation, $\Delta_f G_i^o$, of components as:

$$\Delta_r G^o = \sum_i v_i \Delta_f G_i^o \quad (12)$$

For more detail of the gasification model Haydary (2016). A computer model of the process was developed by combining a user subroutine of the pyrolysis stage with a Gibbs reactor model of Aspen Plus. Aspen Gibbs reactor model uses the equilibrium constants calculated based on Gibbs free energy and Ideal phase equilibrium model for calculation of equilibrium composition (mole fractions) of the reaction products.

4. Results and discussions

Results of thermal decomposition of biomass particles in the pyrolysis stage calculated by the model described above are shown in Figures 3a and 3b. Kinetic parameters were derived from Janse et.al (2000) and material properties data from Park et al. (2010). Spherical particles with the equivalent diameter of 2 mm were considered. At 550 °C, the biomass conversion was completed after 2 s. In the reaction time of 2.5 s, the product yields were calculated for the temperature range from 470 to 590 °C. The product yields from the pyrolysis stage at different temperatures are given in Figure 3. The pyrolysis stage reactor temperature was set to 550 °C. Elemental and proximate composition of char and tar was measured experimentally and they are shown in Table 2. The composition is moisture free based and the content of oxygen was calculated up to 100%. Composition of gas from the pyrolysis reactor measured by an online micro-chromatograph (Susa and Haydary, 2015) is shown in Table 3. The vapours from the pyrolysis reactor entered the catalytic volatile gasification reactor (VG) at 550 °C. Air was supplied to the bottom of the char gasification reactor (CHG).

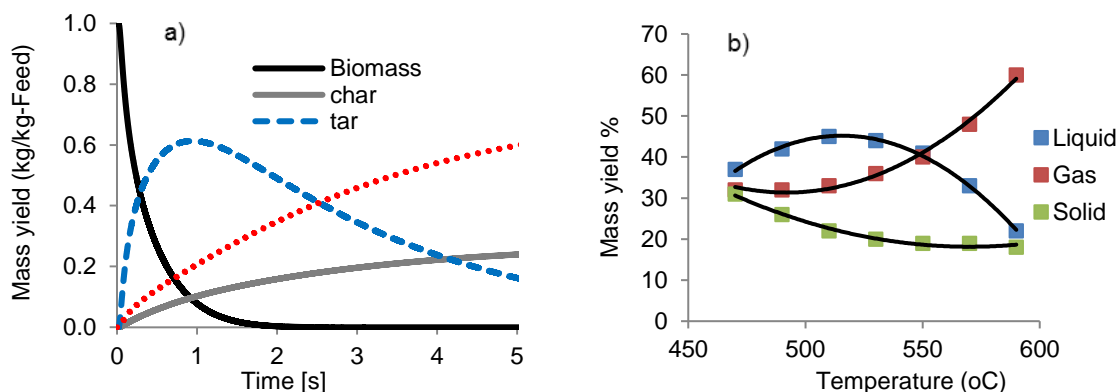


Figure 3: Pyrolysis product yields versus residence time at 550 °C (a) and versus temperature at the residence time of 2.5 s (b).

Table 2: Proximate and elemental composition of solid and liquid products (mass %)

	Moisture	Volatiles*	Fixed C*	Ash*	C*	H*	N*	S*	O*
Char	0	3	83.36	13.64	75.8	2.43	0.68	0.3	7.15
Tar	24	98.04	0	1.96	45.82	4.92	1.15	0.20	45.95

Table3: Composition of gas from the pyrolysis stage (mol.%)

H ₂	CO	CO ₂	CH ₄	Ethane	Propane	n-Butane	i-Butane	n-Pentane	Others
18.33	16.50	25.50	13.75	9.17	4.58	1.83	0.92	0.92	8.50

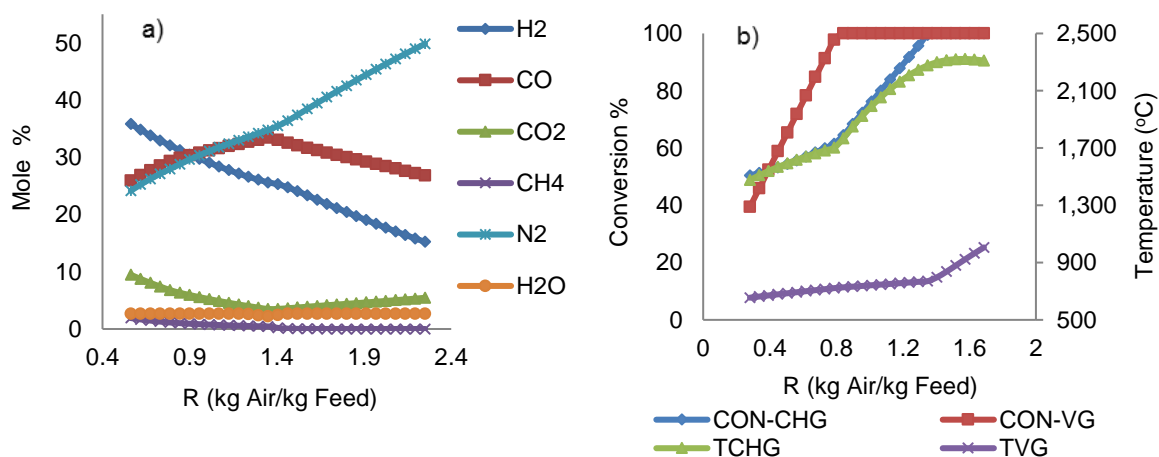


Figure 4: a) Composition of producer gas, b) conversion (CON) and temperature of both gasification reactors (TCHG and TVG) versus air to biomass mass ratio.

Gas product from the CHG reactor was used as the oxidising agent in the catalytic volatile gasification reactor. Figure 4b shows the temperature and carbon conversion in both reactors versus the air to feed mass ratio. Conversion in the CHG reactor was complete at the air to biomass mass ratio (n) of around 0.8; however, at this value of n , temperature in the VG reactor was too low and conversion was only around 0.6. To reach complete conversion in the VG reactor, the air to biomass mass ratio had to be increased to 1.4. At the same time, the temperature in the VG reactor increased to 800 °C.

Composition of the producer gas (content of the major components) is shown in Figure 4a. The equilibrium CO content showed a maximum at $n = 1.35$, which corresponds to the point when complete conversion is reached.

To ensure conversion of 100 % and a reactor temperature of at least 850 °C, an air to biomass mass ratio of 1.5 can be considered as optimal. Hydrogen content of the producer gas at this value of n is 24 mol. %, content of CO is 32 mol.% and gas LHV is 6.6 MJ/Nm³. LHV of producer gas was increased to 11 MJ/Nm³ when technically pure oxygen (99 %) was used; for oxygen rich air (70 % O₂) it was 10.3 MJ/Nm³. The optimal oxidising agent to biomass feed mass ratio was estimated to be 0.35 and 0.45 for technically pure oxygen and oxygen rich air.

5. Conclusions

Two stage pyrolysis/gasification of biomass is an effective method to achieve complete conversion of waste biomass to hydrogen rich producer gas with low tar content. A novel configuration of two stage gasification was modelled in this work. For a mixture of biomass waste at 550 °C, the liquid, solid, and gas yields from the pyrolysis reactor were approximately 40 %, 20 % and 40 % of the biomass feed. An optimal air to biomass mass ratio of 1.5 was estimated for the studied mixture of biomass. At this optimal value of air to biomass mass ratio, the temperature in the catalytic volatile gasification reactor reached 850 °C, the content of hydrogen in producer gas was 24 mol. % and that of CO was 32 mol. %. The gas LHV was calculated to be 6.6 MJ/Nm³ when air is used as the oxidising agent, 10.3 MJ/Nm³, when oxygen rich air was used and 11.0 MJ/Nm³ of technically pure oxygen.

Acknowledgments

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References

- Di Blasi C., 2008, Modeling chemical and physical processes of wood and biomass pyrolysis, *Progress in Energy and Combustion Science*, 34(1), 47-90.
- Hamel S., Hasselbach H., Weil S., Krumm W., 2007, Autothermal two-stage gasification of low-density waste-derived fuels, *Energy*, 32(2), 95-107.
- Haydari J., 2016, Gasification of Refuse-Derived Fuel (RDF), *GeoScience Engineering*, 62, 1, 37-44.
- Haydari J., Susa D., Dudáš J., 2013, Pyrolysis of aseptic packages (tetrapak) in a laboratory screw type reactor and secondary thermal/catalytic tar decomposition, *Waste Management*, 33(5), 1136-1141.
- Henriksen U., Ahrenfeldt J., Jensen T.K., Gøbel B., Bentzen J.D., Hindsgaul C., Sørensen L.H., 2006, The design, construction and operation of a 75 kW two-stage gasifier, *Energy*, 31(10), 1542-1553.
- Higman C., van der Burgt M., 2008, *Gasification*, Second edition, Elsevier, USA, ISBN: 9780750685283
- Janse A.M.C., Westerhout R.W.J., Prins W., 2000, Modelling of flash pyrolysis of a single wood particle, *Chemical Engineering and Processing: Process Intensification*, 39(3), 239-25.
- Kosov V., Zaichenko V., 2016, Two-stage gasification of untreated and torrefied wood, *Chemical Engineering Transactions*, 50, 133-138.
- McIlveen-Wright D.R., Pinto F., Armesto L., Caballero M.A., Aznar M.P., Cabanillas A., Huang Y., Franco C, Gulyurtlu I. McMullan, J. T., 2006, A comparison of circulating fluidised bed combustion and gasification power plant technologies for processing mixtures of coal, biomass and plastic waste, *Fuel processing technology*, 87(9), 793-801.
- Park W. C., Atreya A., Baum H. R., 2010, Experimental and theoretical investigation of heat and mass transfer processes during wood pyrolysis, *Combustion and Flame*, 157(3), 481-494.
- Puig-Arnabat M., Bruno J. C., Coronas A., 2010, Review and analysis of biomass gasification models, *Renewable and Sustainable Energy Reviews*, 14(9), 2841-2851.
- Ruiz J.A., Juárez M.C., Morales M.P., Muñoz P., Mendivil M.A., 2013, Biomass gasification for electricity generation: review of current technology barriers, *Renewable and Sustainable Energy Reviews*, 18, 174-183.
- Sansaniwal S.K., Pal K., Rosen M.A., Tyagi S.K., 2017, Recent advances in the development of biomass gasification technology, A comprehensive review, *Renewable and Sustainable Energy Reviews*, 72, 363-384.
- Sun L., Xu B., Smith R., 2014, Power and chemical production analysis based on biomass gasification processes, *Chemical Engineering Transactions*, 38, 61-66.
- Susa, D., Haydari, J., 2015, Pyrolysis of biomass in a laboratory pyrolysis unit with a screw type reactor and a secondary decomposition reactor, *Sustainable Environment Research*, 25(5), 261-266.