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Gaseous Emissions from Agricultural Biomass Combustion: A Modeling Approach

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Abstract. Previous researches have revealed that gaseous emissions differ significantly according to the combustion technology used and the characteristics of the biomass burned. In order to quantify emissions from agricultural biomass combustion at farm scale under different conditions, a prediction model based on fuel composition will be established. However, most technical articles on simulating combustion systems aim at optimizing design or operation, not predicting emissions. These models also require a detailed and complex description of the thermochemical processes involved during combustion. A simpler approach is based on thermodynamic models which use the assumption of chemical equilibrium. This poster will present an analysis of the existing mathematical models for biomass combustion.

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Introduction

As the price of fossil energy resources and the need to reduce the environmental impacts from energy use increase, biomass fuels have regained interest (Brodeur et al., 2008). Consequently, Québec's agriculture has the will to introduce energy crops for energy purposes such as on-farm combustion. However, the current absence of emission factors for agricultural fuels does not allow a sustainable development of combustion process (Godbout et al., 2012). The variety of existing solid fuels and furnaces complicates the establishment of such reference values. Besides, some studies (Obernberger, 1998; van Loo and Koppejan, 2008; Vassilev et al., 2010) have revealed how physical and chemical characteristics may affect the exit gas composition. In order to consider all these parameters, mathematical modelling could be use as a powerful tool for predicting gaseous emissions from agricultural biomass combustion. The aim of this paper is to analyze the existing models and develop a simple prediction model.

Literature review

Models can be classified according to the number of space dimensions (0D, 1D, 2D, or 3D) and the inclusion of time as a variable (steady state or dynamic) (de Souza-Santos, 2010). They usually consider four steps during combustion: drying, devolatilisation (pyrolysis), gas and char combustion (Figure 1). Biomass combustion is modelled by employing the conservation equations – which track the reactants, the products and heat release rates – over those four phases (Williams et al., 2012). Modelling, mainly used for large scale (packed-bed and fluidized-bed reactors; Tables 1 and 2) development and optimization, is a powerful tool for designing and simulating reactor performances, understanding pollutants evolution, analyzing process transients, and examining strategies for effective control (Di Blasi and Galgano, 2008). At some point, modelling biomass combustion could become really complex and require significant efforts (Ranzi et al., 2008; Williams et al., 2012).

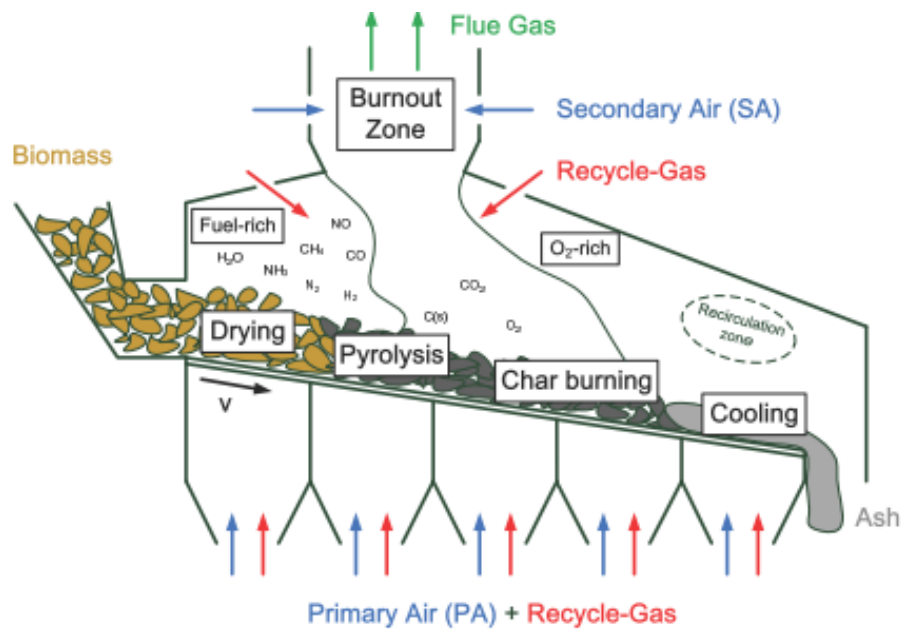


Figure 1. Phases of biomass conversion in the fuel bed (Paces and Kozek, 2011).

Table 1. Combustion model for packed-bed reactors.

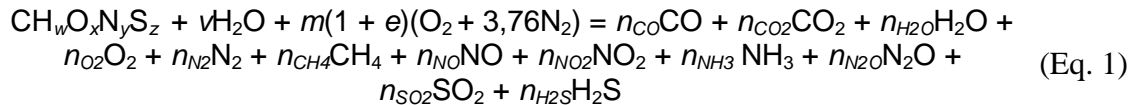
Reference	Combustion equipment	Biomass	Dimension	State	Type ^a
Bruch et al., 2003	Fixed bed	Wood	1D	Transient	5
Collazo et al., 2012	Fixed bed	Wood	3D	Transient	4
Fatehi and Kaviany, 1994, 1997	Fixed bed	Wood	1D	Steady	1
Gort and Brouwers, 2001	Fixed bed	Wood	1D	Steady	1
Haseli et al., 2011	Moving bed	Wood	1D	Transient	5
Johansson et al., 2007ab	Fixed bed	Wood	1D+2D	Transient	4,5
Jöller et al., 2005, 2007	Fixed bed	Wood	1D	Transient	5
Kaer, 2005	Fixed bed	Straw	2D	Steady	3
Kaer, 2004	Vibrating grate	Straw	1D	Transient	2
Klason et Bai, 2007	Fixed bed	Wood	1D	Steady	3
Lu et al., 2008		Poplar	1D	Transient	5
Peters, 2002	Fixed bed	Wood	1D	Transient	5
Peters and Smula, 2010	Fixed bed	Switchgrass	1D	Transient	5
Saastamoinen et al., 2000	Fixed bed	Wood	1D	Steady	1
Scharler and Obernberger, 2000	Travelling grate	Wood	3D	Transient	3
Shin and Choi, 2000	Fixed bed	Wood	1D	Steady	2
Ströhle et al., 2006	Fixed bed	Wood	2D	Steady	4
Thunman and Leckner, 2003, 2005	Fixed bed	Wood	1D+1D	Transient	4,5
van der Lans et al., 2000	Moving bed	Wheat	2D	Steady	2
Wurzenberger et al., 2002	Moving bed	Wood	1D+1D	Transient	4,5
Yang et al., 2003 and 2004	Fixed bed	Wood	1D	Transient	2
Yang et al., 2005ab	Moving bed	Wood	1D	Transient	2
Yang et al., 2005c	Fixed bed	Wood	1D	Transient	5
Yang et al., 2007	Vibrating grate	Wheat	2D	Transient	4
Yang et al., 2008	Fixed bed	Wood	2D	Transient	5
Yu et al., 2010	Fixed bed	Rice	3D	Transient	3
Zhou et al., 2005	Fixed bed	Paille	1D	Dynamique	2

a 1. Packed bed model alone; 2. Packed bed model coupled with the gas-phase processes; 3. Single particle model and solid-phase processes approximated by means of a boundary condition; 4. Combined packed bed and single particle model; 5. Particle model only.

Table 2. Combustion model for fluidized- and pulverized-bed reactors.

Reference	Reactor	Biomass	Dimension	State	Predicted emissions
Desroches-Ducarne et al., 1998	Circulating fluidized bed	Municipal solid waste			CO, NO, N ₂ O, SO ₂ , HCl
Gungor, 2008, 2010	Circulating fluidized bed	Various	2D	Dynamique	CO, NO _x
Khan et al., 2007ab	Bubbling fluidized bed	Wood	1D	Permanent	CO, CO ₂ , CH ₄ , N ₂ , NO, NH ₃ , O ₂ , H ₂ , H ₂ O
Liu and Gibbs, 2002	Circulating fluidized bed	Wood	1D	Dynamique	NO, N ₂ O
Ma et al., 2007	Pulverized bed	Wood	3D	Dynamique	NO _x
Okasha, 2007	Bubbling fluidized bed	Straw	1D	Permanent	CH _x , O ₂ , CO, H ₂ O, CO ₂
Scala and Salatino, 2002	Bubbling fluidized bed	Wood	1D	Permanent	

A simpler approach, described by Ranzi et al. (2011), establishes that, given the biomass composition and the equilibrium temperature, thermodynamic models can simply predict the exit gas composition. Assuming that the products have reached chemical equilibrium, the problem is to determine the proportion of each species that exist in the equilibrium mixture at a known pressure and temperature for a given set of constituents Ragland and Bryden (2011). Therefore, the results of such a thermodynamic model could be used to solve the stoichiometric coefficients of the global reaction (Jenkins et al., 2011):



where w , x , y , and z are the number of atoms of hydrogen, oxygen, nitrogen, and sulfur per number of atom of carbon in the feedstock, respectively; v is the amount of moisture per kmol of feedstock; m is the amount of air per kmol of feedstock; e is the excess air ratio; and n_i are the numbers of mole of species i .

Equilibrium models have been mainly used for pyrolysis and gasification processes (Bratieri et al., 2008). Some authors (de Souza-Santos, 2010; Jarungthammachote and Dutta, 2007) also demonstrated their application in combustion. Equilibrium models have been developed using two approaches: equilibrium constants and minimization of the Gibbs free energy. The former has to define the specific chemical reactions used in the calculation, whereas the latter estimate the concentrations of the products which minimize Gibbs free energy. Since no chemical

reaction needs to be known to find the solution, the minimization method is advantageous and more suitable for complex problems (Jarungthammachote and Dutta, 2008).

Model development

At equilibrium state, the total Gibbs free energy (G) is minimized and defines as

$$G = \sum_{i=1}^N n_i \mu_i \quad (\text{Eq. 2})$$

where μ_i is the chemical potential of species i that can be presented by

$$\mu_i = \bar{G}_i^o + RT \ln \left(\frac{f_i}{f_i^o} \right) \quad (\text{Eq. 3})$$

where R and T are the universal gas constant and temperature. f_i represents the fugacity of species i . The superscripts o and $-$ denote a standard thermodynamic quantity and a molar basis. Eq. 3 can also be presented in terms of pressure. Normally, f and P can take on the same value when the pressure ratio approaches zero. If all gases are assumed as ideal gases at 1 atm, Eq. 3 becomes

$$\mu_i = \bar{G}_{f,i}^o + RT \ln \left(\frac{n_i}{n_{tot}} \right) \quad (\text{Eq. 4})$$

where n_{tot} is the total number of moles of the reaction mixture. $\bar{G}_{f,i}^o$ is the standard Gibbs free energy of formation of species i , and it is set equal to zero for all chemical elements. Substituting Eq. 4 into Eq. 2

$$G = \sum_{i=1}^N n_i \bar{G}_{f,i}^o + \sum_{i=1}^N n_i RT \ln \left(\frac{n_i}{n_{tot}} \right) \quad (\text{Eq. 5})$$

Now, the problem is to find the values of n_i which minimize the objective function G . The appropriate method is the Lagrange multipliers. The constraint of this problem is the elemental balance, i.e.

$$\sum_{i=1}^N a_{ij} n_i = A_j, \quad j = 1, 2, 3, \dots, k \quad (\text{Eq. 6})$$

where a_{ij} is the number of atoms of the j th element in a mole of the i th species. A_j is defined as the total number of atoms of the j th element in the reaction mixture. To form the Lagrangian function (L), the Lagrange multipliers, $\lambda_j = \lambda_1, \dots, \lambda_k$, are used by multiplying with elemental balance constraints, and those terms are subtracted from G as follows

$$L = G - \sum_{j=1}^k \lambda_j \left(\sum_{i=1}^N a_{ij} n_i - A_j \right) \quad (\text{Eq. 7})$$

The partial derivatives of Eq. 7 are set equal to zero in order to find the extremum point

$$\left(\frac{\partial L}{\partial n_i} \right) = 0 \quad (\text{Eq. 8})$$

Eq. 8 can be formed in terms of a matrix that has i rows, and those are solved simultaneously with the constraints as defined in Eq. 6. However, the solutions n_i have to be real numbers in the boundary that $0 \leq n_i \leq n_{tot}$. Eq. 8 creates the set of non-linear equations, and those are solved by an iteration technique (e.g. Newton–Raphson). In order to calculate $\bar{G}_{f,i}^o$ at a specific T , the values of the standard enthalpy of formation ($\Delta\bar{H}_{f,i}^o$) and the standard entropy of formation ($\Delta\bar{S}_{f,i}^o$) are needed because

$$\bar{G}_{f,i}^o = \Delta\bar{H}_{f,i}^o - T\Delta\bar{S}_{f,i}^o \quad (\text{Eq. 9})$$

where

$$\Delta\bar{H}_{f,i}^o = \bar{H}_{f,i} + \int_{T_0}^T \bar{C}_p \partial T \quad (\text{Eq. 10})$$

and

$$\Delta\bar{S}_{f,i}^o = \bar{S}_i^o + \int_{T_0}^T \frac{\bar{C}_p}{T} \partial T \quad (\text{Eq. 11})$$

\bar{C}_p , the specific heat at constant pressure, can be expressed as a polynomial equation of four constants as follows

$$\bar{C}_p = a_1 + a_2T + a_3T^2 + \frac{a_4}{T^2} \quad (\text{Eq. 12})$$

The constants a_1 to a_4 , $\Delta\bar{H}_{f,i}^o$, and $\Delta\bar{S}_i^o$ are given by de Souza-Santos (2010).

Validation

The model will be established on MATLAB according to Gautam's (2010) work. The model will then be adjusted and validated according to future on-farm experiments. The tests will be held at the new laboratory on energy of the Research Institute for the Agri-Environment (IRDA) on the site of the "*Centre de recherche en sciences animales de Deschambault*" (CRSAD) during winter 2013. One hundred and twenty (120) combustion experiments are planned with five (5) energy crops (wood, willow, miscanthus, switchgrass, and reed canary grass) harvested either in fall or spring. The solid fuels will be burned as pellets, briquettes, or chopped material.

Conclusion

In order to calculate gaseous emissions from agricultural biomass combustion at farm-scale, the procedure for a prediction model has been presented. A thermodynamic model based on

chemical equilibrium was retained. The approach involves the minimization of Gibbs free energy. Although theoretical, this method is simple in comparison with other mathematical models employed mostly to design and simulate performances of combustion reactors. The developed model will be validated with lab experiments. A simplified tool will also be developed on Excel so that more users can access and use it.

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