Experimental and Modeling of Biomass Char Gasification

Ruochen Wu
Brigham Young University

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Experimental and Modeling of Biomass Char Gasification

Ruochen Wu

A dissertation/thesis submitted to the faculty of
Brigham Young University
in partial fulfillment of the requirements for the degree of

Doctor of Philosophy

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Experimental and Modeling of Biomass Char Gasification

Ruochen Wu
Department of Chemical Engineering, BYU
Doctor of Philosophy

This investigation provides a comprehensive experimental dataset and kinetic model for biomass gasification, over a wide temperature range (1150-1350 °C) in CO₂, H₂O and the combination of these two reactant gases over the mole fraction ranges of 0 to 0.5 for H₂O and 0 to 0.9 for CO₂. The data come from a unique experimental facility that tracks continuous mass loss rates for poplar wood, corn stover and switchgrass over the size range of 6-12.5 mm. In addition, the data include char size, shape, surface and internal temperature and discrete measurements of porosity, total surface area, pore size distribution and composition. This investigation also includes several first-ever observations regarding char gasification that probably extend to char reactivity of all types and that are quantified in the model. These include: the effect of ash accumulation on the char surface slowing the apparent reaction rate, changes in particle size, porosity and density as functions of burnout, and reaction kinetics that account for all of these changes. Nonlinear least-squares regression produces optimized power-law model parameters that describe gasification with respect to both CO₂ and H₂O separately and in combination. A single set of parameters reasonably describes rates for all three chars. Model simulations agree with measured data at all stages of char conversion.

This investigation details how ash affects biomass char reactivity, specifically the late-stage burnout. The ash contents ratios in the raw fuels in these experiments are as high as 40:1, providing a clear indication of the ash effect on the char reactivity. The experimental results definitively indicate a decrease in char reaction rate with increasing initial fuel ash content and with increasing char burnout – most pronounced at high burnout. This investigation postulates that an increase in the fraction of the surface covered by refractory material associated with either higher initial ash contents or increased burnout decreases the surface area available for reaction and thus the observed reaction rate. A quantitative model that includes this effect predicts the observed data at any one condition within the data uncertainty and over a broad range of fuel types, particle sizes, temperatures, and reactant concentrations slightly less accurately than the experimental uncertainty.

Surface area, porosity, diameter, and density predictions from standard models do not adequately describe the experimental trends. Total surface area increases slightly with conversion, with most of the increase in the largest pores or channels/vascules not measurable by standard surface area techniques but most of the surface area is in the small pores. Porosity also increases with char conversion except for abrupt changes associated with char and ash collapse at the end of char conversion. Char particle diameters decrease during these kinetically controlled reactions, in part because the reaction is endothermic and therefore proceeds more rapidly at the comparatively warmer char surface. SEM images qualitatively confirm the quantitative measurements and imply that the biomass microstructure does not appreciably change during conversion except for the large pore diameters. Extant char porosity, diameter, surface area, and related models do not predict these trends. This investigation suggests alternative models based on these measurements.

Keywords: gasification, char reactivity, porosity, ash effect, kinetic model
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<td>Higher heating value</td>
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1 INTRODUCTION

1.1 Energy background

Interest in renewable energy arises from two sources: (1) increasing concern about global climate change and the environmental impact of fossil energy sources and (2) increasing anxiety regarding the security and longevity of fossil fuel. Approximately 14% of the world's primary energy comes from biomass [1]. However, developing countries significantly affect this number, where biomass is primarily burned to provide domestic heating and cooking. In industrialized countries, biomass provides less than 3% of the primary energy. Only about 40% of the available biofuel potential is used and only in Asia does use currently exceed the available potential [1]. This shows a great potential for increased use of biomass as a sustainable replacement for or supplement to coal. According to a proposed strategy outlined in the report by the US Department of Agriculture and Energy, biomass from forest and agricultural lands could replace up to 30 percent of the current petroleum consumption in the US by 2030 [2].

Biomass and coal are in many ways similar because they are both solid, ash-forming fuels. Raw biomass works much less well as a replacement for natural gas or petroleum. However, existing processes can convert biomass (and coal) to chemical feedstocks or transportation fuels. These processes first convert solids to gases, or gasify the solids, in a gasifier to form syngas (synthesis gas), which is a mixture of primarily CO and H₂ gases with varying amounts of CO₂ and H₂O. The syngas converts to other products in one of a variety of catalytic, pressurized
processes to produce base chemicals, transportation fuels, or finished chemicals. The gasification step in these processes represents over 75% of the capital cost and an even greater amount of the technical risk [3-6]. Gasifiers present major operational and design challenges and, even when installed, generally represent the most troublesome and inelegant portions of the process. Nevertheless, they represent the single most essential step in the most syngas operations. Coal gasification in the modern western world has a very long and storied research history and a much shorter and less successful operational record. However, regimes that have been denied (Nazi Germany and Apartheid South Africa) or have poor access to (China and India) petroleum reserves have successfully operated coal gasifiers to provide strategically substantial contributions to their country’s fuel and chemical supplies. These operating processes combine with a handful of successful government gasification demonstrations and represent the operating fleet of gasifiers today.

Biomass is unique among renewable energy in that most renewable energy sources (hydro, wind, solar, geothermal, etc.) produce electricity and can only contribute to non-electrical energy demands indirectly, whereas biomass has a viable pathway for generating transportation fuels, chemical feedstocks, and finished chemicals directly from renewable sources. However, biomass gasification presents even greater challenges than coal gasification, primarily because of fuel energy density and handling. Biomass fuels commonly exhibit 40-50% volatile yields during pyrolysis in standardized tests and up to 95% yields in practice and in this regard they make better gasification feedstock than coal. Coal, by contrast, typically has 35-45% yields in standardized tests and up to 60% pyrolysis yields in practice – substantially lower numbers than biomass. Indeed, many biomass processes call themselves gasifiers but in fact produce only pyrolysis products and char and are more accurately described as pyrolyzers. By strict definition, and the definition used
in this investigation, gasification involves the heterogeneous reaction of solid particles, typically char, with CO₂, H₂O, and possibly CH₄ to produce CO, H₂, and other gaseous products.

Efficient conversion of biomass to syngas requires char gasification and is the key to unlocking the potentially unique role biomass can play in producing renewable transportation fuels and chemicals. This document reports the results of a biomass gasification investigation using some new and much more highly resolved and accurate diagnostics than have previously been demonstrated. The investigation contributes effective and novel diagnostic techniques and new conceptual and empirical experimental results to gasification science. Much of the foundation for this work comes from coal analyses and in many places the discussion relates biomass results to those typical of coal.

Biomass can and does form transportation fuel and chemicals, but biomass also contributes to electrical power supplies as do most other renewable fuels. Therefore, there are competing demands on biomass. Global climate change concerns may lead to displacing as much coal as possible or cofiring biomass with coal, which contributes nothing to reducing dependence on oil. Energy security concerns lead to displacing petroleum by gasifying or otherwise converting biomass to transportation fuel. This has less favorable impact on climate change, but a larger impact on energy security. Finally, resource depletion concerns could lead to either use – displacing petroleum or possibly replacing natural gas, since petroleum and natural gas are more limited resources than coal. Even if one factors the effects of fracking into the analysis or using biomass in a coal boiler, the amount of useful energy derived from biomass is greater when it is burned (co-fired with coal) than when it is converted to transportation fuel or a syngas. Gasification syngas can also burn in a gas turbine to produce power, in which case it usually includes many other compounds and is called producer gas. On paper, the conversion of fuel to power can be
much higher using a combined-cycle gas turbine and steam generator. In practice, natural gas combined cycle systems can be much more efficient than coal boilers. However, coal and biomass gasification for power generation require hot gas cleanup and other steps that prevent them from significantly exceeding combustion efficiencies despite vast amounts of research and development efforts to do so. However, the results of this investigation pertain equally well to gasification for power generation as they do to other biomass gasification applications.

Table 1. Typical (average) coal and biomass analyses based on many thousands of measurements.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Typical Coal Analysis</th>
<th>Typical Biomass Analysis (dry fuel)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Anthracite</td>
<td>Bituminous</td>
</tr>
<tr>
<td>Moisture</td>
<td>2.27</td>
<td>4.46</td>
</tr>
<tr>
<td>Ash</td>
<td>14.49</td>
<td>11.12</td>
</tr>
<tr>
<td>Volatile Matter</td>
<td>7.40</td>
<td>33.00</td>
</tr>
<tr>
<td>Fixed Carbon</td>
<td>75.90</td>
<td>51.40</td>
</tr>
<tr>
<td>Sum</td>
<td>100.06</td>
<td>99.98</td>
</tr>
<tr>
<td>Carbon</td>
<td>90.22</td>
<td>78.35</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>2.85</td>
<td>5.75</td>
</tr>
<tr>
<td>Oxygen</td>
<td>5.03</td>
<td>11.89</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.93</td>
<td>1.56</td>
</tr>
<tr>
<td>Sulfur</td>
<td>0.96</td>
<td>2.43</td>
</tr>
<tr>
<td>Chlorine</td>
<td>0.03</td>
<td>0.08</td>
</tr>
<tr>
<td>Sum</td>
<td>100.02</td>
<td>100.06</td>
</tr>
<tr>
<td>HHV, dry, Btu/lb</td>
<td>14388</td>
<td>13944</td>
</tr>
</tbody>
</table>

Table 1 summarizes typical (average) fuel properties based on a database maintained in this research group that contains many thousands of measurements. The literature contains additional similar summaries [7-9]. Table 1 reveals that biomass has higher volatile content, more variable ash, lower sulfur, and higher oxygen content than coal. Nitrogen content may be higher or lower, depending on the fuel. The table also shows that biomass properties vary among fuels much more
so than coals, especially in terms of ash content. This table does not include typically ash contents, but they too vary much more among biomass fuels than among coals.

Table 2. Proximate and Ultimate analyses of the three fuels used in the experiments.

<table>
<thead>
<tr>
<th></th>
<th>Corn Stover</th>
<th>Switchgrass</th>
<th>Poplar</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Proximate Analysis (Dry)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Moisture (wt. %)</td>
<td>6.92</td>
<td>8.42</td>
<td>4.30</td>
</tr>
<tr>
<td>Volatiles (wt. %)</td>
<td>67.00</td>
<td>77.60</td>
<td>89.06</td>
</tr>
<tr>
<td>Fixed Carbon (wt. %)</td>
<td>13.00</td>
<td>18.25</td>
<td>10.39</td>
</tr>
<tr>
<td>Ash (wt. %)</td>
<td>20.00</td>
<td>4.15</td>
<td>0.55</td>
</tr>
<tr>
<td><strong>Ultimate Analysis (DAF)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon (wt. %)</td>
<td>49.33</td>
<td>49.51</td>
<td>49.19</td>
</tr>
<tr>
<td>Hydrogen (wt. %)</td>
<td>5.53</td>
<td>7.31</td>
<td>6.00</td>
</tr>
<tr>
<td>Nitrogen (wt. %)</td>
<td>0.88</td>
<td>0.52</td>
<td>0.41</td>
</tr>
<tr>
<td>Sulfur (wt. %)</td>
<td>0.08</td>
<td>0.08</td>
<td>0.00</td>
</tr>
<tr>
<td>Chlorine (wt. %)</td>
<td>0.00</td>
<td>0.00</td>
<td>0.07</td>
</tr>
<tr>
<td>Oxygen by diff. (wt. %)</td>
<td>44.18</td>
<td>42.58</td>
<td>44.33</td>
</tr>
</tbody>
</table>

* measured by GE global research for this project

Table 2 summarizes the properties of biomass fuels used in this investigation. The ash composition of the three biomass fuels appears in Table 3. All the ash components are reported as oxides (i.e., Na₂O, MgO, Al₂O₃, SiO₂, etc.) since they ultimately form oxides during combustion and during the ASTM ash test in air at 750°C [10]. They do not necessarily exist in this form in the unburned fuel. The values of ash compositions are in good agreement with the measurements in the literature [9],[11-12]. As indicated, the fuels show large variations in ash content. Some of the fuels are bulk materials (poplar) while others can form pellets from finer particles (switchgrass and corn stover). The pellets are potentially much less homogeneous and consistent than the poplar. Some of the properties in these tables of most importance to this investigation are the relative similarity of the organic portion of the fuels (C, H, O, N, and S contents) and the large differences in the amount and composition of the inorganic content (ash and ash chemistry). Specifically, the
amount of ash in the three fuels varies but a factor of about 40 whereas the organic content has comparatively little variation on a dry, ash-free (daf) basis.

Both biomass char and raw material are composed of various elements, which have a significant influence on the physical properties of char, char reactivity, char morphology and micro-pore structure, and other important properties. GE Global Research has performed the proximate and ultimate analyses of biomass as shown in Table 2, similar to the approaches to analyze the properties of coal and determine their energy value. Table 2 provides valuable information about the chemical compositions of the three biomass fuels, which are involved in determining the gasification reactivity and ash effects. Note that the dry ash content varies greatly from 0.55% for poplar to 20% for corn stover.

Table 3. Biomass ash composition.

<table>
<thead>
<tr>
<th>Element</th>
<th>Poplar (wt%)</th>
<th>Switchgrass (wt%)</th>
<th>Corn Stover (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>0.77</td>
<td>0.25</td>
<td>0.99</td>
</tr>
<tr>
<td>Mg</td>
<td>11.7</td>
<td>2.09</td>
<td>2.84</td>
</tr>
<tr>
<td>Al</td>
<td>0.70</td>
<td>0.86</td>
<td>4.36</td>
</tr>
<tr>
<td>Si</td>
<td>2.69</td>
<td>34.34</td>
<td>22.31</td>
</tr>
<tr>
<td>P</td>
<td>0.53</td>
<td>2.22</td>
<td>2.19</td>
</tr>
<tr>
<td>S</td>
<td>1.43</td>
<td>1.15</td>
<td>1.03</td>
</tr>
<tr>
<td>K</td>
<td>5.30</td>
<td>6.93</td>
<td>11.98</td>
</tr>
<tr>
<td>Ca</td>
<td>40.69</td>
<td>9.11</td>
<td>9.14</td>
</tr>
<tr>
<td>Ti</td>
<td>0.24</td>
<td>0.14</td>
<td>0.46</td>
</tr>
<tr>
<td>Fe</td>
<td>1.18</td>
<td>1.14</td>
<td>7.00</td>
</tr>
<tr>
<td>Cr</td>
<td>-</td>
<td>-</td>
<td>0.77</td>
</tr>
<tr>
<td>Mn</td>
<td>0.93</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

1.2 Comparison of the relative advantages between fossil fuel and biomass fuel

Unlike fossil fuels, biomass fuels can be renewable and CO₂-neutral in the sense that the CO₂ generated by biomass utilization recycles through the atmosphere as plants extract it back into
plant material during photosynthesis, closing the carbon cycle on a short timescale, resulting in no net accumulation of CO$_2$ in the atmosphere. The CO$_2$ neutrality of biomass depends on the biomass re-growing at the same rate it is harvested. Biomass harvested from rainforests, land clearing, beetle kill or other forest losses, tree thinning or other sources is no more CO$_2$ neutral or greenhouse gas friendly than fossil fuel if the biomass is not replanted and regrown to the same extent as it was when harvested. Biomass comes from living or recently living organisms. Although fossil fuels also ultimately come from biota, the primary difference, as it relates to greenhouse gas emissions, is one of time scale. Fossil fuels removed carbon from the atmosphere many tens or hundreds of millions of years ago, while biomass removes carbon from the atmosphere as it grows or, in the case of harvested biomass, in the comparatively recent past.

While biomass has the potential to be CO$_2$ neutral, some of the largest current biomass utilization processes fall far short of that goal. Specifically, the current use of corn to make ethanol through fermentation is by all measures far from carbon neutral and in some analyses appears to generate more CO$_2$ than fossil fuels. The major issues in this process are that it is a very small fraction of biomass that ultimately makes the ethanol – just the corn fructose – and it requires significant amounts of fossil energy to plant, fertilize, irrigate, harvest, and process the biomass [2]. There are many active research programs targeting cellulosic ethanol production, which could greatly increase the fraction of biomass used for ethanol production.

1.3 Current status of renewable energy consumption in world energy supply

In 2019, biomass energy accounts for nearly 4 % of all energy consumed in the U.S. There is a significant increase in the development of renewable energy, especially biomass energy.
1.4 Future of biomass fuel and the approaches with which to utilize biomass applications

Biomass defines a wide range of energy sources, including woods and plants, agricultural residues, byproducts from biological materials, and municipal sludge wastes [13]. This investigation uses three representative biomass fuels, woody material (poplar), agricultural residue (corn stover), and energy crops (switchgrass as an herbaceous energy crop). Although the primary utilization of biomass energy is via combustion, biomass contributes to energy supplies in both chemical and bio-chemical technologies:

1. Direct combustion to produce steam and generate electricity [14];
2. Gasification to produce syngas, which forms chemicals or fuels [15];
3. Gasification to produce gas, which may drive a high-efficiency, combined-cycle gas turbine [16];
4. Pyrolysis to obtain pyrolysis oil and chemicals [17];
5. Biological or chemical conversion to transportation fuels or chemical feedstocks [2];
6. Fermentation to produce ethanol from the sugar in biomass [18];
7. Anaerobic digestion to produce methane and CO by bacterial in the absence of O₂ [19];

Among these contributions, biomass uniquely contributes to renewable, fungible transportation energy supplies. Due to the large amount of feed-stock and faster conversion rate, gasification has drawn more attention than other technologies. Different mechanisms in the three temperature intervals, namely water evaporation (drying zone) at lower temperatures (0 – 250 °C), thermal decomposition (pyrolysis zone) of biomass to produce volatile materials at medium temperatures (200 – 550 °C) and conversion of biomass into CO and H₂ in CO₂ and/or steam environment (reduction zone) at high temperatures (> 600 °C) govern the behavior of the biomass during gasification process. This project addresses items 2-4 directly and item 1 indirectly.
1.5 Technical understanding of biomass conversion rates and mechanism

Unlike coal, biomass comminution (size reduction) presents nearly insurmountable economic and energetic barriers. Coal comminution or pulverization typically produces particles with average sizes of 40-50 µm and top sizes less than 100-120 µm. High coal friability leads to particle fragmentation under stress and produces many smaller particles. Biomass friability is very low and practical stress-based size reduction usually results in particles many millimeters in their smallest dimension and with very high aspect ratios, resulting in the longest dimensions approaching or exceeding a centimeter. Herbaceous biomass fuels also commonly contain highly abrasive inorganics that erode equipment at rates unimaginably high compared to coal systems. These large sizes and non-equant shapes lead to large temperature and composition gradients in reacting biomass particles, whereas pulverized coal particles typically react at constant temperature. One-dimensional, transient models have described these gradients with some success. However, there is clear evidence that gradients exist in more than one dimension [20].
2 LITERATURE REVIEW

The following literature review covers the following topics:

1. The effects of pyrolysis conditions on char formation or gasification;
2. Models for biomass pyrolysis;
3. BET surface area analysis for chars at different reaction time and char conversion;
4. Kinetics of pyrolysis, combustion and gasification of three biomass fuels;
5. Different types of biomass gasification processes.

2.1 Effects of CO$_2$ pyrolysis conditions on char formation or gasification

Chen et al. reported the preparation of two kinds of char from lignite [21]. In their research, they compared the two different methods, using a drop tube furnace by fast pyrolysis and using a fixed-bed furnace by slow pyrolysis at 1273 K, respectively. They used a thermogravimetric analyzer (TGA) system to gasify the chars into CO$_2$, H$_2$O and their gaseous mixtures, then developed gasification kinetic modeling. To validate the gasification rate equation derived from TGA data, they carried out a fluidized-bed gasification experiment. Both the fast-pyrolysis-char and the slow-pyrolysis-char were mainly composed of dense char [21].

The BET internal surface area of the fast-pyrolysis-char is close to that of the slow-pyrolysis-char, while the external surface area of the fast-pyrolysis-char is almost twice as large as that of slow-pyrolysis-char. After char gasification, they also investigated CO$_2$ gasification in a fluidized-
bed reactor and in an atmospheric TGA system, respectively. The researchers found that the char
gasification reaction rate for the reactants combination of CO\textsubscript{2} and H\textsubscript{2}O was lower than the sum of
the two gasification rates of the char reacting with CO\textsubscript{2} and H\textsubscript{2}O separately, but higher than the
rate of each independent reaction, for both the fast-pyrolysis-char gasification and slow-pyrolysis-
char gasification. This results in the equation below.

\[ r_{\text{mix}} < r_{\text{CO}_2} + r_{\text{H}_2\text{O}} \]  

Both of the results from the TGA system and the fluidized-bed reactor demonstrated that the
char-H\textsubscript{2}O reaction is independent on the char-CO\textsubscript{2} reaction, while the char-H\textsubscript{2}O reaction inhibits
the char-CO\textsubscript{2} reaction because of the competition between CO\textsubscript{2} and H\textsubscript{2}O molecules on the active
reacting sites.

Roberts and Harris discuss the competitive inhibition relationship between CO\textsubscript{2} and H\textsubscript{2}O in
char gasification [22]. They present data acquired from the reaction of coal chars in the mixtures
of CO\textsubscript{2} and H\textsubscript{2}O at high pressures, which shows the rate of reaction in a mixture of CO\textsubscript{2} and H\textsubscript{2}O
is not the sum of the two pure-gas reaction rates. On the contrary, it is a complex combination of
the two rates that appears to be dependent on the competition for the active reaction sites. Based
on the results, the reaction is relatively slow in C–CO\textsubscript{2} reaction, compared to the C-H\textsubscript{2}O reaction.
By applying a Langmuir–Hinshelwood (LH) mechanism assumption, the authors derived the
expression and model for the intrinsic reaction rate. This model provided the basis for a means by
which the competition between the two reactants can be introduced into char gasification models,
either from ‘first principles’ (using values of the LH rate constants) or as a technique to determine
the net reaction rate from known, measured pure-gas reaction rates.

In Watanabe et al.’s experiments[23], they investigate the effect of high CO\textsubscript{2} concentration
on the characteristics of biomass pyrolysis. They mainly use cellulose, lignin, and metal-depleted
lignin to perform their experiments. By using Fourier transform infrared (FTIR) spectroscopy, they obtained the surface area of the chars and the characterizations of the species. Because the content in the ash affected the char formation, the char formed during lignin pyrolysis in CO$_2$ had unique chemical bonds that did not appear in the lignin-derived char prepared in Ar. Also, the researchers indicated that C=O groups, which were found in the chars formed under CO$_2$, were associated with an aromatic ring, but not in those formed in Ar.

2.2 Models for biomass pyrolysis

Gina Rolea et al. have developed a sub-CFD model of the combustion and gasification process [24]. They combined relevant models and data to formulate a new model to predict the simplified volatile composition and char yields in terms of a few simple species. The volatile species considered by this model are CO, CO$_2$, H$_2$O, H$_2$, and some light and heavy hydrocarbons. The model predicts the volatiles as a function of temperature for different types of biomass.

Some researchers have proposed a model for laminar behavior of biomass combustion and compared the model with that of turbulent behavior [25]. They studied the flame stretch, reaction rate and instabilities. From their experiments and model, good agreement was obtained for the combustion flames at 1 bar; however, significant differences were observed for higher pressure cellular flames. They also correlated their model to the data using the Markstein number and Lewis number to better describe the laminar behavior in their modeling. After discussion, they concluded that at 1 bar, the flames were in the laminar zone, which meant the flame behaviors were smooth and stable, thus experimental and theoretical values of laminar burning velocity were in good agreement. At 5 bars, the flame behavior was associated with the onset of cellularity. There was no perfect mechanism for the enhancement of laminar burning velocity by cellularity in the model and the phenomenon precluded reliable determination of corresponding (stretch and instability free)
experimental data. Increased pressure resulted in substantially reduced laminar burning velocity (both theoretical and experimental).

2.3 BET surface area and intrinsic char reaction rate

Yuan et al. [26] studied three types of biomass char produced during rapid pyrolysis in a high-frequency furnace at 800-1200°C. The rapid pyrolysis char produced was isothermally gasified in CO₂ atmosphere in a TGA system. By applying several methods, including Raman spectroscopy, scanning electron microscopy (SEM), and BET surface analysis, they further studied the effects of biomass types, and temperature on intrinsic carbon structures of the pyrolysis char and on the characteristics of the gasification char. They developed a kinetic model to describe the relationship between gasification rates and reacting conditions. Their results indicate that gasification reaction rates drop with increasing pyrolysis temperature. Under some conditions, the morphologic structures produce notable effects on the gasification rates. In general, the higher complexity of morphologic structure, including micro-porosity and internal surface area, induces an increase in reaction rate. In their model, they also considered the existence of melting and shrinkage during the pyrolysis stage, which led to the disappearance of internal pores and the decrease of the specific surface area. In the meantime, they found that, in most conditions, the random pore model (RPM) worked well in predicting the gasification behavior of biomass char, except for the gasification of sawdust char at high temperatures.

Lu and Baxter performed a comprehensive investigation on the combustion behavior of the single biomass particle [20]. They developed a one-dimension model to simulate the drying, rapid pyrolysis, gasification, and char oxidation processes for biomass particles of different shapes and sizes. Some crucial factors are included in this model, such as the particle aspect ratio, volume and surface area for the different shapes (sphere, cylinder and flat plate). They also revealed that the
gradients of composition and temperature in the particles have strong influence on combustion reaction rates, that is to say, large particles react more slowly than that predicted from the isothermal models.

Tremel et al. produced char samples in an entrained flow reactor, at 1600°C and 2.5 MPa [27]. The researchers measured the conversion rate of char in a pressurized thermogravimetric analyzer (PRETA) using CO₂ and H₂O atmospheres. Based on their observations, they concluded that the initial surface area after devolatilization was dependent on pressure, and during the late stage of gasification, they found a significant decrease in the surface area, which was caused by the melting of minerals or ash. They developed the intrinsic model with the combination of surface area data and the thermogravimetric analysis data. With an n<sup>th</sup> order of LH assumption, the model can describe the temperature influence on char-CO₂ reaction rates. In this paper, they listed the activation energy for CO₂ and H₂O char reaction as 200 kJ/mol and 212 kJ/mol respectively. They also found that the activation energies are independent of char preparation conditions, and the pre-exponential factor significantly decreases for a higher heating rate treatment.

### 2.4 Thermodynamics and kinetics of biomass pyrolysis, combustion and gasification

Brown et al. [28] explored a thermo-economic assessment of a biomass gasification energy conversion and gas cleaning process with the multiple objective optimization of a flow sheet superstructure. Industrial operations always involve multiple objectives and trade-offs to maximize the profit. In this paper, the authors addressed the trade-off between total investment costs and the energy efficiency of electricity production for a plant, to determine the operating conditions in the process that minimize tar formation. The researchers adopted a stoichiometric equilibrium model to describe the concentrations of gas, tar, and char, which was comprised of temperature dependent parameters regressions. Assuming that the temperature dependent
parameters are independent of pressure, the equilibrium modeling indicates that tar concentration will increase, and char concentration decrease with increasing pressure.

Senneca [29] compared the micro-structural properties and the intrinsic reactivity among three types of biomass, pine seed shells, olive husk and wood chips, upon pyrolysis, combustion and gasification (with CO₂ and H₂O). Listed in Table 4, the three types of biomass are quite different in terms of O and C contents, and O/C and H/C ratios, of porosimetry structure and of ash content [29]. Based on the morphological characterization and porosimetric characterization of chars, the authors developed a kinetic model to analyze the data and explore the relationship between pyrolysis rate and pore size, pore distribution and temperature. She concluded that olive husk is the most reactive material upon pyrolysis, char combustion and char gasification as well, followed by wood chips and pine seed shells. From their point of view, the microstructural and chemical properties of the biomass material could have a tentative relationship with the biomass reactivity.

<table>
<thead>
<tr>
<th>Table 4. Properties of biomass fuels tested [29].</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
</tr>
<tr>
<td>-----------------------------</td>
</tr>
<tr>
<td>Particle density (g/cm³)</td>
</tr>
<tr>
<td>Particle sphericity</td>
</tr>
<tr>
<td>Char density (g/cm³)</td>
</tr>
<tr>
<td>Char porosity</td>
</tr>
<tr>
<td>LHV (kJ/kg)</td>
</tr>
<tr>
<td><strong>Proximate analysis (wt %)</strong></td>
</tr>
<tr>
<td>moisture</td>
</tr>
<tr>
<td>volatiles</td>
</tr>
<tr>
<td>fixed carbon</td>
</tr>
<tr>
<td>ash</td>
</tr>
</tbody>
</table>
Table 4 continued

<table>
<thead>
<tr>
<th></th>
<th>Pine seed shells</th>
<th>Wood chips</th>
<th>Exhausted olive husk</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Ultimate analysis (dry basis, wt %)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>carbon</td>
<td>48.5</td>
<td>47.3</td>
<td>51.8</td>
</tr>
<tr>
<td>hydrogen</td>
<td>6.1</td>
<td>6.1</td>
<td>5.5</td>
</tr>
<tr>
<td>nitrogen</td>
<td>0.2</td>
<td>0.2</td>
<td>1.2</td>
</tr>
<tr>
<td>sulfur</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>ash</td>
<td>0.9</td>
<td>0.4</td>
<td>5.1</td>
</tr>
<tr>
<td>oxygen (diff)</td>
<td>44.3</td>
<td>46</td>
<td>36.3</td>
</tr>
<tr>
<td><strong>Ash composition (wt %)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaO</td>
<td>39.8</td>
<td>15.3</td>
<td>22.3</td>
</tr>
<tr>
<td>MgO</td>
<td>25.7</td>
<td>3.4</td>
<td>1.8</td>
</tr>
<tr>
<td>K₂O</td>
<td>17.4</td>
<td>12.8</td>
<td>25.6</td>
</tr>
<tr>
<td>Na₂O</td>
<td>7.6</td>
<td>1.9</td>
<td>1.7</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>1.3</td>
<td>3.5</td>
<td>2.8</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>1.5</td>
<td>9.1</td>
<td>6.2</td>
</tr>
<tr>
<td>SiO₂</td>
<td>&lt; 0.03</td>
<td>45</td>
<td>34.8</td>
</tr>
</tbody>
</table>

The analysis of Table 4 [29] indicates that the olive husk has the greatest amount of potassium oxide, which could be the key to the extremely high reactivity of olive husk. At the same time, the author points out that the porous texture of the chars also contributes to their combustion/gasification reactivity. This factor might be a key to explain the patterns of reactivity along with the conversion.

2.5 Different types of biomass gasification processes

Kislov et al. [30] demonstrated that some types of biomass, including those that are difficult to convert by some normal methods, can be efficiently thermal-processed under conditions of super-adiabatic filtration combustion. This finding could significantly lower the cost imposed on
the starting material and provides an opportunity to process this material after minimum preparation.

Song et al. [31] discussed the experimental investigation of hydrogen production from biomass gasification in interconnected fluidized beds. Their results indicated that both a high hydrogen yield and hydrogen content could be obtained from the novel inter-connected fluidized beds. With increasing gasifier temperature, H₂ yield decreased, and CO yield increased. The steam/biomass ratio has a weak effect on the syngas composition. The researchers even showed the optimal solution to maximize hydrogen yield.

Blander [32] put forward a method to avoid fouling and corrosion during combustion, by adopting biomass gasification. He pointed out that biomass gasification at 600-800 °C could produce an effluent gas in a combustor for power production, after removal of the solid products of gasification by hot gas cleanup. This could help eliminate fouling and corrosion. Due to the relatively low temperature, the condensed products for biomass were all solids. According to the author, with well mixed additions, the problem of fouling and corrosion no longer exists.

Dasappa et al. [33] investigated some industrial applications for biomass gasification, the low temperature application and high temperature application. Then they used some balance equations, e.g., energy balances, to analyze the data and get the optimal operating conditions considering many different situations. The system used one gasifier to energize 16 burners in 8 furnaces with different temperature requirements. The modified system has a great advantage for bioenergy and leads to significant economic and environmental benefits.

Xiao et al. [34] showed the design, construction and operation of an Internally Circulating Fluidized-bed Gasifier (ICFG) in detail. This reactor provides a multi-stage gasification process, with bed material acting as the medium for char combustion and heat exchange by its internal
circulation. From the results, the authors discussed the effects of pressure balance, pyrolysis temperature, catalytic temperature and steam/feedstock ratio on the gasifier performance (e.g. product gas yield, gas composition, and tar content). They believed that pressure balance was necessary to ensure the separation of the flue gas and the product gas, which they demonstrated by adjusting the air/steam ratio and the control valve for product gas to realize the optimization. Temperature and steam ratio also had an important role on the gasification process.

2.6 Proposed areas of further research

Generally, biomass char gasification remains highly uncertain compared to coal. Inconsistent results with respect to ash content, biomass type, and reactant appear in the relatively scant experimental data in the field. All existing data come from sampled particles in reacting flows, which lead to discrete data points inherently based on different particle samples. That is, no experiment follows the conversion of the same particles in time. Given the potential very large particle-to-particle variation in biomass properties coupled with inherent experimental error, this leads to great uncertainty in the results. Furthermore, this research group has established the inadequacy of coal-like particle models to describe biomass combustion [20]. Such models nearly universally assume isothermal, spherical particles. It is likely that such models will also be inadequate to describe biomass gasification reactivity. The first and most critical need is for a comprehensive database of reactivity collected under well-characterized and broad range of conditions. This project proposes a technique that can track individual particle behavior with time and can record particle surface temperature, internal (center) temperature, size, shape, and mass as continuous functions of time with discrete measurements of particle total surface area.

The correlation between char conversion and internal surface area may be crucial in developing the kinetic model of biomass char gasification with either in CO\textsubscript{2} or in H\textsubscript{2}O. Unlike
oxidation rates, that usually occur at or near external diffusion limited rates in practice, gasification kinetic rates are slow, and particles commonly react at or near kinetic rates. The internal surface area of the char affects the gas molecules adsorption rates and reaction rates. Surface changes with the extent of reaction but the techniques indicated here cannot track it continuously. The experiments will include surface area measurements at discrete times. This project will also develop biomass reactivity models that describe as much of the measured variation in behavior as possible. These models will include both global and intrinsic reactivity models and will explore different reaction mechanisms. One outcome of this analysis is the extent that the data clearly distinguish different mechanisms or intrinsic vs global reaction rates.
3 OBJECTIVE AND APPROACH

3.1 Objective

The objective of this research is to collect new and highly accurate experimental data on single biomass particles throughout their lifetimes and to describe the gasification reaction rates and mechanism as a function of time for arbitrary shapes and sizes of particles in an approachable computer model. The data include particle internal temperature, surface temperature, shape, size, mass, porosity, and geometrical surface area measured as continuous functions of time and particle total surface area, external surface area, pore size distributions, and morphology at discrete but often highly resolved points in time. This dataset provides details of particle behavior that separately measure particle-to-particle property variations and experimental error by tracking an individual particle in time. Furthermore, the data will include measured temperature gradient and particle size and type effects. This eliminates many sources of error compared to earlier experiments and may provide data sufficient to distinguish different reaction mechanisms. The data provide definitive indications of mass-transfer vs. kinetic limitations and reaction mechanisms. Aside from the data, this project will produce a more sophisticated model than those typically used in large computer simulations, but the intent is to develop a model with sufficient computational efficiency that the model could support such codes in addition to experimental analysis and stand-alone applications.
The experiments include data on three types of biomass particles: wood, switchgrass (an herbaceous energy crop), and corn stover (an herbaceous agricultural residue).

3.2 Approach

The experimental technique uses several first-of-a-kind technologies developed at BYU. This project will improve on these techniques in the following ways:

1. Operate with different gases over wider flow rate ranges.
2. Improve the model for the biomass kinetic gasification mechanisms.
3. Use mass spectrometry to analyze the product gases, especially during the pyrolysis stage.
4. Improve the previous code to better fit experimental data, which works for deriving the diameter ratio and volume plot of the particles.
5. Measure BET surface area for chars at different reaction time and different char conversion. Explore the relationship between BET surface area, and reaction rate and char conversion.

This project is divided into these five tasks:

1. Particle mass loss measurements: The facility in this investigation measures continuous pyrolysis and gasification mass loss data for poplar wood, corn stover and switchgrass over the size range of 6-12.5 mm, over a wide temperature range (1150-1350 °C) in CO₂, H₂O and the combination of these two reactant gases over the mole fraction ranges of 0 to 0.5 for H₂O and 0 to 0.9 for CO₂.
2. Particle temperature measurements: The particle mounting system, including the thermocouples and the data logger measures the surface temperature and center temperature of the particle. The RGB cameras additionally provide images for pixel-by-pixel measurements of the particle surface temperature during the reaction.
3. **Particle surface area and pore size distribution measurements:** The biomass chars will stay in N\textsubscript{2} environment surrounded by cooling jacket so that BET surface area analyzer (TriStar 3000) is able to analyze the surface area and pore size information of biomass chars extracted at successive residence times. A Micromeritics Tristar 3000 surface area and pore size distribution analyzer provides data from the char samples, generally using N\textsubscript{2} adsorption at 77 K. The Brunauer-Emmett-Teller (BET) method and Barrett-Joyner-Halenda (BJH) model determine specific surface area and pore size distribution, respectively.

4. **Particle size, shape, diameter and porosity measurements:** Three CCD cameras record particle images from three orthogonal directions. These images provide continuous particle shape and size changes, and diameter variations. The 3-D particle shape, combined with the surface temperature distribution data, provides spatially and temporally resolved 3-D particle data. Porosity can be calculated since the mass, density and volume of the char are accessible in the experimental measurements.

5. **Pyrolysis gas analysis:** A GC-MS (Gas Chromatography – Mass Spectrometry) system samples a portion of particle off gases from immediately above the reacting particle while the remaining gases are vented to the laboratory exhaust system. Then the GC-MS analyzes the components and composition of pyrolysis gases as a function of residence time.

The following discussion outlines the experimental and theoretical techniques used in this approach.
4 EXPERIMENTAL METHODS AND APPARATUS

Devolatilization and gasification experiments were conducted in a single-particle reactor for biomass particles of different types, sizes and shapes. Measurements of particle mass loss, surface and internal temperature, particle size change, pyrolysis product gases and internal surface area were performed, as described below in data collection parts.

4.1 Raw materials preparation

This investigation processed three types of biomass fuels: poplar wood (ligneous), corn stover (herbaceous agricultural residue) and switchgrass (herbaceous energy crop). The experiments focus on particles of various sizes but with initially cylindrical shapes with aspect ratios (AR = length/diameter) of 1. The poplar samples were bulk wood cut into these shapes while the switchgrass and corn stover were pellets formed from milled material. The following sections will cover the preparation procedures of these three biomass samples respectively.

4.1.1 Wood dowel particles

Three typical shapes of poplar wood particles, cylinder, disc, and near-sphere, were obtained by cutting poplar dowel rod to different AR. Particle sizes are ranging from 3 mm to 12 mm. AR is near 1.0 for spheres, 0.2 to 0.125 for discs, and 5.0 to 8.0 for cylinders. Figure 1 illustrates the poplar particles with different sizes and shapes. A wire gauge #80 drill bit is utilized to drill two
holes on the particle, one on the surface and the other is on the center, to allow thermocouple wires to get through the particle and measure the temperature distribution on both surface and internal of the particle.

Figure 1. Different sizes and shapes of poplar wood particles.

4.1.2 Corn stover particles

Figure 2. Corn stover pellets and raw materials.
For corn stover particles, only cylinder shape is applied because the corn stover samples were compressed into pellets from raw materials and they all have the same length and diameter. The two thermocouple wires were placed into the pellets before they were compressed. Figure 2 illustrates the corn stover raw materials and particles with cylindrical shape (3/8 inch in diameter with different lengths).

4.1.3 Switchgrass particles

Similar with corn stover samples, switchgrass samples were compressed into pellets from raw materials. Figure 3 illustrates the corn stover raw materials and particles with uniform shape (cylinder) and size (3/8 inch both in length and diameter). Figure 3 illustrates the corn stover raw materials and particles with uniform shape (cylinder) and size (3/8 inch both in length and diameter).

Figure 3. Switchgrass pellets and raw materials.
4.2 Single particle reactor

Figure 4: Schematic diagram of the single-particle reactor where the gas feed streams represent some combination of separately metered \( \text{N}_2, \text{Ar}, \text{CO}_2, \text{H}_2\text{O}, \) and \( \text{H}_2 \) [15].

A single-particle reactor produced all the samples and most of the data for this investigation. This reactor and its associated experimental techniques include several unique and innovative approaches for determining particle reactivity. Specifically, particle reactivity depends critically on particle temperature, size, and shape and this facility provides means of measuring these properties, together with mass, as continuous functions of time. The experimental portion of this discussion provides significant detail in the temperature and shape reconstruction algorithms that are unique to this system. In this work, the single-particle reactor with the same optical access features as the entrained-flow reactor, designed and built by Ip [35] and modified by Lu [15],[20],[36-37], provided biomass particle devolatilization and gasification data. More detailed
descriptions of this facility are in these references. The essential characteristics and major changes made for this investigation are illustrated in Figure 4.

The single-particle reactor suspends a single particle from a thermocouple that is in turn placed on a precision balance. The balance records the particle mass as a function of time while the thermocouple provides particle center temperature information. The particle is contained in an atmospheric-pressure reaction chamber or furnace. This investigation went to considerable effort in rebuilding this chamber and the associated equipment to eliminate oxygen from the reaction chamber. Previous investigations centered around char oxidation, where this was less of an issue.

The chamber is ventilated with an arbitrary gas environment that includes CO₂, H₂O, mixtures of the two, with the balance usually N₂ or He. Helium eliminates the ambiguity between CO and N₂ in the mass-spectrometer-based off gas and reactor gas sampling system (not shown). These gases pass through an electrical preheater and a radiation chamber at the bottom of the reactor, both of which allow temperature control. The radiation chamber is optically isolated from the particle (not shown) such that the particle has no direct or even single reflection exposure to the radiating sources. This is important to the optical temperature measurements.

Three orthogonally arranged CCD video cameras (only one is shown in Figure 4) record particle images through three mutually orthogonal view ports. The figure shows all three of these view ports in the same plane while the reactor has one of them rotated 90 degrees from the other two. These cameras record particle profiles orthogonal to the lines of sight of each camera. These cameras provide data from which algorithms reconstruct the particle shape and surface temperature, as typified in Figure 5 below. The RGB cameras form an innovative analysis system that provides both pixel-by-pixel surface temperatures and that reconstructs the three-dimensional particle shape [36]. The temperature measurement is based on the spectral response of the RGB cameras. Figure
5 illustrates that the temperature difference on the particle surface could be as much as 500 K, and the temperature differences decrease with decreasing size. The radial temperature gradients are larger than spatial temperature gradients on the biomass particle surface. The image data in Figure 5 suggests that reconstructing the 3-D particle shape, paired with the size evolution, is feasible. The 3-D particle shape combined with the surface temperature distribution data provides spatially and temporally resolved 3-D particle data.

![Image of particle surfaces and temperature distributions](image)

**Figure 5.** Poplar char particle surface temperature and shape reconstruction (in SPR), Air, AR = 1, MC = 6% (wt), T_w=1273 K, T_g=1050 K [15],[20].

### 4.3 Reacting conditions and data collection

Three types of biomass with widely varying properties (herbaceous and woody material, ash content, pellets vs. bulk materials, etc.) were gasified over a wide range of particle characteristics. Experimental variables include particle size (6 to 12.5 mm), reaction temperature (1150 - 1350 °C),
reactant gas composition (CO₂ from 0-90% and steam from 0-50%) and extent of particle and char burnout (0-100% daf) (Table 5). The steam and CO₂ contents ranged as indicated, both individually and over smaller ranges (up to 50:50) jointly. The particle surface temperature was about 200 Kelvin cooler than the gas temperature due to radiation losses to the comparatively cool reactor walls and the endothermic gasification reactions. Table 2 provides the properties of the biomass fuels used in this investigation.

<table>
<thead>
<tr>
<th>fuel material</th>
<th>poplar, corn stover, switchgrass</th>
</tr>
</thead>
<tbody>
<tr>
<td>particle initial size</td>
<td>¼ inch, ¾ inch, ½ inch</td>
</tr>
<tr>
<td>temperature range</td>
<td>1150-1350 °C</td>
</tr>
<tr>
<td>gas composition</td>
<td>0-90% CO₂, 0-50% H₂O, 0-50% CO₂&amp;H₂O</td>
</tr>
</tbody>
</table>

This system provides essentially continuous measurements of particle mass, size, shape, center and surface temperature, and off-gas composition with further information on porosity, surface area, and pore size distribution based on quenched particle samples. Calibrations of all these measurements provide some protection from systematic and periodic errors. GC-MS collects data continuously during the reaction. The x-axis of a mass spectrum represents the relationship between the mass of a given ion and the number of elementary charges that it carries. And the y-axis of a mass spectrum is an intensity. In GC-MS output files, each component that came out from the reactor has formed a peak at where their mass-to-charge m/z ratio falls. By referring to the GC-MS library, the components of the gases at each time point can be detected.
5 DEVELOPMENT OF SINGLE PARTICLE MODEL

5.1 Technical understanding of biomass conversion rates and mechanism

Unlike coal, pulverizing biomass presents nearly insurmountable economic and energetic barriers. Biomass size reduction usually results in particles many millimeters in their smallest dimension and with aspect ratios of 5-20, resulting in the longest dimensions approaching or exceeding a centimeter. These sizes and shapes lead to large temperature and composition gradients in reacting particles. One-dimensional, transient models have described these gradients with some success. However, there is clear evidence that gradients exist in more than one dimension [20].

Biomass char involves a series of reactions, with potentially complicated mechanisms. A substantial literature describes coal-char reaction mechanisms, and research shows that biomass and coal share great similarity. Most reactions and their reaction rate expressions appear in Table 6, including both heterogeneous (char) and homogeneous (pyrolysis) reactions. The char gasification reaction in the table use power-law expressions for the reactant concentrations. Biomass char gasification may also proceed through Eley Rideal or Langmuir-Hinshelwood mechanisms, as discussed shortly.

some extreme reacting conditions, such as high concentrations of reactant gases (CO₂ and H₂O).
Kajitani et al. studied two kinetic models in entrained flow gasifier, i.e. nth order power-law model and Langmuir-Hinshelwood (L-H) model [45]. The two kinetic models were applied in the gasification reactions with CO₂.
Results show that both nth order and L-H equations predicted the measured data adequately under low partial pressure of reactant gas CO₂. And under high partial pressure of CO₂, L-H model is in better agreement with the experimental data, while the nth order model is twice as more than the measured rate. Thus, it is essential to introduce some sophisticated model, not just simplified power-law model, into some extreme reacting conditions, such as high concentrations of reactant gases (CO₂ and H₂O).

In Table 6, $z_i$ is the volume fraction of component $i$ in the condensed phase where is given by

$$z_i = \frac{1}{\rho_i} \frac{1}{\sum_{i, \text{condensed phase}} \frac{1}{\rho_i}}$$

(2)

and $k_i$ is the reaction rate constant in Arrhenius equation

$$k_i = A_i e^{E_i/RT}$$

(3)

<table>
<thead>
<tr>
<th>Reaction index</th>
<th>$A$ (1/s)</th>
<th>$E$ (kJ/mol)</th>
<th>Reference</th>
<th>Temperature (K)</th>
<th>$\Delta H$ (kJ/kg)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
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<td>[46]</td>
<td>733-878</td>
<td>418</td>
<td>[38]</td>
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<td>[47]</td>
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<td>[46]</td>
<td>733-878</td>
<td>418</td>
<td>[38]</td>
</tr>
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<td>149</td>
<td>[47]</td>
<td>573-873</td>
<td></td>
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<td>$E$ (kJ/mol)</td>
<td>Temperature (K)</td>
<td>Reference</td>
<td>$\Delta H$ (kJ/kg)</td>
<td>Reference</td>
</tr>
<tr>
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<td>-----------------</td>
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</tr>
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<td>[46]</td>
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<td>[48]</td>
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<td>-</td>
<td>[49]</td>
<td>42</td>
<td>[39]</td>
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<td>9</td>
<td>$0.0131 \text{ (m/s K atm)}$</td>
<td>142</td>
<td>-</td>
<td>This investigation</td>
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<td>This investigation</td>
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<tr>
<td>10</td>
<td>$9.57 \times 10^{-5} \text{ (m/s K atm)}$</td>
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<td>-</td>
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<td>11</td>
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<td>[43]</td>
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<td>[50]</td>
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<td>-</td>
<td>[44]</td>
<td>41,600</td>
<td>[40]</td>
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</table>

Table 8. Kinetic parameters for global kinetics gas and particle reaction rate expressions.

<table>
<thead>
<tr>
<th>Reaction index</th>
<th>$A$ (kg char/s m² Pa)</th>
<th>$E$ (kJ/mol)</th>
<th>Temperature range (K)</th>
<th>$\Delta H$ (kJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>$1.31 \times 10^{-5}$</td>
<td>63.21</td>
<td>700-1200</td>
<td>14,370</td>
</tr>
<tr>
<td>10</td>
<td>$1.94 \times 10^{-6}$</td>
<td>38.36</td>
<td>700-1200</td>
<td>10,940</td>
</tr>
</tbody>
</table>
Some published versions of Eley-Rideal and Langmuir-Hinshelwood reaction rates expressions include the following [45],[51]:

\[ r_9 = \frac{k_1 p_{CO_2} + k_4 p_{CO_2}^2}{1 + k_2 p_{CO_2} + k_3 p_{CO}} \]  
\[ r_9 = \frac{C_1 k_1 p_{CO_2}}{1 + k_2/k_3 p_{CO} + k_1/k_3 p_{CO_2}} \]  
\[ r_{10} = \frac{k_5 p_{H_2}O + k_8 p_{H_2}p_{H_2}O + k_9 p_{H_2}O^2}{1 + k_2 p_{H_2}O + k_3 p_{H_2}} \]

For the external-surface-area simplified models (reaction 9 and 10), the reactions kinetic rate coefficients appear in Table 8.

![Figure 6. Traditional example of reaction zones during char oxidation [44].](image)

Lin and Strand explored CO\(_2\) reactivity for eight biomass char samples, prepared from raw wood, miscanthus, and straw under various pyrolysis conditions by thermogravimetric analysis (TGA) [52]. Data included gasification rates at temperatures from 800 °C to 1300 °C. Similar
reactivity behavior was observed for all char samples in the low-temperature range (from 800 °C to 1000 °C), and an improved aerosol-based method characterized the significant differences among the eight char samples at high temperature (from 1000 °C to 1300 °C). Due to the combination of the TGA and improved aerosol-based methods, the intrinsic kinetics were established over a broad temperature range (from 800 °C to 1300 °C) for all char samples, and activation energies were determined: 216-251 kJ/mol for wood char, 177-197 kJ/mol for miscanthus char, and 159-170 kJ/mol for straw chars [52].

![Graph](image_url)

**Figure 7. Influence of the reaction temperature (inverse) on the char conversion rate (logarithmic) within a porous char particle.**

Combustion investigators commonly use the relationship between char gasification and mass transport to define three reaction zones or regimes (Figure 6) [44]. Zone 1 involves kinetically limited reactions with no transport effect on the observed rate and typically occurs at low temperatures, with small particles, or with very slow kinetic rates. In this zone, chemical kinetics control the observed reaction or mass loss rate and the data are most useful for determining kinetic coefficients. Zone 3 involves transport-limited reactions with no kinetic effect on the observed rate.
and typically occurs at high temperatures, with large particles, or with rapid kinetics. In zone 3, the chemical reaction proceeds so rapidly that it reduces the surface concentration of the reactant to near zero, creating the largest possible transport driving force and data that are insensitive to the kinetic rate parameters. Zone 2 exhibits reaction rates with both kinetic and transport effects and lies between the two zones discussed above. However, there are no sharp transitions between each zone and zones 1 and 3 are really limiting behaviors or asymptotic limits with a smooth transition zone between them as indicated by Figure 7.

Tremel and Spliethoof studied char of a lignite coal at three different regimes [53]. The observed char activation energy was 239 kJ/mol in zone 1 and 62 kJ/mol in zone 3. This large decrease in apparent activation energy as combustion approaches zone 3 typifies particle combustion behavior since transport rate temperature dependence is weaker than that of chemical kinetics. Hodge et al. [54] investigated three coal samples at 0.5 MPa partial pressure of CO$_2$ at a total pressure of 2.0 MPa. Zone 1 conditions produced similar activation energies of 242 kJ/mol, 278 kJ/mol and 281 kJ/mol respectively. However, Zone 2, produced large differences in activation energies: 78 kJ/mol, 153 kJ/mol, and 156 kJ/mol, respectively.

5.2 Surface area vs. reaction rate

Unlike oxidation rates, which usually occur at or near external diffusion controlled rates in practice [20], gasification kinetic rates are slow and kinetics commonly influence particles reaction rates. The reactions occur on and near the char particle internal and external surface. Biomass char specific surface areas and particle sizes exceed those of similar fuels, such as coal and black liquor, by large margins, which makes internal surface reactions more significant for biomass chars than most other chars. Several instructive investigations have been performed that shed light on the relationship between gasification reaction kinetics and the characteristics of char morphology,
including the active surface area, particle shape and size, and pore size distribution [26-27],[53],[55-63]. Xu et al. [55] studied coal and biomass blend chars and concluded that the exposed surface area of char determined the intrinsic reaction rate. Bruun [59] related the surface area of biomass char to the capacity to absorb the reactant gas molecules, and Tremel et al. [58] developed a model to describe the loss of active sites on the surface of char, which was caused by either the continuous transformation from active sites to deactivated sites, or the loss of the specific surface area. They also observed that the reaction of char with CO$_2$ and moisture occurred at the microporous char surface. That is, the number of available active sites on the char surface determined the intrinsic reaction rate [27],[53]. Yuan et al. [26] reported that the gasification rates of CL (chinar leaves) char were higher than those of RS (rice straw) char, due to the higher specific surface that CL char presented. Rollinson et al. [62] explored the reactivity of various biomass species and indicated that the reactivity increased with increasing specific surface area. Both Matsumoto et al. [61] and Wu et al. [56] demonstrated that the reactivity scaled with active surface area. Valix et al. [60] developed a theoretical linear model to describe the relationship between intrinsic reactivity and total surface area, along with the characteristic particle size and particle density. Feng and Bhatia [63] proposed the ratio of active surface area (ASA) and total surface area (TSA) to be the standard of determining the char reactivity. To better validate the role of the active surface sites in the intrinsic reaction of char gasification, Roberts and Harris [57] predicted the competitive behavior of CO$_2$ and H$_2$O reactants for the same active sites on the char surface. Their experimental results revealed the significant competitive interactions between CO$_2$ and H$_2$O at high pressures, when most of the active surface sites were occupied [57].

Several mechanisms, including both physical adsorption and chemical adsorption, measure the surface area of porous structures. Physical adsorption has the following features: a) no
destruction of the pore structure; b) comparatively low heat of adsorption; c) a rapid and generally non-activated process; d) highly reversible; and e) effective in determining the pore size through multilayer adsorption. The Brunauer-Emmett-Teller (BET) method is one of the most widely used physical adsorption techniques to determine surface area [64]. N₂ and CO₂ are two common adsorbents in the BET measurements to determine the surface area. N₂ and CO₂ adsorption-desorption isotherms occur at 77 K and 273 K respectively. Because nitrogen is stable, readily available, inexpensive, and provides a wide pressure range, nitrogen adsorption most commonly characterizes porous materials [65].

Most of the surface data in this investigation were undertaken in N₂ adsorption. However, Castello et al. [66] reported that the adsorption-desorption data in the low pressure range (10⁻⁸–10⁻³) were not valuable because of marked downward deviations in the curves. Moreover, during physical adsorption, only the pores whose diameters are larger than that of the adsorbent gas molecule are measured. N₂ and CO₂ have similar molecular sizes, but they produce surface areas that differ markedly. The main reason for the difference is that nitrogen adsorption occurs at low sample temperatures (about 77 K) whereas CO₂ adsorption occurs near room temperature. The surface mobility of the molecules at these two temperatures differs markedly. Biomass chars produce a very narrow micro-porosity size distribution, which makes the diffusion effect significant at low temperature. Therefore, the entry of N₂ molecules into micro-pores becomes kinetically or sterically limited. Higher adsorption temperature increases the surface mobility and diffusion rates and therefore more rapidly enters and leaves the very small pores. As a result, N₂ adsorption at 77 K consistently measures less micro-pore volume than CO₂ adsorption at 273 K [66-69]. To overcome the inadequacy of N₂ adsorption, Sing [65] reviewed several classical and empirical approaches in surface area determination and pore size analysis for different types of N₂.
adsorption isotherms, and concluded that extra caution should be paid to the analysis of micro-pore capacity.

This investigation analyzes gasification properties and kinetic behavior of industrially relevant (< ½ inch or 12.5 mm) particles with systematically analyzed char surface areas. Several widely used traditional kinetic models—including the volumetric model (VM), unreacted shrinking core model (URCM), hybrid model (HM), and random pore model (RPM)—are reviewed in this paper and compared to similar literature reviews [69-71] and to these measured data. The VM assumes [72-73] a uniform distribution of active sites on the surface, and other char properties, such as particle shape and pore structure, remain constant during the reaction. The expression for reaction rate is given by [71],

\[
\frac{dx}{dt} = k_{VM} e^{-E/RT} (1 - x) \tag{7}
\]

where \(x\) is reaction conversion, \(t\) is residence time, \(k_{VM}\) is the pre-exponential factor, \(E\) is the reaction activation energy, \(R\) is the universal gas constant, and \(T\) is the reaction temperature.

The URCM [74] assumes the reaction occurs at the surface of the char with the remaining char left as an unreacted core. The size of the particle shrinks as gasification reactions proceed, but the properties of the unreacted core remain unchanged. The rate expression is given by [71],

\[
\frac{dx}{dt} = k_{URCM} e^{-E/RT} (1 - x)^{2/3} \tag{8}
\]

The HM [70] is an empirical model, and the rate expression is described as,

\[
\frac{dx}{dt} = k_{HM} e^{-E/RT} (1 - x)^n \tag{9}
\]

where \(n\) is an empirical parameter generally derived from experimental data.

The random pore model is one of the most common gas-solid descriptions of surface area. The RPM [75-76] assumes the char reacts on pore surface. The cylindrical pores consist of macro-,
meso-, and micro-pores. The internal surface area and therefore intrinsic reactivity initially increase with conversion as pore diameters increase. This surface area and associated reactivity reach a maximum and then decrease as growing pores overlap or grow into each other. This maximum in surface area represents the defining characteristic of the random pore model. The rate expression is given by [71],

$$\frac{dx}{dt} = k_{RPM} e^{-E/RT} (1 - x) \sqrt{1 - \psi \ln(1 - x)}$$  \hspace{1cm} (10)

where \(\psi\) is a positive-valued dimensionless parameter which represents the initial pore structure of char, and is given by the expression [71],

$$\psi = \frac{4\pi L_0 (1 - \varepsilon_0)}{S_{V,0}^2}$$  \hspace{1cm} (11)

where \(L_0\) is pore length per unit volume, \(\varepsilon_0\) is the solid porosity and \(S_{V,0}\) is the initial surface area per unit volume. A \(\psi\)-value of 0 yields the same results as the volumetric model and indicates that \(\varepsilon_0 = 1\), the asymptotic upper limit of porosity. Very large values of \(\psi\) indicate very little porosity in the solid material. Typical porous material \(\psi\)-values range from 5-20. Each of these models predicts that surface area decreases with increasing char conversion over most of the char conversion range. The random pore model uniquely predicts an increase in surface area with char conversion during the initial stages of char conversion if \(\psi\) is greater than 2. The peak in the surface area in the random pore model occurs at \(1 - \exp\left(\frac{\psi^2}{2\psi}\right) < 1 - \sqrt{1/e} \approx 0.39\) for any finite value of \(\psi\). After this peak, the surface area monotonically decreases with conversion.

The conversion as a function of time normalized by the various \(k\)-values depends strongly on the pore model as shown in Figure 8.

These results represent the solutions to the differential equations above if the \(k\)-values are constant.
These solutions are

\[
X_{VM} = 1 + (X_0 - 1) \exp\left(-k_{VM}e^{-E/RT}t\right) \tag{12}
\]

\[
X_{HM} = 1 - \left( (p - 1)k_{HM}e^{-E/RT}t + (1 - X_0)^{1-p} \right)^{\frac{1}{1-p}} \tag{13}
\]

where \( p = 2/3 \) represents the unreacted-shrinking-core model, and

\[
X_{RPM} = 1 + (X_0 - 1) \exp\left(-\frac{1}{4}e^{-E/RT}k_{RPM}t\left(k_{RPM}t\psi + 4\sqrt{1 - \psi \ln(1 - X_0)}\right)\right) \tag{14}
\]

The essential behavior of these equations becomes more obvious if time is replaced by a normalized time equal to \( \tau = tk \) where \( k = k_{VM}e^{-E/RT} \) and similar for the other expressions. This simplifies the equations and shows how conversion depends strongly on the pore model as shown in Figure 8. The simplified solutions depend only on the normalized time \( \tau \), the model parameters, and the initial conversion as follows

\[
X_{VM} = 1 + (X_0 - 1) \exp(-\tau) \tag{15}
\]

\[
X_{HM} = 1 - \left( (p - 1)\tau + (1 - X_0)^{1-p} \right)^{\frac{1}{1-p}} \tag{16}
\]

where \( p = 2/3 \) represents the unreacted-shrinking-core model, and

\[
X_{RPM} = 1 + (X_0 - 1) \exp\left(\frac{1}{4}\tau(\tau\psi + 4\sqrt{1 - \psi \ln(1 - X_0)})\right) \tag{17}
\]

The equations simplify further under the normal assumption that \( X_0 = 0 \), namely

\[
X_{VM} = 1 - \exp(-\tau) \tag{18}
\]

\[
X_{HM} = 1 - ((p - 1)\tau)^{\frac{1}{1-p}} \tag{19}
\]

\[
X_{RPM} = 1 - e^{\frac{1}{4}\tau(\tau\psi + 4)} \tag{20}
\]
Figure 8. Conversion as a function of time normalized by $k$-values and model parameters.

In each equation, $X_0$ represents the initial char conversion. Normal convention defines this value as 0, but there is no completely objective way to define where pyrolysis ends and char reactions begin in most experimental data and these forms of the equations are useful in reducing such data.

These equations all indicate char conversion begin at 0 and ends at 1, as expected, but the time to reach the final conversion varies from about 1 to over 3 dimensionless units and the intermediate values of char conversion vary quite significantly among the models. The hybrid model produces results identical to or very close to the VM and URCM for $p$ values of $2/3$ and 1, respectively.

The volumetric surface area variations with conversion for these models relate directly to the measurements and model development of this paper.
These are given by

\[
\frac{S_V}{S_{V,0}}_{VM} = 1 - X
\]  
(21)

\[
\frac{S_V}{S_{V,0}}_{HM} = (X - 1)^p
\]  
(22)

where \( p = \frac{2}{3} \) in the plots to represent the unreacted-shrinking-core model, and

\[
\frac{S_V}{S_{V,0}}_{RPM} = (1 - X)\sqrt{1 - \psi \ln(1 - X)}
\]  
(23)

Figure 9. Normalized surface area with conversion for each of the pore models.

The limit of all three of these expressions as \( X \) approaches 0 is 0. A plot of the normalized surface area as a function of conversion for each model indicates how the models affect the observed behavior and relates direction to the data discussed later in this investigation (Figure 9). The kinetically controlled reaction rate scales proportional to this number. This scaling factor
begins at unity and ends at zero for each model, as expected. However, the intermediate values vary substantially and, uniquely in the case of the RPM, may not be bound by the initial and final values. This variation in surface area as a function of burnout represents a first-order term in the overall rate expression and distinguishing the models from one another should be well within the measurement precision of most experiments.

Many investigations find that the RPM performs well under most conditions, and agreement has been observed between experimental data and theoretical models [45],[62],[77]. However, a few studies indicate that the RPM will not work under some conditions, and modification of the RPM becomes necessary [26-27],[56]. Yuan et al. [26] analyzed three biomass chars and found that the RPM is not accurate enough to describe the measured surface area data of PS (pine sawdust) char at high temperatures. Consequently, they developed a modified random pore model to better describe the experimental data. Due to ash melting and the loss of surface area, Tremel et al. [27] added an empirical correlation in the random pore model. Wu et al. [56] evaluated the char reactivity in detail, and employed a shifted extended random pore model to fit the CO$_2$ gasification rate plot.

Coal char surface areas commonly feature a non-monotonic change associated with the pore growth and coalescence that is the basis of the RPM and other char models, as discussed above. The pore structure of metaplast-forming coals bears little resemblance to the initial particle structure. Biomass chars differ in both regards from coal. The observations in this investigation extend the results of previous investigators who observe no decreasing and generally increasing surface area with increasing char conversion [78-80]. The previous results focused primarily on about the first half of char conversion whereas these results cover essentially the entire conversion history. Furthermore, the results below indicate that biomass chars resemble the initial particle
structures to a remarkable extent, at least for the energy crop, agricultural residue, and wood fuels analyzed here. The particles in this investigation are large compared to the largest vascular structures in biomass and it is these structures that are preserved. Powdered biomass, which might destroy these structures, and reactor systems in which tar condenses on char surfaces may behave differently [81-82].

The results reported here agree with many previous investigations on many points but differ in some details. For example, Cetin et al. reported that the biomass chars melted and formed a metaplast during high heating rate gasification conditions [83]. The results discussed in this paper expose particles to relatively high temperatures essentially immediately and in this sense are high heating rate conditions. However, the particles sizes in the cited work ranged from 50 to 2000 microns whereas those in this work reach to larger sizes. Large particles experience rapid surface heating rates with increasingly slower heat rates further from the surface. A common biomass particle specification for entrained-flow combustors is that the particles must pass through a ½ inch mesh, meaning their smallest cross section would be up to 12.5 mm. This paper explores behavior in this general size range (6-12.5 mm). Perhaps for this reason, the SEM images from this research show that the chars retain the biomass particle structure to a remarkable extent and until nearly the completion of char burnout. However, the inorganic material from high-ash fuels becomes much more prominent during devolatilization and oxidation/gasification. Near the end of char burnout, the organic structures of low-ash fuels begin to disintegrate. Campbell et al. concluded that biomass char reactivity exhibited a peak near 10% char conversion, and the char oxidation models were not accurate as the quasi-steady state was not established until relatively late in burnout [84]. The char reactivity analysis of these fuels appears in a separate chapter, but it relates closely to the observations shown here. If the effects of the inorganic material in the fuel
are included, these results show that the char reactivity does not change although the observed reaction rate monotonically decreases as the inert inorganic material occupies increasing fractions of the surface. Klose et al. revealed that the surface area of biomass chars related with the gasification reaction rates are comparable to that of coal chars [80]. This analysis indicates that the surface area is much higher than that of coal chars in similar reacting conditions. Many of these differences could be because of different experimental approaches. The data here record in situ and continuous mass, temperature, size, and shape of a particle that is in simulated entrained flow (no neighboring particles). The surface area, pore size distribution, particle images, and other ex situ measurements occur frequently in the char lifetime but not continuously. Other samples are either collected on filters from entrained flow reactors or are generated with a group of particles in a wire mesh. In both cases, the substantial tar produced during pyrolysis could condense on neighboring particles and render different results than are observed here.

Biomass gasification proceeds through a complex process and char properties such as shape, size, and ash content could influence the char reactivity profoundly [54],[85-86]. The size, shape, and density strongly affect the observed rates. This investigation focusing the relationship between the char reactivities and char properties.

5.3 Ash effects on char reactivity

During pyrolysis, biomass decomposes into three primary products: light gases, tar and char, with most but not necessarily all of the ash remaining in the char [20],[29],[87-92]. The first two products form gases at reaction conditions, with the tar condensing at room temperature. During gasification, biomass typically undergoes pyrolysis and the char rather reacts with gas-phase CO₂, H₂O or (more rarely) H₂ to produce H₂, CO and possibly CH₄ as primary syngas products.
Ash represents the fully reacted, residual, inorganic fraction of the fuel, and is a product of combustion, not a characteristic of the fuel. However, the nearly universal practice treats ash an inert fuel component. The distinction is that some of the inorganic material reacts during fuel conversion, and it is the products of these reactions, not the initial material, that constitutes ash. The initial inorganic material generally has more mass than the ash due to dehydration, carbonate and sulfide/sulfate decomposition, and sometimes vaporization of inorganic species. The exception is fuel such as waste that may contain unoxidized inorganics, such as aluminum, that oxidize during combustion, thus increasing their mass. Inorganic species commonly exhibit catalytic properties with respect to fuel and char reactions [91],[93-95], though this investigation presents evidence of the opposite effect. Biomass pyrolysis creates a highly porous char structure that provides active surface sites for gasification reactions. The available active surface area plays a prominent role in most descriptions of intrinsic char reactivity [27],[53],[61],[63],[96]. Char oxidation and especially gasification proceed slowly during biomass conversion [97]. As a result, char reactivity greatly influences the burnout time [98]. The mass fraction of inert materials (ash) increases as the particle reacts. This investigation provides, for the first time, definitive evidence that this accumulating ash fraction decreases the overall particle reactivity, especially as the particles approach burnout.

Hurt and Davis undertook measurements on the char reactivity near extinction and final burnout. They concluded that the reaction could be divided into two stages: (a) a rapid process consuming approximately 80% of the total char mass, and (b) a slow process consuming the remainder of the char carbon. The authors postulated that intrinsic char reactivity decreases as char burnout increases [99-100].
Some investigations demonstrate the catalytic effects of ash components on biomass gasification. Brown et al. [95] and Sutton et al. [101] illustrated that alkali metals catalyze biomass gasification. However, some contrary observations have been reported. Haykiri-Acma et al. [102] studied the reactivities of five biomass chars with different amounts of ash and observed that the lowest ash contents biomass material had the highest reaction rate. They concluded that the biomass ash inhibited the formation of gas products in gasification reactions, thus reducing the biomass char reactivity [102]. Hurt et al. [103] developed a kinetic model to describe the char reactivity in complete burnout level (0-99%). This model quantitatively performed the analysis of reactivity loss in late stages of reaction and related this phenomenon to ash effects. The ash contents reportedly formed a layer of inorganic material on the char surface through which reactant gases and reaction products must pass to the active surface sites below. As the char gasified, ash preferentially accumulated on the surface, with increasing resistance to mass transfer. In addition, the available active surface sites were occupied by the ash contents [103].

To better explore the distinct behavior of char burnout process, especially in the full range of the heterogeneous reaction, this investigation presents continuous measurements of mass, particle size, shape, internal (center) temperature, surface temperature, together with time-resolved but not continuous measurements of pore surface area, porosity, etc. These detailed experimental data are essential to demonstrate that the accumulation of ash contents on char surface will decrease the reactivity.

5.4 Diameter variation during gasification

Although biomass gasification enjoys an extensive experimental and modeling literature, the models that describe the dynamic char diameter variation and effects of swelling and /or shrinkage are inadequate. Most current biomass gasification models assume 0-dimensinal or, at most, one-
dimensional heat and mass transport [104], and make simplistic assumptions regarding diameter variation, effective surface area and ash content. Tinaut et al. observed that the biomass consumption rate was inversely proportional to the size of biomass particle [105]. Nikoo et al. simulated the biomass gasification process and concluded that the gas products such as H$_2$, CH$_4$ and CO decrease when particle equivalent ratio (ER) increases [106]. This simulation results are consistent with Di Blasi’s observation [107]. Lv et al. explained that gasification reaction rate is mainly determined by kinetics for small particles and by diffusion and transport for large particles [108]. It is generally accepted that biomass particle char has undergone size and diameter change in the gasification process. Some researchers have been exploring the mechanisms of char diameter variation and simulating the models to predict this phenomenon. The swelling factor is the ratio of the maximum char diameter to the initial diameter [109], and it is highly dependent on the reacting conditions and biomass fuel materials. Cetin et al. revealed that swelling phenomenon primarily occurred at lower pressures in small particle as higher pressures usually led to larger particle size [110]. Lu and Baxter quantitatively depicted the influence of particle size on biomass gasification and combustion. Their model precisely predicts both swelling and shrinking behaviors of biomass particle during gasification and oxidation. According to the model, near-spherical particles produce lower volatile yields and higher tar yields compared to the aspherical particles under the same reacting conditions [20],[36]. Hagge and Bryden discussed the effects of shrinkage on char reactivity, density, and product yield. The shrinkage shortened the reaction time and diminished secondary reactions, but this effect weakened with increasing temperature and prompted a more thorough conversion of heavy tar to light hydrocarbons. They also illustrated that the shrinkage amount was related biomass materials, heat flux and temperature [104].
Much of the literature of char forming fuels, primarily biomass and coal, share similar experimental techniques and modeling approaches. However, biomass and coal char formation proceeds by conceptually different mechanisms in most cases, and these differences affect char and pore structure [111]. High-rank coals pass through a metaplast phase in which the fuel considerably softens and commonly forms interior bubbles, sometimes to the extent of cenosphere formation. As the fuel preferentially expels compounds enriched in hydrogen and oxygen during pyrolysis or devolatilization, the residual char undergoes significant molecular transformation. Biomass similarly preferentially loses hydrogen- and oxygen-containing compounds and forms more volatiles and generally forms more tar than coal. However, biomass char retains the initial fuel physical structure and characteristics, often to a remarkable degree [111]. That is, unlike coal, the pores in biomass chars mostly reflect the structure of the original fuel, which generally have a high degree of anisotropy and biologically specific functions that are definitively non-random. Not surprisingly, the pore- and surface-area-development models of the two fuels differ, and these have implications on density and diameter.

The following discussion provides a theoretical model to describe the variations of diameter and density for an arbitrary char-forming biomass particle (poplar, corn stover, and switchgrass) over its entire reaction history and compares this model with experimental data during biomass gasification.

5.5 Biomass pyrolysis

Pyrolysis is a thermochemical decomposition of organic material at elevated temperatures in the absence of oxygen (or any oxidizer). It involves the simultaneous change of chemical composition and physical phase. Pyrolysis is a set of complex reactions observed in organic
materials exposed to high temperatures [112]. During pyrolysis, CO and CO₂ are the main product gases, and the nitrogen from the fuel mainly forms NH₃, HCN and NO. Ammonia is the main the product of the fuel-nitrogen [17]. Pyrolysis occurs rapidly compared to oxidation, which is in turn rapid compared to gasification. Pyrolysis is the initial step in both gasification and combustion.

Lu and Baxter developed a model to predict pyrolysis mass loss data and performed several experiments to prove the reproducibility of this model [20]. Figure 10 shows good agreement via three separate runs. This model predicts the amount of fuel, char, tar, and light gas as a function of time, including the ultimate pyrolysis yield. Typically, dry, ash-free (daf) poplar fractional mass loss during pyrolysis is the highest among the three types of biomass material examined here, usually between 92% and 96%. Pyrolysis daf mass loss is about 88%-90% for switchgrass and corn stover. By comparison, coal pyrolysis mass losses typically are about 60% under similar conditions.

![Figure 10](image-url.com)

**Figure 10.** Overall mass loss data and the predicted model for pyrolysis stage [20].
Char yield is the fraction of the initial daf fuel converted to char, or the daf volatile yield subtracted from unity, and is a good standard to determine biomass reactivity. Char conversion is the fraction of the char yield that has reacted. Biomass chars of different type and size react at different rates. Reaction rates also depend on experimental temperature and reactant concentration. The effects of ash concentration and surface area changes further complicate particle conversion rates. This discussion presents most of the results as a function of char conversion, which establishes a common range for the independent variable that would not be possible if data were plotted as a function of residence time.

5.6 Summary

Factors like ash contents on the surface of the char, and pore structure in the char play a vital role in determining the overall reactivity of biomass char during gasification. However, most literature does not have adequate discussion on this topic. This investigation will elaborate on the effects of ash contents on char reactivity and reveal the variation of particle size, porosity, and density as a function of burnout, and develop models that account for all of these changes. These results include several first-ever observations regarding char gasification that probably extend to char reactivity of all types and that are quantified in the model.
6 RESULTS AND DISCUSSION

The objective of this project is to collect new experimental data on single biomass particles as continuous functions of time under gasification conditions and to describe the reaction rates and mechanism in terms of spatial dimensions and time for arbitrary shapes and sizes of particles. The data include particle internal temperature, surface temperature, shape, size, porosity, geometric surface area, and mass as continuous functions of time and particle internal surface area, external surface area, and pore size distribution at discrete points in time. This will be a much more comprehensive dataset than has been available in the past and will include data that separate particle-to-particle property variations from experimental error by tracking an individual particle in time. Furthermore, the data will include measured temperature gradients or differences and particle size and shape effects. This should eliminate many sources of error compared to earlier experiments and may provide data sufficient to distinguish reaction mechanisms. The data will provide definitive indications of mass-transfer vs. kinetic limitations. Aside from the data, this project will produce a more sophisticated model than those typically used in large computer simulations, though the intent is to develop one or more models with sufficient computational efficiency that they could support such codes.

The experiments include data on three types of biomass particles: wood, an herbaceous energy crop, and an herbaceous agricultural residue. The single-particle reactor provides gasification kinetic data, including: particle surface and internal temperatures from type B or K
thermocouples and the imaging pyrometry; 5-digit mass balance data; images that quantify particle shape and size; and based bulk gas and pyrolysis product composition measurements. The pyrolysis product gases analysis is performed by Agilent 5975C GC-MS (Figure 11). Additional non-continuous data include particle internal surface area data and porosity determined by the Micromeritics ASAP 2020 (BET) surface area analyzer.

![Figure 11. Single particle reactor (left) and GC-MS (right).](image)

This discussion presents the experimental and theoretical results on five topics: kinetic reaction rates, particle diameter dynamics, surface area and porosity evolution, ash effects on char reactivity, and pyrolysis gases analysis.

6.1 Single particle gasification kinetic model

6.1.1 Basis experimental measurements

Figure 12, Figure 13 and Figure 14 illustrate the mass loss data for three different biomass fuels as a function of time. The x-axis is the reaction time in minutes and the y-axis is the normalized mass loss data in grams. The initial ash fraction of the dry mass varies by about a factor
of 40 among these fuels (Table 2), specifically being 0.55%, 4.15% and 20% for poplar, switchgrass, and corn stover, respectively. The corn stover shows a significant change in mass loss rate (slope of line) as conversion increases while the lowest ash content fuel (poplar) shows little or no such curvature except, perhaps, at the end of mass loss. The reactions proceed at near constant-temperature conditions in all three cases. These data illustrate the effect of ash on reaction rates observed in all other analyses, as will be discussed later in this paper.

![Graph](image1.png)

**Figure 12.** Measured mass loss data for poplar as a function of time reacting in a 30% H$_2$O + 5% H$_2$ + balance N$_2$ environment.

![Graph](image2.png)

**Figure 13.** Measured mass loss data for switchgrass as a function of time reacting in a 15% H$_2$O + 5% H$_2$ + balance N$_2$ environment.
Figure 14. Measured mass loss data for corn stover as a function of time reacting in a 50% CO₂ + 5% H₂ + balance N₂ environment.

Figure 15. Illustration of dry, ash free (daf) mass loss as a function of time for three 1/2 inch poplar particles at the reactor temperature of 1050 °C (particle surface temperatures are 743 °C, 742 °C and 743 °C respectively) on three different days. The graph shows the entire (pyrolysis and gasification) daf mass loss history. The three lines are virtually on top of each other.
Figure 16. Illustration of dry, ash-free (daf) mass loss as a function of time for three 3/8 inch switchgrass particles at different temperatures (particle surface temperatures are 713 °C, 742 °C and 816 °C respectively) on three different days. The graph shows the entire (pyrolysis and gasification) daf mass loss history.

Figure 17. Illustration of dry, ash-free (daf) mass loss as a function of time for four 3/8 inch corn stover particles at different temperatures (particle surface temperatures are 799 °C, 827 °C, 787 °C, and 832 °C respectively) on four different days. The graph shows the entire (pyrolysis and gasification) daf mass loss history.
These mass loss data remain very similar among experimental runs for the three biomass fuels (illustrated in Figure 15, Figure 16 and Figure 17), with most of the particle-to-particle and run-to-run variation occurring in the char yield [113]. Figure 15 indicates that poplar particles produce nearly identical mass loss data among runs under the same conditions. The poplar fuel is cut from bulk material, with each sample being essentially identical in shape, composition, and essentially all other properties. Larger but still modest differences between each experiment occur with switchgrass particles (Figure 16). Switch grass particles are pressed into pellets, but the initial fuel is reasonably homogeneous on the scale of a single pellet and does not differ substantially with region of the plant from which it might come. Corn stover particles produce the largest differences among experiments (Figure 17). The mass loss measurements remain accurate but not as repeatable as the poplar particles. Corn stover in these experiments occurs as pellets of individual, smaller particles. The small particles differ significantly in many properties (moisture, ash, density, etc.) depending on the part of the plant it comes from. These differences create relatively large particle-to-particle property variations on scales that are comparable to the pellet. Among other things, the ash contents in poplar samples are more constant than the pellets (corn stover and switchgrass). Specifically, the pellets exhibit significant sample-to-sample property variations that translate into run-to-run variations in reaction rates dominated by different particle behaviors, not experimental uncertainty.

6.1.2 Modeling techniques and optimization results

Non-linear least squares regression methods optimize the kinetic parameters with respect to the experimental data. This process produces a global kinetic model that reasonably describes all three fuels at all sizes and reactant gas concentrations and over a wide temperature range. Table 5 summarizes the test matrix.
Figure 18 illustrates the measured fractional daf mass loss data (blue points/line) as a function of time. The experimental data indicate very high mass loss rates during pyrolysis at the initial stages of reaction and dramatically lower gasification rates for the remaining char, as is typical of biomass and other solid fuels. During gasification, the experimental mass loss rate (slope of the mass loss curve) remains fairly constant even though the reaction temperature increases by 50 K, the particle diameter decreases, and the surface area and porosity increase. The experimental reaction rate decreases dramatically near the end of char conversion. The data show a short region where the reaction rate temporarily approaches zero and then begins again at about the same slope as previously. These experimental vagaries are difficult to eliminate entirely even though they affect the agreement between model and data substantially.

The red line and the dash-dot green line illustrate model predictions for fractional mass loss (daf basis) and reaction rate, respectively. The rate uses the measured particle temperatures, among other parameters and though it is a predicted result, the experimental noise in the temperature measurement introduces some noise in the predicted rate. In this case, the surface temperature ranges from 830 to 870 °C on the surface during char gasification. The center temperature remains about 50 °C lower than the surface temperature. The predicted daf mass loss compares directly with the measurements. The reaction rate depends on porosity, size, shape, and many other parameters not illustrated in the figure in addition to its dependence on time. It is approximately but not precisely equal to the slope of the data. That is, the reaction rate could conceptually change even if the slope of the data does not because of changes in these other measured but not illustrated parameters. The predicted fractional mass loss and rate mirror the measured behavior with allowances for the experimental aberrations in some of the data. Specifically, the rate is nearly constant for most of the char conversion history and decreases near the end of char conversion.
Figure 18. Measured mass loss (blue dots), predicted mass loss using the regressed parameters (red line), and reaction rate derived from the measured data (dot-dashed green line) for a ⅜ inch poplar particle, including the normalizeddaf mass loss (left axis) and overall reaction rate (right axis) while reacting in a 90% CO₂ and 0% H₂O environment with a reactor temperature of 1250 °C.

Figure 19. Measured particle surface temperature (green line) and center temperature (red line) from data logger for a poplar reacting in a 90% CO₂ and 0% H₂O environment and a reactor temperature of 1250 °C.
Figure 20. Measured particle surface temperature (green line) and center temperature (red line) from data logger for a poplar reacting in a 90% CO$_2$ and 0% H$_2$O environment and a reactor temperature of 1250 °C, as continuous functions of time during pyrolysis.

Figure 18 indicates that in this case, the particle yields about 11% of its daf (dry ash free) mass as char, which is consumed by the gasification reactions in about 35 minutes when the CO$_2$ and H$_2$O concentrations are 90% and 0%, respectively. Toward the end of a particle’s lifetime, the remaining char sometimes falls off the balance. Among these three fuels, poplar is especially prone to this behavior since it has such small ash content (0.55%) that the residual ash particle is extraordinarily fragile. The ratio of the surface mole fraction of CO$_2$ to the bulk mole fraction is about 0.95 in this and most of the remaining experiments, indicating that external diffusion resistance to mass transfer is negligible.

Figure 19 illustrates typical surface and center temperature data. The temperature difference arises from both heat loss to the relatively cool reactor walls and because of the endothermic gasification reaction. The particle diameter also decreases during the reaction. Of these effects, the endothermic reaction rate and particle diameter are the largest. Therefore, the temperature difference between the center and the surface of the particle generally decreases somewhat as reaction proceeds. Both temperatures increase about 50 K during reaction. The temperature
difference between the center and external surface in the figure appears to be small during pyrolysis, but the lines have such large slopes that the actual differences are very large (several hundred degrees), as illustrated in Figure 20.

6.1.3 Experimental data illustration

![Graph illustrating experimental data](image-url)

Figure 21. Measured mass loss (blue dots), predicted mass loss using the regressed parameters (red line), and reaction rate derived from the measured data (dot-dashed green line) for a ¾ inch poplar particle, including the normalized daf mass loss (left axis) and overall reaction rate (right axis) reacting in a 50% CO₂ and 0% H₂O environment with a reactor temperature of 1250 °C.

Figure 21 illustrates data from experiments similar to those previously discussed but with lower reactant concentration (¾ inch poplar particle with 50% CO₂ and 0% H₂O at 1250 °C). The reaction rate and reactant concentration both decrease by a nominal factor of 2, as would be expected in these kinetically limited experiments with approximately first-order kinetics. Specifically, the reaction rate (green dot-dashed line) decreases from about 0.07 g/m²s to 0.035 g/m²s during gasification. As a result, the time required for the particle to react completely
increases from 23 minutes at 90% CO$_2$ to about 35 minutes at 50% CO$_2$. The measured char yield also increases slightly.

Figure 22. Measured mass loss (blue dots), predicted mass loss using the regressed parameters (red line), and reaction rate derived from the measured data (dot-dashed green line) for a ⅜ inch poplar particle, including the normalized daf mass loss (left axis) and overall reaction rate (right axis) while reacting in a 50% CO$_2$ and 0% H$_2$O environment with a reactor temperature of 1150 °C.

Figure 22 illustrates similar data at 100 K lower reactor temperature (⅜ inch poplar particle, reacting in 50% CO$_2$ and 0% H$_2$O at 1150 °C). The particle temperature decreases by about 75 K, somewhat less than the decrease in reactor temperature because the reaction rate and hence endothermic cooling decrease and the radiative heat transfer is less significant, among other factors. Compared to Figure 21, the reaction rate decreases by about 17%. The abrupt mass loss near the end of burnout in the measured mass loss line indicates the residual char fell from the mass balance.

These and similar data at differing conditions form the basis for fitting the reaction rate parameters. These optimal parameters derived from these experimental data describe reaction with
particles reacting in CO$_2$. These parameters predict the observed temperature, reactant concentration, and particle size data over the ranges they varied in these experiments.

Reactivity toward H$_2$O and combined H$_2$O and CO$_2$ for a variety of particles yield conceptually similar results. Typical results appear in Figure 23 through Figure 26, which illustrate data for poplar, corn stover, and switchgrass with H$_2$O (steam) and CO$_2$ reactants alone or in combination. Figure 23 shows that the corn stover particle requires about twice as long to react completely as the poplar particle in the same reacting conditions. Corn stover’s higher ash content affects char reactivity during its entire reaction history, with increasing effect as conversion increases, according to the concepts developed in this document. This sensitivity to ash contents explains the differences observed here without the need to adapt different kinetic parameters for different fuels. The ash effect also changes the shape of the mass loss and reaction rate lines, the highest ash content (corn stover) shows a significant change in mass loss rate (slope of line) as conversion increases while the lowest ash content fuel (poplar) shows almost no line curvature, with corn stover indicating intermediate behavior.

The corn stover also has a significantly larger char yield than poplar. These effects combined to result in a slower overall reaction rate for the corn stover than for the poplar. The periodic spikes appearing on the reaction rate line (green line) reflect the same trend in temperature data. Such temperature spikes could produce temperature-dependent data that would allow better kinetic parameters to come from a single particle run. However, the particle response to these spikes is quite slow and they provide little additional data.

Figure 24 illustrates the results for a ¾ inch poplar particle reacting in a combination of 47% CO$_2$ and 47% H$_2$O environment and a reactor temperature of 1250 °C. This is a similar CO$_2$ concentration as the 50% CO$_2$ data shown in Figure 21 with the additional complexity of adding
47% H₂O. As expected, the particle reacts more rapidly than that in a 50% CO₂ environment with otherwise similar conditions. Indeed, reaction rate increases by about a factor of 3, indicating that either H₂O is more reactive with char than CO₂ or that there are synergistic effects between the two that cause the reactivity in the presence of both to be greater than in the presence of just CO₂. The literature review indicates a wide acknowledgement that H₂O reacts more readily with chars than does CO₂ in gasification environments. These observations are consistent with that. However, there is not a consensus regarding the potential synergy or competition between the reactions. The next sets of data determine this with respect to these chars.

Figure 23. Measured mass loss (blue dots), predicted mass loss using the regressed parameters (red line), and reaction rate derived from the measured data (dot-dashed green line) for a ⅜ inch corn stover particle, including the normalized daf mass loss (left axis) and overall reaction rate (right axis) while reacting in a 50% CO₂ and 0% H₂O environment with a reactor temperature of 1250 °C.

Figure 25 illustrates the results for a ⅜ inch poplar particle reacting in 50% H₂O environment, which demonstrates the previous conclusion that H₂O reacts more rapidly with biomass char than CO₂.
Figure 24. Measured mass loss (blue dots), predicted mass loss using the regressed parameters (red line), and reaction rate derived from the measured data (dot-dashed green line) for a ⅜ inch poplar particle, including the normalized daf mass loss (left axis) and overall reaction rate (right axis) while reacting in a 47% CO₂ and 47% H₂O environment with a reactor temperature of 1250 °C.

Figure 25. Measured mass loss (blue dots), predicted mass loss using the regressed parameters (red line), and reaction rate derived from the measured data (dot-dashed green line) for a ⅜ inch poplar particle, including the normalized daf mass loss (left axis) and overall reaction rate (right axis) while reacting in a 0% CO₂ and 50% H₂O environment with a reactor temperature of 1250 °C.
Figure 26. Measured mass loss (blue dots), predicted mass loss using the regressed parameters (red line), and reaction rate derived from the measured data (dot-dashed green line) for a ¾ inch switchgrass particle, including the normalized daf mass loss (left axis) and overall reaction rate (right axis) while reacting in a 0% CO₂ and 15% H₂O environment with a reactor temperature of 1250 °C.

Figure 26 illustrates typical data for a ¾ inch switchgrass particle reacting in a 0% CO₂ and 15% H₂O environment with a reactor temperature of 1250 °C. The switchgrass particle reacts more slowly than poplar, as the total reactant gas concentration (H₂O) is relatively low and switchgrass has more ash than poplar. Figure 27 illustrates data for a ¾ inch corn stover particle reacting in a 0% CO₂ and 30% H₂O environment with a reactor temperature of 1250 °C. When compared to Figure 26, which reacted in H₂O as well, the reaction rate line shows a similar shape for both materials. Corn stover in Figure 27 requires longer to react completely than switchgrass in Figure 26, even though the concentration of reactant gas (H₂O) is lower in Figure 26 for switchgrass. This indicates that the ash effect for the corn stover cannot be ignored. Figure 28 illustrates results from an experiment with a higher furnace temperature (1350 °C) but otherwise identical with the results shown in Figure 21. In this experiment, the total reaction time is less than half of the time required for Figure 21.
Figure 27. Measured mass loss (blue dots), predicted mass loss using the regressed parameters (red line), and reaction rate derived from the measured data (dot-dashed green line) for a ⅜ inch corn stover particle, including the normalizeddaf mass loss (left axis) and overall reaction rate (right axis) while reacting in a 0% CO\textsubscript{2} and 30% H\textsubscript{2}O environment with a reactor temperature of 1250 °C.

Figure 28. Measured mass loss (blue dots), predicted mass loss using the regressed parameters (red line), and reaction rate derived from the measured data (dot-dashed green line) for a ⅜ inch poplar particle, including the normalized daf mass loss (left axis) and overall reaction rate (right axis) while reacting in a 50% CO\textsubscript{2} and 0% H\textsubscript{2}O environment with a reactor temperature of 1350 °C.
6.1.4 Power-law model fits

![Figure 29. Measured mass loss (blue dots), predicted mass loss using the regressed parameters (red line), and reaction rate derived from the measured data (dot-dashed green line) for a ⅜ inch poplar particle, including the normalizeddaf mass loss (left axis) and overall reaction rate (right axis) while reacting in a 50% CO₂ and 0% H₂O environment with a reactor temperature of 1250 °C.](image)

The discussion thus far uses a power-law kinetic model. This model assumes the rate is proportional to the reactant concentrations raised to some power times a temperature-dependent reaction rate constant. Therefore, comparing the results in Figure 29 and Figure 30, in which the two experiments are performed in different reactant concentrations (CO₂ concentrations are 50% and 90%, respectively) but otherwise very similar conditions produces a useful comparison. The comparison is not exact since the char yields, diameter and density/internal surface area vary slightly from run to run. For example, these two experiments produced 11% and 14% char yields, respectively. As seen in Figure 29 and Figure 30, the kinetic parameters describe the behavior of both data sets reasonably well, although they predict the high CO₂ concentration (90%) data in Figure 30 less precisely than the low CO₂ concentration (50%) data in Figure 29. Parameters
optimized with a single data set fit that data better than the globally optimized results, as expected (Figure 31), but such fits are not very useful for describing behavior under a wide set of conditions.

![Figure 30](image_url)

**Figure 30.** Measured mass loss (blue dots), predicted mass loss using the regressed parameters (red line), and reaction rate derived from the measured data (dot-dashed green line) for a ⅜ inch poplar particle, including the normalized daf mass loss (left axis) and overall reaction rate (right axis) while reacting in a 90% CO₂ and 0% H₂O environment with a reactor temperature of 1250 °C.

The models dealing with surface adsorption (Eley Rideal or Langmuir-Hinshelwood) were previously presented and are

\[ r_9 = s_{a,\text{char}} z_{\text{char}} \frac{C_1 k_1 p_{CO_2}}{1 + k_2 / k_3 P_{CO} + k_1 / k_3 P_{CO_2}} \]  

(4)

\[ r_9 = s_{a,\text{char}} z_{\text{char}} \frac{k_1 p_{CO_2} + k_4 p_{CO_2}^2}{1 + k_2 P_{CO_2} + k_3 P_{CO}} \]  

(5)

\[ r_{10} = s_{a,\text{char}} z_{\text{char}} \frac{k_5 p_{H_2}O + k_8 p_{H_2}O + k_9 p_{H_2}O^2}{1 + k_2 P_{H_2}O + k_3 P_{H_2}} \]  

(6)

These three models can be simplified into first-order power expressions if \( k_1 \) or \( k_5 \) dominates the reaction for CO₂ or H₂O, respectively. From the observation, the models fitting the
data without using the other terms in these expressions indicate that those terms are negligible compared to the dominant factors and cannot be determined with any precision from these data. On one hand, it proves that none of the terms in those expressions could be precisely estimated, if all terms above are involved in the optimization process. On the other hand, these models are accurate enough to describe the mechanism without any doubt, but rather that under the experimental conditions in this investigation, the other minor terms never contribute notably enough to the extent that they can be reliably measured.

![Graph](image.png)

**Figure 31.** Measured mass loss (blue dots), predicted mass loss using the improved (unique) regressed parameters (red line), and reaction rate derived from the measured data (dot-dashed green line) for a ¼ inch poplar particle, including the normalized daf mass loss (left axis) and overall reaction rate (right axis) while reacting in a 90% CO₂ and 0% H₂O environment with a reactor temperature of 1250 °C.

The analysis of reaction order in this investigation addresses both the activation energy, which captures the temperature dependence, and reaction order, which indicates the rate dependence on reactant concentration. The experimental data reacting in different temperatures and different gas concentrations determined a preliminary activation energy through least-squares
analysis optimizing the pre-exponential factor and activation energy. A similar least-squares analysis optimized the reaction order, pre-exponential factor and activation energy together using data at different temperatures and with different reactant concentrations. Table 9 summarized the analysis results of reaction order optimization. The optimal solutions of reaction order in the data analysis are 0.95 for CO₂ reaction and 0.94 for H₂O reaction respectively. Although the optimal solution of the reaction order is not 1, a 1st order kinetic model is more theoretically reasonable and fits the data nearly as well as the optimized orders, well within the statistical uncertainty of the orders.

<table>
<thead>
<tr>
<th>Table 9. Optimal reaction order analysis.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
</tr>
<tr>
<td>CO₂ data</td>
</tr>
<tr>
<td>Reaction order</td>
</tr>
<tr>
<td>Sum sq. error</td>
</tr>
<tr>
<td>Difference</td>
</tr>
</tbody>
</table>

### 6.1.5 Summary

Table 10 lists the uniform regressed parameters used in optimizing the global kinetic model, which works for most experimental data in great correlation. Nonlinear least-squares regression of these data produces the pair of \( A \) and \( E \) (Table 10) as global optimal parameters with first-order kinetics. Figure 33 illustrates the 95% confidence interval in this prediction model. The regressed Arrhenius kinetic parameters used in the global model (Table 10) fall into this region. These parameters reasonably predict all of the data, though not within the uncertainty in all cases. Optimization of each fuel type individually produces slightly different parameters. Essentially
every result illustrated thus far would improve by fitting the kinetic coefficients uniquely to the single data set. This suggests, though falls far short of being compelling, that such a model may be justified. The observation that the models fit the data without using the other terms in these expressions indicates that the other terms are small, and that if we were to fit the data using all of these terms, none of the resulting kinetic coefficients estimates would be accurate. This does not mean the expressions are inaccurate but rather that under the broad sets of conditions used here, the other terms never contribute significantly enough to strongly affect the results or to be accurately measured. The simple power-law model seems to suffice for the range of temperatures, reactant mole fractions, and reactants used in these experiments.

Figure 32. Comparison of overall reaction rates between H₂O and CO₂ environment. ln(kH₂O) (red line) and ln(kCO₂) (blue line) using the improved (unique) regressed parameters with a temperature range of 300-2000 K.
Figure 33. 95% confidence intervals for CO$_2$ parameters in the prediction model in this investigation.

Table 10: Regressed Arrhenius kinetic parameters used in the global model.

<table>
<thead>
<tr>
<th>Reactant gas</th>
<th>A (g/Pa m$^2$ s)</th>
<th>E/R (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$</td>
<td>0.001048</td>
<td>5450</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>0.002884</td>
<td>6292</td>
</tr>
</tbody>
</table>

The regressed kinetic parameters explain why biomass gasification reaction proceeds more rapidly in H$_2$O environment than CO$_2$ environment under otherwise similar conditions. The rate constant $k$ of H$_2$O is greater than that of CO$_2$. H$_2$O has higher pre-exponential factor ($A$) and higher activation energy $E$ than CO$_2$, which means each rate constant is higher than the other over some range of temperatures. At all temperatures above about 560 °C, which is all practical temperatures for gasification, H$_2$O reactivity exceeds that of CO$_2$ reactivity with an increasing ratio as temperatures increase (Figure 32).
Biomass gasification global kinetics over broad range of reacting conditions depends on accurate submodels for all the parameters. This and several companion papers document the accuracy of these submodels [111],[113]. The intrinsic reaction depends on the total surface area of biomass particle, which consists of the pores ranging from a few nanometers to many tens of microns. Previously published work indicates that most of this total surface area does not participate materially in particle conversion and that much of the surface area that does participate is in the vascular channels that are too large to be measured by traditional BET isotherm techniques [111]. It is clear that the pores in biomass are not random and do not behave consistent with any of the common pore models. Separate analyses not reported here investigate the intrinsic reactivities and conclude that total surface areas (including micro- or nanopores) represents a poor basis on which to base such kinetics.

6.2 Particle diameter evolution

6.2.1 Theoretical model

Particle diameter generally decreases during char conversion, increasing the reaction rate per unit surface area but decreasing the total mass loss rate. The change in particle diameter with reaction rate depends on many factors, including reactants penetration into the char, structural sintering, porosity changes, etc. In these experiments, the size is measured directly, but in a predictive code, it must be modeled. This model begins with the mass ratio in terms of densities and diameters as follows

\[
\frac{m}{m_0} = \frac{\rho d^3}{\rho_0 d_0^3}
\] (24)
where subscript 0 represents the original value, which can be for either the particle or the char. The quantity $1 - m/m_0$ represents the total burnout when 0 represents the initial particle value. The same quantity represents char conversion when 0 represents the initial char values. From this equation, the diameter is given by

$$d = d_0 \left( \frac{m \rho_0}{m_0 \rho} \right)^{\frac{1}{3}}$$

(25)

This expression is rigorous. However, it involves the particle density, and one usually does not know how density varies with conversion or time. A useful empirical relationship between density and mass is

$$\frac{\rho}{\rho_0} = \left( \frac{m}{m_0} \right)^n$$

(26)

which yields

$$d = d_0 \left( \frac{m}{m_0} \right)^{\frac{1-n}{3}}$$

(27)

where $n = 0$ corresponds to a constant-density process, $n = 1$ corresponds to constant-diameter process, $n > 1$ represents particle swelling behavior, and $n < 0$ represents particle sintering or some other mechanism by which diameter decreases without or at least faster than mass change. Intermediate values represent some intermediate behavior among these defined points. A suitable choice for $n$ renders this equation exact if it can vary with conversion, but the equation is most useful if the value of $n$ remains nearly constant.

Geometric-surface-area-based particle models usually use empirically determined values for $n$. Intrinsic-kinetics-based models can predict the effective $n$ theoretically with an appropriate pore model. Commonly, the change in diameter associated with a change in mass differs significantly during pyrolysis compared to heterogeneous reactions, with the former process
commonly leading to swelling (at least for coal and black liquor) and in any case more rapid diameter changes during pyrolysis or devolatilization compared to heterogeneous char reaction. This equation can describe both processes, but usually with different parameters and in the case of heterogeneous reactions (oxidation and gasification), \( m_0 \) and \( d_0 \) most usefully refer to initial char properties and \( m \) and \( d \) refer to the mass and diameter of the char particle.

Nearly all particles contain organic material in the form of biomass or char, relatively refractory inorganic material or ash, and moisture. All quantities represented here are on a dry basis. Refractory material can be the total ash or any component of the ash that does not leave the particle, which normally includes compounds that contain silicon, aluminum, titanium, and calcium. Some potassium and sodium occur in modes that might be less refractory. Sulfur occurs in many modes, all of which are non-refractory at high temperature but some of which may reform as the particle cools. The refractory material, by definition, does not leave the particle and therefore provides a means to estimate the overall mass loss, as follows

\[
m^0 x^0_a = m x_a \tag{28}
\]

\[
\frac{m}{m^0} = \frac{x^0_a}{x_a} \tag{29}
\]

where \( x \) is a mass fraction and subscript \( a \) represents refractory material (ash or an ash component).

This equation combines with the previous result to indicate how the particle diameter depends on the refractory material mass fraction as

\[
d = d_0 \left(\frac{x^0_a}{x_a}\right)^{1-n} \tag{30}
\]
If the ash mass fraction is \( x_a \), the dry ash free (\( daf \)) mass ratio is

\[
\frac{m_{daf}}{m_{daf}^0} = \frac{x_a^0(1 - x_a)}{x_a(1 - x_a^0)} = \frac{m(1 - x_a)}{m^0(1 - x_a^0)} = \frac{\rho d^3(1 - x_a)}{\rho_0 d_0^3(1 - x_a^0)}
\]  \( (31) \)

where \( \rho \) and \( \rho_0 \) are the particle density and initial density, respectively. This leads to a particle diameter expression of

\[
d = d_0 \left( \frac{m \rho_0}{m_0 \rho} \right) \frac{1}{3} = d_0 \left[ \frac{m_{daf}(1 - x_a^0)}{m_{daf}^0(1 - x_a)} \left( \frac{\rho_0}{\rho} \right) \right] \frac{1}{3}
\]  \( (32) \)

This model differentiates behavior of the ash and the organic material (char). The dry ash-free (\( daf \)) char experiences density and size changes during reaction. These changes occur at the finest scales as reactions proceed.

Separate reactions affect the initial refractory or inorganic material in the fuel. This discussion distinguishes this initial refractory material from ash, although most of the literature uses these terms interchangeably. The initial refractory material can include hydrated clays and salts, carbonates, sulfates, sulfides, oxides, sub-oxides and other materials that dry, decompose, oxidize, or otherwise transform during particle reaction. These transformations produce the ash as measured by standardized fuel characterization procedures. These procedures specify conditions designed to oxidize fully all of the material, to decompose carbonates, sulfates, and sulfides, and to dehydrate salts, clays, and minerals. Nevertheless, common practice uses the term ash as if it refers to a raw fuel component rather than the product of these reactions. The model development below recognizes that the ash is a product of these reactions.

This particle model assumes that the particle comprises several mutually exclusive constituent masses and that the volumes occupied by these masses add with individual scaling factors and densities. Mass and elemental components add quantitatively, but volumes do not necessarily add directly. Specifically, the particle includes liquid (generally water but sometimes
oil), solid fuel, char, and inorganic material. The liquid represents moisture or any component that reacts in a zero-order, vaporization-type process. Water, in fact, exists both as free water that vaporizes and chemically complexed water that dehydrates [36]. In detailed models, the solid fuel can react to form an organic liquid such as a tar or metaphase, but in simple models, the liquid is generally moisture. Additionally, biomass chemically binds some moisture as hydrates or similar chemical forms. Solid fuel represents raw biomass, coal, black liquor or similar condensed-phase fuel that decomposes to form gaseous, liquid, or solid products. The solid product of this reaction is char, which does not thermally decompose but rather reacts heterogeneously to form gases. The transition from initial organic fuel to char involves a transition that is not easy to define objectively. That defining quantitative char yields from biomass involves a measure of subjectivity and in any case depends on many experimental and fuel conditions. The inorganic material transforms into a product that, in aggressive oxidizing environments, eventually becomes ash [113]. Each of these four particle constituents has a mass and a density, and the associated volumes (mass divided by density) sum to the overall particle volume. Typical particle histories start with no char and progress through drying, solid fuel decomposition to release gases (pyrolysis or devolatilization) and form char, and finally heterogeneous char reaction with the gas phase, although there is nothing in this or most models that requires that these reactions be sequential and, indeed, for large particles they vary with both time and particle location and, at times, proceed simultaneously. Inorganic material transforms to ash through many mechanisms that include dehydrating, carbonate/sulfate/sulfide decomposition, vaporization, oxidation, and melting, generally in parallel with the other reactions. Many models simplify these steps and treat the inorganics as inert.

Scaling factors of unity conserve volume and assume, for example, that moisture occupies a volume in a wet biomass particle comparable to the volume occupied by pure water of the same
amount. This implies that drying the particle creates porosity equal to the volume of the water that vaporizes. Non-unity scaling factors accommodate the observed behavior that particles often shrink, and sometimes swell, through bulk structure rearrangement as the particle constituents react. Including these shrinking/swelling parameters result in a mathematical form of the model as follows.

\[ m_p = m_w + m_f + m_c + m_i \]  \hspace{1cm} (33)

\[ V_p = f_w V_w + f_f V_f + f_c V_c + f_i V_i \]  \hspace{1cm} (34)

where \( m, f, \) and \( V \) represent mass, scaling factor, and volume, respectively. And subscripts \( p, w, f, v, \) and \( i \) represent particle, moisture, fixed carbon, volatiles and inorganic matters (ash), respectively. The scaling factor formulation appears shortly. Standard fuel measurements determine moisture, ash, volatiles and fixed carbon contents of the fuel. Common practice equates the ash measurement with the initial inorganic fraction, though as the previous discussion indicates this is not actually the case. However, under this assumption, the sum of the fixed carbon and volatiles measurements become the organic fuel fraction. The present model indicates how to include the ash transformations in the particle size description and how to use the common assumptions, which treat the ash as inert, to obtain a simplified and more tractable model.

These assumption lead to the following relationship for the densities

\[ \rho_p = \frac{m_p}{V_p} = \frac{m_w + m_f + m_c + m_i}{f_w \frac{m_w}{\rho_w} + f_f \frac{m_f}{\rho_f} + f_c \frac{m_c}{\rho_c} + f_i \frac{m_i}{\rho_i}} = \frac{1}{f_w \frac{x_w}{\rho_w} + f_f \frac{x_f}{\rho_f} + f_v \frac{x_v}{\rho_v} + f_i \frac{x_i}{\rho_i}} \]  \hspace{1cm} (35)

or, in a less concise but more computationally efficient expression,

\[ \rho = \frac{f_w x_w \rho_f \rho_v \rho_i + f_f x_f \rho_w \rho_v \rho_i + f_v x_v \rho_w \rho_f \rho_i + f_i x_i \rho_w \rho_f \rho_v}{\rho_w \rho_f \rho_v \rho_i} \]  \hspace{1cm} (36)
Particles that conserve volume \((f_j = 1\) for all components\) have overall inverse densities that scale with the mass-fraction-weighted inverse densities of the components. That is, for volume conservation,

\[
\frac{1}{\rho} = \frac{x_w}{\rho_w} + \frac{x_f}{\rho_f} + \frac{x_v}{\rho_v} + \frac{x_i}{\rho_i}
\]  

(37)

In general, the scaling factors depend on composition and component mass loss in complicated ways. A convenient representation of these scaling factors is that each component density scales with that component’s mass ratio (current component mass over initial component mass) according to a power-law expression similar to that used previously.

\[
\frac{1}{\rho} = \frac{x_w}{\rho_w^0 \left( \frac{m_w}{m_w^0} \right)^p} + \frac{x_f}{\rho_f^0 \left( \frac{m_f}{m_f^0} \right)^q} + \frac{x_v}{\rho_v^0 \left( \frac{m_v}{m_v^0} \right)^r} + \frac{x_i}{\rho_i^0 \left( \frac{m_i}{m_i^0} \right)^s}
\]  

(38)

where the mass ratios equal 1-conversion of the four fractions, respectively, and a superscript 0 represents the initial values. The exponents quantify the extent to which the density of the fractions varies as each of the fractions reacts. As before, values of 0 and 1 represent components in which the density or the diameter/volume, respectively, remain constant as the particle reacts. Intermediate values represent intermediate behavior. Values larger than 1 represent swelling while negative values represent sintering or some similar volume-reducing reaction that does not consume mass. The exponents may be functions of burnout.

Typical biomass particle behavior involves the following:

- \(p\) close to zero (density of remaining water is unaffected drying),
- \(q\) close to zero (density of remaining raw fuel is unaffected by char formation),
- \(r\) depends on the degree of kinetic (near one) or diffusion (near zero) influence on the reaction, and
- \(s\) is unimportant since the mass ratio \(m_i/m_i^0\) is near one – identically one of ash is refractory and used to represent inorganic material generally. Near the end of particle burnout, \(s\) drops below zero if all char reacts and ash sinters.
Particle drying generally decreases fuel density. This model describes this decrease by $\rho_f^0$ being the density of dry fuel, not by $p$ being close to one. A finite positive value of unity indicates that the remaining liquid density decreases as the particle dries, which is not typical. Similarly, pyrolysis commonly causes particles to swell. This model describes such swelling (or shrinking) as the char density being less than the fuel density, not by the parameter $q$ being greater than one (or less than zero). The parameter $q$ exceeds one if, for example, the reaction of some biomass to char causes the remaining biomass component density to decrease, which is not typical.

The simple application of this model below assumes that values tabulated above for the exponents in the model. However, the model still requires a relationship between the initial char and particle density, or some other means to calculate an initial char density. This relationship is the swelling factor, which is unity if the initial char is the same size as the initial particle and greater or less than unity if the char is larger or smaller, respectively, than the initial particle. A swelling factor of unity indicates the initial char size equals that of the initial particle, which in turn implies than the char density equals the initial dry particle density multiplied by the char yield. The discussion below uses this swelling factor to determine the char density and the diameter factor $n$ to determine how the char diameter changes during burnout.

The particle consists of only char and ash after devolatilization and during heterogeneous gasification. Under these circumstances, the equation above for the volume fraction of char is expressible in terms of overall particle daf mass loss, initial ash mass fraction, and char and ash densities.

The following derivation uses the relationship for dry, ash-free burnout $b_{daf}$

$$b_{daf} = \frac{\left(1 - \frac{x_{a,0}}{x_a}\right)}{1 - x_{a,0}} = \frac{b}{1 - x_{a,0}}$$ (39)
and assumes that the particle consists only of ash and char, namely

\[ x_a = 1 - x_c \]  

(40)

and finally the relationship between burnout (not daf) and ash mole fraction

\[ x_a = \frac{x_{a,0}}{1 - b} \]  

(41)

\( z_c \) is the volume fraction of char in the particle, which is given by,

\[ z_c = \frac{x_c}{x_a \rho_c + x_a \rho_a} = \frac{1}{1 + \frac{x_a \rho_c}{(1 - x_a) \rho_a}} = \frac{1}{1 + \frac{\rho_c}{\rho_a} \frac{x_{a,0}}{(1 - b - x_{a,0})}} = \frac{\rho_a(1 - b - x_{a,0})}{\rho_a(1 - b - x_{a,0}) + \rho_c x_{a,0}} \]  

(42)

Another important relationship is the variation of particle diameter with burnout. The particle density (assuming \( f_i = 1 \)) is

\[ \frac{1}{\rho_p} = \sum_j \frac{x_j}{\rho_j} \]  

(43)

For a particle that consists only of char and ash

\[ \frac{1}{\rho_p} = \frac{x_a}{\rho_a} + \frac{x_c}{\rho_c} = \frac{x_a}{\rho_a} + \frac{1 - x_a}{\rho_c} = \frac{\rho_c x_a + \rho_a (1 - x_a)}{\rho_a \rho_c} = \frac{x_{a,0} (\rho_c - \rho_a) + \rho_a}{\rho_a \rho_c} \]  

(44)

or

\[ \rho_p = \frac{\rho_a \rho_c}{x_{a,0} (\rho_c - \rho_a) + \rho_a} = \frac{(1 - b) \rho_a (\rho_c - \rho_a)}{(1 - b) \rho_a + (\rho_c - \rho_a) x_{a,0}} \]  

(45)
The terms $b_0$ and $b_{daf,0}$ represent the particle burnout on a total mass and a daf basis at some reference condition. Subscript 0 in $\rho_{a,0}$, $\rho_{c,0}$ and $x_{a,0}$ refers to the initial particle/char properties. Subscript 1 in $\rho_{p,1}$ the char property at the beginning of gasification (or the end of devolatilization). However, the subscript can also refer to the initial char properties, or the particle properties at the end of devolatilization, in which case $b_0$ and $b_{daf,0}$ range from about 0.8 to 0.95, depending on fuel and reactor conditions.

A rigorous and general expression for the dependence of the diameter on burnout is

$$\frac{m}{m_0} = 1 - b = \frac{\rho_p d_p^3}{\rho_{p,0} d_{p,0}^3}$$

or

$$d_p = d_{p,0} \left[ \frac{\rho_{p,1}}{\rho_p} (1 - b) \right]^{\frac{1}{3}} = d_{p,0} \left[ \frac{\rho_{p,0}}{\rho_p} \left( 1 - b_{daf}(1 - x_{a,0}) \right) \right]^{\frac{1}{3}}$$

where $d_{p,0}$ is the diameter at reference conditions 0, which again can be either the initial particle or the initial char.

The previous equation for the ratio of the particle densities and its dependence on burnout,

$$d_p = d_{p,0} \left[ \frac{\rho_{p,1}}{\rho_p} (1 - b) \right]^{\frac{1}{3}} = d_{p,0} \left[ \frac{x_{a,0} \rho_c + \rho_a (1 - b_{daf}) (1 - x_{a,0})}{x_{a,0} (\rho_{c,0} - \rho_{a,0}) + \rho_{a,0}} \cdot \frac{\rho_{a,0} \rho_{c,0}}{\rho_a \rho_c} \right]^{\frac{1}{3}}$$

is
This expression is rigorous and general. It is reasonable to assume that the ash density is constant but that the char density changes with burnout. Char porosity models describe the changes in the char density and porosity with burnout. As mentioned earlier, a convenient and rational model for the change in char density with burnout is

$$\frac{\rho_c}{\rho_{c,0}} = (1 - b_{daf})^n = \left(1 - \frac{b}{1 - x_{a,0}}\right)^n$$

where $n$ is 0 for constant density behavior, 1 for constant diameter behavior, greater than 1 for swelling behavior, and generally between 0 and 1 for oxidation and gasification reactions. This substitution and a constant $\rho_a$ assumption lead to

$$d_p = d_{p,0} \left[ \frac{\rho_{p,0}}{\rho_p} (1 - b)^{\frac{1}{3}} \right]$$

$$= d_{p,0} \left[ \frac{x_{a,0}\rho_c (1 - b_{daf})^n + (1 - b_{daf})(1 - x_{a,0})}{1 - x_{a,0}} + \frac{x_{a,0}\rho_{c,0}}{\rho_{a,0}} \right]^{\frac{1}{3}}$$

Density and diameter changes during pyrolysis usually differ markedly from those during char oxidation, with diameter often but not always increasing during pyrolysis. Quantitative pyrolysis behavior characteristically involves a swelling factor and a pyrolysis or char yield. These factors can be included in the above description as follows:
\[
d_p = d_{c,0} \left[ \frac{(c_0 - b_c - x_{a,0})^{1-n}(1 - x_{a,0}) + x_{a,0} \rho_{c,0}}{1 - x_{a,0} + x_{a,0} \rho_{c,0}/\rho_a} \right]^{1/3}
\]

(52)

\[
= d_{p,0,s} \left[ \frac{(c_{0,daf} - b_{c,daf})^{1-n}(1 - x_{a,0}) + x_{a,0} \rho_{c,0}}{1 - x_{a,0} + x_{a,0} \rho_{c,0}/\rho_a} \right]^{1/3}
\]

Where \(d_{c,0}\) is the initial char diameter and \(c_0\) is the char yield on a with-ash basis, and where \(s = \frac{d_{c,0}}{d_{p,0}}\) is the swelling factor.

This provides a quantitative expression for biomass particle diameter (size) as a function of burnout. The remainder of this discussion compares this expression with measured data. These data use equant (aspect ratio = 1) cylindrical particles and sphere-equivalent diameters, although practical biomass fuels come in widely varying sizes and shapes. Previous work documents how these shapes affect fuel conversion rates and quantitative modeling approaches for describing this size effect [20].

### 6.2.2 Dynamic char diameter variation

Although the shape of the particle in the experiments is considered as cylinder, the introduction of the spherical-equivalent diameter is still necessary [20]. In this model, a spherical particle with the same volume as the cylindrical particle is calculated. For a cylindrical particle, the diameter or radius of the base and the height is accessible, with which to calculate the volume [114].
Figure 34. a) Normalized sphere equivalent diameter based on the 3-D optical camera image data, y-axis is the normalized diameter over initial diameter $d_0$ and x-axis is residence time, b) Normalized height, y-axis is the normalized diameter over initial diameter $h_0$ and x-axis is residence time, c) Normalized diameter of the base, y-axis is the normalized diameter over initial diameter $D_0$ and x-axis is residence time.

Figure 34 illustrates the equivalent diameter results corresponding to kinetic data in Figure 21. The results in Figure 34(a) reveal that particle size has a much larger influence on the reaction rates than is commonly acknowledged. The measured diameter, normalized by the initial diameter, changes from 0.75 to 0.65, while the measured mass, normalized by the initial mass, is about 0.88, which implies a diameter ratio of 0.49 is necessary to maintain a constant particle density. The diameter of the base and the height of the cylindrical particle show the same trend in Figure 34(b)
and Figure 34(c). Despite the spikes in Figure 34(a), which is probably caused by an error in the shape of the particle due to the brightness of the images, the trends in the diameter generally agree with the kinetic data in Figure 21 if one assumes a combustion regime in which density changes much more than diameter. As gasification is kinetically limited at these experimental conditions, the diameter of the char should stay constant after devolatilization. However, the trends in Figure 34(a) indicate different results. Initially the diameter drops rapidly during the last stages of devolatilization. The diameter change is much more modest during gasification. Neither a constant diameter nor a constant density model accurately describes the observed diameter changes. Isothermal particles whose diameters change during reaction frequently also have internal (pore) mass transport limitations. However, these particles are not isothermal. The endothermic gasification reaction cools the center of the particle such that, even under kinetic control, it reacts more slowly than the surface. Therefore, in these cases the shrinking particle size with time is not indicative of mass transfer affecting the reaction.

6.2.3 Diameter model development

Figure 35 illustrate 3/8-inch poplar char diameter variation data. The green and orange bands show the single-point and multiple-point prediction bands for the newly developed diameter model in this investigation. The red solid line shows the prediction data by the traditional diameter model derived from equation 27. The red prediction line matches well with the measured data (green dots) especially during the first stage of gasification process. However, the red prediction line deviates from the measured data when it is approaching the end of char conversion. Consequently, it is essential to develop a new model to precisely predict the char diameter variation during its entire life. The crucial change to the diameter model is to recognize that the factor n cannot be constant during burnout. No real particle can have a value of 1 under the conditions in this investigation.
because (1) the temperature gradient, and (2) the net flow of gas out from the particle. These effects
will cause the outer layers to burn faster than the inner layers, and as they do, they will generate
high specific surface area, which will make them burn even faster. As a result, as char conversion
progresses, the factor n should change. This investigation empirically developed the new diameter
model in the dependence of n on burnout depends on many things (surface area model, kinetic
model, temperature gradient model, etc.), but the effect is more than linear.

\[
\frac{d_p}{d_{p,0}} = s \left( \frac{(1 - b_{daf})^{1-n(1+ab_{daf}^2)} + d}{1 + d} \right)^{1/3}
\]  

(53)

Where \(d_{p,0}\) is the initial particle diameter and \(d = (\frac{x_{a,0}}{1-x_{a,0}}) \cdot \frac{\rho_c}{\rho_a}\) is the parameter
determined by char property, and \(a\) is the empirical parameter in this new diameter model.

Figure 35. Illustration of experimental (dots) and predicted (solid line) poplar char
diameter data. Red line shows the prediction line derived from traditional diameter model,
y-axis is the normalized diameter ratio and x-axis is char conversion.
Figure 36. Illustration of 3 experimental (dots) and predicted (solid lines) poplar char diameter data, y-axis is the normalized diameter ratio and x-axis is char conversion.

Figure 37. Examples of joint confidence intervals of a and n in the diameter model.

For the three poplar particles analyzed in Figure 36, this gave the following results (s and d were calculated from initial properties for all three fuels, namely the initial char particle diameter
over the initial particle diameter 0.8 and 0.015, respectively. Figure 36 indicates great fit to the three experimental trends using the new diameter model, especially for the late stage of burnout. The statistical analysis gives the joint confidence intervals of $\alpha$ and $n$ in Figure 37, which shows that each case has in Figure 36 has a unique set of optimal parameters $\alpha$ and $n$.

### 6.3 Char surface area and porosity dynamics

#### 6.3.1 Surface area vs char conversion

Chars produced with the reactor temperature of 1150 °C at different residence times in different reacting conditions, which are 50% CO$_2$ + 7% H$_2$ + balance N$_2$, 90% CO$_2$ + 7% H$_2$ + balance N$_2$, and 30% H$_2$O + 7% H$_2$ + balance N$_2$. The 7% H$_2$ eliminates potential residual O$_2$ in the reactor, which is measured to be < 0.1%. The surface area measurements were undertaken by N$_2$ adsorption at 77 K.

![Figure 38. Surface area from N$_2$ adsorption for ¼ inch poplar wood in different reacting conditions (50% CO$_2$, 90% CO$_2$, and 30% H$_2$O) at 1150 °C as a function of conversion.](image)
Char yield is the fraction of the initial daf (dry ash free) fuel converted to char, or the daf volatile yield subtracted from unity. Char conversion represents the fraction of char yield converted to gases and provides a convenient means to compare experiments under widely differing conditions of temperature, reactant composition, particle size, and particle properties. The surface area data are converted from residence time to char conversion (Figure 38).

![Char conversion graph](image)

**Figure 39.** Predicted normalized gravimetric surface areas as a function of conversion for the random pore, shrinking core, and volumetric pore models assuming the density varies with conversion as $\rho_{p,0}(1 - X)^n$. The data indicate that $n$ in these experiments lies closer to 0 and that these pore models would predict behaviors intermediate between those illustrated here and those indicated in Figure 9.

Figure 38 illustrates the development of char $N_2$ specific surface area as a function of poplar char conversion during gasification with varying amounts of $CO_2$ and $H_2O$. $N_2$ specific surface areas range from 300 to 600 $m^2/g$. Each data set includes duplicates indicating reproducibility. In general, specific surface area increases with char conversion, and remains relatively constant near the end of burnout. The specific surface area of three different chars produces almost the same
values, with slight difference, especially near the beginning of gasification. Chars in 50% CO₂ show the lowest specific surface area, while chars in 90% CO₂ show the highest specific surface area, and the differences are statistically significant. The N₂ specific surface areas illustrated here develop differently that those predicted by any of the previously mentioned surface area models (URCM, VM or RPM). The mechanisms driving these changes appear to differ from those from coal chars on which the other models are based.

The specific surface area, \( S_g \), in Figure 38 relates to the volumetric surface area, \( S_V \), in Figure 9, as follows:

\[
S_V = \frac{S}{V_p} = \frac{S}{m_p/\rho_p} = \rho_p S_g
\] (54)

A useful relationship between the particle density and mass conversion comes from

\[
\frac{\rho}{\rho_0} = \left(\frac{m}{m_0}\right)^n = (1 - X)^n
\] (55)

where \( n = 0 \) corresponds to a constant-density process, \( n = 1 \) corresponds to constant-diameter process, \( n > 1 \) represents particle swelling behavior, and \( n < 0 \) represents particle sintering or some other mechanism by which diameter decreases without or at least faster than mass change. Intermediate values represent some intermediate behavior among these defined points. A suitable choice for \( n \) renders this equation exact if \( n \) can vary with conversion, but the equation is most useful if the value of \( n \) remains nearly constant. Using this expression,

\[
S_V = \rho_p S_g = \rho_{p,0} \left(\frac{m}{m_0}\right)^n S_g = \rho_{p,0} (1 - X)^n S_g
\] (56)

or

\[
\frac{S_g}{S_g^0} = \frac{S_V}{S_V^0} (1 - X)^{-n}
\] (57)
Particles that react at constant diameter \((n = 0)\) produce identical normalized volumetric and normalized gravimetric surface areas. Particles that react with varying diameters produce normalized gravimetric surface areas that can differ markedly from the normalized volumetric surface areas and that do not necessarily become zero as conversion approaches 1. In these experiments, the empirically measured values of \(n\) are relatively small, in which case the gravimetric surface area behavior differs modestly from the volumetric trends illustrated previously in Figure 9. A value of \(n = 0.5\) predicts normalized gravimetric surface areas that vary with conversion for the various models as indicated in Figure 39.

It is clear that the data of Figure 38 cannot be even qualitatively described by any of the pore models discussed in the introduction that commonly describe coal chars. Specifically, the data show unambiguous though modest surface area increases of 25-50% over the entire char lifetime and over a range of reactant concentrations while all the models indicate surface area decreases in the last half of char conversion, with only the random pore model showing any increase, but this is limited to low char conversions and even then only with high parameter values. The central feature of the pore models is that pore diameters grow and begin coalescing as they overlap with each other. This gives rise to a specific surface area that decreases with increasing conversion. The data reveal no such increase even at high char conversions. It is clear that the models fail to capture the observed behavior, and the assumption of coalescing pores lies at the core of this discrepancy, as demonstrated shortly.

Figure 40 illustrates typical mass loss and global reaction rate data as a function of time for poplar char gasifying in a 50% \(\text{CO}_2\) and 0% \(\text{H}_2\text{O}\) environment, identical to the reactant gas compositions in Figure 38. The gasification global reaction rate (based on particle external surface area and surface reactant composition) remains constant after devolatilization for most of char
conversion, decreasing rapidly in the final moments of char reaction. The occasional spikes in reactivity correspond to measured spikes in particle temperature that figure into the kinetic analyses discussed separately.

Figure 40. Measured mass loss (blue dots), predicted mass loss using the regressed parameters (red line), and reaction rate derived from the measured data (dot-dashed green line) for ¼ inch poplar particle, including the normalized daf mass loss (left axis) and overall reaction rate (right axis) while reacting in a 50% CO₂ and 0% H₂O environment with a reactor temperature of 1150 °C.

The reaction rate in Figure 40 remained constant while the specific surface area in Figure 38 increased with char conversion. This indicates that the specific surface area measured by N₂ adsorption is not proportional to the intrinsic reaction rate, as is very commonly assumed. At least three possibilities could explain these data: 1) the number of effective sites on the surface remains constant during the reaction despite increasing surface area; 2) the gasification reaction is a balance between the formation and destruction of effective sites due to increasing, overlapping and
consumption of pores in the chars; and 3) the specific surface area measurements do not track the surface area involved in the reactions because of pore size or other effects.

6.3.2 Surface area among three fuels

Table 11 summarizes the measurements of N2 adsorption on chars generated near complete char burnout (> 90% char conversion) in different gasification conditions. Consistent with the literature conclusions [59],[71], switchgrass chars generate lower surface area than poplar char, which is due to the difference in ash content between these two chars. Although most publications suggest that ash content acts as a catalyst in gasification reactions, the kinetic data collected in this paper definitively establish that ash decreases reaction rates because of its effect on available surface area. Herbaceous materials nearly always have much higher alkali and alkaline earth contents than ligneous materials, and these are the two most common classes of ash compositions associated with catalytic effects. The herbaceous materials with high ash contents tend to exhibit lower specific char surface area than woody samples under identical reacting conditions (Table 11).

<table>
<thead>
<tr>
<th></th>
<th>N2 BET Surface area m²/g</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>30% H2O</td>
</tr>
<tr>
<td>Poplar</td>
<td>508</td>
</tr>
<tr>
<td>Switchgrass</td>
<td>369</td>
</tr>
<tr>
<td>Corn stover</td>
<td></td>
</tr>
</tbody>
</table>

Table 11. Surface area from N2 adsorption for biomass in different reacting conditions (50% CO2, 90% CO2, and 30% H2O) at 1150°C with full char conversion.
6.3.3 Pore diameter vs surface area

Pore size distribution determines accessibility and diffusion rates in and out of pores and, together with surface area, characterizes char characteristics important to reactivity. Essentially all pore development theories predict that pore sizes increase with increasing char conversion. Figure 41 illustrates this increase for the chars produced from different reacting conditions in terms of average pore diameter, which ranges from 1.5 nm to 2.5 nm. As to the pore size distribution, over 90% of the pores in the char are in micro size (Figure 42). As shown in Figure 42, over 90% of the pores in the char are in micro size. The great majority of the pore volume and area lies well below one mean-free path (about 500 µm) of the gas molecules under the experimental conditions. Such pores lie well within the Knudsen diffusion regime and contribute relatively little to overall surface area availability.

Figure 41. N\textsubscript{2} adsorption average pore diameter (4V/A by BET) for ¼ inch poplar wood in three different reacting conditions (50% CO\textsubscript{2}, 90% CO\textsubscript{2}, and 30% H\textsubscript{2}O) at 1150\degree C with char conversion. The unit for diameter is nm.
The following discussion benefits from a clear definition of terms that lead to confusion in the literature. Isotherm surface area analysis commonly refers to a total external surface area, or an external surface area, which is the surface area contained in the meso and macro pores but excludes the surface area in the micro- or nano-pores. The kinetics and catalysis literature frequently uses the same term (external surface area) to indicate the geometric surface area of a sphere or other particle of a specific shape. These numbers differ substantially in both concept and quantitative measure. To avoid this confusion, this discussion defines external surface area as the meso- and macro-pore surface area as is reported by the BET analysis and the term geometric surface area as the surface area of a sphere or other geometric shape of a given size.

![Figure 42. Pore size distribution (incremental pore area and incremental pore volume) for ¼ inch poplar char reacting in a 0% CO₂ and 30% H₂O at 1150 °C.](image)

Tremel et al. [27] concluded that char gasification with CO₂ and steam (H₂O) occurred mostly at the surface of micro-pores. Figure 40 implies that the reaction rate is almost constant after devolatilization, which means the micro-pore surface area stays constant while the surface area of meso-pores and macro-pores increase. Figure 43 illustrates the essentially constant surface area of the micro-pores and the slightly increasing total external surface area.
Figure 43. Micro-pore area (a) and external surface area (b) for ¼ inch poplar wood in three different reacting conditions (50% CO$_2$, 90% CO$_2$, and 30% H$_2$O) at 1150°C with char conversion. The unit for surface area is m$^2$/g.

6.3.4 Porosity vs char conversion

Biomass char exhibits high porosity and surface area and is a common source of activated carbon. Porosity is an important parameter in determining the reactivity. The porosity ($\phi$) is calculated as the ratio between the void (pore) volume ($V_p$) and total volume ($V_t$) of the char particles, which is given by,

$$\phi = \frac{V_p}{V_t} = \frac{V_p}{V_p + V_s} = 1 - \frac{V_s}{V_t}$$  \hspace{1cm} (58)

where $V_s$ stands for solid volume.

The image data taken by the RGB cameras provide the information to calculate the total volume of the char particles. The solid volume relates to the weight of the char particles ($m_{char}$) and the true density ($\rho_t$), as follows

$$V_s = \frac{m_{char}}{\rho_t}$$  \hspace{1cm} (59)
Therefore, the porosity is described as,

\[
\phi = 1 - \frac{m_{\text{char}}}{\rho_t V_t}
\]  

(60)

Figure 44. Porosity for ¼ inch poplar wood in three different reacting conditions (50% CO₂, 90% CO₂, and 30% H₂O) at 1150°C with char conversion.

This investigation did not directly measure true density. The true density depends quite strongly on experimental technique and definition and cannot be determined completely objectively. The main complication is that different techniques find increasingly smaller pore volumes, including smallest pores comparable to molecular sizes and distances between crystalline layers in molecular structures. Impure, non-crystalline carbon materials such as biomass chars have molecular structures that are especially difficult to characterize in this regard. The literature discusses mercury porosimetry data with a wide range of true densities. However, those that exclude micro-pores from the solid mass indicate true densities of 1.5 and 3 g/cm³ [115-116]. Other investigators report pycnometry results that suggest a true density of 1.9 g/cm³ [117]. Diamond density (3.5 g/cm³) and graphite density (2.2 g/cm³) place logical upper limits on char true density. Figure 44 exhibits measured porosity for ¼ inch poplar char in three reacting
conditions (50% CO$_2$, 90% CO$_2$ and 30% H$_2$O) at 1150 °C assuming a true density of 1.9 g/cm$^3$, which is from Mermoud’s investigation. Lower true densities yield lower porosities. The porosity increases monotonically with char conversion. The porosity of the chars generated from 50% CO$_2$ is slightly lower than the porosity of chars generated from the other two reacting conditions. The char porosity, much like the surface area, increases monotonically with conversion. However, the changes in average pore diameter (Figure 41) do not even approximately account for the change in porosity.

6.3.5 Pore structure evolution

![Figure 45. Single point adsorption total pore volume for ¼ inch poplar wood in three different reacting conditions (50% CO$_2$, 90% CO$_2$, and 30% H$_2$O) at 1150°C with char conversion. The unit for pore volume is cm$^3$/g.](image-url)
Pore volume analyses further confirm these trends. Some literature indicates that biomass char shares a similar chemical structure with coal, hence some models which were developed for coal char could be applied in predicting biomass char reactivity [8],[20],[118-119]. However, the pore models discussed previously all incorrectly describe the observed surface area and pore structure of biomass char in this investigation both qualitatively and quantitatively. All of the models indicate surface areas decreases during the last stages of conversion.

![Figure 46](image_url)

**Figure 46.** Micro pore volume for ¼ inch poplar wood in three different reacting conditions (50% CO₂, 90% CO₂, and 30% H₂O) at 1150°C with char conversion. The unit for pore volume is cm³/g.

Uniquely, the RPM predicts a local maximum in surface area and char reactivity for coal char during conversion. The surface area decreases after this maximum point because pores begin to overlap and merge as they grow. The surface area of biomass char increases continuously as the char conversion proceeds until the end of burnout (Figure 38). Furthermore, these biomass chars are highly porous, more so than coal chars, and would normally be expected to enter the
overlap/merge stage of pore growth at earlier stages of char conversion than do coal chars if they had similar pore structures. The increases in total pore volume (Figure 45) together with the increases in surface area (Figure 38) result from pore enlargement. Meanwhile, the micro-pore volume is almost constant for all three reacting conditions (Figure 46), which when combined with the pore surface areas measurements, indicates that the number and size of micro-pores stays constant, while the size of larger pores increases, consistent with the observations in Figure 41 and Figure 43.

6.3.6 Qualitative SEM indications

SEM images of the biomass particles confirm the essential findings of the quantitative analyses indicated above. Figure 47 illustrates SEM images of the cross-grain (left) and surface (right) features of poplar particles at the earliest stages of char conversion. These initial char images are most notable for their vascular structure and rather remarkable preservation of essentially every detail of the organic structure despite losing over 90% of the initial mass during pyrolysis. In addition to the vascular vessels, the particles include fracture planes and organic features that span a considerable distance through the grain. Particle drying, but not necessarily pyrolysis, creates some of the fracture planes while organic growth patterns create other similar features. These large-scale features become much more important in much larger particles [117]. They play a minor role in these experiments. During most of char gasification, the particle images show how the particle maintains a similar shape and size (Figure 48). However, the photographic images show that in the final stages of burnout, changes in the particle shape and size become more pronounced and SEM images confirm that the well-formed cells and structure apparent during nearly all of the char conversion begin to finally disintegrate, with only a skeleton of the cellular structure remaining and an exceptionally fragile and porous framework (Figure 49).
Figure 47. SEM images of the cross-grain (left) and surface (right) features of poplar particles at the earliest stages of char conversion.

Figure 48. Typical continuous examples of poplar char gasification reaction approaching burn-out. The first two images illustrate the particle shape and size for char conversions of 0-90+%. The remaining images illustrate the last approximately 3% or so of char conversions.
Figure 49. SEM image of the fragile surface of poplar particles at late char conversion.

The particle surface temperature somewhat exceeds that of the particle core primarily because the endothermic reaction creates a temperature profile that decreases in the direction of the particle center. Therefore, the particle surface reacts somewhat faster than the core. In the latest stages of char combustion, this difference in reaction rate leads to the surface of the particle disintegrating prior to its core. In the data of Figure 48, this disintegration of the particle surface begins at char conversions exceeding 90%. As particle size increases, this effect becomes larger, consistent with the measurements on particles much larger than these [117].
These results suggest that the vascular structure of the chars effectively transports reactants and products through the particle structure for over 90% of char conversion. Most of the reaction occurs on the walls of these vascular channels, which are too large to be measured by BET techniques but are evident in the particle porosity changes. The data indicate essentially no change in micro- and meso-pore sizes during char conversion and only modest changes in macro pore sizes. The porosity data exhibit the greatest sensitivity to char conversion, consistent with the walls of the vascular channels being the most actively consumed regions of the char. Pore size distributions indicate that the char exhibits essentially no change in the smallest but highest surface area micropores despite losing more than 90% of the char mass. This indicates that the vascular channel walls, which have high micro-porosity, gasify to uncover similar microporous structures below them but that the micro- and meso-pores themselves do not appreciably grow.

The conceptual image of gasification indicated by these data involves reactants moving through the biomass char vascular structure and gaining essentially unimpeded access to the entire particle. Gasification occurs primarily on the walls of these vascular tubes, with no change in the traditional micro- and meso-pores and measurable but relatively minor change in the traditional macro-pores. The vascular network enables much more effective reactant penetration than would occur in a randomly porous particle and drives changes in surface area and porosity that differ markedly from those of randomly porous materials [111]. The vessel walls thin as they react. However, they only lose structural integrity in the final stages of burnout, as evidenced by the SEM images. All of this process is in stark contrast to metaplast-forming chars, such as coal and black liquor chars [120], which have more random porosity (at least for high-rank coals) and much less efficient transport through these pores.
6.4 Non-catalytic ash effects

Refractory material such as ash contents on the surface of particles should affect reaction rates, though literature rarely discusses and even more rarely document this effect. The data collected in this investigation definitively establish two primary effects of inorganic material with both theoretical and practical implications. One effect is on the particle size and the second is on the available surface area for reaction. The first is included in most models though rarely explicitly discussed. The second is rarely included in models but has a pronounced effect on observed rates. The three fuels and their corresponding ashes used in this investigation differ markedly in their ash contents (Table 2), providing a good basis for investigating the effects of ash on reactivity.

6.4.1 Ash model

![Graph showing the ash effect on predicted mass loss and reaction rate](image)

**Figure 50. Illustration of the ash effect on predicted mass loss and reaction rate for ⅛ inch poplar fuel reacting in 50% CO₂, 0% H₂O and balance N₂ at 1250 °C.**
Figure 51. Illustration of the ash effect on predicted mass loss and reaction rate for ⅜ inch switchgrass fuel reacting in 50% CO₂, 0% H₂O and balance N₂ at 1250 °C.

Figure 52. Illustration of the ash effect on predicted mass loss and reaction rate for ⅜ inch corn stover fuel reacting in 50% CO₂, 0% H₂O and balance N₂ at 1250 °C.
Figure 50 through Figure 52 illustrate measured and predicted mass loss data (left axis) and predicted reaction rates (right axis) of three different biomass fuels of the same initial size (3/8-inch cylindrical pellets with aspect ratio of 1) and reacting conditions of gas composition (50% CO₂, 0% H₂O, balance N₂) and temperature (1250 °C). As before, the predicted mass loss and reaction rate data show result including and excluding this ash effect. As seen, the differences are slight when there is little ash in the fuel but become increasingly larger, to the point of a first-order consideration, as the ash content increases.

Figure 50 typifies the kinetic behavior of 3/8 inch poplar char reacting in 50% CO₂, 0% H₂O and balance N₂ at 1250 °C. In this case, measured oxygen concentrations are about 0.045% and close to the equilibrium values at the temperatures of the heating elements, and measured particle temperatures on the surface and reactor center vary during the reaction, which ranges from 830 to 870 °C on the surface during gasification, increasing with increasing extent of reaction, and with center temperature about 50 °C lower than the surface temperature during gasification. The differences in center and surface temperature are many hundreds of degrees during pyrolysis. During gasification that endothermic reaction cools the particle interior and results in a difference of a few tens of degrees. Pyrolysis usually lasts for 1 minute, which represents a rapid process of mass loss. The predicted mass loss lines with ash effect and without ash effect overlap until about 20 minutes of the gasification reaction and diverge afterwards. Char with no ash content reacts slightly faster than ash-containing char based on the particle model, though the difference in this case is quite small.

Similar trends are founded in the kinetic reaction rate lines. The reaction rate with no ash effect remains nearly constant after the end of devolatilization except at the instant of final burnout, where it drops considerably. The reaction rate of char with ash effect is slower and starts to drop
earlier during the gasification process. By comparison to the next sets of data, these differences are also fairly small. Although the particle temperature slightly increases during char conversion, the reaction rate slightly drops. This drop is caused by a slowly decreasing particle size which more than compensates for the effects of the slightly increasing temperature on overall reaction. All of the predicted rates shown here use the measured particle temperatures as part of the prediction. These measured temperatures feature occasional spikes, which increases the range of particle temperature behaviors in an experiment that otherwise contains relatively little change in temperature. These spikes appear as instantaneous in the figures but actually last for many measurement points.

Figure 51 and Figure 52 illustrate the kinetic behavior of 3/8 inch switchgrass char and corn stover char, respectively, reacting in conditions nominally identical with that of the poplar char in Figure 50. The switchgrass and corn stover fuels produce about 4.15% and 20.0% ash, respectively, compared with the poplar ash of 0.55% (Table 2). These are increases in ash of approximately a factor of 8 and 40, respectively. The data in Figure 51 and Figure 52 show qualitatively similar trends with Figure 50, but the difference between the predicted mass loss lines with and without including the ash effect increases significantly as the amount of ash increases. The ash content of residual char increases continuously from the initial values shown in Table 2 to 100 percent as these fuels approach total burnout. However, the high ash content fuels reach high ash fractions much sooner than the low ash content fuels. The rate of curvature in the predicted and measured mass loss curves reflects the effect of the increasingly higher amounts of ash on reaction rate, as discussed shortly.

The reaction rates with the ash effect are lower than that with no ash effect, which indicates the negative effect of ash contents on the observed reaction rate. It is possible that there are also
catalytic effects here, though this is unlikely as discussed below. Whatever catalytic effects there might be, the effects seen here predominantly come from non-catalytic behavior in that they decrease rather than increase the observed reactivity. The model described below quantitatively describes these effects over this broad range of initial ash contents (factor of 40) and during the entire char conversion history. The data definitively establish these first-order effects of ash on char reactivity for the first time and the quantitative model predictions capture these effects convincingly enough sand over a broad enough range of conditions that its conceptual framework is very compelling. Due to this ash effect, the total reaction time of poplar char is the shortest, while the total time of corn stover char is the longest even though the reactivity of the organic portion of the fuel is comparable [113].

6.5 Size effects

The external-surface-area (global kinetics) rate of a first-order reaction frequently used to model heterogeneous reactions depends on a reaction rate coefficient and reactant concentration as

\[-r = -\frac{1}{A} \frac{dm}{dt} = e k y_s p = \frac{e k y_b p}{1 + \frac{k e d R T_f}{D_{AM} S h \theta_m}}\]  

(61)

where \(A\) is the external surface area, \(\epsilon\) is an efficiency factor, \(m\) is the mass of the char, \(t\) is time, \(k\) is the reaction rate constant, \(y_b\) is the bulk mole fraction, \(y_s\) is the surface mole fraction, \(p\) is the total pressure, \(d\) is the diffusion distance, \(R\) is the gas constant, \(T_f\) is the film temperature, \(D_{AM}\) is the effective diffusivity, \(Sh\) is Sherwood number, and \(\theta_m\) is the mass transfer blowing factor. The first expression represents the rate in terms of the surface partial pressure of the reactant and the second expression is the rate in terms of the bulk partial pressure. The rate, expressed as
moles or mass per unit external surface area per unit time, is independent of particle diameter if reacting under kinetically controlled conditions (surface and bulk reactant concentrations equal) with no pore diffusion resistance. The rate increases with decreasing diameter as external diffusion become increasingly important. The kinetic rate never decreases with decreasing diameter. In stark contrast, the rate of mass loss,

\[ -\frac{dm}{dt} = AMr = \frac{\pi d^2 M \phi \epsilon p y_b}{1 + \frac{k \epsilon d R T_f}{\mathcal{D}_A M S h \theta_m}} \tag{62} \]

which is measured in units of mass change per unit time, depends strongly on diameter and in all cases should decrease with decreasing diameter unless there are temperature effects that compensate for size changes. In the kinetic limit, the rate decreases proportional to \( d^2 \), with a slightly weaker dependence as external diffusion becomes more important. In all cases, the mass loss rate approaches zero as the diameter decreases. The particle mass also approaches zero and scales proportional to \( d^3 \), which is a stronger dependence than the mass loss rate, which is why the particles burns out in finite time and why neither the particle dry-ash-fee mass nor the mass loss rate asymptotically approaches zero, even if the particle contains no ash.

The presence of a refractory component (ash) in the particle prevents the particle diameter from ever becoming zero, with the limiting size being larger as the initial ash content increases. Biomass generally produces relatively small char yields and the corresponding increase in ash can be quite pronounced. Unlike oxidation, which often occurs at or near external-diffusion-limited rates, gasification is comparatively slow and particles can react at or near kinetically limited rates. The ratio of the surface mole fraction of reactants to the bulk mole fraction is 0.95 or higher in these experiments, with typical values being about 0.98, indicating that external diffusion resistance to mass transfer is negligible.
\[
\chi = \frac{k_{rxn} \cdot P_{CO2, surface}}{v \cdot h_m \cdot C_{CO2,\infty}} = \frac{k_{rxn} \cdot P_{CO2, surface}}{v \cdot h_m \cdot \frac{P_{CO2,\infty}}{R \cdot T_{gas}}}
\] (63)

As a result, our experiments measure the mass loss rate under conditions with minimal external diffusion influence. The analysis includes transport effects, but their influence on the results is small.

Particle diameter changes affect reaction rates of isothermal, homogeneous particles according to the following classical trends:

1. Particles with significant transport resistance exhibit nearly constant-densities and shrinking diameters and their mass loss rate (as opposed to mass flux) decreases toward the end of their lifetimes as their diameters decrease. They decrease more rapidly if they have minimal amounts of refractory than if they have large amounts of refractory, regardless of whether kinetics, external transport, or a combination controls the reaction rate. In equation 62, External diffusion limited mass loss rates should decrease approximately proportional to the diameter if the reaction rate coefficients remain unchanged.

2. Particles reacting with constant diameters and changing densities should show no change in mass loss rates with particle diameter but may show changes associated with reactive surface area.

Essentially all particles in this investigation exhibit particle diameter decreases during char conversion despite being kinetically controlled. The relatively large, highly porous particles have low thermal conductivities and the endothermic reactions decrease the center temperature relative to the surface temperature, causing the surfaces to react more rapidly than the center even though the reactant concentration has relatively little gradient.
The ash-induced changes in reaction rates increase as the char conversion increases and ash mass fractions approach unity. As the ash content increases, so does the minimum particle diameter. The effects of ash on particle size and mass loss rate become decreasingly observable as initial ash content increases. However, these changes are difficult to ascertain from discrete kinetic data with low char conversion resolution. The changes in reaction rate could be interpreted either as changes in kinetic parameters or changes in reactive surface area with such data. The present continuous analysis provides definitive evidence that at least these char reaction rates do not involve changes in kinetic parameters but rather changes in reactive surface area and may provide a more fundamental and accurate explanation for changes of apparent kinetic reactivity in late stages of burnout.

![Figure 53](image)

**Figure 53.** Change in particle reaction rates as particle diameter approaches zero for external diffusion control (dashed, red line) and kinetic control (solid line). Time/particle conversion increases from right to left in this plot. Residual ash contents that result in particle sizes of 5 microns or more would largely eliminate an observable change in slope.

Figure 53 illustrates the change in particle reaction rates as particle diameter approaches zero for external diffusion control (dashed, red line) and kinetic control (solid line). Time/particle
conversion increases from right to left in this plot. Note that residual ash contents that result in particle sizes of 5 microns or more would largely eliminate an observable change in slope, and that the slope only changes under kinetic control. However, under kinetic control, the slope changes markedly in the last stages of burnout. Constant-diameter particle reaction results in mass loss rates independent of diameter (horizontal lines in this plot).

If the kinetic rate is not first order with respect to reactant concentration, the equations above change and, for arbitrary order, result in implicit forms. However, for any positive reaction order, the qualitative trend is the same – observed mass loss rates should decrease with decreasing diameter and the rate of decrease should be larger for particles with lower initial ash contents.

### 6.5.1 Available surface area effects

A refractory material also affects kinetic rates by reducing the fraction of the surface area that is reactive. It is not reasonable that a particle reacting under kinetically controlled rates and that contains measurable amounts of refractory material on the surface will react at the same rate as a particle with no refractory material. Under external diffusion control, the effects of refractory are possibly less significant since the upper limit of a reaction rate could be the same diffusion-limited rate with or without a fraction of the surface being inert if the reactant gas diffuses significantly in curvilinear directions in the boundary layer. Even then, however, observed reaction rate should decrease as increasingly larger portions of the surface become inert.

The effect of the refractory fundamentally depends on many unknown things. For example, a few refractory particle inclusions probably affect observed kinetic and mass loss rates differently than an equal mass of material uniformly distributed on the surface. The former provides a conceptual model of the effects of mineral inclusions such as silica deposits in biomass and the latter of the effect of organically complexed inorganics such as potassium and much of the calcium.
One tractable approach for describing this effect involves the volume fraction of refractory in the particle, which is generally calculable with only modest amounts of information and has a rigorous theoretical underpinning in a generalization of the stereological principle of Delesse et al. [121]. This theory contemplates a material containing two (or more) phases randomly arranged but not necessarily intimately mixed. For such a material, randomly sampled lines, surfaces, and volumes of the material contain, on average, the same fraction of any one phase as the overall volume fraction of that phase in the material. More specifically, 10% of a random char particle surface should contain ash if the particle contains 10% ash by volume. More generally, the fraction of any random surface occupied by one of the phases in that material should be proportional to the volume fraction of that phase in the body. This theory includes several important assumptions, including that the surface and all the phases (char and ash) randomly appear in the body. There is good reason to believe that the ash might preferentially accumulate on the surface as the char reacts and the surface recedes, but this principle still provides a quantitative starting point and a lower bound on the fraction of the surface occupied by ash (or any other phase) and the effects of such a refractory material on char reactivity. An additional factor could enhance it to accommodate the effect of preferential ash accumulation on the surface. The same description should pertain to any surface, specifically, to both the external surface area and the total (internal) surface area. The theory depends on the volume fractions, not mass or mole fractions. The volume fractions relate to the mass fractions as described below.

The volume fraction of component \( i \) in a particle, \( f_i \), is given by

\[
 f_i = \frac{x_i \rho_i}{\sum_j x_j \rho_j} \tag{64}
\]
where $x_i$ is mass fraction and $\rho_i$ can be any form of density (true, apparent, etc.) so long as it is the same for each phase. If the only components of the fuel are char and ash, represented by subscripts $c$ and $a$, respectively,

$$f_c = \frac{x_c}{\rho_c + x_a \rho_a} = \frac{1 - x_a}{\rho_c + x_a \rho_a} = \frac{(1 - x_a) \rho_a}{(1 - x_a) \rho_a + x_a \rho_c} = \frac{1}{1 + \frac{x_a \rho_c}{(1 - x_a) \rho_a}}$$

which ultimately depends on the two dimensionless parameters $x_a$ and $\rho_c/\rho_a$.

As char conversion progresses, the mass fraction of a refractory component increases from its initial value and depends on the residual char fraction as

$$\frac{m}{m^0} = \frac{x_a^0}{x_a}$$

In terms of normalized dry, ash-free mass ratio, the mass fraction is

$$m_{daf} = m(1 - x_a) \Rightarrow m = \frac{m_{daf}}{1 - x_a}$$

$$\frac{m_{daf}}{m_{daf}^0} = \frac{x_a^0 (1 - x_a)}{x_a (1 - x_a^0)} = \frac{m(1 - x_a)}{m^0 (1 - x_a^0)}$$

and the ash fraction is

$$\Rightarrow x_a = \frac{x_a^0}{m_{daf}^0 (1 - x_a^0) + x_a^0}$$

Perhaps most conveniently, in terms of relative daf mass loss or burnout, $g = 1 - \frac{m_{daf}}{m_{daf}^0}$, the fraction of the surface that is char and is capable of reacting, is

$$f_c = \frac{1}{1 - \frac{x_a^0 \rho_c}{(g - 1)(1 - x_a^0) \rho_a}}$$
which depends on two approximately constant dimensionless numbers, $x_a^0$ and $\rho_c/\rho_a$ and a third transient dimensionless number, the char burnout, $g$.

As mentioned earlier, this correction presumes randomly arranged ash and char with no preferential ash accumulation on the surface. Adjustments for preferential accumulation of ash on the surface depend on resistance of the ash layer to gas diffusion, the amount of preferential accumulation, and other parameters. However, the assumption of randomly distributed ash quantitatively explains the ash-surface area effect for all data collected in these experiments. Preferential ash accumulation seems conceptually logical, but in these cases, it appears that either the ash does not accumulate over the carbonaceous ash surface or it does not present any significant barrier to reactant access to the underlying carbonaceous material. However, it does represent an increasing fraction of the total surface area that is inert. Since ash densities exceed char densities by a large fraction, $\frac{\rho_c}{\rho_a}$ is a small number and the fraction of the surface occupied by the ash is small compared to the ash mass fraction. This ash effect becomes most evident and increases most rapidly near complete char burnout, as the ash fraction becomes very large.

This expression for available char surface area modifies the kinetic expression used to describe mass loss. In the simple case of a first-order reaction as used above, this would be

$$r = f_c e^{k y_a p} = \frac{f_c e^{k y_b p}}{1 + \frac{k e d R T_f}{D_{AM} Sh \bar{\theta}_m}} \quad (70)$$

Alternative expressions should similarly be modified to describe the decrease in available surface area associated with the increasing ash volume/mass fraction.

The predictions in Figure 50 to Figure 52 that best match the data points include this correction with no further modification to the reaction rate expressions. These corrections quantitatively capture the observed effects as a function of both initial ash content and of burnout.
This correction allows the same set of kinetic parameters to describe the reaction rates of all three fuels with reasonably accuracy. No alternative explanation for the burnout-dependent observed rate of reaction or the differences in the rates with respect to ash content appears likely to describe these data. This ash effect appears fundamental to char conversion.

![Figure 54](image.png)

**Figure 54. Illustration of the impact of ash on available reaction surface area as a function of fuel ash assuming a char to ash density ratio of 0.05 and for conditions otherwise similar to biomass fuels.** The correction for the low-ash fuel is small until the daf mass loss exceeds about 99% while the correction for the high-ash fuel becomes apparent much earlier. All corrections scale non-linearly with burnout.

This correction depends strongly on both initial ash content and extent of reaction. Figure 54 illustrates predicted results for three fuels with ash contents similar to those tested in this investigation: an initially high-ash fuel (dot-dashed black line, $x_a^0 = 0.20$), intermediate ash fuel (dashed blue line $x_a^0 = 0.040$) and low-ash fuel (solid red line, $x_a^0 = 0.0055$) for conditions otherwise similar to biomass fuels. The correction for the low-ash fuel is small up until the daf mass loss exceeds about 99% while the correction for the high-ash fuels becomes apparent much earlier. The magnitude of the correction (departure from unity) increases monotonically with
increasing mass loss in all cases. This is consistent with the expectation that ash in a low-ash fuel occupies less volume than in a high-ash fuel, and hence has a smaller effect on available surface area. The monotonic trend in the magnitude of the correction indicates that the ash mass and volume fractions increase with increasing burnout, increasingly removing available surface area.

Figure 55. Illustration of the ash impact on observed normalized mass loss for an initially high-ash fuel (dashed red line, $x_a^0 = 0.25$) and an initially low-ash fuel (solid blue line, $x_a^0 = 0.03$) for conditions otherwise similar to biomass fuels. The correction for the low-ash fuel is small up until the daf mass loss reaches about 99% while the correction for the high-ash fuel becomes apparent much earlier, both monotonically increasing with increasing mass loss. Time is normalized to approximate value required for 100% mass conversion.

These results show that high-ash fuels should exhibit an observable and gradual drop in mass loss rate during the last 10% of mass loss caused by loss of surface area to refractory material, with the drop becoming increasingly important and ultimately dominant as the particle approaches burnout. By contrast, ash-induced surface area losses in low-ash fuels occur only in the last 1% or so of mass loss and may not be distinguishable from noise. Figure 55 illustrates the predicted effects on mass loss.
6.6 Analysis of devolatilization/pyrolysis process and gas products

The pyrolysis process involves many complex reactions and product gases. The experiments here monitor CH$_4$, C$_2$H$_2$, CO, NO, CO$_2$, C$_6$H$_6$ and C$_7$H$_8$. CO is a difficult to analyze with the GC-MS because N$_2$ and CO have the same molecular weight and mass-to-charge ratio (m/z). To overcome this difficulty, argon is used as purge gas to create an atmosphere nearly free of N$_2$. Example data from this task appear in Figure 56, which displays gas species during pyrolysis of ⅜ inch poplar in 50% CO$_2$ and 0% H$_2$O at 1150 °C. The data show that H$_2$O appears first, followed rapidly by benzene and toluene, then by C$_2$H$_2$, CH$_4$ and NO. The sharp cutoff at the end of the process represents limitations in sampling high molecular weight gases in this manner, not an abrupt termination of pyrolysis. Indeed, pyrolysis tails off slowly with the heaviest compounds becoming increasingly larger fractions of the mass loss as tar.

![Figure 56. Analysis of pyrolysis gases for a 3/8 inch poplar wood in 50% CO$_2$ and 0% H$_2$O environment with a reactor temperature of 1150°C.](image-url)
7 CONCLUSIONS

Poplar, corn-stover, and switchgrass biomass particles reacted via heterogeneous gasification with H\textsubscript{2}O and CO\textsubscript{2} over a broad range of both reacting gas concentration (0-90\%) and reactor temperature (1150 °C - 1350 °C).

Despite the model is simplified due to the assumptions above, and some neglected terms, certain important properties of the particle and the intrinsic reactions are obtained based on the experimental data in the model, such as the swelling factor, char yield, diameter ratio, surface area, density, ash content and relative velocity of the reactant gases. The data regarding these terms and the analyses in the experiments are as follows:

1. Biomass raw materials in the experiments are mainly obtained from heartwood, corn stover and switchgrass, with an extensive range of both organic and inorganic components, nevertheless, no cardinal differences appear in the char gasification parameters.
2. H\textsubscript{2}O and CO\textsubscript{2} are the two reactant gases in biomass gasification reactions, namely particles are gasified in H\textsubscript{2}O and CO\textsubscript{2} either alone or in combination with different concentrations, both reactant gases have low activation energies.
3. Particle reactions proceed more rapidly with H\textsubscript{2}O than with CO\textsubscript{2}, as is commonly observed.
4. Over a broad temperature range (1150 °C-1350 °C), and for different concentrations of CO\textsubscript{2}, H\textsubscript{2}O, and combination of CO\textsubscript{2} and H\textsubscript{2}O, the first-order power-law global reaction rate expressions discussed in this study are accurate enough to predict most experimental data.
5. There is no substantial indication that adsorbed H$_2$O and CO$_2$ species play a role in the kinetics or compete for similar sites and therefore enter the rate expressions for each other.

6. Some publications suggest that CO and H$_2$ are absorbed on particle surface. Howbeit, no statistically significant absorption is indicated, which affects the gasification reaction rates. Therefore, the diffusion of CO and H$_2$ molecules are negligible in this model.

7. The reaction conditions indicate that the rates are strongly kinetically limited, even at the average pore diameter. Nevertheless, the endothermic nature of the reactions creates a particle temperature gradient that causes the outside (warmer) regions of the particle to react somewhat faster than the inside. This causes the particle diameter to slowly decrease as reaction proceeds, though the decrease is slow compared to constant-density particle burning.

8. The ash exclusion effect indicates that char becomes more refractory with the increasing of ash content for different material of biomass fuel. As the reaction proceeds, the reaction rates are reduced owing to more ash produced on the surface area. Besides, the formed ash changes the particle size, especially near the end of burnout, which also affects the reaction rates in a negative way. The negative ash effect is evident in the experimental data, though the ash content is widely considered to act as catalyst in biomass gasification reactions.

9. The pre-fixed experimental conditions determine that the reaction is kinetically limited, not diffusion limited, indicating that advanced and accurate surface-reaction-based model is not necessary.

10. The varying of biomass particle shape and size influences the reaction rates in profound ways, which cannot be described with any simple kinetic model. Better assumption and treatment should be developed to fit the data in this stage.
Char-yield represents a critical and often poorly estimated parameter but is required for accurate gasification estimates, which is to say, predicted char-yield errors can lead to large errors both because of imputed size effects and because of the mass remaining to react.

Pores in biomass char differ markedly from coal char because of their vascular structure and the commonly used pore models, such as the random pore model, predict trends in porosity, pore size distributions, and surface area inconsistent with the observations. Char conversion appears primarily in the largest pores, which account for a small fraction of the total pore volume, with strikingly little change in pore structure aside from pore wall thickness. Large pore diameter and surface area increase essentially monotonically through char conversions from 0 to well over 90%. The last 3% or so of char conversion sometimes involves a catastrophic collapse of pore structure as the residual inorganic material either rapidly sinters or structurally fails. SEM micrographs of char particles qualitatively confirm the quantitative data. Although these experiments occur under strongly kinetically limited conditions, the gasification reactions are endothermic and tend to cool the particle interior. The particle shape and size do not change significantly for the first 90+% of the reaction. The vascular structure of the biomass chars appears to effectively transport reactants and products through the particle, with most of the reaction occurring and the walls of these vessels. There are modest changes in the sizes of the macro pores and essentially not change in the sizes of the micro and meso pores.

As to the non-catalytic ash effects, experimental data from three chars exhibit the significant effects of inert material (ash) content on char reactivity, which become more pronounced as ash content or char burnout increases. The samples contain amounts of inorganic material that differ by factors of up to 40. The observed effect increases with increasing fuel ash content and is highly nonlinear for all fuel ash contents as burnout approaches unity.
A simple theoretical description of this inert ash effect based on stereological principles quantitatively describes the observed effects as a function of initial ash content and of burnout:

1. The three biomass fuels, widely differing in ash contents, provide great basis for exploring ash effects on kinetic reactivity.

2. This nonlinear, least-square regression technique adequately describes the kinetic behavior of biomass char over a broad reacting condition. The difference between the predicted line with ash effect and predicted line with no ash effect effectively illustrates the impact of ash contents on the reaction.

3. Poplar particle data has the highest repeatability in mass fraction loss than the other two materials, due to the differences in ash contents.

4. The ash effects influence the line curvature of the mass loss, as the highest ash content fuel shows a pronounced change in the slope of mass loss line, while the lowest ash content fuel shows no line curvature.

5. The ash content of the fuel changes gasification rates in profound ways, the importance of which differ strongly with differing ash contents and which include:
   
   a. Increasingly inert char surface area as reaction proceeds and ash content increases – these are the first data of which we are aware that establish this and they are quite definitive in this regard;
   
   b. Changing the size history of the particle, especially near the end of burnout.

The ash exclusion effect indicates that char becomes more refractory with the increasing of ash content for different material of biomass fuel. As the reaction proceeds, the reaction rate is reduced owing to more ash produced on the surface area. Besides, the formed ash changes the particle size, especially near the end of burnout, which also affects the reaction rates in a negative
way. Although the ash content is widely considered to act as catalyst in biomass gasification reactions, the net effect on the reaction is negative, which is evident in the experimental data.

In sum, this investigation provides substantial development and improvement in predicting the reactivity of biomass particle over broad reacting conditions. Both the experimental measurements and theoretical models indicated that the biomass char reactivity is influenced by several key factors, such as swelling factor, char yield, diameter ratio, surface area, density, ash content and relative velocity of the reactant gases. The modeling works developed in this investigation are able predict the kinetic behavior of biomass particle in great agreement with measured data. It should be noted that most of the remaining differences between measured data and predicted data may be due to uncertainties in material physical properties, model assumptions and tolerated systematic errors.
8 REFERENCES


