

Modelling biomass gasifiers

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Abstract

This work analyzes and discusses the general features of biomass gasifiers modeling. The particle model is described both by proposing a detailed kinetic scheme for the devolatilization and combustion of biomasses and by the basic mass and transport equations governing the phenomenological aspects. Volatile components released by the solid particles are involved in gas phase pyrolysis/combustion reactions described with a detailed kinetic scheme. Experimental data from a drop tube reactor has been used for evaluating the model predictions. A sensitivity analysis to inter- and intra-phase thermal resistance shows the great importance of the overall external heat transfer coefficient. The satisfactory agreement with experimental data makes the model capable to contribute to a better design and understanding of industrial gasifiers.

Keywords: Biomass; pyrolysis; modeling; devolatilization; gas phase kinetics

1. Introduction

The key to understanding the complex phenomena occurring inside the process units lies in the characterization of the initial biomasses, in describing the primary devolatilization phase, the released products, the gasification phase and the secondary or successive gas phase reactions. Therefore models need an appropriate description in relation both to a mechanistic kinetic model of biomass gasification and pyrolysis and to transport phenomena.

Designing the transports along the reactor requires the solution of mass, energy and momentum equations both inside each particle and in the continuous surrounding gas phase. Phase changes should be properly taken into account as well as pressure contribution to mass and energy transfers. The whole system is described by a large set of partial differential equations in time and space length. The use of the discretization approach on space coordinate reduces the system to an ordinary differential equation in the time domain which still maintains a huge complexity due to its size and to the degree of stiffness. The paper will describe a model that aims to cover the above items. A set of comparisons with experimental data will also be included.

2. Kinetic model

The devolatilization of the biomass is considered a straightforward combination of the pyrolysis of three reference components: cellulose, hemicellulose and lignin. Although extractives, either soluble in water or in organic solvents, usually account for less than 10% of the total biomass, they are ignored as participating to its characterization. Predictions from these models reproduce correctly the experimental thermo gravimetric (TG) curves during the pyrolysis of several biomasses. [Manya et al., 2003; Becidan et al., 2007; Miranda et al., 2007]. A more complete picture of biomass pyrolysis by taking into account the total devolatilization and gas evolution has been recently proposed by [Radmanesh et al., 2006; Yanik et al., 2007; de Jong et al., 2007]. Table 1 reports a

novel revision of the kinetic model adopted for the devolatilization of the biomass through the three different constituents, cellulose (CELL) hemicellulose (HEC) and Lignin (LIG-C, LIG-H, LIG-O).

The secondary gas phase reactions of the released gas and tar species are mainly pyrolysis type reactions in conjunction with combustions when oxygenated components are present. Several authors have extensively studied the kinetic equations related to this phenomena. The scheme proposed by Ranzi et al. (2001) is strongly suggested and here adopted.

Char combustion, i.e. the overall set of heterogeneous reactions of oxygen with the solid residue are responsible for the autothermic behaviour of the whole gasification process. They are summarized in Table 2.

3. Particle model

A simplified scheme of the elemental gas-particle module indicating the gas-solid interactions and the release of *tar* components is reported in Figure 1. The biomass particle, which consists of a mixture of reference components and ash, is assumed as a homogeneous sphere with NS internal sectors that account for possible heat and mass transfer resistances.

Gases are released by the particle to the surrounding gas phase while surrounding gases diffuse into the solid particle. Gas phase is considered as a perfectly stirred reactor inside the cell module.

Convective fluxes or flowrates entering and exiting the module are allowed, both for gas and solid phase. This elemental module is flexible and suitable for simulating different process alternatives, such as fixed or moving bed gasifiers and combustors, updraft or downdraft configurations and also the entrained (drop tube) flow reactor. The ODE system is solved by using BzzMath library, available on the Internet and is downloadable as freeware software for non-commercial use from www.chem.polimi.it/homes/gbuzzi/. Physical and mathematical details on the overall complexity of this problem are described by Pierucci and Ranzi 2008.

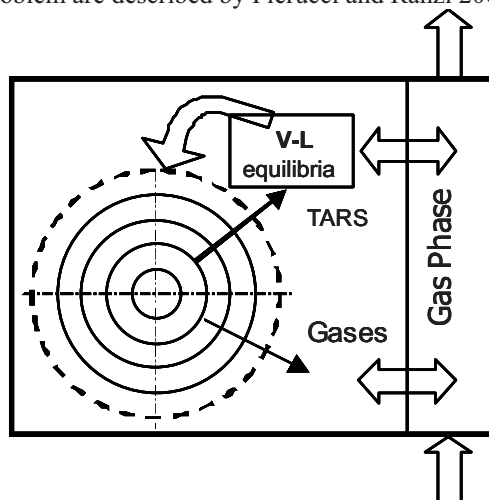


Figure 1. Scheme of the elemental gas-particle module

Table 1: Kinetics of Cellulose, Hemicellulose and Lignin devolatilization

	k [s ⁻¹], kmol, m ³ , K
CELL > CELLA	$8 \times 10^{11} \exp(-46000/RT)$
CELLA > 0.95 C ₂ H ₄ O ₂ + 0.25 C ₂ H ₂ O ₂ + 0.2 CH ₃ CHO + 0.25 C ₆ H ₆ O ₃ + 0.2 C ₃ H ₆ O + 0.16 CO ₂ + 0.23 CO + 0.1 CH ₄ + 0.9 H ₂ O + 0.61 CHAR	$10^9 \exp(-30000/RT)$
CELLA > C ₆ H ₁₀ O ₅	$4 \times T \exp(-10000/RT)$
CELL > 5.0 H ₂ O + 6.0 CHAR	$8 \times 10^7 \exp(-32000/RT)$
HEC > 0.4 HCE1 + 0.6 HCE2	$10^{10} \exp(-31000/RT)$
HCE1 > 0.75 GH ₂ + 0.125 H ₂ O + 0.8 CO ₂ + 1.4 CO + 0.5 CH ₂ O + 0.125 C ₂ H ₅ OH + 0.25 CH ₃ OH + 0.625 CH ₄ + 0.25 C ₂ H ₄ + 0.675 CHAR	$3 \times 10^9 \exp(-27000/RT)$
HCE1 > C ₅ H ₈ O ₄	$3 \times T \exp(-11000/RT)$
HCE2 > 0.125 H ₂ O + 0.2 CO ₂ + 0.5 CH ₄ + 0.25 C ₂ H ₄ + 0.7 CH ₂ O + 0.125 C ₂ H ₅ OH + 0.25 CH ₃ OH + 0.8 GCO ₂ + 0.8 GCOH ₂ + CHAR	$10^{10} \exp(-33000/RT)$
LIG-C > 0.35 LIG _{CC} + 0.1 C ₉ H ₁₀ O ₂ + 0.08 C ₆ H ₆ O + 0.41 C ₂ H ₄ + H ₂ O + GCOH ₂ + 0.495 CH ₄ + 0.32 CO + 5.735 CHAR	$4 \times 10^{15} \exp(-48500/RT)$
LIG-H > LIG _{OH} + C ₃ H ₆ O	$2 \times 10^{13} \exp(-37500/RT)$
LIG-O > LIG _{OH} + CO ₂	$10^9 \exp(-25500/RT)$
LIG _{CC} > 0.3 C ₉ H ₁₀ O ₂ + 0.2 C ₆ H ₆ O + 0.35 C ₃ H ₄ O ₂ + 0.7 H ₂ O + 0.65 CH ₄ + 0.6 C ₂ H ₄ + GCOH ₂ + 0.8 GCO + 6.4 CHAR	$5 \times 10^6 \exp(-31500/RT)$
LIG _{OH} > LIG + 0.1 GH ₂ + H ₂ O + CH ₃ OH + 1.4 GCO + 0.6 GCOH ₂ + 0.45 CH ₄ + 0.2 C ₂ H ₄ + 4.15 CHAR	$10^{13} \exp(-49500/RT)$
LIG > C ₁₁ H ₁₂ O ₄	$10^5 \exp(-20500/RT)$
LIG > H ₂ O + 0.2 CH ₂ O + 0.2 CH ₃ CHO + 0.4 CH ₃ OH + 0.5 CO + 0.2 C ₃ H ₆ O + 0.6 CH ₄ + 0.65 C ₂ H ₄ + GCO + 0.5 GCOH ₂ + 5.5 CHAR	$80 \times T \exp(-12000/RT)$
GCO ₂ > CO ₂	$10^5 \exp(-24000/RT)$
GCO > CO	$10^{13} \exp(-50000/RT)$
GCOH ₂ > CO + H ₂	$5 \times 10^{11} \exp(-65000/RT)$
GH ₂ > H ₂	$5 \times 10^{11} \exp(-75000/RT)$

Table 2: Char combustion

	kmole, m ³ , K, s
CHAR + O ₂ > CO ₂	$5.7 \times 10^9 \exp(-38200/RT) [\text{O}_2]^{0.78}$
CHAR + 0.5 O ₂ > CO	$5.7 \times 10^{11} \exp(-55000/RT) [\text{O}_2]^{0.78}$
CHAR + H ₂ O > CO + H ₂	$7.9 \times 10^9 \exp(-52000/RT) [\text{H}_2\text{O}]^{0.7}$

4. Comparison with experiments

A drop tube reactor of 0.075 m internal diameter and 1-meter length is heated by an electric oven that can reach a maximum temperature of 1300 K. The reactor is fed with pure N_2 that is injected at the top and then passes through an electric preheater. A constant flow rate of solid is injected at the top of the reactor by pneumatic transport. Under the explored conditions, the gas flow is highly laminar ($Re < 2000$). The experiments were conducted by Dupont C., CEA, Grenoble, DTN/SE2T/LPTM.

Figure 2 and 3 report some comparisons between experiments and predictions at different temperatures and for different particle size: The results clearly show the role of secondary pyrolysis reactions: acetylene is only a product of the secondary gas phase dehydrogenation of ethylene and it is favoured by high temperatures.

In agreement with experimental results, char yields reach values of 14-16 wt% of the initial dry biomass. The initial composition of the biomass $C_6H_{8.8}O_{3.9}$ significantly changes at the reactor outlet and becomes $C_6H_{2.9}O_{1.1}$ at 1073 K. At higher temperature, the charification process is further completed and the composition of the solid residue becomes $C_6H_{1.4}O_{0.5}$. These results are in agreement with the experimental measurements indicating a composition of $C_6H_{2.7}O_{0.8}$ at 1073 K and $C_6H_{1.5}O_{0.4}$ at higher temperatures. No comparisons with the experimental measurements are available for *tar* species, since these species are not measured in the gas phase.

Since the transport processes have a strong influence on the devolatilization of large particles, a simple sensitivity analysis to the overall heat transfer coefficient and to the effective thermal conductivity of the biomass particle is shown in Figure 4. The reference value of the overall external heat transfer coefficient was increased of 50% (dashed lines) and decreased of 50% (dotted lines). The same variations were applied to biomass thermal conductivity. The overall external heat transfer coefficient significantly affects the heating and the devolatilization process. Thermal conductivity plays a minor role. This analysis supports and confirms the conclusions of Janse et al. 2000 that extensive description of internal mass transport phenomena in flash pyrolysis modelling is not necessary, while accurate knowledge of reaction kinetics and heat transfer parameters is crucial.

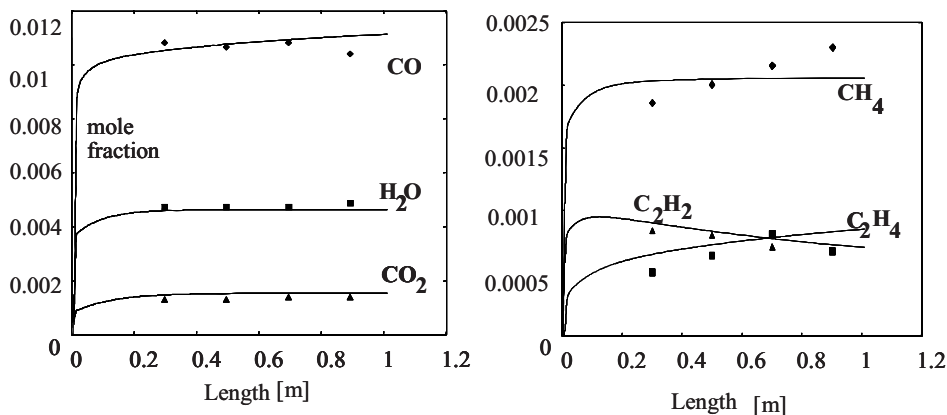


Figure 2: Comparisons with experiments (points) and predictions (lines) for beech wood particles of 0.20 mm at 1273 K

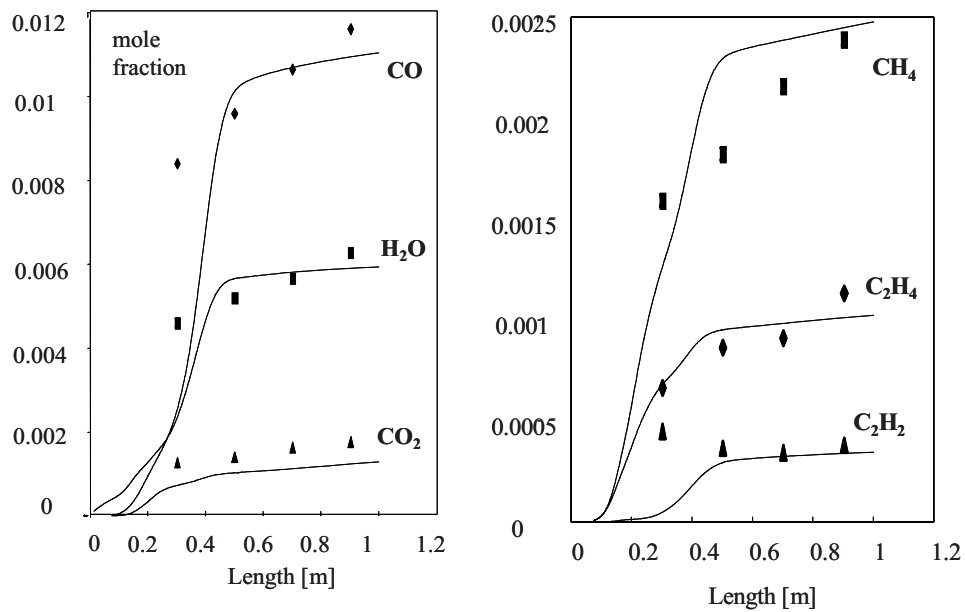


Figure 3: Comparisons with experiments (points) and predictions (lines) for beech wood particles of 0.67 mm at 1073 K

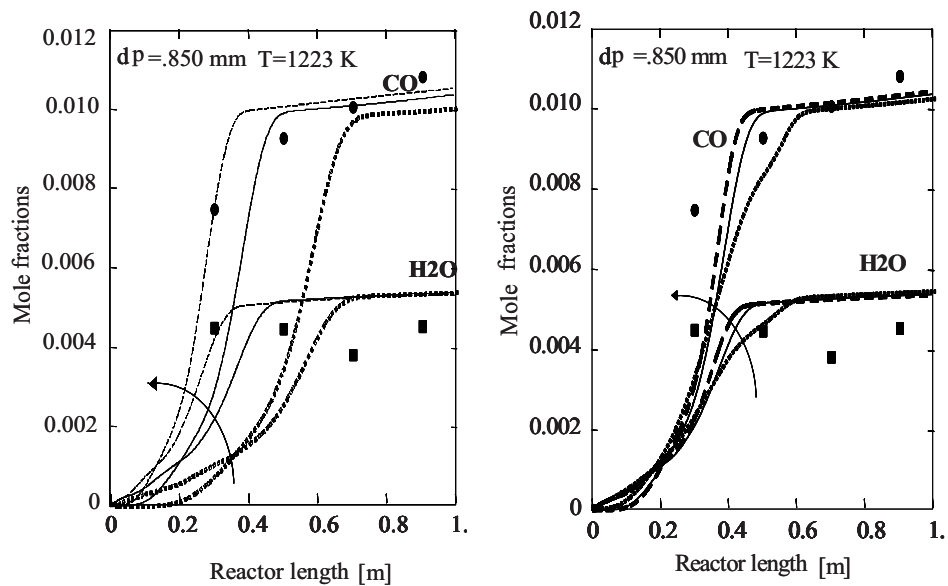


Figure 4: CO and H₂O vs. reactor length for 0.850 mm Beech wood particles at 1223 K. Sensitivity to heat transfer coefficient (left) and solid thermal conductivity (right)

5. Conclusions

A novel detailed kinetic scheme for the devolatilization and combustion of biomasses has been presented and tested with experiments. The adopted particle model is described by the basic mass and transport equations governing the phenomenological aspects. Experiments have been performed at high temperatures (1073–1273 K) and fast heating rates ($> 500 \text{ K s}^{-1}$) in an entrained flow reactor with different wood particles of different sizes. These results have been used to further validate a semi detailed kinetic model of biomass pyrolysis. These comparisons show that the main experimental trends are well-reproduced by the model. The crucial influence of the particle size can be seen under these conditions. For small particles, the decomposition of the biomass components is completed after about 0.3 s and leads to total gas yields higher than 70 wt% at the reactor outlet, and a char yield of about 10 to 15 wt%. The major gas is largely CO, followed by H₂. CH₄ and CO₂ are present in smaller amounts. There is a clear effect of temperature on the C₂ species behaviour. For large particles, the decomposition still proceeds at the end of the reactor after about 0.5 s, due to internal heat transfer limitations. The satisfactory agreement with experimental data makes the model capable to contribute to a better design and understanding of industrial gasifiers

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