An unsteady-state two-phase kinetic model for corn stover fluidized bed steam gasification process

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ABSTRACT

A complex unsteady-state two-phase kinetic model including reaction kinetics and fluid dynamics was developed for corn stover fluidized bed steam gasification process. The gasification model included an unreacted core shrinking model for char–gas reactions, and a pyrolysis model considering the effect of the particle size on the pyrolysis time and pyrolysis products. In this model, fuel particles stay in the fluidized bed and take part in chemical reactions until their size decreases to a critical size, and then are entrained out of the bed. The kinetic model developed in this study is capable of predicting concentration profiles of gas in the bubble phase and the emulsion phase along the height of the reactor, the evolution of particles in the bed with time, and the particle size distribution in the fluidized bed under different operating conditions (temperature, steam/biomass ratio, and gas superficial velocity). Results show that the water–gas shift reaction and the residence time play important roles in determining the gasification results in terms of the gas volumetric fraction and yields of char and dry tar-free gas.

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1. Introduction

Corn stover is the largest quantity of biomass residue available annually in the United States, which makes it one of the most promising biomass renewable energy sources. Gasification is a successful option for chemical production and energy production from biomass feedstocks. The products of gasification syngas that contain CO, CO_2, H_2O, CH_4, H_2, char, alkali compounds, tar, and other hydrocarbons can be used in engines, turbines, boilers, and for conversion to methanol and gasoline. Fluidized bed steam gasification is an attractive thermo-chemical process due to its ability to handle a wide range of feedstocks, rapid heat and mass transfer, and high energy content of syngas produced [1].

The authors of this paper performed extensive analysis of combined heat and power generation using corn stover [2]. It is found that although fluidized bed gasification of many sources of biomass such as wood, grass, waste, and wheat straw has been widely studied, corn stover has not received as much attention either through experiments or simulation. There are only a few experimental studies available [3,4], and only two papers mention simulation of corn stover fluidized bed gasification [5,6]. De Kam et al. [5] developed a non-stoichiometric equilibrium model based on minimization of system Gibbs free energy using Aspen Plus software, with the yields of char, C_6H_6O, C_2H_4, and C_2H_6 fixed according to experimental data. Wang et al. [6] created a stoichiometric equilibrium model for the corn stover steam gasification process, and

yields of gasification products (yield of char was given) were determined by solving atom balance equations and relationships between moles of gasification products and chemical equilibrium constants. However, several challenges exist for the simulation study of corn stover fluidized bed steam gasification. First, although these two modeling approaches [5,6] are essentially of the same concept [7], they predict different results in terms of yields of gasification products, higher heating value (HHV), and gas volumetric flow rate. Second, the two models are equilibrium models based on an assumption that the entire system is in chemical equilibrium state. Because high residence time is required for the system to reach an equilibrium state [8,9], thermodynamic equilibrium may not be achieved in many cases especially when the temperature of the reactor is less than 800 °C [1,7,10,11]. Therefore, although this kind of model is easy to understand and use, it may not give accurate results. Third, equilibrium models can only give a maximum estimation of yields of gases, but cannot reflect the effects of residence time, gas superficial velocity, or gasifier structure on gasification product distribution at the gasifier exit or across the gasifier, which is important for reactor design and improvement. Moreover, equilibrium models cannot predict the yield of char, which must be specified before simulation, and thus, they cannot accurately predict the yields of species with high Gibbs free energy [12]. Therefore, it is of vital importance to develop a better model to study corn stover fluidized bed steam gasification.

Since gasification is a very complex process involving both reaction kinetics and fluid dynamics, two-phase kinetic models considering both reaction kinetics and fluid dynamics are widely used to model the gasification process. To facilitate simulation, researchers have

made many simplifications of the real process. Some researchers assume that diffusion does not exist and only convection exists for gases [13,14], and many researchers assume that solid fuel remains in the bed all of the time [15,16]. In addition, most researchers divide the gasification process into pyrolysis and char gasification, and assume pyrolysis occurs instantaneously and fail to consider the effect of particle size on char gasification [16,17], which is not true for large particles [18]. Furthermore, most researchers deal with fuel in terms of mass with no sense of particle size, thus those models provide no information on particle size distribution or evolution [16,17].

The authors of this paper conducted extensive work on kinetic model development and comparison between different models [19]. The objectives of this article are to 1) develop an unsteady-state two-phase kinetic model for corn stover fluidized bed steam gasification process, and 2) investigate the effects of temperature, steam/biomass ratio, gas superficial velocity, and particle size on gasification results. The model a) considers both convection and diffusion for gases, b) includes the effect of particle size on char gasification and pyrolysis, c) includes solid entrainment, and d) is able to predict particle size distribution in the bed and evolution of particle size with time.

2. Model development

The fuel studied in this paper is corn stover, and its properties are shown in Table 1. In addition, the properties of wood used for model validation are also provided in Table 1.

2.1. Assumptions

The following were assumed for modeling the corn stover fluidized bed steam gasification process:

1) An unsteady state mathematical model including both reaction kinetics and fluid dynamics.
2) The temperature of the reactor is uniform.
3) The gasification process is divided into two stages: devolatilization/pyrolysis and gasification both of which are controlled by reaction kinetics. Products of pyrolysis and gasification include char, ash, CO, CO_2, H_2, H_2O, CH_4, C_2H_x, and tar. The other high-molecular gases such as C_2H_2, C_2H_4, and C_2H_6 are included in C_2H_x in order to simplify simulation.
4) Char is pure carbon. Ash is inert, and does not take part in reactions.
5) Fuel particles experience pyrolysis when they first enter the gasifier, and then pyrolysis (if there is still unpyrolyzed biomass) and char gasification take place simultaneously until the particles reach a small enough size where they are entrained out of the bed. Fuel particles are spherical, consisting of an un-pyrolyzed biomass core and a shell which is a mixture of carbon and ash. Ash peels off of particles

Table 1
Properties of fuels.

	Corn stover [5,20]	Birch wood [21]	Pine sawdust [10]
Particle size, mm	0.3	0.5–0.8	0.5
Moisture (wt %, wet)	8.0	5	8.5
HHV (MJ kg^{-1}, dry)	17.93	–	–
Bulk density, kg/m3			
Raw material	300		
Char	90		
Ultimate (wt %, dry)			
Carbon	45.44	48.25	41.99
Hydrogen	5.52	5.58	6.22
Nitrogen	0.69	0.20	0.20
Oxygen	41.49	45.66	50.39
Sulfur	0.04	0	0
Chlorine	0.1	0	0
Ash	6.72	0.3	1.2

immediately after carbon is consumed during chemical reactions. Char deactivation and particle fragmentation are not modeled due to the lack of related theories. Particles are isothermal and non-penetrative, and gas–solid reactions take place on the surface of particles.

6) The entire reactor is divided into two parts: fluidized bed and freeboard. The fluidized bed is modeled as a two-phase system (emulsion and bubble described below), and remainder of the gasifier, called freeboard, is modeled as a one-phase system (gas only). Only gas–gas reactions exist in the freeboard.
7) The fluidized bed consists of a bubble phase and an emulsion phase as shown in Fig. 1. The emulsion phase consists of gases, char, and bed material (sand), while the bubble phase contains only gases. Flow of gas in excess of the minimum fluidization velocity passes through the bed in the form of bubbles. The voidage of the emulsion remains constant, and is equal to that at incipient fluidization. Mass exchange takes place between the bubble phase and the emulsion phase.
8) Due to rapid mass transfer, fuel particles of different sizes are well mixed and homogeneously distributed inside the fluidized bed, and the mass balance for solid phase in the fluidized bed section is global [13]. Difference in gas concentration in the radial direction is neglected. Gas concentration gradients exist only in the axial direction for both bubble and emulsion phases.

2.1.1. Model development for the entire reactor

The entire reactor is divided into a series of infinitely thin vertical elemental cylinders of *dz* thickness up to the gasifier outlet, and governing equations are established for each gas species of each phase in each element. Fluid dynamics parameters are shown in Table 2.

For specifies *i* in element *j* in the bubble phase of the fluidized bed, mass increase during unit time equals mass entering this element by convection and diffusion minus mass leaving this element by convection and diffusion during this amount of time. Therefore, based on the mass balance, the governing equation for species *i* in element *j* in the bubble phase of the fluidized bed is:

$$\frac{\partial\left(C_{b,i,j}A_{b,j}\Delta Z\right)}{\partial t} = \left(A_{b,j-1}C_{b,i,j-1}U_{b,j-1} - A_{b,j-1}D_b\frac{\partial C_{b,i,j-1}}{\partial z}\right)$$
$$- \left(A_{b,j}C_{b,i,j}U_{b,j} - A_{b,j}D_b\frac{\partial C_{b,i,j}}{\partial z}\right)$$
$$- K_{be}\left(C_{b,i,j} - C_{e,i,j}\right)A_{b,j}\Delta Z + R_{b,i,j}A_{b,j}\Delta Z$$

$$\frac{\partial C_{b,i,j}}{\partial t} = \left(\frac{A_{b,j-1}U_{b,j-1}}{A_{b,j}\Delta Z}C_{b,i,j-1} - \frac{A_{b,j-1}D_b}{A_{b,j}\Delta Z}\frac{\partial C_{b,i,j-1}}{\partial z}\right)$$
$$- \left(\frac{U_{b,j}}{\Delta Z}C_{b,i,j} - \frac{D_b}{\Delta Z}\frac{\partial C_{b,i,j}}{\partial z}\right) - K_{be}\left(C_{b,i,j}C_{b,i,j} - C_{e,i,j}\right) + R_{b,i,j}.$$

Similarly, mass balance for species *i* in element *j* in the emulsion phase of the fluidized bed is:

$$\frac{\partial\left(C_{e,i,j}A_{e,j}\Delta ZE_{mf}\right)}{\partial t} = \left(A_{e,j-1}U_{e,j-1}C_{e,i,j-1} - E_{mf}A_{e,j-1}D_e\frac{\partial C_{e,i,j-1}}{\partial z}\right)$$
$$- \left(A_{e,j}U_{e,j}C_{e,i,j} - E_{mf}A_{e,j}D_e\frac{\partial C_{e,i,j}}{\partial z}\right) \quad (3)$$
$$+ K_{be}\left(C_{b,i,j} - C_{e,i,j}\right)A_{b,j}\Delta Z + R_{e,i,j}A_{e,j}\Delta ZE_{mf}$$
$$+ \frac{n_{p,i}}{V_e}A_{e,j}\Delta ZE_{mf}$$