Modeling the impact of bubbling bed hydrodynamics on tar yield and its fluctuations during biomass fast pyrolysis¹

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Abstract The impact of bubbling bed hydrodynamics on temporal variations in the exit tar yield for biomass fast pyrolysis was investigated using computational simulations of an experimental laboratory-scale reactor. A multi-fluid computational fluid dynamics model was employed to

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simulate the differential conservation equations in the reactor, and this was combined with a multi-component, multi-step pyrolysis kinetics scheme for biomass to account for chemical reactions. The predicted mean tar yields at the reactor exit appear to match corresponding experimental observations. Parametric studies predicted that increasing the fluidization velocity should improve the mean tar yield but increase its temporal variations. Increases in the mean tar yield coincide with reducing the diameter of sand particles or increasing the initial sand bed height. However, trends in tar yield variability are more complex than the trends in mean yield. The standard deviation in tar yield reaches a maximum with changes in sand particle size. The standard deviation in tar yield increases with the increases in initial bed height in freely bubbling state, while reaches a maximum in slugging state.

Keywords: Biomass fast pyrolysis; Bubbling bed hydrodynamics; Multi-fluid model; Tar yield fluctuation; Slugging

1. Introduction

Biomass pyrolysis for producing high energy-density transportable bio-oil has attracted increased considerable interest in recent years [1]. Under external heating in the absence of oxidizer agent, lignocellulosic biomass is rapidly decomposed into three primary products: condensable liquids (also called tar), non-condensable gases, and biochar [2]. The non-condensable gases and biochar can be used to make high-value coproducts or used as fuel for process heat, while the condensable liquids contain hydrocarbons that can be used to produce liquid fuels via catalytic upgrading [3].

Because the potential output of bio-oil is directly dependent on the initial pyrolysis tar yield and composition, there is considerable interest in experimental [4-8] and computational [9-22]

investigations of how tar yield is affected by the biomass type and also by the employed conditions for pyrolysis. This interest should include both the mean tar yield as well as its variability, since large fluctuations in the condensable hydrocarbon stream used for catalytic upgrading would significantly complicate the process control. With this in mind, we focused our attention in this study on simulating how the operation of a bubbling bed pyrolysis reactor might affect both mean tar yield and its variability.

Many versions of biomass fast pyrolysis have been implemented in bubbling fluidized-bed reactors because of their excellent solid mixing and heat transfer [4]. Some general guidelines regarding the effects of operating conditions on overall tar yields have been proposed in the literature [5, 6]. The effects of inlet gas velocity [16], sand particle size [23], biomass particle size [19], reactor temperature [24], reaction atmosphere [22, 25], etc., on overall tar yields have been extensively investigated. However, it appears that the issue of temporal fluctuations in the exit gases from such reactors has rarely been addressed. Since the hydrodynamics and transport processes in bubbling bed reactors include inherent fluctuations associated with the multi-phase flow, one would expect this to create some degree of fluctuations in the flow and composition of the pyrolysis products leaving the reactor. This latter issue is of particular concern in this study because of its potential impact on processes involving direct catalytic upgrading of the chemically unstable products in raw bio-oil.

2. Modeling Approach

In this study, the effects of different operating parameters on the fast pyrolysis products exiting the reactor were simulated using computational fluid dynamics (CFD) to account for the multi-phase hydrodynamics. Compared with time-consuming and costly experiments, multi-

phase CFD is able to provide detailed information on the spatiotemporal variations in species concentrations, flows, and temperatures within the reactor with reduced effort and developing circle. This makes CFD a promising platform to account for physical relationships that are beyond the capability of direct experimental measurements [7-15]. To make sure that the simulated reactor conditions were relevant, we based the simulations in the present study on an experimental laboratory-scale bubbling fluidized-bed pyrolyzer located at Iowa State University [16]. Assumptions concerning inlet gas flow, biomass feed rate, initial bed height, and bed solids properties were based on realistic variations about the published nominal operating conditions for this reactor.

Following previous experience with similar reactor simulations, we adopted the multi-fluid modeling (MFM) approach for CFD [17-21, 26, 27] for this study. Compared with discrete particle models [28-30], MFM models treat all phases as continua through volume fraction averaged conservation equations, hence considerable computational effort is saved. The relevant conservation equations for MFM can be found in our previous papers [17, 23], and thus they are not described here. The momentum and energy transfer coefficients between gas and solids were modeled by the Gidaspow drag model [31] and Gunn heat transfer model [32], respectively.

The multi-component, multi-step devolatilization scheme proposed by Miller and Bellan [33] was employed to model the biomass fast pyrolysis reactions, since it includes both the effects of the initial biomass composition and secondary tar cracking [34]. The Miller and Bellan devolatilization scheme includes the following major reactions:

Virgin biomass is assumed to consist of cellulose, hemicellulose, and lignin with prescribed mass fractions. In this reaction network, each reaction is assumed to be first-order irreversible, and detailed data on the reaction rate constants and heats are listed in Table 1.

The open-source code MFIX developed at National Energy Technology Laboratory was used to conduct the numerical study [35]. The stiff ordinary chemistry solver was launched each time step to integrate the reaction kinetics and a time-split scheme [36] was utilized to couple the multiphase flow solver with the chemical reaction solver.

3. Simulation details

The experimental laboratory-scale bubbling fluidized-bed reactor at Iowa State University [16] on which the present simulations were based is illustrated schematically in Fig. 1. This reactor has been used in many CFD studies [19, 26, 37] to provide high-fidelity comparisons with computational predictions. The inner reactor diameter and total height are 3.81 cm and 34.29 cm, respectively. The bulk of the reactor bed is composed of sand particles with density of 2.649 g/cm³ and diameter (d_s) of 0.052 cm. These are typically added to the reactor vessel to an initial height (h_{ini}) of 5.5 cm and a void fraction of 0.41. Biomass particles are injected into the reactor 1.33 cm above the reactor bottom. The reactor exit is open to atmospheric pressure where products are collected for post-processing. The temperature of the side wall is maintained at 773 K. The assumed biomass feed in this study was red oak, with a mean diameter of 0.04 cm and a composition of 41% cellulose, 32% hemicellulose, and 27% lignin on mass basis [16].

To begin, we used a reference operating condition that included a feed rate of uniformly distributed pure nitrogen from the bottom of the bed at 773 K to give a superficial velocity of $u_{in} = 36$ cm/s. The nominal red oak feed rate was 100 g/h at temperature of 300 K. Based on the reactor height and gas velocity, the residence times for both biomass and tar are approximately 1 s, which further confirms that biomass was under fast pyrolysis. To investigate the effects of changing operating conditions, variations from the reference case were made in the gas velocity, the sand particle size, and the static bed height. All of the operating states included in this study were constrained to fall within the characteristic Geldart Group B bubbling regime in order to avoid defluidization or the turbulent regime.

To reduce computation time, all of the results reported here were simulated using a two-dimensional (2D) Cartesian grid, based on previous investigations that demonstrated consistency between 2D and 3D simulations for this reactor [16]. Using trial simulations of the reference case for different spatial resolutions, computational independence was confirmed for a grid resolution of uniform 20 horizontal $\times$ 180 vertical cells. To maintain the same biomass particle volume fraction in the bed, the biomass injection rate for 2D simulations was changed to 32.75 g/h, consistent with [38]. A variable time step was also employed to reduce the computational cost. For simulations lasting 100 s of physical time, the transient mass flux of tar at the reactor exit was recorded at 0.05 s intervals. After the initial simulation transients were discarded (typically lasting < 5 s), the convergent statistical properties of the exit tar flux variations were evaluated as described below.

4. Results and discussion

4.1 Characterizing tar yield dynamics

Instantaneous tar production, i.e., the mass flux of tar exiting the reactor, is calculated as

$$F_{tar} = \int_{exit} \varepsilon_g \rho_g X_{tar} \mathbf{V}_g \cdot \mathbf{n} d\mathbf{x}, \quad (4)$$

where ε_g is volume fraction of the gas phase, ρ_g is gas density, $\mathbf{V}_g$ is gas velocity and X_{tar} is mass fraction of tar in the gas phase; $\mathbf{x}$ is elemental surface at the reactor exit and $\mathbf{n}$ is the outward vector normal to $\mathbf{x}$. It can be seen that because of the flow characteristics in bubbling bed, ε_g and $\mathbf{V}_g$ at the reactor exit show insignificant variations. Thus, the temporal fluctuation of F_{tar} will be mainly determined by the extent of variations from ρ_g and X_{tar} . The temporal evolution of F_{tar} in the reference case with time interval of 0.05 s is shown in Fig. 2. Because of the composition of the biomass feedstock, reactor geometry, and operating conditions, the resulted tar yield is about 70% of the fed biomass. It can be seen that after a rapid increase, F_{tar} converges to a time series of fluctuations around a mean value. The predicted mean for the reference case is close to the experimental observation with relative error less than 5%, supporting the basic validity of the computational approach.

The temporal fluctuations in F_{tar} arise at the reactor exit due to the inherent hydrodynamic instability of the bubbling fluidized bed, e.g., the spontaneous flow fluctuations caused by the nonlinear drag interactions between the fluidized particles and gas. The gas-particle flow instabilities generate regions of low solids density (gas bubbles) that travel upward, coalesce, and finally erupt at the bed surface. Vertical fluctuations also occur in the bed height, and the particles slosh from side-to-side in wave-like patterns. Because of the strong coupling among the gas-particle flows, local chemical species concentrations, and the pyrolysis reactions, fluctuations also occur in the local fluxes of reaction products.

Example snapshots of the above spatial variations are illustrated in Fig. 3 at the times marked in Fig. 2. At the reactor exit, the net outflow of tar fluctuates in response to all the variations in the zones below. In addition to using the mean tar exit concentration to indicate overall reactor performance, the amplitude of the fluctuations in F_{tar} can be represented in terms of the standard deviation, σ_F , of the distribution of F_{tar} . We found it convenient to use the estimated mean exit tar flow, $\bar{F}_{tar}$, and the tar flow standard deviation to track the statistical convergence of each simulation. Examples of this are illustrated in Fig. 4 as the time interval T over which these statistics are averaged is increased. For the conditions of interest here, we found that statistical convergence is completed by 50 s. Therefore, all the statistics reported here are based on the last 50 s from each simulation. We also found that another statistic, the coefficient of variation, S_F , which is the ratio of σ_F to $\bar{F}_{tar}$, is useful for understanding trends. This is a widely used statistic that gives a standardized measure of statistical dispersion for contexts where the relative size of oscillating quantities is important. Small values of S_F imply relatively high average yield and relatively low variability, so it might be useful for optimizing the pyrolysis reactor.

4.2 Simulation results for variations in u_{in} , h_{ini} , and d_s

Figure 5 illustrates the predicted trends in $\bar{F}_{tar}$ and S_F as u_{in} was varied. In this case, d_s and h_{ini} were fixed at 0.052 cm and 5.5 cm, respectively. The increase of $\bar{F}_{tar}$ with the increases in u_{in} is consistent with the trend reported in previous studies of the same bubbling bed reactor [16, 19, 23]. The largest contributing factor here is the reduction of gas residence time in the bed with increasing gas flow, resulting in less opportunity for the initially released tar vapors to undergo cracking before they escape the bed. With less cracking, more tar is left in the exit gas and thus should potentially provide more condensable material for upgrading to bio-oil.

Interestingly, the fluctuations in exit tar flux, as indicated by S_F , were also predicted to increase with u_{in} . The trend we observed in the present simulations appears to be similar to that reported by others for the overall pressure fluctuations. For example, in [39] it is reported that in the bubbling bed regime (where the gas flow is below the transition level from bubbling to turbulent fluidization), the standard deviation of the dynamic overall pressure fluctuations can be related to u_{in} as

$$S_F = a(u_{in} - u_{mf})^{0.4} + b(u_{in} - u_{mf}), \quad (5)$$

where u_{mf} , a , and b are the minimum fluidization velocity, and empirically derived parameters, respectively. This is because in the bubbling fluidization regime, more energy is carried into the reactor through the increased gas flow, leading to larger bubbles and greater amplitude fluctuations.

The predicted impacts of d_s on $\bar{F}_{tar}$ and S_F are shown in Fig. 6, when u_{in} and h_{ini} were fixed at 36 cm/s and 5.5 cm, respectively. Over the particle size range evaluated, we observed a steady drop in $\bar{F}_{tar}$ with increasing d_s . Since the gas flow was fixed, increasing the bed particle size shifted the hydrodynamic state closer to minimum fluidization, reducing the fluidization intensity and thus reducing the heating rate of the injected biomass particles. The net result was a predicted drop in tar generation rate.

The predicted trend in S_F with bed particle size was characteristically different from the mean exit tar flux as illustrated in Fig. 6. Specifically, we found that S_F first increases and then decreases with increasing d_s , reaching a maximum in the present case for bed particles between 0.05 and 0.06 cm. The increase of S_F with the increases in d_s is similar to that found by Svoboda,

et al. [40] for pressure fluctuations. In their study, it was discovered that the standard deviation of pressure fluctuation increased as d_s became larger. However, with increasing d_s beyond a certain value, e.g., ~ 0.05 cm, S_F decreased. We conjectured that this complex variation of S_F with d_s may be explained by a transition in the fluidizing state of the bed from a near slugging condition (very large bubbles at the bed surface) for smaller bed particle sizes to a more freely bubbling condition (small bubble sizes at the bed surface) as particle size is increased. As illustrated in Fig. 7, increases in bed particle size above the transition point tend to reduce the exiting bubble size and amplitude of the bed surface fluctuations. Decreasing bed particle size below the transition point results in larger bubbles in slugging state, which seems to decrease the fluctuation of tar yield as will be discussed in the following on the effects of h_{ini} . Also, the overall amplitude of the bed fluctuations appears to be reduced because the smaller bed particles have less inertia and are able to move more freely. Taken together these effects appear to be responsible for the peak in tar fluctuations at an intermediate bed particle size. If the above conjecture is correct, proper selection of the bed particle size should be an important consideration in pyrolyzer operation. It is worth noting that d_s was chosen to be larger than 0.04 cm to make the bed in bubbling state. When d_s is less than 0.04 cm, the bed may enter turbulent fluidization and bed hydrodynamics could be more complex than that in bubbling fluidization. The trends of tar yield and its fluctuations with particle size in turbulent fluidization are hard to predict based on the information obtained from bubbling fluidization and require further investigations.

The predicted trends in $\bar{F}_{tar}$ and S_F with respect to h_{ini} when u_{in} and d_s were fixed at 24 cm/s and 0.052 cm, respectively, are shown in Fig. 8. The increases in $\bar{F}_{tar}$ with increases in h_{ini} are consistent with an increasing biomass particle residence time in the bed, allowing more

devolatilization to occur before the biomass particles exit. The increases in S_F with increases in h_{ini} may be because for higher h_{ini} , the bed becomes heavier and more energy is required to be carried by the inlet gas to fluidize the sand and ultimately produce larger S_F by the elevated amplitude of spontaneous bed fluctuation.

The predicted trends in $\bar{F}_{tar}$ and S_F with respect to h_{ini} when u_{in} and d_s were fixed at 36 cm/s and 0.052 cm, respectively, are shown in Fig. 9. The predicted trend for S_F with increases in h_{ini} under such u_{in} was similar to that seen for d_s , i.e., S_F increased at first but then decreases at higher h_{ini} . The decreases in S_F with increases in h_{ini} are conjectured as follows. Under such operating condition, i.e., $u_{in} = 36$ cm/s, changes in bed height can result in a bubbling-slugging transition similar to changes in bed particle size. When h_{ini} is sufficiently low, slugging cannot occur, as is illustrated in Fig. 10. With modest increases in h_{ini} around 4.5 cm which is also the point where S_F turns from increasing to decreasing, slugging begins. Slugging seems to favorably produce smaller amplitude of fluctuations, thus further increases in h_{ini} results in reduced S_F . We noted here that our simulation results for this case exhibited relatively wide scattering in the S_F trend. This may be possibly due to the fact that even longer simulations are required to minimize statistical scattering. Another explanation is that the dominant mechanisms with the changes of h_{ini} may be more complex than what we proposed above and deserve further investigation.

5. Conclusion

An experimental laboratory-scale bubbling fluidized-bed reactor for biomass fast pyrolysis was simulated using a multi-fluid CFD model combined with a global multi-component, multi-step reaction kinetics scheme. The numerical simulation was able to predict mean tar yields

consistent with experimental observations. The effects of bubbling bed hydrodynamics on tar yield and its fluctuations are

- a) Increasing levels of fluidizing gas flow resulted in increases in both the tar yield and amplitude of its fluctuations.
- b) Increases in bed particle size led to the decreases in the tar yield and the maximum of amplitude of its fluctuations.
- c) Increases in static bed height predicted increases in the tar yield. At relatively low levels of fluidizing gas flow, the amplitude of tar yield fluctuations increases with the increases in static bed height, while reaches a maximum at relatively high levels of fluidizing gas flow.

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Table 1 Reaction rate constants for biomass fast pyrolysis reactions.

Components	Reaction	Y	A (s^{-1})	E (J/mol)
Cellulose	k_{1c}	0.35	2.8×10^{19}	2.424×10^5
	k_{2c}		3.28×10^{14}	1.965×10^5
	k_{3c}		1.3×10^{10}	1.505×10^5
Hemicellulose	k_{1h}	0.6	2.1×10^{16}	1.867×10^5
	k_{2h}		8.75×10^{15}	2.024×10^5
	k_{3h}		2.6×10^{11}	1.457×10^5
Lignin	k_{1l}	0.75	9.6×10^8	1.076×10^5
	k_{2l}		1.5×10^9	1.438×10^5
	k_{3l}		7.7×10^6	1.114×10^5
Tar	k_4		4.25×10^6	1.08×10^5

Fig. 1 The simulated laboratory-scale bubbling fluidized bed for biomass fast pyrolysis

Fig. 2 The temporal evolution of the tar mass flux at the reactor exit; A , B , C are snapshot times as depicted in Fig. 3; T is an averaging timespan as depicted in Fig. 4

Fig. 3 Snapshots of gas volume fraction, axial gas velocity, and mass fraction of tar at the marked instants in Fig. 2

Fig. 4 Variations of $\overline{F}_{tar}$ and σ_F with respect to T

Fig. 5 Variations of $\overline{F}_{tar}$ and S_F with respect to u_{in} when d_s and h_{ini} are fixed at 0.052 cm and 5.5 cm; Dash curves represent the fitted trends

Fig. 6 Variations of $\bar{F}_{tar}$ and S_F with respect to d_s when u_{in} and h_{ini} are fixed at 36 cm/s and 5.5 cm; Dash curves represent the fitted trends

Fig. 7 Snapshots of gas volume fraction for different d_s (cm) at $t = 60$ s

Fig. 8 Variations of $\bar{F}_{tar}$ and S_F with respect to h_{ini} when u_{in} and d_s are fixed at 24 cm/s and 0.052 cm; Dash curves represent the fitted trends

Fig. 9 Variations of $\bar{F}_{tar}$ and S_F with respect to h_{ini} when u_{in} and d_s are fixed at 36 cm/s and 0.052 cm; Dash curves represent the fitted trends

Fig. 10 Snapshots of the gas volume fraction distribution with different h_{ini} (cm) at $t = 60$ s