Coupling DAEM and CFD for simulating biomass fast pyrolysis in fluidized beds¹

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Abstract We report results from computational simulations of an experimental, lab-scale bubbling bed biomass pyrolysis reactor that include a distributed activation energy model (DAEM) for the kinetics. In this study, we utilized multiphase computational fluid dynamics (CFD) to account for the turbulent hydrodynamics, and this was combined with the DAEM kinetics in a multi-component, multi-step reaction network. Our results indicate that it is possible

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to numerically integrate the coupled CFD-DAEM system without significantly increasing computational overhead. It is also clear, however, that reactor operating conditions, reaction kinetics, and multiphase flow dynamics all have major impacts on the pyrolysis products exiting the reactor. We find that, with the same pre-exponential factors and mean activation energies, inclusion of distributed activation energies in the kinetics can shift the predicted average value of the exit vapor-phase tar flux and its statistical distribution, compared to single-valued activation-energy kinetics. Perhaps the most interesting observed trend is that increasing the diversity of the DAEM activation energies appears to increase the mean tar yield, all else being equal. These findings imply that accurate resolution of the reaction activation energy distributions will be important for optimizing biomass pyrolysis processes.

Keywords: Biomass fast pyrolysis; Distributed activation energy model; Multi-fluid model; Gaussian distribution; Logistic distribution

1. Introduction and Background

Computational fluid dynamics (CFD) simulation of biomass fast pyrolysis in fluidized beds has gained increased attention in the last decades [1-17] because of its versatility and economy compared with experiments. Through judicious use of computational simulation, detailed information about the links between dynamic conditions inside pyrolysis reactors and key operating and design parameters can significantly reduce development cost and time [18-23]. Also, computational simulations of experiments can provide information about important details that are simply not accessible through direct measurements, especially when the process conditions of interest are harsh [24].

In simulating biomass fast pyrolysis reactors, the dynamic behavior of the product streams depends heavily on the nonlinear interactions between the multiphase hydrodynamics, the heat and mass transport, and the chemical reaction rates. The product stream dynamics are important in turn, because they become direct inputs to subsequent processing operations, such as condensation and catalytic upgrading. So to account for these interactions in computational simulations, it is important to include sufficient details about key pyrolysis operating parameters, such as the biomass and bed solid physical and chemical properties, the turbulence and interphase transport submodels used, and the boundary conditions and computational domain discretization. Each of these issues has been individually investigated [25-42], and the computational modeling community appears to be approaching a consensus on many of the issues associated with computational modeling of bubbling fluidized bed reactors.

It is important to recognize, however, that biomass pyrolysis in bubbling fluidized beds involves some unique challenges. This is especially true where the goal is to maximize the quality and yield of key hydrocarbon species needed for upgrading raw bio-oil vapors into feedstock for fuels or other commercial products. One key reason that biomass fast pyrolysis is so challenging is that the chemical reactions involved are themselves highly complex, involving many thousands of intermediate products, many parallel reaction pathways, and catalysis due to intrinsic ash. In turn, these reactions couple strongly with the turbulent flow and transport processes in the reactor, creating even higher levels of complexity. So predicting even general trends for products generated under such conditions requires resolving how the dominant reactions couple with the spatiotemporal transport dynamics in the reactor. This is where CFD, appropriately linked to both chemistry and transport, can be a powerful tool.

Our initial challenge in the present study was to identify an appropriate reaction mechanism that would help reveal basic trends without adding too much complexity. We first considered the reaction mechanisms studied in other pyrolyzer CFD studies such as that by Xiong, et al. [43], Xiu, et al. [44], Simone, et al. [45], and Mellin, et al. [46]. In all these cases, each reaction step is assumed to have a single value for the activation energy. To include the effects of reaction rates, we decided to focus on the reaction mechanism proposed by Miller and Bellan [47] which involves both competitive decompositions to produce tar (condensable liquids), permanent gas, and biochar, and secondary tar cracking was utilized to represent biomass devolatilization. The biomass devolatilization reactions included in this mechanism are

Given the interest in maximizing condensable hydrocarbon liquids vs. char and light gases in bio-oil production, we felt this mechanism included the most important general pathways (albeit in a very lumped form), without adding too many overwhelming computational details.

Based on prior studies of the kinetics of coal devolatilization [48], we expect that it is probably more realistic to assume that biomass devolatilization kinetics are also likely to involve distributed activation energies. Considering this possibility, we were motivated to see how use of these alternate models can affect the expected biomass pyrolyzer performance.

Distributed activation energy models (DAEMs) [49], in which the activation energy of every biomass decomposition reaction distributes over a range, provide a way to account for the inherent non-uniformity of chemical bonds in biomass. So far, studies of how DAEM kinetics might affect the resulting products have been restricted to cases where the focus was on individual fixed particles [50-53]. The impacts of the turbulent mixing and transport that are characteristic of bubbling bed reactors on the resulting reaction products have not been considered so far.

In this study we selected the DAEM approach summarized in [47] and combined it with a CFD model of an existing experimental pyrolyzer at Iowa State University [54]. The reactor simulations were carried out using a multi-fluid model (MFM) [18,26], which simulates all phases as interpenetrating continua. Details on MFM can be found in our previous papers [18,55] and are not repeated here. However, in the discussion below we focus on the DAEM kinetics and how they were coupled to CFD and transport in MFM to generate pyrolyzer simulations, assuming two different activation energy distribution functions: Gaussian and Logistic.

2. Distributed activation energy model

2.1 Theory of DAEM

In contrast to conventional Arrhenius kinetics, DAEM assumes that activation energies are distributed over a range, and thus they are described in terms of probability density functions $f(E)$. This implies that the rate for first-order irreversible reactions can be expressed as

$$\frac{\partial[dm(E)]}{\partial t} = -A \exp\left(-\frac{E}{RT}\right)[dm(E)], \quad (4)$$

96 where A , R , and T are frequency factor, universal gas constant, and temperature, respectively. In
 97 DAEM, $dm(E)$ is related to the total mass of biomass m as

$$98 \quad dm(E) = f(E)mdE. \quad (5)$$

99 Therefore, the integrated reaction rate on total biomass becomes

$$100 \quad \frac{\partial m}{\partial t} = -Am \int_0^{\infty} \exp\left(-\frac{E}{RT}\right) f(E) dE. \quad (6)$$

101 It can be seen from the above description that $f(E)$ is the key feature in DAEM. In the
 102 application of DAEM to biomass fast pyrolysis, there are two distribution functions, the
 103 Gaussian and the Logistic, that are most frequently employed. The Gaussian distribution is
 104 centered at E_0 with standard deviation σ and is expressed as

$$105 \quad f(E) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left[-\frac{(E-E_0)^2}{2\sigma^2}\right]. \quad (7)$$

106 The Logistic distribution was initially proposed [56] to account for the structural asymmetry that
 107 exists in many types of biomass materials, such as grape residuals. It is typically written as

$$108 \quad f(E) = \frac{\pi}{\sigma\sqrt{3}} \frac{\exp[-\pi(E-E_0)/(\sigma\sqrt{3})]}{\{1 + \exp[-\pi(E-E_0)/(\sigma\sqrt{3})]\}^2}, \quad (8)$$

109 where E_0 and σ are the mean value and standard deviation, respectively. It should be mentioned
 110 that in some applications of DAEM to biomass fast pyrolysis [57,58], the frequency factor, A ,
 111 has also been assumed to vary with T or E_0 . In the present study, A was held constant, but it
 112 would certainly be possible to include variations in this parameter in future studies using the

approach described below. The reaction rate constant for the Miller and Bellan mechanism that used in this study is listed in Table 1.

2.2 Numerical implementation of DAEM

Because of the nonlinearity of Eq. (6), it was numerically integrated to determine reaction rates. The accuracy for numerical integration of Eq. (6) with various choices of integration space and number of intervals are summarized in Table 2. It can be seen that if the integration space was chosen to be $(E_0-5\sigma, E_0+5\sigma)$ and divided into 200 equal intervals, the accuracy would be very high with relative error to the analytical solution less than 0.05%. It should be mentioned that the analytical solution is calculated by choosing the integration space to be $(E_0-10\sigma, E_0+10\sigma)$ and the integration intervals of 1000. In such case, the computational overhead for numerically integrating the DAEM reaction rates is about 1.7% of the time-consuming part to solve ordinary differential equations (ODEs) for source terms to be used in CFD partial differential equations (PDEs). Thus, in all simulations, DAEM reaction rates were numerically integrated on $(E_0-5\sigma, E_0+5\sigma)$ over 200 equal intervals.

The joint integration of the reaction kinetics and transport processes was implemented with the so-called time-split approach [59], which is frequently used in reactive flow modeling to effectively decouple processes at different time and length scales. In the time-split scheme, local reaction rates are first calculated based on local state variables such as temperature and species concentrations. The calculated reaction rates and their associated exothermic or endothermic heat releases are then used as source terms in the conservation equations for updating field variables at each location. This procedure is summarized schematically in Fig. 1.

3. Experimental Setup

The experimental atmospheric pressure pyrolysis reactor used as the basis for this study is used for biomass research at the Iowa State University [54]. Its inner diameter and height are 3.81 cm and 34.29 cm, respectively. Sand particles with density of 2.649 g/cm^3 and mean diameter of 0.052 cm are initially packed to the height of 5.5 cm with voidage of 0.41. The temperature of side wall is maintained at 773 K and pure nitrogen of 773 K at velocity of 36 cm/s is supplied continuously and uniformly from the reactor bottom. Under such properties, the calculated minimum fluidization velocity is about 14 cm/s. Additional details about the reactor configuration and operating conditions can be found in previous publications [18,43]. The assumed biomass feedstock for our simulations was red oak, with an initial composition of 41% cellulose, 32% hemicellulose, and 27% lignin with density of 0.4 g/cm^3 and mean diameter of 0.04 cm. The injection tube for biomass is located 1.33 cm above the gas distributor with inner diameter of 0.73 cm. The mass flux of inlet biomass is maintained at 100 g/h.

The reactor was simulated in two dimensions using the open-source code MFIX and the domain was discretized into a 20×180 uniform grid. It has been proved [18,54] that two-dimensional simulation can qualitatively reproduce the characteristics of the reactor. A physical time of 100 s was performed for each case and the last 50 s was used for data analysis.

4. Results and Discussion

4.1 Exit product flow characteristics with DAEM kinetics

We first evaluated the effects of including distributed reaction activation energies in the kinetics by comparing the product yields and flows for simulations using either single-value activation energy kinetics with simulations using activation energies having Gaussian or Logistic distributions with $\sigma = 0.06E_0$. The predicted temporal variations of the tar flux at the reactor exit

for these three cases are depicted in Fig. 2. One important difference revealed in this figure is that the mean predicted tar yield with distributed activation energy reaction kinetics is noticeably higher. This boost in the mean tar yield from DAEM can be explained as the result of the presence of a few sites with lower activation energy, which can boost the overall reaction rates. This can also be stated mathematically in the following way: When $f(E)$ is Gaussian or Logistic distributed, within the parameters of activation energy in Table 1, it can be obtained that

$$\frac{\int_0^{\infty} \exp(-\frac{E_2}{RT}) f(E_2) dE_2}{\int_0^{\infty} \exp(-\frac{E_3}{RT}) f(E_3) dE_3} \geq \frac{\exp(-\frac{E_2}{RT})}{\exp(-\frac{E_3}{RT})}. \quad (9)$$

Therefore, more biomass is converted into tar in the primary reactions when their activation energies are distributed, which ultimately produces higher levels of tar. Interestingly, this implies that, at least in some cases, biomass feed stocks with greater levels of heterogeneity (all else being equal) should be expected to generate higher tar yields.

We also evaluated the possibility that introduction of the DAEM kinetics might affect other flow and temperature profiles in the reactor. As depicted in Figure 3, it appears that the time-averaged axial profiles of the gas pressure, stream-wise gas velocity, stream-wise velocity of biomass solid phase, and gas temperature were negligibly affected by the shift in reaction rates. So at least for the conditions in this study, the concentration of biomass is too low to significantly impact the reactor hydrodynamics and transport processes. This is perhaps not surprising [43] and implies that it may be possible to ignore this type of feedback in low-order models of biomass pyrolysis as long as the conditions are similar. However in the future, it would be important to reassess this result when higher biomass feed rates are of interest.

4.2 The effects of σ (activation energy diversity)

Perhaps not surprisingly, we also observed that increasing the level of variability in the DEAM activation energies is predicted to increase the exit tar yield, as might be expected from the above discussion. This is illustrated in Figure 4, where the mean tar flux at the exit is plotted versus the standard deviation (σ) of both the Gaussian and Logistic DEAM distributions. In this case, the effect appears to be greater for the Logistic distribution, possibly because of the heavier tails in this distribution.

Given the turbulent character of bubbling bed hydrodynamics, it is not surprising that the product flows exiting the pyrolyzer exhibit significant fluctuations. We were also concerned here with how the DEAM kinetics might affect those fluctuations. One way to quantify the relative intensity of such fluctuations is the coefficient of variation, C_F , of the predicted exit tar flux with respect to σ as shown in Fig. 5. As it is used here, C_F provides a way to normalize the standard deviation with the mean value [60]. Thus it is perhaps not too surprising that, with the increases in σ , our simulations predicted a slight decrease in C_F , since the mean tar flux was also increased. Again the impact appeared to be larger for the Logistic distribution than for the Gaussian distribution, possibly because of the extended tails of the former.

The impact of the DEAM kinetics can also be seen in the higher-order moments of the simulated tar fluxes as depicted in Figs. 6 and Fig. 7, respectively. For both activation energy distribution functions, the skewness, S_F , of the exit tar fluctuations reaches a peak and the kurtosis, K_F , reaches a minimum as the activation energies become very highly dispersed. This illustrates the highly nonlinear and complex relationship between the DEAM kinetics and the

exiting pyrolysis product stream. This implies that having good models for the pyrolysis kinetics will be critical for optimizing pyrolysis process performance.

5. Conclusions

For the experimental bubbling bed biomass pyrolyzer conditions studied, our computational simulation results indicate the following:

- Inclusion of DEAM reaction kinetics (reaction kinetics with distributed versus single-valued activation energies) has a significant impact on the mean value and distribution of fluctuations in the exit tar flux.
- With the same mean values for the kinetic parameters, greater diversity in the activation energies appears to increase the mean tar yield, with possible implications for blending of biomass feeds.
- Coupling between the bed hydrodynamics and reactions appears to be primarily unidirectional, with minimal feedback between the reaction kinetics and the major flow and temperature profiles in the studied reactor.
- It appears to be possible to numerically integrate the coupled CFD-DAEM reactor models without significantly increasing computational overhead.
- Having good models for the pyrolysis kinetics will be important for optimizing pyrolysis process performance.

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Table 1 Reaction rate constants for biomass fast pyrolysis reactions.

Components	Reaction	$A \text{ (s}^{-1}\text{)}$	$E_0 \text{ (J/mol)}$	$\sigma \text{ (J/mol)}$
Cellulose	k_{1c}	2.80×10^{19}	2.424×10^5	0
	k_{2c}	3.28×10^{14}	1.965×10^5	$0.02 \sim 0.10 \times E_0$
	k_{3c}	1.30×10^{10}	1.505×10^5	$0.02 \sim 0.10 \times E_0$
Hemicellulose	k_{1h}	2.10×10^{16}	1.867×10^5	0
	k_{2h}	8.75×10^{15}	2.024×10^5	$0.02 \sim 0.10 \times E_0$
	k_{3h}	2.60×10^{11}	1.457×10^5	$0.02 \sim 0.10 \times E_0$
Lignin	k_{1l}	9.60×10^8	1.076×10^5	0
	k_{2l}	1.50×10^9	1.438×10^5	$0.02 \sim 0.10 \times E_0$
	k_{3l}	7.70×10^6	1.114×10^5	$0.02 \sim 0.10 \times E_0$
Tar	k_4	4.25×10^6	1.080×10^5	0

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340 Table 2 Relative errors (%) of numerical integration to analytical solution for DAEM using
341 different integration parameters (in the form of Gaussian/Logistic)

	50	100	200	400
$(E_0-3\sigma, E_0+3\sigma)$	2.7/3.4	1.9/2.6	1.7/2.3	1.4/1.8
$(E_0-4\sigma, E_0+4\sigma)$	0.46/0.66	0.21/0.39	0.15/0.29	0.11/0.25
$(E_0-5\sigma, E_0+5\sigma)$	0.22/0.26	0.10/0.11	0.03/0.04	0.02/0.03
$(E_0-6\sigma, E_0+6\sigma)$	0.22/0.26	0.10/0.11	0.03/0.04	0.02/0.03

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Fig. 1 Flowchart of the coupling between DAEM and CFD

Fig. 2 Predicted temporal evolutions of tar fluxes at the reactor exit for the three cases

Fig. 3 Distributions of gas pressure, stream-wise gas velocity, stream-wise velocity of biomass solid phase, and gas temperature along with reactor height

Fig. 4 Variation of $\bar{F}_{tar}$ with respect to σ for both Gaussian and Logistic distribution functions

Fig. 5 Variation of C_F with respect to σ for both Gaussian and Logistic distribution functions

Fig. 6 Variation of S_F with respect to σ for both Gaussian and Logistic distribution functions

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Fig. 7 Variation of K_F with respect to σ for both Gaussian and Logistic distribution functions