ORNL/TM-2016/69

Development of a Low-Order Computational Model for Biomass Fast Pyrolysis: Accounting for Particle Residence Time

C. Stuart Daw
Gavin Wiggins
Qingang Xiong
Emilio Ramirez

February 1, 2016

OAK RIDGE NATIONAL LABORATORY
MANAGED BY UT-BATTELLE FOR THE US DEPARTMENT OF ENERGY

ORNL/TM-XXXX/XXX

Engineering and Transportation Science Division
Sustainable Transportation Program

DEVELOPMENT OF A LOW-ORDER COMPUTATIONAL MODEL FOR BIOMASS FAST PYROLYSIS: ACCOUNTING FOR PARTICLE RESIDENCE TIME

C. Stuart Daw
Gavin Wiggins
Qingang Xiong
Emilio Ramirez

???, 2016

Prepared by
OAK RIDGE NATIONAL LABORATORY
Oak Ridge, TN 37831-6283
managed by
UT-BATTELLE, LLC
for the
US DEPARTMENT OF ENERGY
under contract DE-AC05-00OR22725

CONTENTS

LIST OF FIGURES v
ACKNOWLEDGEMENTS vii
ABSTRACT 1
1. INTRODUCTION 1
2. BACKGROUND 2
2.1 MEASURING EXPERIMENTAL PARTICLE RESIDENCE TIMES 2
2.2 PARTICLE RESIDENCE TIME DISTRIBUTION MODELS 2
2.2.1 1D Continuum Dispersion Model 3
2.2.2 Series CSTR Model 4
2.2.3 Van de Vusse Multi-Zone Model 5
2.2.4 Weibull Distribution Model 5
2.3 SIMULATING PYROLYSIS REACTOR YIELDS 6
3. RESULTS AND DISCUSSION 8
4. CONCLUSIONS 13
5. RECOMMENDATIONS 14
6. REFERENCES 14

LIST OF FIGURES

1 Example low-order simulation of feed particle size effect on yield. 10
2 Example low-order simulation of moisture effect on yield. 11
3 Example low-order simulation of particle shape impact on yield. 11
4 Example low-order simulation of particle residence time impact on yield. 12
5 Pyrolysis yields predicted by the Liden et al (1988) poplar model vs. post-heat up particle RTD. 12
6 Pyrolysis yields predicted by the Liden et al (1988) poplar model vs. gas residence time. 13

ACKNOWLEDGEMENTS

We are grateful to James E. Parks and Jae-Soon Choi for their assistance in reviewing this report and providing helpful suggestions for improvements. Our colleagues at the National Renewable Energy Laboratory in Golden, Colorado, also provided important technical insights and information about their biomass experiments. Finally, we also wish to acknowledge the support for this research from the Bioenergy Technologies Office of the Energy Research and Renewable Energy Program of the U.S. Department of Energy under contract DE-AC05-00OR22725.

ABSTRACT

We summarize literature on low-order modeling of bubbling and circulating fluidized bed reactors relevant to the residence times and conversion of biomass particles during fast pyrolysis. Previous studies have shown that biomass fast pyrolysis yields depend critically on the residence time distribution (RTD) of the pyrolyzing particles, which is a function of the intrinsic feed properties as well as the reactor design and operating conditions. Experimental measurements indicate that it should be possible to represent the RTDs for biomass particles in both reactor types with relatively simple functional approximations involving only two or three physically relevant parameters. We demonstrate how particle RTDs represented by such functional models can be combined with reaction kinetics and simplified reactor mass balances to create low-order fast pyrolysis models that can be used to summarize, interpret, and extrapolate observed pyrolysis trends in experiments and more detailed computational simulations. We expect similar approaches can also be used to model the impact of catalyst particle residence time in vapor phase upgrading reactors.

1. INTRODUCTION

The two most common reactor configurations used for carrying out fast pyrolysis of biomass are bubbling fluidized beds and circulating fluidized beds, also known as riser reactors [Cui and Grace (2007), De Souza-Santos (2010), Bridgwater (2012)]. Both of these reactor types are designed to contact biomass particles with hot up-flowing inert gases (e.g., nitrogen) and solids (e.g., sand) under multiphase flow conditions. In bubbling beds, the gas flow is sufficient to cause turbulent mixing of the solids and gas, but it is typically not sufficient to entrain most of the particles, with the exception that much of the char generated from the biomass often can escape out the top of the reactor vessel. In circulating fluidized beds on the other hand, the gas flows are much higher and the solids are typically smaller, so that most or all of the solids are entrained out the top of the reactor vessel. In this case, the entrained solids are separated from the gas and most of them are recirculated back through the reactor with fresh gas, hence the name circulating beds.

Previous studies over many years have demonstrated that there are three major factors determining the conversion performance of biomass fast pyrolysis (that is the yield and composition of the pyrolysis vapors) in both circulating and bubbling fluidized bed pyrolyzers:

- The heating rate and maximum temperature of the biomass particles;
- The biomass particle residence time distribution (RTD) in the reactor; and
- The residence time distribution and gas-solid contacting of vapors released from the biomass particles.

The present study was initiated to review previous work on how biomass particle RTD behavior in bubbling and circulating fluidized bed reactors has been modeled in the past and how it has been coupled with reaction kinetics to simulate overall conversion performance. Our overall objective is to identify low-order reactor approximations based on this information that can be used to guide, interpret, and correlate lab and pilot-scale experiments on pyrolysis-based bio-oil generation now being carried out at national laboratories in support of the Department of Energy's (DOE's) Bioenergy Technology Office (BETO). We also seek to provide tools for consolidating information from more detailed computational reactor simulations [e.g., see the recent studies by Trendewicz et al (2014, 2015)] and improving high-level process simulations of bio-oil production needed for techno-economic analyses.

2. BACKGROUND

2.1 MEASURING EXPERIMENTAL PARTICLE RESIDENCE TIMES

Many different experimental techniques have been employed to measure solids motion and mixing in bubbling and circulating fluidized beds. Some have relied on direct visual imaging of optically accessible beds [e.g., Busciglio et al (2011) and Goldschmidt et al (2003)], but these experiments typically involved significant perturbations of the dynamics (e.g., 2D bed construction) in order to obtain the optical access. Less intrusive methods based on capacitance, X-ray, and magnetic resonance imaging and magnetic and radioactive particle tracking have also been employed to follow the motion of fluidized particles with high precision in 3D [e.g., see Halow and Nicoletti (1992), Larachi et al (1997), and Halow et al (2012)]. While these experiments have provided unprecedented information about the details of particle motion, they have not typically provided a means to directly quantify particle RTDs.

The experimental methods that have provided the most direct measurement of particle RTDs have relied on measurements of the exit times of distinctive particles (e.g., particles with some distinctive physical characteristic such as color, size, or chemical composition that can be readily detected) after they have been injected as pulses into experimental bubbling or circulating fluidized beds. Typically, the particles that were measured have been classified either as Geldart A or B type, which characterizes the flow patterns they tend to exhibit [Geldart (1973), Kunii and Levenspiel (1991)].[1] Some of the most relevant articles on these experiments include: Yagi and Kunii (1961a), Helmrich et al (1986), Berruti et al (1988), Ambler et al (1990), Smolders and Baeyens (2000), Harris et al (2003a&b), Bhusarapu et al (2004), and Andreux et al (2008). All of these studies have reported some common features in the observed RTDs:

- A small percentage of particles travel very rapidly through the reactor, probably due to being captured in turbulent flow streams that bypass most of the reactor volume.
- Most particles reach the exit after some significant delay in time that is longer than the average gas residence time.
- It is most common to observe one peak in the RTD but there are some instances when two have been seen.
- There is almost always an extended tail in the RTD that can sometimes extend over an order of magnitude range in time.

As discussed below, the above features of particle RTDs are actually analogous to features seen in many types of flow reactors, both single and multiphase. So it is possible to draw on an even larger body of literature in chemical reaction engineering to search for useful modeling approaches.

2.2 PARTICLE RESIDENCE TIME DISTRIBUTION MODELS

The chemical reaction engineering literature has dealt extensively with analytical, statistical, and computational dynamics models that can simulate the complex flow processes common to many types of flow reactors, both single and multiphase [see for example Levenspiel (1999) and Fogler (2006)]. So the issue of modeling biomass particle RTDs in flash pyrolysis is, in fact, a subset of a much more general problem that has received considerable attention for over 50 years [e.g., see Van de Vusse (1962) and Naor and Shinnar (1963)]. Many of the general modeling approaches developed for chemical reactors

[1] Geldart (1973) and Kunii and Levenspiel (1991) provide more information on particle groups. Briefly, Geldart A particles are small, cohesive, and not easily flowing. Geldart B particles are larger in size than Geldart A particles and flow more freely.

have been adapted for modeling particle RTDs in bubbling and circulating beds. Some relevant articles in the literature that discuss RTD modeling in this context include the following: Yagi and Kunii (1961a), Verloop et al (1968), Berruti et al (1988), Ambler et al (1990), Smolders and Baeyens (2000), Harris et al (2002), Bhusarapu et al (2004), and Andreux et al (2008). As with the modeling approaches used for the more general problem in chemical reactors, particle RTD models for bubbling and fluidized beds have adopted one of three basic approaches, listed below in increasing order of complexity:

- Analytical relationships derived from simplified assumptions that combine the flow and mixing characteristics of one or more types of ideal reactor configurations (e.g., continuous stirred tanks and/or plug flows);

- Statistical models that treat particle motion as single or serial stochastic processes that are parameterized in terms of probabilities associated with sequential random events (e.g., Markov chains); or

- Computational fluid dynamic models that solve the multiphase Navier-Stokes relationships to provide highly detailed simulations of the solids motion.

In general, the level of computational overhead required for each of the above approaches increases by at least an order of magnitude as one advances down the list. While the statistical and computational approaches should (in principle) be more fundamentally informative, they involve empirical relationships and uncertainties in key model parameters that require the use of external correlations and assumptions that can have a significant impact on the predictions. Thus, it is usually most useful to use statistical and computational models selectively when there are specific concerns (e.g., the selection of a different experimental feed system) about an experiment or reactor design that can afford the large investment of time and effort involved.

The simplicity and generality of the simplified RTD models, while less fundamental and specific to individual experiments, are likely to make them more flexible and readily accessible for correlating experimental data sets and evaluating general trends in biomass fast pyrolysis. Also, in spite of their ideal assumptions, such models are still based on physical principles and thus can presumably provide some level of physical insight. A relatively complete summary of all the simplified RTD models that have been previously considered is given in Verloop et al (1968). The RTD approximations that appear most promising for the present modeling needs for biomass particle pyrolysis are:

- The 1D continuum dispersion model [see for example Berruti et al ((1988), Levenspiel (1999), and Smolders and Baeyens (2000];

- The series continuous stirred tank reactor (CSTR) and plug flow reactor (PFR) model [e.g., see Berruti et al (1988), Levenspiel (1999), and Fogler (2010)];

- The multi-zone tank model [see Van de Vusse (1962) and Berruti et al (1988)]; and

- The Weibull distribution [see Halow etal (2012) and Daw and Halow (2014)].

These are briefly described in more detail below.

2.2.1 1D Continuum Dispersion Model

The 1D continuum dispersion model approximates the trajectory of particles as if they were being transported uniformly in a turbulent fluid flowing down a pipe. This basic approach has been proposed for

describing the RTDs of both fluid species and particles entering and leaving reactors (Berruti et al (1988), Levenspiel (1999)]. The differential mass balance for this situation leads to the following partial differential equation (PDE):

$$\frac{\partial C}{\partial t} = \left[\frac{D}{UL}\right]\frac{\partial^2 C}{\partial z^2} - \frac{\partial C}{\partial z} \qquad \textbf{(1a)}$$

In (**1a**) above, ***C*** is the concentration of transiting fluid or particles [Number/L^3], and ***z*** is axial position [L]. D represents a dispersion coefficient [L^2/T], ***U*** is an average fluid velocity [L/T], and ***L*** is a characteristic mixing length [L]. The ratio ***D/UL*** is an effective dimensionless dispersion number (i.e., the reciprocal of the Peclet number). To obtain the RTD, one introduces an impulse at the reactor inlet and then observes how ***C(t)*** varies at the exit. Normalizing the integral of ***C(t)*** to a value of 1 yields the RTD, often designated as ***E(t)***. When the dispersion ratio is very large, the exit time behavior (measured by ***C(t)***) tends to approach the limit of a single-stage continuous stirred tank reactor (CSTR). When this ratio tends toward zero, the exit time behavior of the particles approaches an ideal plug flow. Thus this type of RTD is parameterized by a single dimensionless parameter, the dimensionless dispersion or Peclet number.

Application of (**1a**) can be somewhat problematic because it also requires information about the inlet boundary conditions, and there is not a general analytical solution. Instead, it is necessary to numerically integrate (**1a**) to obtain the RTD in general. However, it has been shown that the RTD can be approximated analytically in the limits of very small and very large dispersion with specific assumptions about the inlet and exit boundary conditions [Levenspiel (1999)]. These approximations are typically expressed in terms of the RTD variance, which is sometimes the most convenient way to fit experimental measurements. One example of this is the following relationship that can be used when the dispersion is known to be large

$$\sigma^2 = 2\bar{t}^2\left(\frac{D}{UL}\right) - 2\left(\frac{D}{UL}\right)^2\left(1 - e^{-\left(\frac{UL}{D}\right)}\right) \qquad \textbf{(1b)}$$

where $\boldsymbol{\sigma^2}$ is the RTD variance and $\bar{\boldsymbol{t}}$ is the mean transit time. The corresponding RTD approximation is given by

$$E(t) = \frac{U}{\sqrt{4\pi Dt}}\exp\left[-\frac{(L-Ut)^2}{4Dt}\right] \qquad \textbf{(1c)}$$

If the dimensionless dispersion number is specified, it is still necessary to specify two more parameters from among ***L***, ***U***, or ***D*** in order to obtain ***E(t)*** from equation **1c**.

2.2.2 Series CSTR Model

Another RTD model that can closely approximate 1D continuum dispersion is that developed for continuous stirred tank reactors (CSTRs). In this case, particles are assumed to progress along the reactor in a unidirectional fashion between a series of well-mixed zones (or tanks) that act like CSTRs. It is typically assumed that each of the mixing zones (tanks) is identical, and the number of zones can vary between 1 and a very large number (all integers). The size of each zone is analogous to an effective axial mixing length, so like the ratio ***D/UL***, the resulting RTD behavior of the reactor can vary between a single well-mixed tank (where ***N***=1 which is analogous to large ***D/UL*** in the dispersion model) and plug flow (where ***N*** is very large, which is analogous to very small ***D/UL***). When the number of zones and average

total residence time (or average residence time in each zone) are specified, the RTD is analytically represented by:

$$E(t) = \left(\frac{t}{\tau_i}\right)^{N-1} \left(\frac{1}{\tau_i(N-1)!}\right) e^{-t/\tau_i} \quad \textbf{(2)}$$

In (**2**), ***E(t)*** is the probability density function for particle exit times, τ_i is the average residence time in each stage (equal to the total reactor residence time divided by the number of stages), and ***N*** is the effective number of mixing stages.

2.2.3 Van de Vusse Multi-Zone Model

An important limitation of the series CSTR model is that it cannot account for large-scale back mixing between the stages. To address this, Van de Vusse [1962] proposed a modification of the series CSTR model that accounts for both the small-scale intra-stage mixing and large-scale inter-stage circulation. The result is summarized in Equations **3a-c**. While originally developed for simulating liquid mixing processes in agitated tanks, this model has also been demonstrated to work well for describing particle RTDs in bubbling fluidized beds [Berruti et al (1988)]. The analytical RTD result for this model is represented by:

$$E(t) = \left(\frac{q}{r+q}\right)\left(\frac{r+q}{r}\right)^{\frac{N-1}{N}} \left(\frac{N}{\tau}\right) e^{-\frac{Nt}{\tau}} g(at) \quad \textbf{(3a)}$$

$$a = \frac{N}{\tau}\left(\frac{r}{r+q}\right)^{1/N} \quad \textbf{(3b)}$$

$$g(at) = \frac{1}{N}\sum_{k=0}^{N-1} \exp\left[at\left\{cos\left(\frac{2\pi k}{N}\right) + i\, sin\left(\frac{2\pi k}{N}\right)\right\} + \frac{2\pi i k}{N}\right] \quad \textbf{(3c)}$$

In the equations above, ***N*** is the number of mixing stages in each circulation loop, ***q*** is the volumetric feed rate at the inlet [L^3/T], ***r*** is the internal volumetric recirculation rate [L^3/T], and τ is the overall average residence time [T]. Upon inspection of equations **3a** and **b**, it is clear that the critical flow parameter is the ratio of ***r/q***, which represents the relative magnitude of internal circulation flow to the incoming flow. Thus there are actually only three parameters required to specify the RTD, the ratio ***r/q***, ***N***, and τ. When ***r/q***=>0, the result from equation **(3a-c)** converges toward the series CSTR limit.

2.2.4 Weibull Distribution Model

The Weibull distribution has been used extensively for describing the probability distributions of repetitive processes involving component failures and particle fragmentation [e.g., see Brown and Wohletz (1995)]. A key aspect of these previous applications is that the rate of predicted events of interest is proportional to a power of time. More recently, magnetic tracking of simulated biomass particle motion in bubbling fluidized beds has been shown to be consistent with a type of correlated random walk that can be represented with Weibull statistics [Daw and Halow (2014)]. For these experiments, the Weibull model also appeared to account for particle size and density segregation effects, which are not considered in the above models. For time-based applications, the functional form of the standard Weibull distribution can be written as

$$E(t) = \frac{K}{\theta}\left(\frac{t}{\theta}\right)^{K-1} e^{-\left(\frac{t}{\theta}\right)^{K}} \quad for\ t \geq 0 \qquad \textbf{(4)}$$

The two required parameters are $\boldsymbol{K}$ and $\boldsymbol{\theta}$, which are frequently referred to in the literature as the shape and scaling parameters, respectively. Although the physical meaning of these parameters seems less obvious for the reactor RTD context, comparisons with the series CSTR and Van de Vusse models suggests that $\boldsymbol{\theta}$ can represent a characteristic time scale for particle movement, and $\boldsymbol{K}$ can indicate mixing complexity.

A three-parameter version of the Weibull distribution has also been frequently used for cases where there is a time delay (also referred to as dead time) before any event occurs. In this case, $\boldsymbol{t}$ in the above equation is replaced by $\mathbf{t' = t - t_d}$, where $\mathbf{t_d}$ is a delay time. This is appropriate for describing particle exit times relative to when a particle first enters a reactor, since there should always be a minimum finite time involved for particles to reach the exit, even if they move in a straight line.

2.3 SIMULATING PYROLYSIS REACTOR YIELDS

Simulation of pyrolysis reactor performance (e.g., estimating the relative yields of tar, light gases, and char) requires that biomass particle RTDs be coupled to reaction kinetics. One of the most thoroughly validated low-order models for biomass pyrolysis reactors proposed so far is that by Liden et al (1988). The approach used by these investigators traces back even further to earlier studies by Yagi and Kunii (1961 b&c) for other types of fluidized bed reactors. The main assumptions used by Liden et al include the following:

- Steady-state operation so that there is no net accumulation of biomass or biomass products in the reactor;
- Except for the released pyrolysis vapors, no other gaseous reactants are present (e.g., the main gas flow is inert);
- The biomass particles are exposed to conditions that are effectively isothermal (relatively minor temperature gradients exist within the reactor);
- Biomass particle concentrations within the reactor are essentially uniform, so that is there is no significant segregation (concentration gradients) in space;
- The biomass particle residence time can be approximated by a single mean value; and
- The released pyrolysis vapors transit through the reactor in plug flow, with a mean residence time different from the biomass particles.

The original context for the Liden et al model was a bubbling fluidized bed pyrolyzer; so, it is reasonable that some revisions to the above assumptions will be needed for circulating fluidized beds. Perhaps most importantly, the Liden et al model does not consider the impact of widely distributed biomass particle residence times, which are known to be important in both bubbling and circulating beds. Nevertheless, the Liden et al approach provides a reasonable starting point that has been extensively validated with experiments using a wide range of biomass feedstocks [Scott and Piskorz (1982), Scott et al (1984), and Scott et al (1985)].

In addition to the above reactor assumptions, Liden et al proposed the following global reaction sequence to describe the kinetics:

Initial Reactions 1&3 (parallel):
Biomass => Tar (rate constant k1) **(5a)**

Biomass=> Char + Gas (rate constant k3) **(5b)**

Reaction 2 (following Reaction 1):
Tar=> Gas **(5c)**

Another important part of this scheme (which has been similarly stated with variations by other investigators) is the inclusion of a secondary reaction that results in decomposition of tar that is initially produced in the first steps of pyrolysis. This is important because it accounts for loss of potentially condensable hydrocarbon oils (tar) when the initially released vapors are retained for too long a period at high temperature in the reactor. Based on extensive reviews of experimental results both Kim (2015) and Brown (2015) note that vapor phase tar reactions can significantly affect overall yields of bio-oil, although the details of these reactions are still poorly understood. The effect of these reactions appears to be similar to reactions noted in earlier studies with coal pyrolysis, which also led to losses in liquid yield [Kathelakis et al (1990)].

When Liden et al integrate the differential mass balance for tar over the reactor with the above assumptions, they arrive at a final result for tar yield summarized by:

$$\varphi = \varphi^{*}[1 - \exp(-k_1\tau_{s)}]\frac{[1-\exp(-k_2\tau_g)]}{k_2\tau_g} \quad \textbf{(6a)}$$

where $\boldsymbol{\varphi}$ is the moisture and ash-free fractional tar yield, $\boldsymbol{\varphi^*}$ is a maximum theoretical tar yield, $\boldsymbol{k_1}$ is the global 1st-order rate constant for the initial tar production reaction [1/T], $\boldsymbol{k_2}$ is the global 1st-order rate constant for the tar decomposition reaction [1/T], $\boldsymbol{\tau_s}$ is the average biomass particle residence time (after the particle is heated) [T] and $\boldsymbol{\tau_g}$ is the average gas phase residence time [T]. Based on their experimental pyrolysis measurements, Liden et al recommend the following Arrhenius expressions for the global rate constants:

$$k_1 = 1 \times 10^{13}\exp(-\frac{183.3}{R_gT}) \quad \textbf{(1/s)} \quad \textbf{(6b)}$$

$$k_2 = 4.28 \times 10^{6}\exp(-\frac{107.5}{R_gT}) \quad \textbf{(1/s)} \quad \textbf{(6c)}$$

where $\boldsymbol{R_g}$ is the ideal gas constant (kJ/mole K) and $\boldsymbol{T}$ is the reactor temperature (K). It is clear from the above that the secondary reactions tend to reduce the initial tar yield (producing more light gas instead) the longer the gas remains in the reactor. It does not appear that Liden et al explicitly recommended expressions for the 3rd reaction rate constant that produces char and gas in the initial stage of pyrolysis. In the absence of that, an alternative approach for estimating the gas and char yields is to utilize an overall volatiles mass balance with some additional assumptions as illustrated below.

Liden et al do not directly specify an approach for estimating the gas and char yields, but it is possible to estimate the net gas yield by accounting for the gas made from tar and the difference between the ideal conversion limit (**φ***) and the proximate volatile matter:

$$\varphi_{gt} = \varphi\left(1 - \frac{[1-\exp(-k_2\tau_g)]}{k_2\tau_g}\right) \Big/ \left[\frac{[1-\exp(-k_2\tau_g)]}{k_2\tau_g}\right] \quad \textbf{(7a)}$$

$$\varphi_{gc} = (VM - \varphi^*)[1 - \exp(-k_1\tau_s)] \quad \textbf{(7b)}$$

$$\varphi_g = \varphi_{gt} + \varphi_{gc} \quad \textbf{(7c)}$$

$$\varphi_c = 1 - \varphi_g \quad \textbf{(7d)}$$

In equation **7**, φ_{gt} is the gas generated from tar, φ_{gc} is the gas generated in parallel with char, φ_g is the total gas yield, and φ_c is the char yield.

The above kinetics do not account for transport limitations (e.g., associated with intra-particle heat and mass transfer); so, we expect that additional corrections to the predicted rates are needed to deal with differences in particle size. The impacts of transport were correlated from experimental data by Di Blasi and Branca (2003) and more recently summarized in detail by Di Blasi (2008). One of the most convenient correlations arising out of this work is an expression for estimating the devolatilization time summarized in equation **8** below. Other investigators [notably de Diego et al (2003)] included additional terms (shown below) to account for the effects of moisture. According to Di Blasi and Branca (2003), the time required for a particle to reach 95% of complete devolatilization, t_v, is given by

$$t_v = Ad^n \quad \textbf{(8a)}$$

where ***n*** is an exponent reflecting the effect of particle size (typically = 1.2), and ***A*** is a prefactor given by

$$A = 0.8e^{1525/T} \quad \textbf{(8b)}$$

According to de Diego et al (2003), the effects of moisture can be estimated by multiplying the result from **8a** by the factor

$$k_M = 1 + 1.7 \times 10^{-2}M \quad \textbf{(8c)}$$

where ***M*** is the weight percent moisture. The above relationships lead to the result that the devolatilization time increases with increasing particle size and moisture, implying that the pyrolysis reactions slow with size and moisture. As we demonstrate below, these relationships provide a way to adjust the reaction rates and tar yield predicted by equations **6(a-c)** to account for size and moisture.

3. RESULTS AND DISCUSSION

Based on the background summarized above, we hypothesize that it should be possible to combine a simplified reactor modeling approach such as that proposed by Liden et al (1988) with appropriate global reaction kinetics (modified for particle size and moisture) and low-order particle RTD functions to simulate the expected trends for fast pyrolysis in both bubbling bed and circulating bed reactors. To

increase our confidence in the reliability of the RTD functions, we evaluated the ability of each function above to fit the experimental RTD results for Group B particles in both bubbling and circulating fluidized beds reported by the following investigators: Helmrich et al (1986), Berruti et al (1988), Ambler et al (1990), Smolders and Baeyens (2000), Harris et al (2003a&b), Bhusarapu et al (2004), and Andreaux et al (2008). We observed that all of the above RTD functions can give reasonably close agreement to the reported RTDs using appropriate parameter values, especially considering the significant measurement errors that were explicitly reported or implied. Of all four functions evaluated, it appeared that the Van de Vusse RTD model is the most flexible and able to handle more unusual features (e.g., the occasional appearance of a secondary probability peak). This is probably due to the fact that the Van de Vusse model accounts for both small and large mixing scales, which is likely to be important in at least some reactors where internal or external recycle are significant.

The reaction rates and conversion for each individual particle can be determined according to equations **6(a-c)** above, based on the reaction temperature and the particle's residence time in the reactor. These can also be adjusted for the effects of particle size, particle shape, and moisture using correlations such as those described in equations **8(a-c)**. As a starting point, we suggest adjusting the first reaction rate constant according to

$$k_1' = k_1 k_{Mr} \tau_{vr} / (k_M \tau_v) \qquad \textbf{(9)}$$

where $\boldsymbol{k_1'}$ is a rate constant for reaction 1, $\boldsymbol{k_{Mr}}$ and $\boldsymbol{\tau_{vr}}$ are the moisture factor and devolatilization time for reference particles used to estimate the original kinetics and $\boldsymbol{k_M}$ and $\boldsymbol{\tau_v}$ are for the specific particles under consideration (see equations **7(a-c)**). We also note here that the same basic approach for determining the global yields of tar, gas, and char for each particle can be used with different kinetics schemes as long as the reactions are first order and similar assumptions are made concerning the reactor mass balances.

Figures 1-4 illustrate how all of the factors associated with intrinsic biomass particle properties: particle size, moisture, and particle shape individually affect the moisture and ash free (MAF) yields of tar, gas, and char for a specific set of conditions. Of these factors, it appears that moisture has the least impact on yields, possibly because the effects of water reactions with gas phase species and solid carbon are not accounted for in the simplified kinetics and because the reactor energy balance (which should be significantly affected by the latent heat of water vaporization) is not included in the present reactor model. Clearly these other effects need to be included in future pyrolysis modeling efforts.

To simultaneously account for the effects of variations in intrinsic particle properties along with mixing in the reactor, we propose using linear superposition of the primary reaction conversions determined from the adjusted kinetic rates and the simplified reactor model for each particle size class and the RTD for that class. This is possible because the primary steps in all the kinetics mechanisms and the reactor differential mass balances are 1st order. Thus the composite reaction rates and conversion of each particle class and increment of the RTD for that class can be determined separately and then added to the rates and conversions of all the other classes to obtain a global result. Based on this, we sequentially apply equations **6(a-c)**, **7(a-d)**, **8(a-c)** and **9** above to each particle size class and each segment of the RTD for that class in the feed to obtain a weighted overall average tar yield:

$$\overline{\varphi} = \sum_i^{N_d} \sum_j^{N_\tau} w_j \, w_i \, \varphi'_{ij} \qquad \textbf{(10)}$$

In equation **10**, $\boldsymbol{N_d}$ is the total number of particle size classes, $\boldsymbol{N_\tau}$ is the number of time segments in the RTD, $\boldsymbol{w_j}$ is the mass of particles falling in the jth time segment of the RTD, $\boldsymbol{w_i}$ is the mass of particles in the ith size class, $\boldsymbol{\varphi'_{ij}}$ is the tar yield associated with the ith particle size class in the jth time segment of

the RTD. An example result for different RTDs (expressed in terms of the probability density functions, PDFs) is illustrated in Figure 5. It should be noted that the RTD assumed here does not include an initial period for particle heating.

One more remaining factor in pyrolysis reactor operation and design deserves attention: the gas residence time. As noted above, tar decomposition in the gas phase appears to be responsible for a significant loss of tar due to the secondary reactions. To illustrate the significance of this factor, the simulated tar, gas, and char yields for a single type of feed particle with varying gas residence times are depicted in Figure 6. It is clear from this that tar conversion to light gases can become a serious issue when gas residence times exceed just a few seconds.

The above relationships comprise the final form of the preliminary low-order model we propose for simulating biomass pyrolysis yields for both bubbling and circulating fluidized bed reactors. A computer code implementing these relationships is currently being completed and will be posted on the CPC website after thorough testing. Of course the usefulness of this model for prediction is dependent on having access to experimental data or more detailed multiphase computations that provide the information needed to fit the particle RTDs, and different kinetic rate parameters and intrinsic particle properties may be needed when different feedstocks are considered. The code being constructed will be structured to allow input of this new information. Nevertheless, we believe the present approach provides a useful structure for understanding and accounting for the dominant physical processes that control pyrolysis yield.

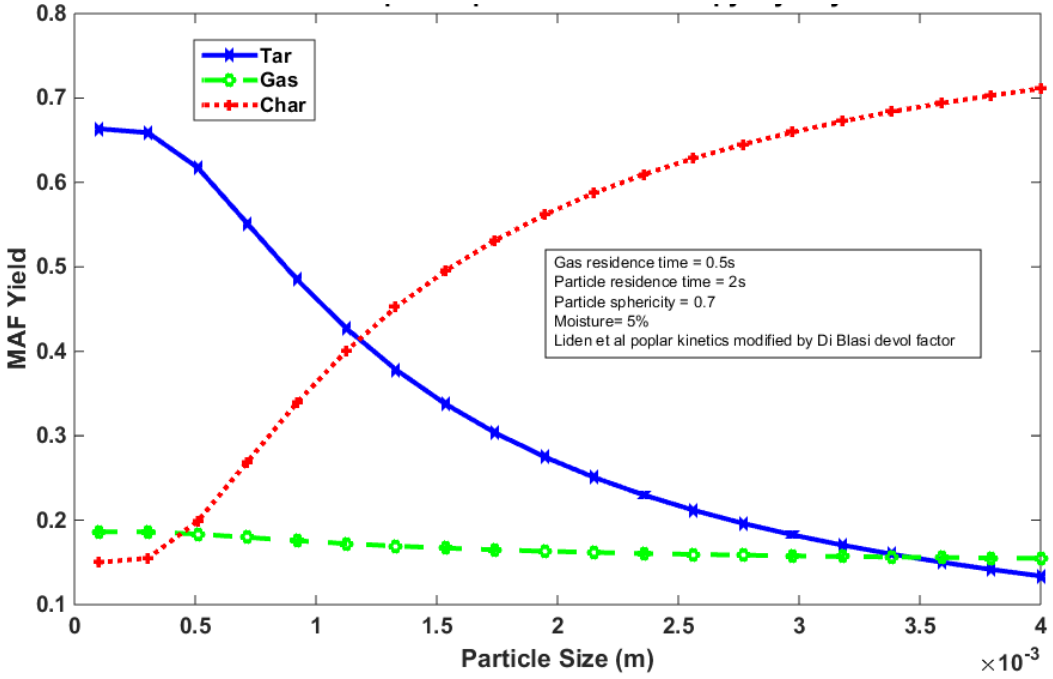

Figure 1. Example low-order simulation of feed particle size effect on yield.

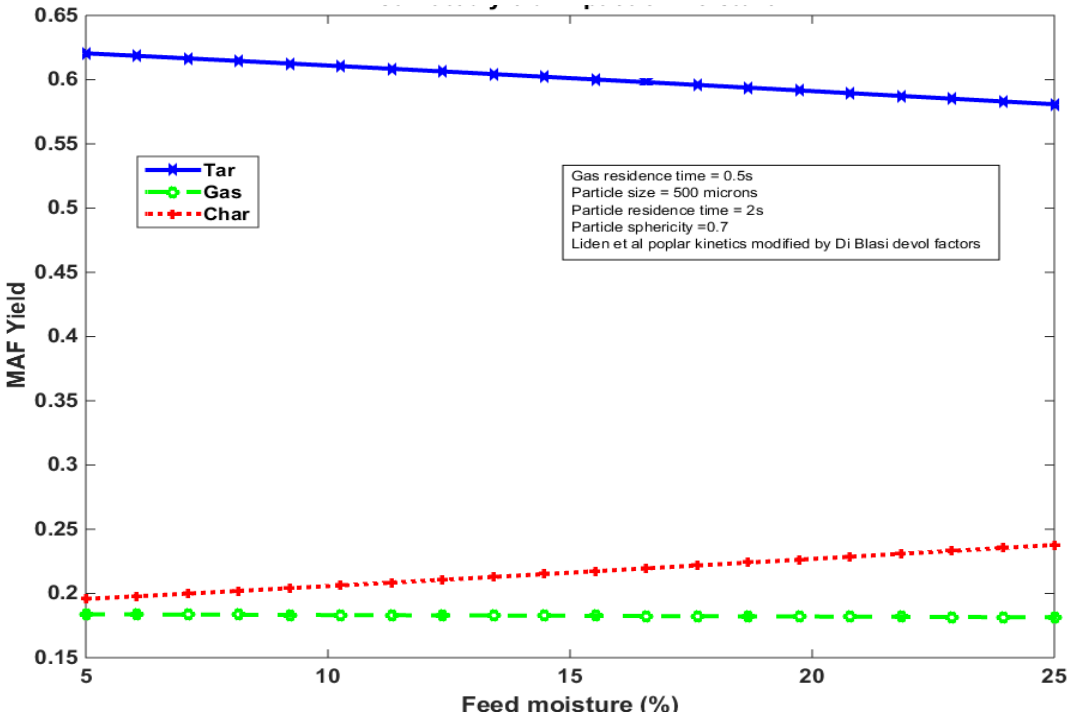

Figure 2. Example low-order simulation of moisture effect on yield.

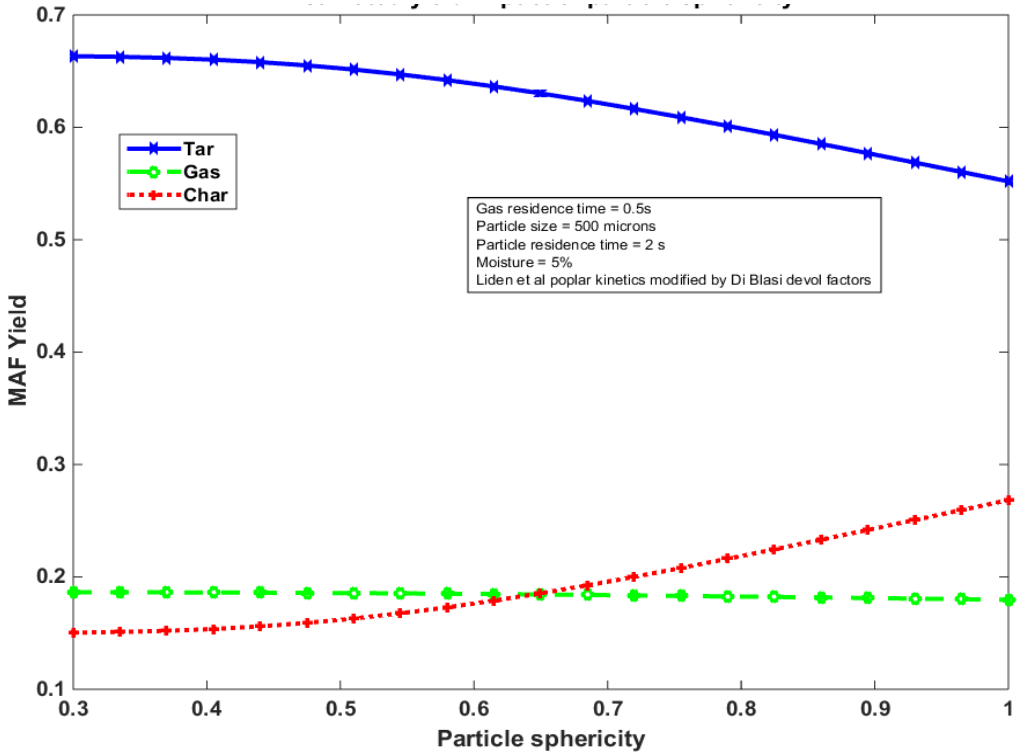

Figure 3. Example low-order simulation of particle shape impact on yield.

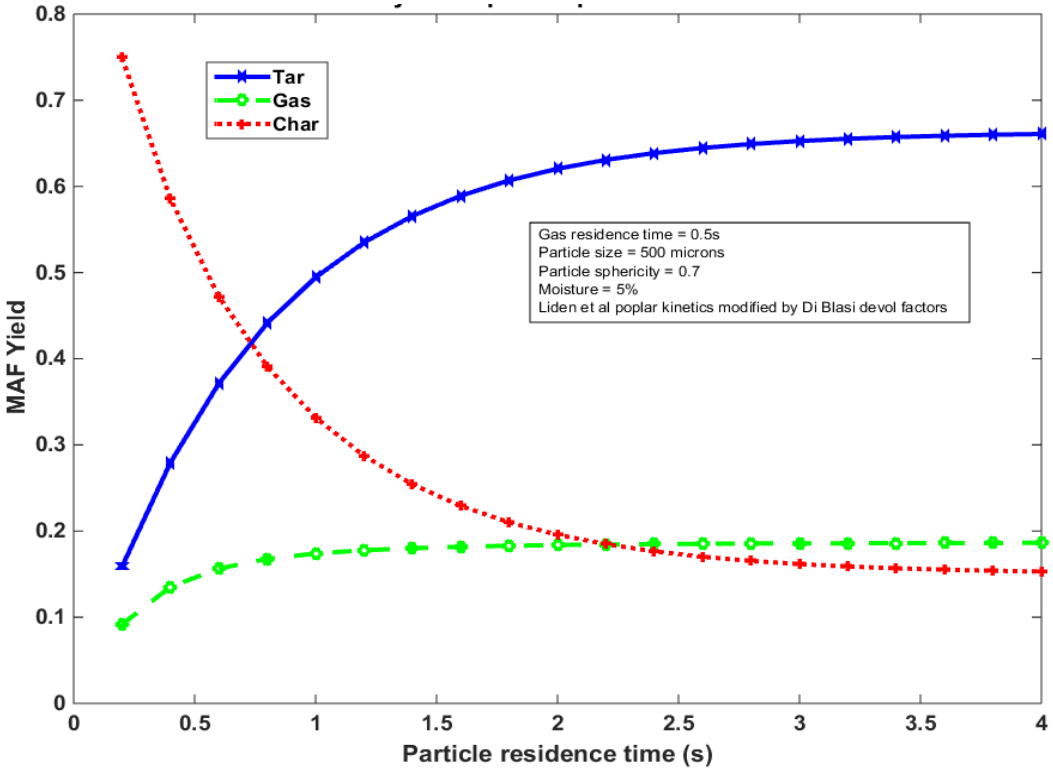

Figure 4. Example low-order simulation of particle residence time impact on yield.

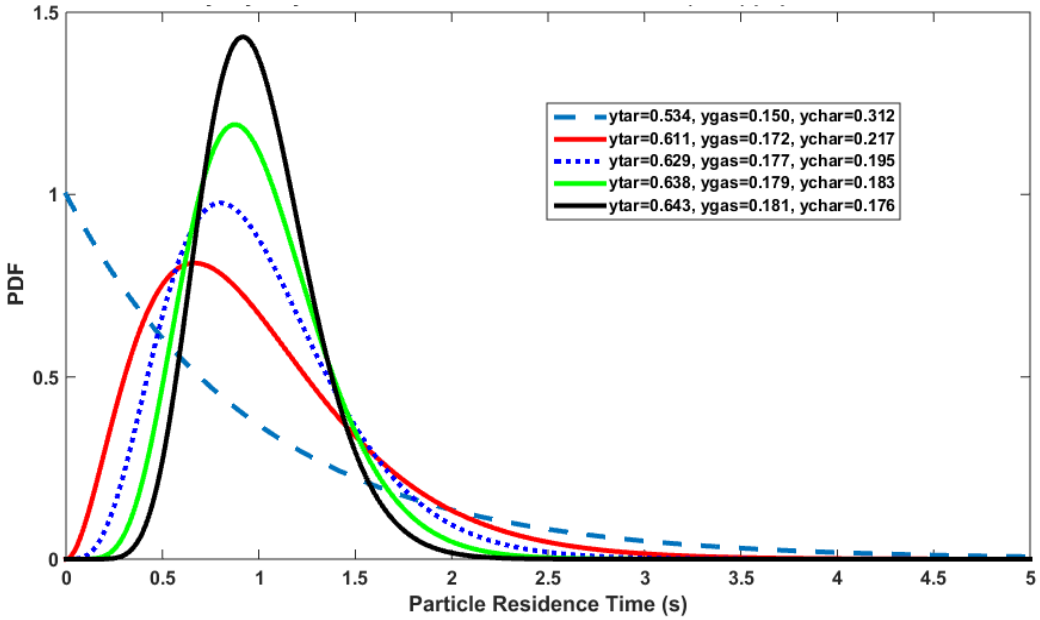

Figure 5. Pyrolysis yields predicted by the Liden et al (1988) poplar model vs. post-heat up particle RTD.

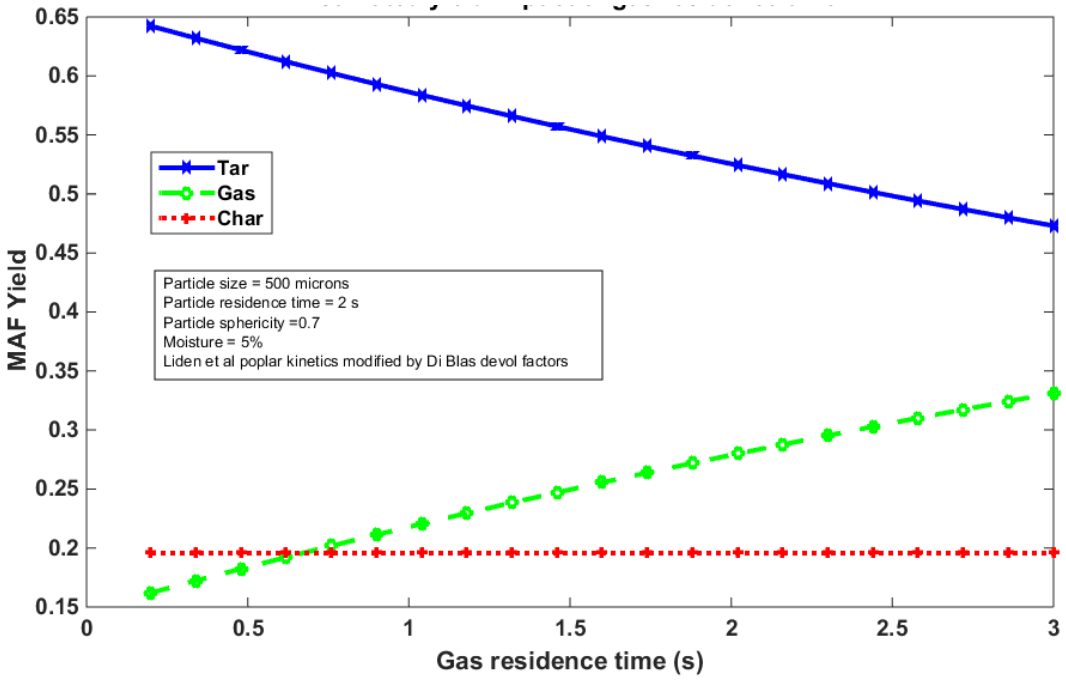

Figure 6. Pyrolysis yields predicted by the Liden et al (1988) poplar model vs. gas residence time.

4. CONCLUSIONS

Based on our review of the available literature for bubbling and circulating fluidized bed reactors, we conclude the following:

- All of the experimentally measured residence time distributions (RTDs) reported for Group B particles in both bubbling and circulating fluidized bed reactors appear to exhibit similar features that include one (or in some cases two) probability peaks, followed by extended tails that often extend several times beyond the mean residence time.

- At least four low-order RTD models have been previously proposed that appear to replicate (within measurement error) the major features of the observed particle RTDs for both bubbling and circulating beds.

- Both computational fluid dynamics simulations and additional experimental measurements will be needed to resolve which of the low-order particle RTD models is most suitable for representing biomass particle RTDs during fast pyrolysis in the reactors included in the BETO lab and pilot-scale demonstrations.

- When the low-order RTD models for biomass are linked with appropriate reaction kinetics and simplified integral reactor models, the resulting yield estimates for tar, gas, and char appear to be consistent with experimental values reported in the literature.

- The general similarities in the reported RTDs for both Group B and Group A particles suggest that it should be possible to use a similar low-order approach for modeling the impact of catalyst particle residence time on the performance of vapor phase catalytic upgrading reactors.

- The effects of the vapor phase tar reactions are likely to be most important where gas residence times are extended (e.g., where fluidization gas velocities are low, in tall bubbling or circulating beds, and in ex situ vapor phase upgrading where transfer times between the pyrolysis and catalytic upgrading reactors are more than a few seconds).

5. RECOMMENDATIONS

- At least some experimental measurements of biomass particle RTDs using tracer particles (e.g., actual biomass particles or 'fiducial' surrogate solids) should be made for experimental pyrolyzers used to generate significant amounts of lab bio-oil data or pilot-scale demonstrations. This information will be critical to making accurate estimates of the impact of scale-up on bio-oil yields.

- Experimental measurements using tracer gas should also be made to determine pyrolyzer gas RTDs.

- Additional studies are needed of the chemistry and kinetics of vapor phase tar decomposition. If possible, these need to include the effect of vapor exposure to devolatilized char and ash particles. This could prove crucial for ex situ vapor-phase upgrading.

- Selective multiphase computational fluid dynamics simulations of experimental bubbling and circulating bed pyrolyzers are needed to confirm and/or revise of the assumptions of the low-order model described above. These simulations should be closely coordinated and validated with experiments.

6. REFERENCES

Ambler, P.A., Milne, B.J., Berruti, F., and Scott, D.S., "Residence Time Distribution of Solids in a Circulating Fluidized Bed: Experimental and Modeling Studies," Chemical Engineering Science, 45, No. 8 (1990), pp. 2179-2186.

Andreaux, R., Petit, G., Hemati, M., and Simonin, O., "Hydrodynamic and solid residence time distribution in a circulating fluidized bed: Experimental and 3D computational study," Chemical Engineering and Processing, 47 (2008), pp. 463-473.

Berruti, F., Liden, A.G., and Scott D.S., "Measuring and Modelling Residence Time Distribution of Low Density Solids in a Fluidized Bed Reactor of Sand Particles," Chemical Engineering Science, 43, no. 4 (1988), pp. 739-748.

Bhusarapu, S., Al-Dahhan, M., and Dudukovic, M.P., "Quantification of solids flow in a gas-solid riser: single radioactive particle tracking," Chemical Engineering Science, 59 (2004), pp. 5381-5386.

Bridgwater, A.V., "Review of fast pyrolysis of biomass and product upgrading," Biomass and Bioebergy, 38 (2012), pp. 68-94.

Brown, R.C., "Understanding reaction pathways of Fast Pyrolysis," University of Iowa, March 2015, personal communication.

Brown, W.K. and Wohletz, K.H., "Derivation of the Weibull distribution based on physical principles and its connection to the Rosin-Rammler and lognormal distributions," Journal of Applied Physics, 78, No. 4 (1995), pp. 2758-2763.

Busciglio, A., Vella, G., Mangano, E., Micale, G., and Rizzuti, L., "Digital image analysis technique for mixing pattern measurements in bi-dispersed 2D gas fluidized beds," Chemical Engineering Transactions, 24 (2011), pp. 1423-1428.

Cui, H. and Grace, J.R., "Fluidization of biomass particles: A review of experimental multiphase flow aspects," Chemical Engineering Science, 62 (2007), pp. 45-55.

Daw, C.S. and Halow, J.S., "Random Walk Model for Biomass Particle Mixing in Bubbling Fluidized Beds," Industrial and Engineering Chemistry Research, 53 (2014), pp. 15836-15844.

De Diego, L.F., Garcia-Labiano, F., Abad, A., Gayan, P., and Adanez, A., "Effect of Moisture Content on Devolatilization Times of Pine Wood Particles in a Fluidized Bed," Energy and Fuels, 17 (2003), pp. 285-290.

De Souza-Santos, M., *Solid Fuels Combustion and Gasification*, 2nd Edition, CRC Press (2010), pp. 315-341, ISBN 978-1-4200-4749-3.

Di Blasi, C., "Modeling chemical and physical processes of wood and biomass pyrolysis," Progress in Energy and Combustion Science, 34 (2008), pp. 47-90.

Di Blasi, C. and Branca, C., "Temperatures of Wood Particles in a Hot Sand Bed Fluidized by Nitrogen," Energy and Fuels, 17 (2003), pp. 247-254.

Fogler, H.S., *Elements of Chemical Reaction Engineering*, 4th Edition, Prentice Hall (2006), pp. 867-993, ISBN 0-13-047394-4.

Geldart, D., "Types of Gas Fluidization," Powder Technology, 7 (1973), pp. 285-292.

Goldschmidt, M.J.V., Link, J.M., Mellema, S., and Kuipers, J.A.M., "Digital image analysis measurements of bed expansion and segregation dynamics in dense gas-fluidized beds," Powder Technology, 138, no. 2-3 (2003), pp. 135-159.

Halow, J.S., Holsopple, K., and Crawshaw, B., "Observed Mixing Behavior of Single Particles in a Bubbling Fluidized bed of Higher Density Particles," Industrial and Engineering Chemistry Research, 51 (2012), pp. 14566-14576.

Halow, J. and Nicoletti, P., "Observations of fluidized bed coalescence using capacitance imaging," Powder Technology, 69 (1992), pp. 255-277.

Harris, A.T., Davidson, J.F., and Thorpe, R.B., "The influence of the riser exit on the particle residence time distribution in a circulating fluidized bed riser," Chemical Engineering Science, 58 (2003b), pp. 3669-3680.

Harris, A.T., Davidson, J.F., and Thorpe, R.B., "Particle residence time distributions in circulating fluidized beds," Chemical Engineering Science, 58 (2003a), pp. 2181-2202.

Harris, A.T., Thorpe, R.B., and Davidson, J.F., "Stochastic modelling of the particle residence time distribution in circulating fluidized bed risers," Chemical Engineering Science, 57 (2002), pp. 4779-4796.

Helmrich, H., Schügerl, K., and Janssen K., "Decomposition of NaHCO3 in Laboratory and Bench-Scale Circulating Fluidized Bed Reactors," *Circulating Fluidized Bed Technology: Proceedings of the First International Conference on Circulating Fluidized Beds*, P. Basu ed., Pergamon Press (1986), pp. 161-166, ISBN 0-08-031869-X.

Kathelakis, I.E., Shi-Lin, L., Bartle, K.D., and Kandiyoti, R., "Effect of freeboard residence time on the molecular mass distributions of fluidized bed pyrolysis chars," Fuel, 69 (1990), pp. 172-176.

Kim, S.W., "Prediction of product distribution in fine biomass pyrolysis in fluidized beds based on proximate analysis," Bioresource Technology, 175 (2015), pp. 275-283.

Kunii, D. and Levenspiel, O., *Fluidization Engineering*, 2nd Edition, Butterworth-Heinemann (1991), ISBN 0-409-90233-0.

Larachi, F., Chaouki, J., Kennedy J.G., and Dudukovic, M.M., *Non-invasive Monitoring of Multiphase Flows*, Elsevier, New York (1997), ISBN 0-444-825215.

Levenspiel, O., *Chemical Reaction Engineering*, 3rd Edition, Wiley (1999), ISBN 978-0-471-25424-9.

Liden, A.G., Berruti, F., and Scott, D.S., "A Kinetic Model for the Production of Liquids from the Flash Pyrolysis of Biomass," Chemical Engineering Communications, 65 (1988), pp. 207-221.

Naor, P. and Shinnar, R., "Representation and Evaluation of Residence Time Distributions," Industrial and Engineering Chemistry Fundamentals, 2, no. 4 (1963), pp. 278-286.

Scott, D.S., Piskorz, J., and Radlein D., "Liquid Products from the Continuous Flash Pyrolysis of Biomass," Industrial and Engineering Chemistry Design and Development, 24 (1985), pp. 581-588.

Scott, D.S. and Piskorz, J., "The Continuous Flash Pyrolysis of Biomass," The Canadian Journal of Chemical Engineering, 62 (1984), pp. 404-412.

Scott, D.S. and Piskorz, J., "The Flash Pyrolysis of Aspen-Poplar Wood," The Canadian Journal of Chemical Engineering, 60 (1982), pp. 666-674.

Smolders, K. and Baeyens, J., "Overall solids movement and solids residence time distribution in a CFB-riser," Chemical Engineering Science, 55 (2000), pp. 4101-4116.

Trendewicz, A., Ziegler, J., Pannala, S., Dutta, A., Robichaud, D. J., Foust, T. D., and Braun, R.J., "Nonreactive Simulations of a Biomass Pyrolysis Riser: Development of One-Dimensional Steady-State Models Through Three-Dimensional Simulation and Experimental Comparisons," Personal Communication, September (2015).

Trendewicz, A., Braun, R., Dutta, A., and Ziegler, J., "One dimensional steady-state circulating fluidized-bed reactor model for biomass fast pyrolysis," Fuel, 133 (2014), pp. 253-262.

Van de Vusse, J.G., "A new model for the stirred tank reactor," Chemical Engineering Science, 17 (1962), pp. 507-521.

Verloop, J., de Nie, L.H., and Heertjes, P.M., "The residence time of solids in gas-fluidized beds," Powder Technology, 2 (1968), pp. 32-42.

Yagi, S. and Kunii, D., "Fluidized-solids reactors with continuous solids feed-III: Conversion in experimental fluidized-solids reactors," Chemical Engineering Science, 16 (1961c), pp. 380-391.

Yagi, S. and Kunii, D., "Fluidized-solids reactors with continuous solids feed-II: Conversion for overflow and carryover particles," Chemical Engineering Science, 16 (1961b), pp. 372-379.

Yagi, S. and Kunii, D., "Fluidized-solids reactors with continuous solids feed- I: Residence time of particles in fluidized beds," Chemical Engineering Science, 16 (1961a), pp. 364-371.