

Quasi-equilibrium thermodynamic model with empirical equations for air–steam biomass gasification in fluidized-beds



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ABSTRACT

Gasification is one of the most promising technologies for converting biomass into a fuel. This study presents a simple and practical biomass gasification model based on thermodynamic equilibrium to find effective operating conditions of the air–steam gasification system in fluidized-beds. The carbon conversion fraction empirically obtained was involved in a global gasification reaction. Two empirical equations as the non-equilibrium factor expressing the deviation from equilibrium were derived as the function of the equivalence ratio (*ER*) from 43 experimental data sets of various operating conditions and different feedstocks. An energy balance was also solved for determining the gasification temperature (*T*). After the producer gas composition with respect to *ER* and steam to biomass ratio (*SBR*) was obtained from the air–steam biomass gasification (ASBG) model, process performances such as lower heating value, heat efficiency, net heat efficiency, and H₂/CO molar ratio were evaluated. An effective operating area was suggested from the contour plot of the process performances with respect to *ER* and *SBR* in the auto-thermal gasification temperature from 700 to 830 °C.

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1. Introduction

Gasification has received the most attention among thermal conversion processes due to its high efficiency compared to direct combustion, pyrolysis and liquefaction [1–3]. Gasification is the conversion of biomass into the mixture of combustible and non-combustible gases by partial oxidation at temperatures around 700–900 °C. Syngas from biomass gasification is a mixture of carbon monoxide, carbon dioxide, hydrogen, water, nitrogen and a small amount of light hydrocarbons. The syngas has been used for power or heat generation via combustion, and for a feedstock of fuel synthesis processes [4].

Fluidized-beds now find a wide application in biomass gasification [5–14]. The fluidized-bed gasifiers have several advantages: good gas–solid contact, excellent heat transfer characteristics, an easily controlled temperature, good degree of turbulence and high volumetric capacity [15]. The bubbling fluidized-bed (BFB) has been used for biomass gasification with air or air–steam as the gasifying agent [10,12,13]. The circulating fluidized-bed (CFB) gasifier typically consists of the riser, cyclone, downcomer and loop-seal, where the bed-material circulates to enhance gas–solid contact and heat transfer [5,7]. The dual circulating fluidized-bed (DFB) gasification, including a gasifier and a combustor,

produces a syngas having a high heating value of 12–20 MJ/Nm³ due to the separation of combustion gas from syngas [8,16].

Air is the widely used agent in demonstration or commercial scale biomass gasification owing to its low-cost. However, the producer gas from air-blown gasification has a low heating value of 4–7 MJ/Nm³ [7, 13]. Steam gasification producing a medium calorific value of 10–14 MJ/Nm³ requires heat for endothermic gasification reaction. One way for supplying heat is to introduce some air or oxygen to the gasifier so that an autothermal gasification proceeds [7]. Many researchers have been devoted to the air–steam mixed biomass gasification [5,7,10,13, 17].

The existing fluidized-bed gasification models can be classified as thermodynamic equilibrium, chemical kinetics, steady-state, and transient models. Among them, the thermodynamic equilibrium model is considered as the simplest, giving the syngas composition for various biomass types at selected gasification temperatures with reasonable accuracy [6,14,18–22].

In a downdraft gasifier, Jarunghammachote and Dutta [21] and Melgar et al. [18] predicted the syngas composition from various biomass types using a thermodynamic equilibrium model at a fixed equivalence ratio. Zainal et al. [19] presented an equilibrium gasification model for three kinds of biomass wood (paddy husk, paper and municipal waste) in a downdraft gasifier, where a global gasification reaction was used for the atomic element balance. Karmakar and Datta [6] developed a thermodynamic equilibrium model for fluidized-bed gasification

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of biomass with steam to produce hydrogen-rich gas. In the study of Buragohain et al. [20], the thermodynamic equilibrium approach of biomass gasification was investigated on various parameters such as the type of biomass, temperature of gasification, equivalence ratio, and gasification agent.

The thermodynamic equilibrium model is not valid for real processes, since gasification reactions are influenced by kinetics and mass transfer so that some components never achieve equilibrium [5]. The quasi-equilibrium approach accounting the deviation from the equilibrium reactions improved the accuracy of the prediction of gas composition [11]. Using quasi-equilibrium thermodynamic models, our recent studies [8,9] presented optimum sets of the operating condition of DFB biomass gasifiers for Fischer–Tropsch (FT) synthesis and electric power generation (EPG), where steam was used as a gasifying agent.

Nevertheless, few researchers have addressed the thermodynamic equilibrium approach for biomass gasification in air–steam fluidized-beds. There remains a need for a simple and practical model taking into account auto-thermal gasification. Furthermore, a systematic way is necessary to figure out the deviation from the thermodynamic equilibrium theory by utilizing numerous experimental data published until now.

This study presents a simple approach for the modeling of air–steam biomass gasification (ASBG) in fluidized-beds. The carbon conversion fraction is empirically obtained from data published in the literature. Since thermodynamic equilibrium is hardly achieved in practical processes, two non-equilibrium factors to compensate the deviation from the equilibrium theory are introduced into the ASBG model. The two non-equilibrium factors are estimated from experimental data. After the model parameter estimation, the parametric study of equivalence ratio (*ER*) and steam to biomass ratio (*SBR*) is performed within the auto-thermal temperature zone in terms of process performance criteria such as lower heating value of syngas (LHV_{syn}), heat efficiency (η_e), net heat efficiency ($\eta_{e,net}$), and H_2/CO molar ratio (ϕ_{HC}).

2. Air–steam biomass gasification (ASBG) model

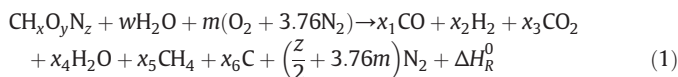
This section presents how the ASBG model based on thermodynamic equilibrium is integrated with the non-equilibrium factors.

2.1. Thermodynamic equilibrium model

At chemical equilibrium, a reacting system achieves its most stable composition when the Gibbs free energy is minimized. The ASBG model proposed in this study is derived from the thermodynamic equilibrium reaction with the following assumptions:

- (1) The carbon content in biomass is converted into a gaseous form by gasification and combustion. The residence time is high enough to achieve thermodynamic equilibrium. The products taken into account are CO, CO₂, H₂, CH₄, N₂, and water. Carbon unconverted to gas is assumed to be pure carbon and flows out as fly ash. Hydrocarbons other than CH₄ were assumed negligible in syngas and were not taken into account. Tar formation is also neglected.
- (2) Ash in the feedstock is assumed to be inert in all gasification reactions, although it holds active typically only for reaction temperatures less than 700 °C.
- (3) All gaseous products are assumed to act as ideal gases. This assumption will not lead to significant error for the fluidized-bed gasifier operated at low pressure and high temperature. The pressure drop inside the gasifier is also supposed to be negligible.
- (4) Sulfur and chlorine contents in biomass are neglected since they are less than 0.6% in most biomass feedstocks.

The substitution fuel formula of biomass by $CH_xO_yN_z$ can be obtained from its ultimate analysis. The air–steam gasification of the biomass is written in one global reaction [19]:



where *w* and *m* are the molar quantity of water and oxygen per mole of biomass, respectively. ΔH_R^0 is the heat of the global reaction at the standard temperature and pressure (STP) of 25 °C and 1 bar. *w* and *m* are determined as a function of the steam to biomass ratio (*SBR*, kg/kg) and the oxygen molar ratio for complete combustion of biomass, respectively, which is called the equivalence ratio (*ER*, kmol/kmol).

$$w = (SBR + w_w) \times \frac{M_{bm}}{18} \quad (2)$$

$$m = ER \times \left(1 + \frac{x}{4} + \frac{y}{2}\right) \quad (3)$$

where w_w is the moisture mass fraction in biomass and M_{bm} is the inlet mass of biomass. For convenience, M_{bm} (kg/h) is defined as a mass for both 1 kmol/h of dry biomass and moisture content.

$$M_{bm} = \frac{12 + x + 16y + 14z}{1 - w_w} \quad (4)$$

For a given ultimate analysis (see Table 1), the inlet mass of biomass (M_{bm}) is about 24.5 kg/h.

In Eq. (1), the element balances of carbon, hydrogen and oxygen elements are given below:

$$x_1 + x_3 + x_5 + x_6 = 1 \quad (5)$$

$$x + 2w = 2x_2 + 2x_4 + 4x_5 \quad (6)$$

$$y + w + 2m = x_1 + 2x_3 + x_4 \quad (7)$$

Since there are just three element equations for the six variables (x_1 – x_6) of syngas compositions and unconverted carbon, three equations should be more defined. In this study, two thermodynamic equilibrium reactions and an empirical model for carbon conversion are introduced.

2.1.1. Two equilibrium constants

The water–gas shift reaction is assumed at equilibrium in gas phase:



The other equilibrium reaction is the formation of methane:

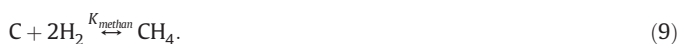


Table 1
Biomass property used in parametric study [7].

Ultimate analysis (wt.%)		Proximate analysis (wt.%)	
Carbon (C)	50.30	Moisture	8.0
Hydrogen (H)	6.17	Volatiles	69.8
Oxygen (O)	37.40	Fixed carbon	20.1
Nitrogen (N)	0.69	Ash	2.1
Others	5.44		
Subtotal	100		100

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