Pyrolysis and Hydrodynamics of Fluidized Bed Media

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ABSTRACT

Interest in non-traditional fuel sources, carbon dioxide sequestration, and cleaner combustion has brought attention on gasification to supplement fossil fueled energy, particularly by a fluidized bed. Developing tools and methods to predict operation and performance of gasifiers will lead to more efficient gasifier designs. This research investigates bed fluidization and particle decomposition for fluidized materials.

Experimental methods were developed to model gravimetric and energetic response of thermally decomposing materials. Gravimetric, heat flow, and specific heat data were obtained from a simultaneous thermogravimetric analyzer (DSC/TGA). A method was developed to combine data in an energy balance and determine an optimized heat of decomposition value. This method was effective for modeling simple reactions but not for complex decomposition.

Advanced method was developed to model mass loss using kinetic reactions. Kinetic models were expanded to multiple reactions, and an approach was developed to identify suitable multiple reaction mechanisms. A refinement method for improving the fit of kinetic parameters was developed. Multiple reactions were combined with the energy balance, and heats of decomposition determined for each reaction. From this research, this methodology can be extended to describe more complex thermal decomposition.

Effects of particle density and diameter on the minimum fluidization velocity were investigated, and results compared to empirical models. Effects of bed mass on pressure drop through fluidized beds were studied. A method was developed to predict hydrodynamic response of binary beds from the response of each particle type and mass. Resulting pressure drops of binary mixtures resembled behavior superposition for individual particles.
Dedication

This thesis is dedicated to my husband Joshua Free and to coffee. I love you both.

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I would like to acknowledge Dr. Brian Lattimer for always pointing me in the right direction throughout my graduate experience. I have often struggled with the transition from undergraduate narrow thinking into the more introspective graduate academic experience, but I realize my ability to think has changed and matured in my tenure here. I believe that is largely due to you letting me struggle, asking me why, and always pushing me forward.

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Photos by author, 2010.
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<tr>
<th>SYMBOL</th>
<th>DESCRIPTION</th>
<th>UNITS</th>
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<tbody>
<tr>
<td>$C$</td>
<td>specific heat capacity of solid material</td>
<td>J/kg-K</td>
</tr>
<tr>
<td>$e$</td>
<td>fraction of active mass remaining</td>
<td>--</td>
</tr>
<tr>
<td>$h$</td>
<td>enthalpy</td>
<td>J/kg</td>
</tr>
<tr>
<td>$\Delta h_{\text{d}}$</td>
<td>heat of decomposition</td>
<td>J/kg</td>
</tr>
<tr>
<td>$k$</td>
<td>thermal conductivity</td>
<td>W/m-K</td>
</tr>
<tr>
<td>$m$</td>
<td>solid material mass</td>
<td>kg</td>
</tr>
<tr>
<td>$m_{\text{g}}$</td>
<td>mass flow rate of pyrolysis gases</td>
<td>kg/s</td>
</tr>
<tr>
<td>$m_{\text{g}}^\prime$</td>
<td>mass flux of pyrolysis gases</td>
<td>kg/m$^2$-s</td>
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<tr>
<td>$q$</td>
<td>heat flow</td>
<td>W</td>
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<td>$q''$</td>
<td>heat flux</td>
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<td>$R$</td>
<td>universal gas constant, 8.314</td>
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<td>$t$</td>
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<td>s</td>
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<td>$T$</td>
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<td>K</td>
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<td>$T_{\text{ref}}$</td>
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<td>K</td>
</tr>
<tr>
<td>$V$</td>
<td>volume</td>
<td>m$^3$</td>
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</table>

### Greek

- $\rho$: solid material density, kg/m$^3$
- $\Delta$: change in the following parameter, --

### Subscripts

- $d$: decomposed (char) material
- $g$: pyrolysis gases
- $s$: sample
- $v$: virgin material
Abbreviations

TGA – Thermogravimetric Analysis
DSC – Differential Scanning Calorimeter/Calorimetry
STA – Simultaneous Thermogravimetric Analyzer
PMMA – Polymethylmethacrylate
VARTM – Vacuum Assisted Resin Transfer Molding
CHAPTER 1 - Introduction

Predicting the response of solid materials when exposed to high temperatures has historically been of primary interest in the areas of material of fire flammability and reentry applications. Many combustion reaction types have previously been studied including homogenous gas phase reactions, surface reactions, and pyrolysis reactions. Pyrolysis reactions represent the solid to gas decomposition reactions and are not as well understood as the other reaction types.

Knowledge of pyrolysis reactions is needed in order to understand the energetic response of the material. The energy term associated with the solid to gas phase change is the heat of decomposition. Once the energetics of the decomposition are understood, this enables prediction of material energetic response under various thermal loads.

Furthermore, since the material degradation is not instantaneous, a kinetic model that predicts the mass loss with temperature is crucial. Combining the kinetic and energetic behaviors results in a comprehensive model that can effectively predict the expected energy release and mass degradation with temperature for a material with an incident heat flux. This is particularly useful for understanding how to harvest useful fuels from non-traditional fuel sources.

More recently, interest in using non-traditional fuel sources, including biomass, as well as a focus on carbon dioxide sequestration and cleaner combustion has brought a focused attention on gasification as a means to supplement fossil fueled energy. A process that benefits from this insight, and is making gains to compete with the traditional fossil fuel driven market, is gasification. While there are several ways to employ this process, a promising method to harness gasification is through a fluidized bed gasifier. This combines combustible product gas harvesting from solid fuels with fluidization.

Solid fuel particles on the range of 500 – 1120 µm are fluidized with a jetting heated gas that has limited oxygen content in order to minimize combustion of the volatile organic compounds (VOC’s) released by the solids. Fluidization is ideal because of the temperature uniformity likely experienced by the bed. Particle decomposition behavior can therefore be predicted by the kinetic and energetic modeling.

However, a fluidized bubbling bed can have varying characteristics based on the observed behavior of the bed media. The most important operating characteristic for fluidized bubbling beds is the minimum fluidization velocity. This velocity depends largely on the characteristics of the bed media such as particle diameter and density. Once this minimum fluidization velocity is exceeded, assumptions such as uniform mixing can be applied to the bed, and the kinetic and energetic models can be used to assess the bed.

The result is an ability to predict operating temperature, pressure drop across the bed, a fuel flow rate, and VOC production rate for the gasification process. This research is aimed at developing the framework to accomplish this.
Energetic models are developed for several materials to determine the heat of decomposition using experimental data assuming a single global reaction. Then the capability is expanded to incorporating kinetic models that predict the mass loss of the material within the energy balance. This allows for complex degradation behavior that can be captured well by using multiple reactions.

Last, the impact of particle density and diameter on the minimum fluidization velocity is investigated for three well-characterized particles. The traditional method for determining minimum fluidization velocity uses a volume of material that is in height equal to the length of one diameter of the fluidization chamber. In this study, partial bed volumes were also investigated to determine the effect on the pressure drop across the bed. Results from the bed mass investigation are then used to estimate the hydrodynamic behavior for a binary mixture of particles. Minimum fluidization velocities are predicted by mass-driven and particle-centric empirical models and compared to actual results.

This thesis is formatted in a non-traditional method. It is structured as a compilation of three journal articles. Each article of the thesis focuses on different aspects of the research objectives. First, the use of STA measured data to determine heat of decomposition is discussed. Next, the development of a kinetic model and incorporation with the STA to determine heat of decomposition is presented. Last, the topic of the fluidization of bed materials in a lab-scale apparatus is discussed.
CHAPTER 2 - Experimental Determination of Heat of Decomposition

Motivation

Predicting the response of solid materials when exposed to high temperatures has historically been of primary interest in the areas of material of fire flammability and reentry applications. More recently, interest in using non-traditional fuel sources, including biomass, as well as a focus on carbon dioxide sequestration and cleaner combustion has brought a focused attention on gasification as a means to supplement fossil fueled energy. Gasification, which is a method to sublime solid fuels (fossil fuels, biomass and other wastes) into either a combustible gas or a synthesis gas for subsequent utilization, offers the potential both for clean power and chemicals production (Michener [1]). In order to better harness this phenomenon and apply it to non-traditional fuel sources, it is crucial to understand the gravimetric response and energetics required for decomposition.

Limited data exists in the literature on the energetics required to decompose solid materials into gas. This in part, is due to the fact that experimental methodologies have not been developed and validated.

Specific heat capacity and mass loss of the material at elevated temperatures are routinely performed using a differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), respectively. There are ASTM standards in place that prescribe methods for conducting DSC experiments to obtain quantitative specific heat capacity (ASTM E-1269 [12]) as well as running TGA with the intent of quantifying mass loss behaviour (ASTM E-1641 [16]). Sample preparation is also a significant issue in DSC/TGA experiments. ASTM E-1641 [16] recommends powdered samples for TGA given the very high surface-to-volume ratio in the sample. However, powdered samples yield poor DSC results due to the slow heat transfer within the sample. Stoliarov and Walters [17] prepared samples in chunks of various size and mass that did not cover the sample pan surface, which goes against the direct recommendation by ASTM E-1269 [12]. Goodrich [7] researched sample preparation techniques for use in an STA (TGA/DSC combined apparatus) and established guidelines that were employed in this research.

Studies have been done that use only one high temperature data collection apparatus. Staggs [15] used TGA data to create a kinetic model that predicts the mass loss of polymers. The results were then correlated to a bond energy calculation based on the breaking of chemical bonds during degradation. The energy model uses calculated steady state surface temperature and steady state mass flux values of the sample based on applied heat flux. However, from this analysis, an instantaneous heat of gasification was calculated and found to vary with temperature.

Stoliarov and Walters [17] also tested samples of polymers in a power-compensated DSC and as a result had to incorporate a test procedure that would ramp the temperature and hold at several intervals in order to effectively account for heat loss. The resulting intervals were combined and used in an energy model that distinguished between a heat of melting and a heat of decomposition. The model does not account for mass loss or the evolution of gas products.
Several studies have been aimed at determining heat of decomposition values based on combining the individual results of TGA and DSC.

Henderson [6] presented a method that combines DSC data with TGA data results measured at the same heating rate. During degradation, the material changes state from virgin to decomposed, and Henderson [6] suggests a method for combining the two properties to represent the sensible specific heat capacity across the full temperature range. The DSC measures apparent specific heat capacity values which combines the sensible and latent specific heat value. A graphical method is employed to interpret the heat of decomposition. This method, however, does not include the effects of the evolved gas products.

Lattimer, et al. [5] provides a more comprehensive approach. Composite material and balsa wood samples were investigated for use in Navy sandwich composites. Samples were prepared in various stages of decomposition and then physical properties determined at each stage using a Thermal Decomposition Apparatus. Then properties of the samples were determined across the full temperature range by combining the stage properties. Data was measured separately using a TGA to decompose samples in Argon environment and a DSC to decompose samples in Nitrogen. Samples were prepared as both fragments and powders for separate TGA and DSC testing. Kinetic models were also developed from the TGA results in order to predict the material response to temperature. Heat of decomposition values were determined by combining the TGA mass loss data with the apparent specific heat data from the DSC in an energy balance. Gas products for the samples were measured separately by Southwest Research Institute [8] and incorporated into the model. The results from the TGA and DSC were also validated by the TDA results with the energy model; however, the properties of propane gas were used for the evolved gas product. An improvement to the use of combining DSC results with TGA would be to test a sample simultaneously.

A Simultaneous Thermogravimetric Analyzer (STA) combines the DSC and STA in a single apparatus. There is very little in the literature where researchers used an instrument that simultaneously does both DSC and TGA on the same sample, which has the distinct advantage of ensuring that all conditions regarding the instrument and measurement are identical between the two types of data. This research goes an additional step and utilizes an STA to remove any differences associated with running two samples on two instruments to obtain both the kinetic and energetic material response.

The focus of this research was to develop a methodology to determine the heat of decomposition for any material directly using experimental data. The heat of decomposition is determined by optimizing an energy model using experimental data. A Simultaneous Thermogravimetric Analyzer (STA) was used to measure both mass loss and heat flow data as functions of temperature in the same experiment. Virgin and decomposed material properties were developed from the experimental data across a wide temperature range. The STA data is combined with an energy model that accounts for mass loss as well as evolved gas products. The resulting energy balance is optimized to determine a best-fit heat of decomposition value.
Experimental Description

A Netzsch STA 449 F1 Jupiter Simultaneous Thermogravimetric Analyzer/Differential Scanning Calorimeter (TGA/DSC) shown in Figure 2.1 was used to characterize the gravimetric and energetic response of materials during heating. The STA is a testing apparatus that can subject a sample to a predetermined temperature profile. This includes a controlled heating rate of up to 50°C/min as well as sustained isothermal temperatures to a maximum of 1500°C. The resulting data collected from the apparatus includes mass loss data, heat flow (i.e., heat transfer to the sample), and apparent specific heat all as a function of time or temperature.

The apparatus consists of a vertical tube furnace with a platinum platform for the sample and integrated Type S thermocouples as shown in Figure 2.1. The platform supports two cups, one for the sample and one for the reference measurements. Lids with single 0.25 mm diameter holes can be used during testing. Note that there is no lid on the sample crucible to show where the sample is located. The STA can be used with cups of various materials (platinum, aluminum, ceramic) depending on the maximum temperature of the test. In these tests, the chamber is closed and taken to 92-95% vacuum and then refilled with pure nitrogen to maintain an inert environment. Nitrogen was used in the testing to prevent char oxidation of samples. Nitrogen continues to enter the chamber at a rate of 50 mL/min for the duration of the experiment.

Figure 2.1. Netzsch STA 449 F1 Jupiter external view and sample holder

The STA uses a common furnace to control the heating conditions in the chamber so that the sample cup and reference cup experience the same thermal conditions. This is known as a heat-flux compensated DSC. The user sets a temperature profile for the test (ramping rates and isotherms), and the sample and reference cup temperatures are recorded. During the test, a difference in temperature between the sample cup and the reference cup indicates a heat flow to or from the sample. This is recorded as the DSC signal for the sample in units of volts. The
voltage signal can be converted to heat flow in Watts by loading a calibration file prior to conducting the test.

Mass of the sample during the heating is continuously measured using a balance attached to the base of the tube supporting the sample platform. The platform balance has a 25 ng resolution at a weighing range of 5g. Mass measurements were obtained in each STA experiment performed.

The temperature conditions can be controlled by either the sample thermocouple or the furnace thermocouple. As recommended by the manufacturer, furnace temperature control was used in all experiments, as it gives better temperature accuracy and prevents temperature control problems from occurring as a result of reactions (melting, decomposition, etc) in the sample. When using furnace temperature control, the instrument will ramp until the furnace thermocouple reaches the selected temperature. This final temperature will always be higher than the sample temperature, which lags due to heat loss from the furnace and placement of the thermocouple within the furnace. The magnitude of the temperature lag depends on the exact temperature, but can range from 10-50°C. The heating rate of the sample is the same as that of the furnace, and all plots are done using sample temperature.

Baseline and Calibration Tests

A series of baseline and calibration tests must be performed using the STA to produce quantitative mass and heat flow data. Without these additional tests, the instrument will only provide qualitative results on the material response.

The baseline test establishes the mass and heat flow response of the instrument over the tested temperature range without a sample in the STA. The baseline test is performed using two empty sample cups at the same conditions the sample will be tested. It is important that the test be conducted with the identical temperature profile, sample cups, gas type, and flow rates. The baseline measurement of mass and DSC signal over the range of temperatures are subtracted from the sample measurements to determine the actual response for the sample only. Once the baseline measurement is recorded, the sample can be loaded in the STA and the actual test can be conducted.

A calibration test is also required to obtain quantitative specific heat capacity data. The calibration test was performed in general accordance with ASTM E-1269 [12]. This standard specifies that the calibration test be conducted with one cup containing aluminum oxide (sapphire) reference material, which has a known specific heat capacity value at elevated temperature. Similar to the baseline test, the calibration test must be performed using the same condition and sample cups that will be used to test the sample. The calibration test provides a DSC signal that can be related directly to a known specific heat capacity. The methodology for using these results to determine the specific heat capacity of a sample is outlined in the next section.
Samples and Preparation

A previous study by Goodrich [7] determined that optimized DSC results depend on samples being prepared in the same manner. Sample materials for use in the STA were prepared into solid discs, 6 mm in diameter, in order to fit snugly into the STA crucible. The thickness of the sample was then reduced to allow the sample mass range to fall within 27-55 mg. Sample thicknesses were on the order of 15 – 75 mils. Sample crucibles and lids were platinum, ceramic, or aluminum depending on the temperature requirements of the testing. The best method to prepare the sample was to core drill the material to the required diameter and then hand sand or file down to the required thickness. However, caution was used to minimize thermal effects on the material and complete filing by hand was done when necessary as in the case of the PMMA sample preparation. For comparison to sapphire in the specific heat determination, samples were prepared so that the average mass of the sample agreed with the sapphire mass during the experiment.

Sample Description

Three materials were investigated in this study – E-glass/vinyl ester composite material, Polymethylmethacrylate (PMMA), and red oak wood.

The composite laminate material evaluated in this study was E-glass/vinyl ester laminate. Laminates contained Vetrotex 324B fibers in a 55/45 woven roving with a 4.826 mm nominal width and 813.75 g/m² density. The resin was Derakane 411-350 vinyl-ester resin. The laminates were manufactured using the vacuum-assisted resin transfer molding (VARTM) process. In this process, layers of woven roving glass were placed under a vacuum bag and the resin is drawn in via a vacuum pump. A package consisting of 1.5% methyl ethyl ketone peroxide (MEKP), 0.06% acetylacetone, and 0.2% CONAP® as percentages of the total resin mass was used to cure the resin. Panels used in this study had a 6 mm nominal thickness and were not post-cured after fabrication. E-glass/VE samples were cut from larger panels, primarily using a hacksaw, and the material was cored using the core drills.

The PMMA samples were cut from 30 cm by 60 cm panels of PMMA polycast BK-2025 black semi-opaque material manufactured at 0.635 cm thickness. The PMMA sample is comprised of over 97% PMMA with remaining residuals consisting of carbon black, heat stabilizers, ultra-violet absorbers, and MMA monomer. The density for this material is 1180 kg/m³, and the molecular weight is approximately 900,000 to 1,000,000 kg/kmol. Care was taken to obtain samples away from the panel edge to avoid material that had been thermally compromised when panel was cut. In addition, the samples were hand sanded to meet the sample preparation target size and reduce effects of machine friction heating.

The red oak wood samples were cut from a 7.5 cm by 30 cm panel with 0.635 cm thickness. The panels were first acclimatized to the monitored environmental conditions of the lab space housing the STA. The sample was core drilled to the correct diameter and then hand sanded to meet the sample thickness and mass requirements. In addition, all red oak samples underwent a dehydration process prior to testing in order to minimize the effects of water evaporation on the STA measurements. Samples were dehydrated by ramping them to 110°C at
10°C/min in the STA and holding them isothermally for one hour before cooling and conducting the test.

Theory

An analysis in this section provides a methodology for using the heat flow and mass data from the STA to determine the solid material specific heat capacity and the heat required to change the solid material into a gas (heat of decomposition). The energy required to heat materials may be composed of a sensible part and a latent part. The sensible energy is simply the energy required to raise the temperature of the solid material, which is the specific heat capacity of the solid material. The latent energy for heating a material is associated with decomposing the material (liquid or solid) into a gas. The heat flow measurement from the STA is a measure of the overall energy required to heat the sample. If there is no mass loss, the STA heat flow is directly related to the sensible specific heat capacity of the solid material. When mass loss occurs, the heat flow measurement is a combination of the energy to heat the solid (sensible part) and the latent energy due to solid decomposition into gas. This is known as the apparent specific heat capacity. Using the energy equation and existing standards on the DSC, this section outlines the development of methods for determining the specific heat capacity of the solid as well as the heat of decomposition using data from the STA.

Sensible Specific Heat Capacity

The specific heat capacity of the sample was determined in general accordance with the procedure outlined in ASTM E-1269 [12]. Revisions were made to this methodology to allow for the determination of decomposing samples. This section provides an overview of this methodology with no material decomposition, while the following section will provide details on making measurements when decomposition occurs.

ASTM E-1269 [12] method for obtaining specific heat by the differential scanning calorimeter is a ratio method that uses the heat flow curve from the sapphire calibration test to determine the specific heat of the sample. Assuming that the same cups are used for both experiments, the specific heat of a sample is determined as follows. The sample is assumed to have lumped heat capacity, which is a good assumption for the very small samples used for DSC, and the basic specific heat equation is then applied:

\[ \dot{Q} = mC_p \frac{dT}{dt} \Rightarrow C_p = \frac{\dot{Q}}{m \frac{dT}{dt}} \]

Equation 2.1

In Equation 2.1, \( \frac{dT}{dt} \) is the user defined heating rate. The mass value used in the DSC signal is the initial mass of the sample.

Quantitative results for specific heat capacity are determined using the calibration factor:
\[ C_p = \frac{E \dot{Q}}{m \frac{dT}{dt}} \]  

Equation 2.2

The calibration factor \( E \) is determined using the DSC signal from the calibration test on sapphire, which has a known specific heat capacity. The data from the STA is used to calculate the value of \( E \):

\[ C_{p,st} = \frac{E \dot{Q}_{st}}{m_{st} \frac{dT}{dt}} \Rightarrow E = \left( \frac{dT}{dt} \right) (m_{st} C_{p,st}) \]  

Equation 2.3

The calibration factor can then be applied to a given DSC signal for any sample material and the specific heat curve determined:

\[ C_{p,s} = \frac{E \dot{Q}}{m_s \frac{dT}{dt}} \]  

Equation 2.4

The ASTM E-1269 [12] standard specifies that the mass of the sample should not change by more than 0.3% during the sample DSC run. When samples decompose, the sample mass is not constant and the methodology presented in ASTM E-1269 [12] is not completely valid. Analysis of data for decomposing samples is presented in the next section.

**Apparent Specific Heat Capacity and Heat of Decomposition**

Samples that decompose in the STA provide a DSC signal that is composed of both the sensible and latent specific capacity of the material. To provide material properties, the sensible specific capacity must be separated from the latent specific heat capacity. The latent specific heat capacity is the energy required to decompose the materials from a solid into a gas. Analysis is developed in this section to predict the heat of decomposition from the latent portion of the specific heat capacity.

The heat of decomposition is determined by using the data collected from the STA and considering the energy balance developed in this section. One-dimensional heat transfer models have been developed by Murty Kanury and Blackshear [2] and Kung [3]. These models are based on material degrading under heat and a unidirectional gas flow of the pyrolysis products. It is assumed that the material can be modeled as having constant and uniform heating incident on the exposed surface. In addition, thermal equilibrium is assumed between the solid material
and the evolved pyrolysis gas products. For the experimental set up in the STA, these assumptions are acceptable.

**Mass Balance and Energy Balance**

The mass and energy balance are derived based on one-dimensional heat flow, which is well suited to the experimental configuration (Lattimer, et al. [14]). The mass balance and general energy balance equations for the system are:

\[
\frac{\partial m_s}{\partial t} + \frac{\partial \dot{m}_g}{\partial x} \delta x = - \frac{\partial m}{\partial t} \quad \text{Equation 2.5}
\]

\[
\frac{\partial (m h + m_g h_g)}{\partial t} + \frac{\partial (\dot{m}_g h_g)}{\partial x} \delta x = \frac{\partial}{\partial x} \left( k \frac{\partial T}{\partial x} \right) V \quad \text{Equation 2.6}
\]

Expansion of the energy equation results in:

\[
m \frac{\partial h}{\partial t} + h \frac{\partial m}{\partial t} + m_g \frac{\partial h_g}{\partial t} + h_g \frac{\partial m_g}{\partial x} \delta x + m_g \frac{\partial h_g}{\partial x} \delta x + h_g \frac{\partial \dot{m}_g}{\partial x} \delta x = \frac{\partial}{\partial x} \left( k \frac{\partial T}{\partial x} \right) V \quad \text{Equation 2.7}
\]

From the definition of enthalpy:

\[
h = C_p T \quad \text{Equation 2.8}
\]

Combining Equation 2.8 with Equation 2.7, the expanded energy equation can be rewritten:

\[
\left( m C_p + m_g C_{p,g} \right) \frac{\partial T}{\partial t} + h \frac{\partial m}{\partial t} + h_g \frac{\partial m_g}{\partial x} \delta x + m_g C_{p,g} \frac{\partial T}{\partial x} \delta x = \frac{\partial}{\partial x} \left( k \frac{\partial T}{\partial x} \right) V \quad \text{Equation 2.9}
\]

The energy equation is now in mass form. By substituting the mass balance from Equation 2.5 with the manipulated energy balance from Equation 2.9, this reduces the energy balance:

\[
\left( m C_p + m_g C_{p,g} \right) \frac{\partial T}{\partial t} + (h - h_g) \frac{\partial m}{\partial t} + m_g C_{p,g} \frac{\partial T}{\partial x} \delta x = \frac{\partial}{\partial x} \left( k \frac{\partial T}{\partial x} \right) V \quad \text{Equation 2.10}
\]

The first term in Equation 2.10 contains the product of the mass and specific heat for both the solid material as well as the gases, which are assumed to be within the void spaces of the mass of the solid material and therefore less than the overall volume of the sample. For testing in the STA, the sample is evacuated and flooded with nitrogen, and it is assumed that the void spaces are now filled with nitrogen. Therefore the specific heat values measured by the STA during
experimentation include the composite of the solid material as well as the nitrogen trapped in the void spaces of the sample. The energy balance can be rewritten again:

\[ mC_p + m_g C_{p,g} \approx mC_p \Rightarrow (mC_p) \frac{\partial T}{\partial t} + \left( h - h_g \right) \frac{\partial m}{\partial t} + \dot{m}_g C_{p,g} \frac{\partial T}{\partial x} \delta x = \frac{\partial}{\partial x} \left( k \frac{\partial T}{\partial x} \right) V \]  

Equation 2.11

This approximation assumes that the mass and specific heat of the nitrogen is equivalent to those of the gas products. While this may not be accurate throughout the degradation, this is assumed to be valid for the development of this energy balance.

The sample material for use in the STA is prepared as a thin disk. The sample is sufficiently thin so as to assume no conduction effects across the material. The experimental set up for the STA and the sample material preparation allow the sample to be treated as having a lumped capacitance. In addition, within the STA the sample is contained in a small well-insulated chamber during testing so that the STA measures heat flow into the material, which is equal to the temperature rise of the material.

The lumped capacitance assumption can be applied to Equation 2.11 to produce Equation 2.12 and rearranged to Equation 2.13. Included in these equations is the calibration factor E as developed previously in Equation 2.3. As a result, these equations can be used to determine a quantitative measurement from apparent specific heat capacity:

\[ (mC_p) \frac{\partial T}{\partial t} + \left( h - h_g \right) \frac{\partial m}{\partial t} = E\dot{Q} \]  

Equation 2.12

\[ \left( mC_p + \left( h - h_g \right) \frac{\partial m}{\partial T} \right) \frac{\partial T}{\partial t} = E\dot{Q} \Rightarrow mC_{app} \frac{\partial T}{\partial t} = E\dot{Q} \]  

Equation 2.13

The apparent specific heat from the STA represents the sensible specific heat term and the enthalpy terms in parentheses. Separation of the apparent specific heat is detailed in the next section. Again considering the definition of enthalpy, the enthalpies in Equation 2.13 are defined below:

\[ h = \Delta h_d + \int_{T_{ref}}^{T} C_p \partial T \]  

Equation 2.14

\[ h_g = \int_{T_{ref}}^{T} C_{p,g} \partial T \]  

Equation 2.15

In the above equations, \( \Delta h_d \) represents the heat of decomposition, and the specific heat terms are integrated from \( T_{ref} = 273K \). Equation 2.13 along with Equation 2.14 and Equation 2.15 represent the model for determining the heat of decomposition.
Separation of Sensible and Apparent Specific Heat Capacity

Specific heat values measured using the STA for a decomposing sample are the apparent specific heat. The apparent specific heat is a combination of the sensible component of the specific heat, which accounts for the heat flow associated with the temperature change in the material, as well as the latent specific heat associated with the phase change during the decomposition reaction. A method is employed to separate the sensible portion of the specific heat from the latent.

During the decomposition of the material, it is assumed that the sample properties transition from virgin to decomposed properties simultaneously with the extent of the reaction. A method of combining the properties of the two states involves the use of a progress variable (Henderson [4]). In this manner, the material properties can be captured for a wide range of temperatures. The progress variable, e, for the decomposition is based on normalizing the instantaneous sample mass by the virgin and fully decomposed masses. This variable also represents a weighted mass fraction of the sample. Now, the reaction progress variable goes from 1 in the initial virgin state to 0 in the fully decomposed state:

\[ e = \frac{m - m_d}{m_v - m_d} \]  

Equation 2.16

The specific heat properties of the sample will change as the material degrades and changes state. Prior to decomposing the material, the sample’s properties correspond to the virgin state. In addition, when the sample is fully decomposed the sample properties correspond to the fully decomposed state. By comparing the apparent specific heat data with the reaction progress variable, the virgin and decomposed portions of the specific heat can be isolated. For example, the sample material might be considered in the virgin state for a reaction progress variable range of 1 to 0.95 and fully decomposed at 0.05 to 0.

Specific heat properties for both states must be determined over the full temperature range, specifically the temperature region between the two stages where the decomposition is occurring. A polynomial fit can be performed on the data and the result extended over the full temperature range. This was accomplished by a built in MATLAB function, and a second order polynomial fit was used. The results of the polynomial fits performed on E-glass/vinyl-ester at 20°C/min are shown in Figure 2.2.
The specific heat properties in both the virgin and decomposed states can be combined in the same equation based on weighting the states with the progress variable:

\[ C_p = eC_v + (1 - e)C_d \]

Equation 2.17

The specific heat term in Equation 2.17 is the sensible specific heat for all states. This effectively isolates the sensible component of the specific heat. Results for separating the sensible specific heat from the apparent specific heat for the E-glass/vinyl-ester at a heating rate of 20°C/min are shown in Figure 2.3.
Figure 2.3 – Sensible specific heat separated from the STA measured apparent specific heat and plotted with apparent specific heat for E-glass/vinyl ester (20 °C/min).

**Enthalpies of Solid and Evolved Gases**

The enthalpy is defined as the integration of the sensible specific heat term from a reference temperature to the state temperature as shown in Equation 2.14. This is accomplished by numerically integrating the sensible specific heat term using a reference temperature of 273 K. A trapezoidal numerical integration scheme was used to determine the enthalpy from the sensible specific heat terms.

The enthalpy of the evolved gases is based on the mixture of products released during the decomposition. The evolved products and their associated mass fractions are used to determine a mixture specific heat as shown in Equation 2.18 where $N$ is the total number of compounds, $y_i$ and $C_i$ are the mass fraction and specific heat associated with a compound:

$$C_{g,mix} = \sum_{i=1}^{N} y_i C_i$$

Equation 2.18

This mixture specific heat is then integrated with temperature to determine the enthalpy for the evolved gases as shown in Equation 2.15.
Data measured by the STA consists of mass, heat flow, and apparent specific heat all as functions of temperature. Note that all the terms in Equation 2.13 have been obtained or developed with the exception of the heat of decomposition. The mass values and mass derivative values are used directly and the sensible specific heat term is derived. Next, the sensible specific heat term is integrated to develop the enthalpy term for the solid. Based on the products evolved for each material, the enthalpy for the gas products can be calculated. The heating rate is constant and known. The calibration factor is then determined and applied to the DSC signal to represent the corrected heat flow experienced by the material during the testing. Equation 2.13 was used to determine the heat of decomposition.

An optimization scheme was employed in MATLAB to determine the heat of decomposition value. All data were imported into MATLAB as arrays with temperature and combined to represent the energy equation. Then, a user-specified range of values for the heat of decomposition was input into the code. Using a least squared difference minimizing technique, with terms evaluated at each temperature node, the program returned the optimum heat of decomposition value to satisfy the energy balance by finding the minimum residual term \( R \) and its associated heat of decomposition:

\[
\sum_{T=\text{Initial}}^{\text{Final}} \left[ (m(T)C_p(T) + \left( h(T) + \Delta h_d - h_g(T) \right) \frac{\partial m(T)}{\partial T}) \frac{dT}{dt} - E(T)\dot{\mathcal{Q}}(T) \right]^2 = R_i \quad \text{Equation 2.19}
\]

Results and Analysis

The gravimetric and energetic response of E-glass/vinyl ester composite laminate, Polymethylmethacrylate (PMMA), and red oak wood are presented in this section. In addition, analysis was performed to determine the heat of decomposition of each sample using the method outlined in the previous section. Prior to testing, red oak samples were dehydrated by ramping them to 110°C at 10°C/min in the STA and holding them isothermally for one hour before cooling and conducting the test. Gravimetric response of each material was measure at 5, 10, 20, and 40°C/min while the energetic and gravimetric response was measured at 20°C/min. Data at 20°C/min was used to determine the heat of decomposition.

Gravimetric Response

The raw mass loss data for the e-glass/vinyl-ester is shown in Figure 2.4. While the initial mass was easily controlled the final mass varied for each sample. The variation in residual mass for this particular material was addressed by Goodrich [7] and attributed to the scale of the samples (6.35 mm diameter, ~0.6 mm thick), which was small enough that the volume fraction
of the fabric, which was woven in 4.8 mm widths could vary between samples depending on the position at which samples were taken from the panel.

Figure 2.4. STA raw data for E-glass/vinyl-ester at all heating rates
When the mass loss data is normalized using the weighted mass fraction transformation (Equation 2.16), the resulting curves illustrate the effect of the heating rate on the mass loss behavior. It is evident from Figure 2.5 that a doubling of the heating rate shifts the mass loss to a higher temperature, about 15°C. The overall shape of each curve is the same at each heating rate, a single shoulder mass loss curve. There is a slight declension from the starting temperature to about 350°C. Then the dominating mass loss occurs between 350°C and 500°C. The initiating temperature for this behavior varies by heating rate. After this dramatic loss, there is another slight decline until the material achieves the fully decomposed state.

![Figure 2.5. E-glass/vinyl-ester data at all heating rates refined by weighted mass fraction](image)

The raw mass loss data for PMMA is shown in Figure 2.6. For this material, the solid material degrades almost completely during the decomposition process. Only a small amount of residual mass remained after testing. This behavior is observed at all heating rates.
Figure 2.6. STA raw data for PMMA at all heating rates

When the PMMA data is refined by the mass fraction, as shown in Figure 2.7, the effect of the heating rate is again observed. As the heating rate is doubled, the mass loss curves shift by about 14°C. The general shape of the single shoulder mass loss is similar to the vinyl ester. There is very little mass loss from the starting temperature until around 300°C. Then the major mass loss occurs from about 350°C and finishes at 450°C. The initiating temperature for the major mass loss shifts with the increase in heating rate.
The raw mass loss data for the Red Oak materials are shown in Figure 2.8. This data is significantly different from the e-glass/vinyl-ester and the PMMA. All of the mass loss curves demonstrate more complex shapes, and this is more evident when the mass loss data is refined by the weighted mass fraction.

Figure 2.7. PMMA data at all heating rates refined by weighted mass fraction

Figure 2.8. STA raw data for red oak at all heating rates
The effect of the heating rate is again observed in the red oak wood material. The curves in Figure 2.9 demonstrate the shift in mass loss curves of about 10°C with a doubling of the heating rate. All curves show a plateau region from the starting temperature to about 200°C. Next, the first shoulder is observed from about 200°C to about 350°C. Then a perceptible change in the slope of the mass loss curve occurs from about 350°C to about 400°C. After this, the curves all have very long tails and come to the fully decomposed state at the rather high temperature of about 950°C.

Figure 2.9. Red oak data at all heating rates refined by weighted mass fraction
Determination of Heat of Decomposition

The details on the determination of the heat of decomposition are provided in this section using the data for E-glass/vinyl-ester. Following the detailed description of how the method is applied, results for the PMMA and the balsa wood are provided.

**E-glass Vinyl Ester**

The calibration factor needs to be determined prior to analyzing a sample. For this, a sapphire sample is tested in the STA at a heating rate of 20°C/min. The results were compared to the established specific heat values for sapphire documented in ASTM E1269 [12]. This data was used to determine the calibration factor. A plot of the calibration factor from the sapphire is shown in Figure 2.10 as a function of temperature.

![Figure 2.10. Calibration factor determined by sapphire sample tested at 20°C/min](image)

A sample of E-glass/vinyl-ester was prepared and tested in the STA at a heating rate of 20°C/min. The raw data DSC signal for the E-glass/vinyl-ester is shown in Figure 2.11. The DSC signal shown in Figure 2.11 is effectively the heat flow per initial mass. In order to determine the actual heat flow experienced by the sample, the DSC signal is multiplied by the initial sample mass and then corrected by the calibration term, E. This becomes the heat flow term on the right hand side of Equation 2.13. As previously mentioned, a Type S thermocouple is used in the STA. The thermocouple is more accurate at higher temperatures and not as accurate at the lower temperatures. The shape of the calibration curve is likely a direct result of the capabilities of the instrumentation. However, for the purposes of this investigation, the behaviors at the higher temperatures are the primary focus.
The apparent specific heat term needs to be determined for use in the analysis as shown in Equation 2.4. To determine the specific heat capacity, the original DSC signal must be corrected to reflect the instantaneous mass and calibrated with the calibration factor from the sapphire test. The result of the manipulation leads to the apparent specific heat as shown in Figure 2.12.

![Graph showing DSC Signal](image)

**Figure 2.11.** Raw data DSC Signal for E-glass/vinyl-ester at a heating rate of 20°C/min

![Graph showing Apparent Specific Heat](image)

**Figure 2.12.** Apparent specific heat curve for E-glass/vinyl-ester as determined from data.
The apparent specific heat capacity was then used to separate the sensible and latent portions of the specific heat term. Results for identifying the virgin and decomposed portions of the specific heat via the reaction progress variable, e, were previously shown in Figure 2.2. Virgin and decomposed properties are then combined to form the sensible specific heat term for all material states from Equation 2.17. The outcome of this method applied to e-glass/vinyl-ester was shown previously in Figure 2.3.

The sensible specific heat term was integrated using a trapezoidal numerical integration technique to determine the enthalpy of solid material defined in Equation 2.14. As for the gas products, the Southwest Research Report results for e-glass/vinyl-ester were used to determine the mixture specific heat based on the amount and species of gas products evolved. For the E-glass/vinyl ester, Southwest Research Institute [8] previously reported the evolved product gases and amounts for vinyl ester under the same conditions as the STA. Specific heat values as a function of temperature for each compound were either referenced from previously published values [9] or the Joback Method [10] was employed to determine the specific heat based on the molecular structure of the compound. Details on the evolved gas compounds and amounts for all three materials are tabulated in Appendix A.

A second-order polynomial curve fit was determined for the resulting mixture specific heat curve from a built in MATLAB function. This aided in the calculation of the enthalpy term, which is the integration of the mixture specific heat curve with temperature (Equation 2.15).

All terms of the energy balance are now known except for the heat of decomposition value, \( \Delta h_d \). The user specifies a range of heat of decomposition values, and the program calculates the squared residuals for each heat of decomposition value as shown in Equation 2.19. The sums of squared difference terms are then plotted with the heat of decomposition value. The optimized heat of decomposition value for the material is determined from the lowest squared residual.
Figure 2.13. Sum of squared difference terms plotted against a user-defined range of heat of decomposition values

The least squared difference results for the E-glass/vinyl-ester composite are shown in Figure 2.13. The range of -1000 J/g to -800 J/g was investigated for the heat of decomposition of e-glass/vinyl-ester. As shown in Figure 2.13, there exists a minimum sum of squared differences. The heat of decomposition value associated with this minimum is identified as the material heat of decomposition. In this case, the heat of decomposition for E-glass/vinyl-ester was determined to be -910 kJ/kg. The MATLAB code then inserts the determined heat of decomposition value into the energy balance and plots the resulting heat flow determined by the model against the experimental data. The results for the E-glass/vinyl-ester are shown in Figure 2.14.
The analysis detailed above was also used to determine the heat of decomposition of PMMA and balsa wood. As described above, this analysis requires the specific heat capacity of the gas products from the decomposition. PMMA evolved products are based on gas measurements in flash pyrolysis of PMMA [11]. Balsa wood evolved gas products were taken from the Southwest Research Institute report [8]. A gas mixture specific heat was determined from the listed components.

The heat of decomposition for the PMMA and balsa wood was determined to be -1180 kJ/kg and -360 kJ/kg, respectively. Heat of decomposition values for PMMA from this study are shown in Table 2.1 along with other values reported in the literature. The predicted and measured heat flow results for the two materials are shown in Figure 2.15 and Figure 2.16. The prediction for the balsa wood is not as good as for the E-glass/vinyl-ester and PMMA.
Figure 2.15. PMMA experimental and predicted heat flows for 20° C/min

Figure 2.16. Red oak experimental and predicted heat flows for 20° C/min
Table 2.1 Experimentally determined heat of decomposition values

<table>
<thead>
<tr>
<th>Material</th>
<th>Heat of Decomposition, kJ/kg</th>
<th>Literature Values for Heat of Decomposition, kJ/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMMA</td>
<td>-1180</td>
<td>-870 ± 200(^1)</td>
</tr>
<tr>
<td>PMMA</td>
<td>-1180</td>
<td>-1600(^2)</td>
</tr>
<tr>
<td>PMMA</td>
<td>-1180</td>
<td>-840(^3)</td>
</tr>
<tr>
<td>Red Oak</td>
<td>-360</td>
<td>--</td>
</tr>
<tr>
<td>Balsa Wood(^*)</td>
<td>--</td>
<td>-500(^4)</td>
</tr>
</tbody>
</table>

\(^1\) Stoliarov [17], \(^2\) Tewarson [13], \(^3\) Staggs [15], \(^4\) Lattimer [5] \(^*\) Similar material shown for comparison

**Discussion**

The method for determining heat of decomposition worked well for the E-glass/vinyl-ester and PMMA but not as well for the balsa wood. An inherent assumption of this analysis is that the decomposition can be represented as a single global decomposition reaction.
The gravimetric data for the E-glass/vinyl-ester indicates that the material decomposition can be well represented using a single global mechanism. A plot of the iso-conversional lines for E-glass/vinyl-ester is created from the STA data for multiple heating rates.

![Ea (kJ/mol) vs. log(A) log(1/s) vs. Fractional Mass Loss](image)

Figure 2.17. E-glass/vinyl-ester plot of estimated activation energies and pre-exponential factors for each iso-conversional value.

Figure 2.17 indicates that there are three significant reaction regimes during the decomposition for E-glass/vinyl-ester: an early reaction, a dominant middle reaction from 0.05 to 0.95 fractional mass loss, and a final reaction. The dominant reaction enables the decomposition to be treated as a single reaction. This corresponds to the reaction having only one heat of decomposition value. As a result, the method outlined here provides heat flow results with a mean absolute percentage error 2.75% of the measured values over the entire temperature range.
The gravimetric data for the PMMA indicates that the material decomposition can be fairly well represented using a single global mechanism. A plot of the iso-conversional lines for PMMA is created from the STA data for multiple heating rates.

Figure 2.18. PMMA plot of estimated activation energies and pre-exponential factors for each iso-conversional value.

Figure 2.18 indicates that PMMA activation energy is dependent on mass loss. However, the range of values for the activation energy and pre-exponential factor during the decomposition is relatively narrow. This narrow range enables the decomposition to be treated as a single reaction. This corresponds to the reaction having only one heat of decomposition value. As a result, the method outlined here provides heat flow results within 25% of the measured values.
The gravimetric data for the red oak indicates that the material decomposition cannot be well represented using a single global mechanism. A plot of the iso-conversional lines for red oak is created from the STA data for multiple heating rates.

![Graph](image)

**Figure 2.19.** Red oak plot of estimated activation energies and pre-exponential factors for each iso-conversional value.

Figure 2.19 indicates that the activation energy is approximately constant for the fractional mass loss range of 0 to 0.75. Beyond 0.75 fractional mass loss, the activation energy and pre-exponential factor values experience peaks and valleys. Looking at the scale, the range in which the both values exist is quite large. Treating the decomposition as a single reaction does not fully capture the complex behavior of the red oak decomposition process. As a result, the method outlined here does not provide good heat flow results compared to the measured values.

Heat of decomposition values from this study are compared to previously published results in Table 2.1. Because of the nature of composite, results for composite laminate of E-glass/vinyl-ester in the same configuration as the sample used in this study are not available. On the other hand, PMMA has been widely studied. Previously reported results were both obtained from methods using DSC measurements, and the results from this analysis are within 35% of the previously reported values. As for red oak, heat of decomposition data was not available specifically for red oak; however, a comparison is shown for balsa wood. Results from the balsa wood study are also based on a method using DSC measurements, and the results presented here are within 28% of the balsa wood value.

For a single global mechanism with one heat of decomposition value, predicted results for E-glass/vinyl-ester are within 2.75% of the data across the temperature range. The general shape of the resulting heat flow curve is quite close to the experimental curve, particularly during the decomposition. However, the optimized heat of decomposition term does not match the peak height seen in the experimental curve. This may be a result of using a global reaction to predict
the mass loss when additional information suggests that there is more than one reaction regime. A different method should be considered to capture the multiple reaction behavior.

Using the single global mechanism with one heat of decomposition value, predicted results for PMMA are within 25% of the data. The general shape of the resulting heat flow curve is similar to the experimental curve; however, not all of the behavior is sufficiently captured particularly at the peak. The optimized heat of decomposition term does not do well to achieve the peak height seen in the experimental curve. The molecular structure of PMMA is \( (C_5O_2H_8)_n \). Perhaps during decomposition, oxygen is released from the PMMA structure and allowed to combust with other evolved products. This may explain why the model is not able to predict the experimental peak heat flow (Figure 2.15).

When the single global reaction model is applied to red oak, the predicted results for red oak do not replicate the data. The fit at the beginning and end tails are mediocre. The behavior during the actual reaction is not well matched by this method. This is likely attributed to the shortfall of using the global reaction mechanism model to capture the complex behavior. As can be seen in Figure 2.16, the experimental heat flow curve for the red oak has two valleys in the reaction region between about 580 and 700 K. The global reaction mechanism model produces optimized results for a single valley only. A different method should be considered to capture the complex behavior.

**Conclusion**

A method was developed to predict the heat of decomposition for a single global reaction representing the decomposition process using TGA and DSC data. The method developed can be used to effectively determine the heat of decomposition, but there are limitations to its use. The method assumes a single global reaction for the decomposition. Single global reactions were applicable for E-glass/vinyl-ester and PMMA, but did not produce good results for the red oak.

Previously published heat of decomposition values were not available for E-glass/vinyl-ester or red oak for comparison; however, PMMA results were within 25% of previously reported values obtained from a similar method. Balsa wood results obtained from a similar method were used as a comparison to red oak; the balsa wood heat of decomposition value was within 28% of the red oak value.

Materials that have more complex decomposition require a more sophisticated approach for representing the decomposition process, such as incorporating multiple reactions. This would allow multiple heats of decomposition to be defined, resulting in a better representation of the heat flow process. Results could also be improved by measuring the gas products evolved through the decomposition process in the tests being used to determine the heat of decomposition values.
References


# Nomenclature

<table>
<thead>
<tr>
<th>SYMBOL</th>
<th>DESCRIPTION</th>
<th>UNITS</th>
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<tbody>
<tr>
<td>$A$</td>
<td>pre-exponential factor</td>
<td>Hz</td>
</tr>
<tr>
<td>$C$</td>
<td>specific heat capacity of solid material</td>
<td>J/kg-K</td>
</tr>
<tr>
<td>$E_a$</td>
<td>activation energy</td>
<td>J/gmol</td>
</tr>
<tr>
<td>$e$</td>
<td>fraction of active mass remaining</td>
<td>--</td>
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<tr>
<td>$h$</td>
<td>enthalpy</td>
<td>J/kg</td>
</tr>
<tr>
<td>$\Delta h_d$</td>
<td>heat of decomposition</td>
<td>J/kg</td>
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<tr>
<td>$k$</td>
<td>thermal conductivity</td>
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<td>$m$</td>
<td>solid material mass</td>
<td>kg</td>
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<td>$m_{g}$</td>
<td>mass flow rate of pyrolysis gases</td>
<td>kg/s</td>
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<tr>
<td>$m_{g}''$</td>
<td>mass flux of pyrolysis gases</td>
<td>kg/m$^2$-s</td>
</tr>
<tr>
<td>$n$</td>
<td>order of reaction</td>
<td>--</td>
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<tr>
<td>$q$</td>
<td>heat flow</td>
<td>W</td>
</tr>
<tr>
<td>$q''$</td>
<td>heat flux</td>
<td>W/m$^2$</td>
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<tr>
<td>$R$</td>
<td>universal gas constant, 8.314</td>
<td>J/gmol-K</td>
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<tr>
<td>$t$</td>
<td>time</td>
<td>s</td>
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<tr>
<td>$T$</td>
<td>absolute temperature</td>
<td>K</td>
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<tr>
<td>$T_{ref}$</td>
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<tr>
<td>$V$</td>
<td>volume</td>
<td>m$^3$</td>
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**Greek**

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<tr>
<td>$\rho$</td>
<td>solid material density</td>
<td>kg/m$^3$</td>
</tr>
<tr>
<td>$\Delta$</td>
<td>change in the following parameter</td>
<td>--</td>
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**Subscripts**

<table>
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<th>SYMBOL</th>
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<tbody>
<tr>
<td>$d$</td>
<td>decomposed (char) material</td>
</tr>
<tr>
<td>$g$</td>
<td>pyrolysis gases</td>
</tr>
<tr>
<td>$s$</td>
<td>sample</td>
</tr>
<tr>
<td>$v$</td>
<td>virgin material</td>
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</table>
Abbreviations

TGA – Thermogravimetric Analysis
DSC – Differential Scanning Calorimeter/Calorimetry
STA – Simultaneous Thermogravimetric Analyzer
VARTM – Vacuum-Assisted Resin Transfer Molding
CHAPTER 3 - Modeling Thermo-gravimetric Response of Materials

Motivation

Predicting the response of solid materials when exposed to high temperatures has historically been of primary interest in the areas of material of fire flammability and reentry applications. This includes being able to predict material degradation with temperature and gain insight into the energetics of the decomposition. A methodology was developed previously in Chapter 2 to model the energetics required to decompose solid materials into gas. This model assumes a single global reaction. A significant shortcoming from the results of the previous methodology was the inability to account for multiple reactions occurring during the degradation. In addition, there was no stand-alone kinetic model to provide insight into the mass loss. Experimentally determined mass loss data was used directly in the model. With the development of a kinetic model, thermal scenarios other than the testing configuration can be predicted.

Several kinetic models have been developed to predict the kinetic response of materials, particularly on single coal particles ([4],[14],[15],[18], [19], and [20]), that are able to account for dual-competing reactions associated with devolatilization and char formation. These models are also able to predict when char combustion is complete, and details about the structural change of the particle are captured degradation.

Kinetic models have also been developed to predict the thermal response of materials at a larger scale. Kinetics of cardboard were investigated by Loulou, Salvador, and Dirion [3], and a numerical procedure was developed to simultaneously determine kinetic parameters from TGA data. Stoliarov and Lyon [2] developed a versatile model called ThermaKin to predict the behaviors of materials exposed to fire that includes transient thermal energy transport, chemical reactions, and transport of gases. This model also predicts charring. Lautenberger, et al. [1] assesses TGA data to determine a kinetic model to predict the decomposition kinetics on overall pyrolysis behavior. Several model reaction mechanisms are evaluated in this study, including a single reaction and a three-reaction model. But the ability to connect the kinetic behavior with the energetics of the reaction is not well understood.

Limited data exists in the literature on the energetics required to decompose solid materials into gas. This in part, is due to the fact that experimental methodologies have not been developed and validated.

Specific heat capacity and mass loss of the material at elevated temperatures are routinely performed using a differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), respectively. There are ASTM standards in place that prescribe methods for conducting DSC experiments to obtain quantitative specific heat capacity (ASTM E-1269 [12]) as well as running TGA with the intent of obtaining kinetic parameters (ASTM E-1641 [13]).

Several studies have been aimed at determining heat of decomposition values based on combining the individual results of TGA and DSC.
Henderson [6] presented a method that combines DSC data with TGA data results measured at the same heating rate. During degradation, the material changes state from virgin to decomposed, and Henderson [6] suggests a method for combining the two properties to represent the sensible specific heat capacity across the full temperature range. The DSC measures apparent specific heat capacity values which combines the sensible and latent specific heat value. A graphical method is employed to interpret the heat of decomposition. This method, however, does not include the effects of the evolved gas products.

Lattimer, et al. [5] provides a more comprehensive approach. Composite material and balsa wood samples were investigated for use in Navy sandwich composites. Samples were prepared in various stages of decomposition and then physical properties determined at each stage using a Thermal Decomposition Apparatus. Then properties of the samples were determined across the full temperature range by combining the stage properties. Data was measured separately using a TGA to decompose samples in Argon environment and a DSC to decompose samples in Nitrogen. Samples were prepared as both fragments and powders for separate TGA and DSC testing. Kinetic models were also developed from the TGA results in order to predict the material response to temperature. Single and multiple step reactions were incorporated. Heat of decomposition values were determined by combining the TGA mass loss data with the apparent specific heat data from the DSC in an energy balance. Gas products for the samples were measured separately by Southwest Research Institute [8] and incorporated into the model. The results from the TGA and DSC were also validated by the TDA results with the energy model; however, the properties of propane gas were used for the evolved gas product. An improvement to the use of combining DSC results with TGA would be to test a sample simultaneously by way of the STA.

Analysis in Chapter 2 used experimental gravimetric and heat flow from the STA to determine the heat of decomposition. This analysis inherently assumed that the decomposition process could be determined through a single global reaction. There are two issues with using this type of approach. First, the heat of decomposition value is directly related to the gravimetric response of the material. The gravimetric response of a material is usually predicted with an Arrhenius kinetic model. The Arrhenius kinetic model is likely to produce different results from the data, and then the heat of decomposition determined using the gravimetric data will not produce the same heat flow response as that determined using the kinetic model gravimetric results. Second, the approach in Chapter 2 does not allow for multiple reactions to be used. The use of multiple reactions by definition requires developing an Arrhenius kinetic reaction model that includes multiple, potentially simultaneously occurring reactions.

The focus of this research was to develop a methodology to determine the heat of decomposition for any material directly using experimental data combined with a kinetic model. Heat of decomposition values can be determined for multiple reactions by optimizing an energy model that combines experimental data and a kinetic model. A Simultaneous Thermogravimetric Analyzer (STA) was used to measure both mass loss and heat flow data as functions of temperature in the same experiment. Virgin and decomposed material properties were developed from the experimental data across a wide temperature range. Properties for the as evolved gas products are also incorporated into the model. The STA mass loss data is evaluated to form a kinetic model and combined in an energy balance. The resulting energy balance is optimized to determine heat of decomposition values for each reaction.
Experimental Description

A Netzsch STA 449 F1 Jupiter Simultaneous Thermogravimetric Analyzer/Differential Scanning Calorimeter (TGA/DSC) was used to characterize the gravimetric and energetic response of materials during heating. The STA is a testing apparatus that can subject a sample to a predetermined temperature profile. This includes a controlled heating rate of up to 50°C/min as well as sustained isothermal temperatures to a maximum of 1500°C. The resulting data collected from the apparatus includes mass loss data, heat flow (i.e., heat transfer to the sample), and apparent specific heat all as a function of time or temperature.

The apparatus consists of a vertical tube furnace with a platinum platform for the sample and integrated Type S thermocouples. The platform supports two cups, one for the sample and one for the reference measurements. Lids with single 0.25 mm diameter holes can be used during testing. The STA can be used with cups of various materials (platinum, aluminum, ceramic) depending on the maximum temperature of the test. In these tests, the chamber is closed and taken to 92-95% vacuum and then refilled with pure nitrogen to maintain an inert environment. Nitrogen was used in the testing to prevent char oxidation of samples. Nitrogen continues to enter the chamber at a rate of 50 mL/min for the duration of the experiment.

The STA uses a common furnace to control the heating conditions in the chamber so that the sample cup and reference cup experience the same thermal conditions. This is known as a heat-flux compensated DSC. The user sets a temperature profile for the test (ramping rates and isotherms), and the sample and reference cup temperatures are recorded. During the test, a difference in temperature between the sample cup and the reference cup indicates a heat flow to or from the sample. This is recorded as the DSC signal for the sample in units of volts. The voltage signal can be converted to heat flow in Watts by loading a calibration file prior to conducting the test.

Mass of the sample during the heating is continuously measured using a balance attached to the base of the tube supporting the sample platform. The platform balance has a 25 ng resolution at a weighing range of 5g. Mass measurements were obtained in each STA experiment performed.

The temperature conditions can be controlled by either the sample thermocouple or the furnace thermocouple. As recommended by the manufacturer, furnace temperature control was used in all experiments, as it gives better temperature accuracy and prevents temperature control problems from occurring as a result of reactions (melting, decomposition, etc) in the sample. When using furnace temperature control, the instrument will ramp until the furnace thermocouple reaches the selected temperature. This final temperature will always be higher than the sample temperature, which lags due to heat loss from the furnace and placement of the thermocouple within the furnace. The magnitude of the temperature lag depends on the exact temperature, but can range from 10-50°C. The heating rate of the sample is the same as that of the furnace, and all plots are done using sample temperature.
Baseline and Calibration Tests

A series of baseline and calibration tests must be performed using the STA to produce quantitative mass and heat flow data. Without these additional tests, the instrument will only provide qualitative results on the material response.

The baseline test establishes the mass and heat flow response of the instrument over the tested temperature range without a sample in the STA. The baseline test is performed using two empty sample cups at the same conditions the sample will be tested. It is important that the test be conducted with the identical temperature profile, sample cups, gas type, and flow rates. The baseline measurement of mass and DSC signal over the range of temperatures are subtracted from the sample measurements to determine the actual response for the sample only. Once the baseline measurement is recorded, the sample can be loaded in the STA and the actual test can be conducted.

A calibration test is also required to obtain quantitative specific heat capacity data. The calibration test was performed in general accordance with ASTM E-1269 [12]. This standard specifies that the calibration test be conducted with one cup containing aluminum oxide (sapphire) reference material, which has a known specific heat capacity value at elevated temperature. Similar to the baseline test, the calibration test must be performed using the same condition and sample cups that will be used to test the sample. The calibration test provides a DSC signal that can be related directly to a known specific heat capacity. The methodology for using these results to determine the specific heat capacity of a sample is outlined in the next section.

Samples and Preparation

A previous study by Goodrich [7] determined that optimized DSC results depend on samples being prepared in the same manner. Sample materials for use in the STA were prepared into solid discs, 6 mm in diameter, in order to fit snugly into the STA crucible. The thickness of the sample was then reduced to allow the sample mass range to fall within 27-55 mg. Sample thicknesses were on the order of 15 – 75 mils. Sample crucibles and lids were aluminum. The best method to prepare the sample was to core drill the material to the required diameter and then hand sand or file down to the required thickness. For comparison to sapphire in the specific heat determination, samples were prepared so that the average mass of the sample agreed with the sapphire mass during the experiment.

Sample Description

E-glass/vinyl ester samples were prepared and tested at heating rates of 5, 10, 20, and 40°C/min in this research. The composite laminate material evaluated in this study was E-glass/vinyl ester laminate. Laminates contained Vetrotex 324B fibers in a 55/45 woven roving with a 4.826 mm nominal width and 813.75 g/m² density. The resin was Derakane 411-350 vinyl-ester resin. The laminates were manufactured using the vacuum-assisted resin transfer molding (VARTM) process. In this process, layers of woven roving glass were placed under a vacuum bag and the resin is drawn in via a vacuum pump. A package consisting of 1.5% methyl
ethyl ketone peroxide (MEKP), 0.06% acetylacetone, and 0.2% CONAP® as percentages of the total resin mass was used to cure the resin. Panels used in this study had a 6 mm nominal thickness and were not post-cured after fabrication. E-glass/VE samples were cut from larger panels, primarily using a hacksaw, and the material was cored using the core drills.

Theory

This theory provides an approach for predicting the heat of decomposition for a material using the results from an Arrhenius kinetic model predicting the heat of decomposition and the apparent specific heat capacity measured using the STA. The approach can be used for either a single reaction mechanism or multiple reactions occurring simultaneously.

Single Global Reaction

For this analysis, the sample material is assumed to have a lumped capacitance. Using this assumption, the resulting energy balance is summarized by Equation 3.1. This approach was previously developed in Chapter 2. The enthalpy terms for the energy balance are further defined in Equation 3.2 and Equation 3.3 where Δh_d represents the heat of decomposition:

\[
\left( mc_p + \left( h - h_g \right) \frac{\partial m}{\partial T} \right) \frac{\partial T}{\partial t} = E \dot{Q}
\]

Equation 3.1

\[
h = \Delta h_d + \int_{T_{ref}}^{T} C_p \partial T
\]

Equation 3.2

\[
h_g = \int_{T_{ref}}^{T} C_{p,g} \partial T
\]

Equation 3.3

Kinetic Equations

Mass loss data from multiple heating rates is measured using the STA. A kinetic model is developed to predict the mass loss as a function of temperature and subsequently the mass loss differential with temperature. This is achieved by first normalizing all the data by means of the reaction progress variable:

\[
e = \left( \frac{m - m_d}{m_v - m_d} \right)
\]

Equation 3.4

Solid material decomposition was previously modeled by directly using the experimental data measured by the STA. For this analysis, an nth order Arrhenius decomposition kinetic model is used to describe the mass loss:

\[
\frac{\partial e}{\partial t} = \left[ e \right]^n A \exp \left( -\frac{E_a}{RT} \right), \quad k = A \exp \left( -\frac{E_a}{RT} \right)
\]

Equation 3.5
In this equation, \( e \) is the normalized weighted mass fraction, which represents the reaction progress and is a measure of active mass. A single reaction is represented by the reaction mechanism in Figure 3.1, where \( k_1 \) is the reaction rate and is equivalent to the product of the pre-exponential factor and the exponential term in Equation 3.5.

\[
A \xrightarrow{k_1} B
\]

Figure 3.1. Single reaction kinetic mechanism

The Arrhenius expression has the ability to be used to correlate the mass loss rate data for degrading materials at different heating rates (Dollimore [15]). After manipulation, the desired expression is achieved, where \( \frac{dT}{dt} \) is the heating rate:

\[
\frac{\partial e}{\partial T} = \left[e\right]^n A \exp\left(\frac{-E_a}{RT}\right) \frac{dT}{dt}
\]  
Equation 3.6

The kinetic parameters are represented by the activation energy, \( E_a \), the pre-exponential factor, \( A \), and the reaction order, \( n \). Once kinetic parameters are determined for this single reaction, \( e \) can be solved for as a function of temperature and transformed to mass as a function of temperature using Equation 3.4. In addition, the expression of the differential of \( e \) with respect to temperature can be directly transformed to the mass differential. Both of these terms are then used directly in the energy balance Equation 3.1.

Combining the kinetic equation with the remaining terms in the energy balance forms the basic model for this analysis. A single kinetic reaction equation can be combined and results in one heat of decomposition value associated with the reaction.

**Sensible Specific Heat Capacity, Enthalpies, and Calibration Factor**

As a result of the decomposition behavior, specific heat values determined by the STA represent an apparent specific heat. The apparent specific heat combines the sensible component of the specific heat, which accounts for the heat flow associated with the temperature change in the material, as well as the latent specific heat associated with the phase change during the decomposition reaction. As done in Chapter 2, the sensible portion can be separated from the apparent specific heat by using Equation 3.4 again, the reaction progress variable, to identify the virgin and decomposed material properties. The properties are then combined to predict the sensible specific heat capacity properties across the full temperature range, particularly during the decomposition.

The enthalpy is defined as the integration of the sensible specific heat term from a reference temperature to the state temperature as shown in Equation 3.2. This is accomplished by numerically integrating the sensible specific heat term using a reference temperature of 273 K. A trapezoidal numerical integration scheme was used to determine the enthalpy from the sensible specific heat terms. The enthalpy of the evolved gases is based on the mixture of products released during the decomposition. The evolved products and their associated mass
fractions are used to determine a mixture specific heat. The result is then integrated with temperature to determine the enthalpy for the evolved gases as shown in Equation 3.3.

A calibration factor $E$ is determined using the DSC signal from the calibration test on sapphire, which has a known specific heat capacity. The specific heat capacity of the sample was determined in general accordance with the procedure outlined in ASTM E-1269 [12]. ASTM E-1269 [12] method for obtaining specific heat by the differential scanning calorimeter is a ratio method that uses the heat flow curve from the sapphire calibration test to determine the specific heat of the sample. Revisions were made to this methodology to allow for the determination of decomposing samples. The calibration factor can then be applied to the given DSC signal (heat flow) for the sample material.

**Determination of Heat of Decomposition from data and model**

Data measured by the STA consists of mass, heat flow, and specific heat all as functions of temperature. By using the kinetic model, the mass loss behavior is instead captured by the kinetic reaction. As a result, all the terms in Equation 3.1 have been obtained or developed with the exception of the heat of decomposition. A kinetic model was developed with a single reaction that predicts the mass loss behavior with temperature. The kinetic model governs the mass values and mass differential values. The sensible specific heat term was derived. Next, the sensible specific heat term was integrated to develop the enthalpy term for the solid. Based on the products evolved for each material ([8], [9], [10], [11]), the enthalpy for the gas products was calculated. The heating rate was constant and known. Last, the calibration factor was determined and applied to the DSC signal to represent the corrected heat flow experienced by the material during the testing.

An optimization scheme was employed in MATLAB to determine the heat of decomposition value. The kinetic model was solved in MATLAB using a built-in ordinary differential equation solver. All remaining data were imported into MATLAB as arrays with temperature and combined to represent the energy equation. Then, a user-specified range of values for the heat of decomposition was input into the code. Using a least squared difference minimizing technique, with terms evaluated at each temperature node, the program returned the optimum heat of decomposition value to satisfy the energy balance by finding the minimum residual term $R$ and its associated heat of decomposition:

$$
\sum_{T=T_{\text{Initial}}}^{T_{\text{Final}}} \left[ m(T)C_p(T) + \left( h(T) + \Delta h_{d,i} - h_g(T) \right) \frac{\partial m(T)}{\partial T} \right] \frac{dT}{dt} - E(T) \dot{Q}(T) \right] = R_i \quad \text{Equation 3.7}
$$

A single reaction is shown in Equation 3.7; however, this method was extended to multiple reactions as well.
Multiple Reactions

For this analysis, the sample material is again assumed to have a lumped capacitance. For multiple reactions, the mass loss is governed by multiple kinetic equations. Each kinetic reaction accounts for a portion of the mass loss, and therefore has its own associated heat of decomposition value. The heats of decomposition terms, $\Delta h_d$, have been rearranged to be included with the enthalpy terms for clarity. Using this assumption, the resulting energy balance is:

$$
\left( m_1 C_p + (h + \Delta h_1 - h_s) \frac{\partial m_1}{\partial T} \right) \frac{\partial T}{\partial t} + \\
\vdots \\
\left( m_n C_p + (h + \Delta h_n - h_s) \frac{\partial m_n}{\partial T} \right) \frac{\partial T}{\partial t} + \\
(m_{\text{inactive}} C_p) \frac{\partial T}{\partial t} = E \dot{Q}
$$

Equation 3.8

where $h = \int_{T_{\text{ref}}}^{T} C_p \partial T$  

Equation 3.9

$h_s = \int_{T_{\text{ref}}}^{T} C_{p,g} \partial T$  

Equation 3.10

In Equation 3.8, the energy balance is written for $n$ kinetic reactions and therefore has $n$ number of associated heat of decomposition values. The term $m_{\text{inactive}}$ refers to any material that remains after the decomposition process. Clearly, it experiences a change in temperature during the experiment, thus the sensible heat of the inactive mass affects the heat flow so it is included. But, by virtue of remaining, the material does not experience decomposition and therefore does not have any associated heat of decomposition value. The enthalpy terms are summarized in Equation 3.9 and Equation 3.10.

Kinetic Equations

A multiple kinetic reaction model is an expansion of the kinetics previously developed. The first step is normalizing all the data by means of the reaction progress variable:

$$
e = \left( \frac{m - m_{d_e}}{m_f - m_d} \right)
$$

Equation 3.11

Mass loss data from multiple heating rates is measured using the STA. Solid material decomposition was previously modeled by using one $n$th order Arrhenius decomposition kinetic model. For this analysis, several Arrhenius expressions are combined to represent the kinetic model. In Figure 3.2, two consecutive reactions are combined to represent a kinetic model.
Each reaction rate, $k_1$ and $k_2$, are defined by their own set of kinetic parameters $A$, $E_a$, and $n$. The generic form for reaction $k_n$ as a function of temperature is:

$$\frac{\partial e_{kn}}{\partial T} = \left[ e_{kn} \right]^{\nu_n} A_{kn} \exp \left( -\frac{E_{a,kn}}{RT} \right) \frac{dT}{dt}$$

Equation 3.12

In this equation, $e_{kn}$ is a portion of the normalized weighted mass fraction, which when summed together represents the reaction progress and is a measure of active mass. Each reaction accounts for a portion of the change in the active mass.

Once a kinetic mechanism is selected and kinetic parameters are determined for multiple reactions, each kinetic reaction can be solved for $e$ as a function of temperature and transformed to mass as a function of temperature using Equation 3.11. In addition, the expression of the differential of $e$ with respect to temperature can be directly transformed to the mass differential. All of these terms are then used directly in the energy balance Equation 3.8.

Combining the kinetic equation with the remaining terms in the energy balance forms the basic model for this analysis. For multiple kinetic reactions, all of the equations are combined and result in a heat of decomposition value is associated with each reaction. The sensible specific heat capacities, enthalpies, and calibration factor for the heat flow are all determined in the same method as with the single kinetic reaction model.

**Determination of Heat of Decomposition from data and model**

Data measured by the STA consisted of mass, heat flow, and specific heat all as functions of temperature. By using the kinetic model, the mass loss behavior was instead captured by the kinetic model. All the terms in Equation 3.8 have been obtained or developed with the exception of the heats of decomposition. A kinetic model was developed with multiple reactions to capture the mass loss behavior with temperature. The kinetic model governs the mass values and mass differential values. The sensible specific heat term was derived from the data, and then the sensible specific heat term was integrated to develop the enthalpy term for the solid. Based on the products evolved for each material, the enthalpy for the gas products was calculated. The heating rate was constant and known. Last, the calibration factor was determined and applied to the DSC signal to represent the corrected heat flow experienced by the material during the testing.

An optimization scheme was employed in MATLAB to determine the heats of decomposition values. The kinetic equations are combined in MATLAB and solved simultaneously using a built-in solver for a system of ordinary differential equations. All remaining data were imported into MATLAB as arrays with temperature and combined to represent the energy equation. Then, a user-specified range of values for the heats of decomposition was input into the code. Using a least squared difference minimizing technique,
with terms evaluated at each temperature node, the program returned the optimum heats of decomposition values to satisfy the energy balance by finding the minimum residual term $R$ and its associated heats of decomposition:

$$
\sum_{T=\text{Initial}}^{T=\text{Final}} \left[ m_i(T)C_p(T) + \left( h(T) + \Delta h_d - h_g(T) \right) \frac{\partial m_i(T)}{\partial T} \right] \frac{dT}{dt} + \\
\vdots \\
\left[ m_n(T)C_p(T) + \left( h(T) + \Delta h_d - h_g(T) \right) \frac{\partial m_n(T)}{\partial T} \right] \frac{dT}{dt} + \\
\left( m_{\text{inactive}}C_p \right) \frac{\partial T}{\partial t} - E(T)\dot{Q}(T) \right]^2 = R_i
$$

Equation 3.13

Results and Analysis

The kinetic and energetic response of E-glass/vinyl ester composite laminate is presented in the section. Kinetic models were developed with the aid of *Thermokinetics* software. In addition, analysis was performed to determine the heats of decomposition for this sample using the methods outlined in the previous section. A single reaction kinetic model is used, and then expanded to multiple reactions.

**Single Reaction Kinetic Model**

Kinetic parameters were determined for a single reaction by using *Thermokinetics* software in conjunction with the STA experimental data. *Thermokinetics* is a software module for the kinetic evaluation of thermal measurements. While *Thermokinetics* has the capability to model multiple reactions, it is limited to unimolecular products and reactants. In this analysis, *Thermokinetics* is used primarily for preliminary estimation of a kinetic model. It also has some useful built in tools that provide insight and are discussed later.

Experiments were performed on the E-glass/vinyl ester at heating rates of 5, 10, 20, and 40°C/min. All mass loss data values were transformed to the normalized weighted mass fraction (active mass) values for analysis by *Thermokinetics*. The transformation results for E-glass/vinyl-ester are shown in Figure 3.3.
A model-free approximation is used to determine the initial kinetic parameters by the Ozawa-Flynn-Wall method [16], [17]. The Ozawa-Flynn-Wall [16], [17] method is based on considering sample iso-conversional lines for multiple heating rates and correlating the slopes to the activation energy and the intercepts to the pre-exponential factor. Kinetic parameters determined for the global kinetic model by Thermokinetics are shown in Table 3.1.

Table 3.1. Optimized kinetic parameters for global reaction determined by Thermokinetics

<table>
<thead>
<tr>
<th>Activation Energy, $E_a$ (kJ/mol)</th>
<th>Pre-exponential factor, A ($\log_{10} (1/s)$)</th>
<th>Reaction order, n</th>
</tr>
</thead>
<tbody>
<tr>
<td>176.2755</td>
<td>10.9067</td>
<td>0.5978</td>
</tr>
</tbody>
</table>

The resulting kinetic behavior is compared to the weighted mass fraction data. Figure 3.4 shows the comparison between the data and the optimized fit by Thermokinetics for a single kinetic reaction using the estimates from the model-free approximation.
The resulting kinetic model captures the general behavior of the reaction. The model does not accurately predict the mass loss at the beginning and the end of the reaction; however, the dominant reaction is well matched. The kinetic parameters define a kinetic model and are combined with the STA data in MATLAB to represent the energy balance. Results of the optimization scheme to determine the heat of decomposition using the kinetic parameters are shown in Figure 3.5.
Figure 3.5. E-glass/vinyl-ester experimental and predicted heat flows for 20° C/min

The results shown in Figure 3.5 are the optimized results with a heat of decomposition value of -870 kJ/kg. Compared to the data, this model indicates a fit that has an average of 4.5% difference between the data and the model across the entire temperature range; however, the peak heat flow of the model does not align well with the experimental data. Recall the energy balance includes a differential mass loss term. Since the kinetic model was created based on the mass loss itself and not the differential, the mismatch is due to a lack of agreement in the slope of the mass loss behavior.

Refined Reaction Kinetic Model

A refinement is made to the kinetic parameters by considering the derivative of the fractional mass loss with temperature. The predicted mass loss derivative of the model is compared to the actual mass loss derivative of the data. Using Mathematica to manipulate the kinetic model, the mass derivative peaks are aligned by adjusting the kinetic parameters, shown in Figure 3.6.
Figure 3.6. Plot of model differential mass loss matched to experimental data for E-glass/vinyl-ester at 20°C/min

By manipulating the kinetic parameters of the model to match the differential mass loss experimental data, a new set of refined kinetic parameters are obtained. These refined values, shown in Table 3.2, are relatively close in value to the parameters determined by *Thermokinetics*.

Table 3.2. Refined kinetic parameters for global reaction determined by Mathematica

<table>
<thead>
<tr>
<th>Activation Energy, $E_a$ (kJ/mol)</th>
<th>Pre-exponential factor, $A$ ($\log_{10} (1/s)$)</th>
<th>Reaction order, n</th>
</tr>
</thead>
<tbody>
<tr>
<td>216.5</td>
<td>14</td>
<td>0.9</td>
</tr>
</tbody>
</table>
Figure 3.7. Fractional mass loss data of E-glass/vinyl-ester at 20°C/min compared to two kinetic models

A comparison of the experimental mass loss data and the two models is shown in Figure 3.7. From the perspective of the mass loss behavior, the refined model does not differ greatly from the Thermokinetics determined model. The refined model still captures the general shape of the reaction, but now makes a better approximation of the mass loss slope.

The refined kinetic parameters were used to define a new kinetic model and are combined with the STA data in MATLAB to represent the energy balance. Results of the optimization scheme to determine the heat of decomposition using the refined kinetic parameters are shown in Figure 3.8. Mass loss results using the Thermokinetics determined model are within 1.5% compared to the actual data. By implementing the refinement procedure, the mass loss results become with 1.1% compared to the actual data. While the refinement results for E-glass/vinyl-ester may achieve only a slight improvement in predicting the mass loss, the improved energetic results are more significant.
Figure 3.8. E-glass/vinyl-ester experimental and predicted heat flows for 20° C/min using refined parameters

The results shown in Figure 3.8 are the optimized results with a heat of decomposition value of -870 kJ/kg. Compared to the data, this model indicates a fit that has an average of 3.5% difference between the data and the model across the entire temperature range. The peak heat flow of the model now aligns well with the experimental data. The optimized Thermokinetics model and the refined model are compared with the experimental data in Figure 3.9.
The heats of decomposition determined for both kinetic models as well as the data driven model determined from Chapter 2, which is also based on a global kinetic reaction, are shown in Table 3.3.

Table 3.3. Comparison of Heat of Decomposition Values

<table>
<thead>
<tr>
<th>Thermokinetics Kinetic Parameters</th>
<th>Refined Kinetic Parameters</th>
<th>Data Driven Model</th>
</tr>
</thead>
<tbody>
<tr>
<td>-870 kJ/kg</td>
<td>-870 kJ/kg</td>
<td>-910 kJ/kg</td>
</tr>
</tbody>
</table>

Overall, the model generally matches the data quite well throughout most of the reaction. The peak has an improved alignment and the model generally replicates the beginning and end tail behaviors. Using a single kinetic reaction model enables material behavior prediction for other thermal circumstances. But, by only considering one reaction, complex decomposition behaviors are simplified in an attempt to achieve a best fit over the entire temperature range.

Multiple Reaction Kinetic Model

From Thermokinetics, a closer look at the results from the Ozawa-Flynn-Wall [16], [17] model-free approximation provides direction for the multiple reaction model. Thermokinetics summarizes the iso-conversional information in an energy plot shown in Figure 3.10.
This energy plot shows how the activation energy and pre-exponential value estimates vary with mass loss. The shape of the plot indicates that there are at least three significant reaction regimes. There is an early stage reaction between 0 and .05 fractional mass loss with an associated activation energy approximately equal to 125 kJ/mol and pre-exponential factor of $10^8$ 1/s. The dominant reaction occurs between .05 and .95 fractional mass loss with associated activation energy of around 175 kJ/mol and pre-exponential factor of $10^{11}$ 1/s. Finally, there is a third reaction stage from .95 to 1.0 fractional mass loss with associated activation energy of around 275 kJ/mol and pre-exponential factor of $10^{17}$ 1/s.

Kinetic parameters obtained for the single reaction (Table 3.2) are similar to the values suggested for the dominant middle reaction. An appropriate multiple reaction scheme would also include a reaction to predict the early decomposition and a final reaction at the end. *Thermokinetics* contains a multivariate nonlinear regression analysis package to determine kinetic parameters for multiple reactions with up to six reactions. Some examples of the various types of multiple reaction mechanisms that *Thermokinetics* can investigate are shown in Figure 3.11.
Figure 3.11. Examples of one, two, and three-step reaction schemes that *Thermokinetics* is capable of handling.

However, the software does not contain reaction schemes that allow for the evolution of multiple products. A simplified reaction scheme, Figure 3.12, is used to ascertain initial estimates for the kinetic parameters governing each reaction.

\[
A \xrightarrow{k_1} B \xrightarrow{k_2} C \xrightarrow{k_3} D
\]

Figure 3.12. Multiple reaction scheme used in *Thermokinetics* for E-glass/vinyl-ester decomposition

This kinetic model does not fully capture the intent of the decomposition. A comprehensive model accounts for intermediate solids and the separate evolution of gas products during each reaction. The kinetic parameters determined for Figure 3.12 are used as initial guesses for a more comprehensive model. The proposed reaction mechanism used for this analysis is shown in Figure 3.13.

\[
A \xrightarrow{k_1} \nu_1 B_{\text{inter}} + (1 - \nu_1)C_{\text{gas}} \\
A \xrightarrow{k_2} \nu_2 D_{\text{inter}} + (1 - \nu_2)E_{\text{gas}} \\
A \xrightarrow{k_3} F_{\text{gas}}
\]

Figure 3.13. Multiple reaction mechanism for E-glass/vinyl-ester decomposition

During the first and second reactions, it is assumed that the reaction produces an intermediate solid and gas products. The coefficient \(\nu\) allows for evolution of separate gas and
solid products governed by the same kinetic reaction parameters (Lautenberger, et al. [1]). Finally, the last reaction is assumed to evolve gas products only from the remaining active mass.

The estimated kinetic parameters are refined just as the single reaction kinetics were by considering the mass loss differential. In this case, the kinetic parameters determined by Thermokinetics are combined within the framework of the comprehensive kinetic model. All kinetic parameters are then refined, and the coefficient ν’s determined, by comparing the solid species to the experimental data in terms of mass loss differential with temperature. The coefficient terms roughly correspond to the reaction progress variable values that separate the reaction regions. The values of the kinetic parameters and the coefficients for each reaction are shown in Table 3.4.

Table 3.4. Kinetic parameters for multiple reaction scheme

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Activation Energy, $E_a$ (kJ/mol)</th>
<th>Pre-exponential factor, $A$ (log$_{10}$ (1/s))</th>
<th>Reaction order, n</th>
<th>Coefficient, ν</th>
</tr>
</thead>
<tbody>
<tr>
<td>First Reaction</td>
<td>38.6239</td>
<td>1.4665</td>
<td>1.0</td>
<td>0.97</td>
</tr>
<tr>
<td>Second Reaction</td>
<td>223.8</td>
<td>14.5706</td>
<td>0.97</td>
<td>0.05</td>
</tr>
<tr>
<td>Third Reaction</td>
<td>90.2901</td>
<td>9.9615</td>
<td>3.0</td>
<td>--</td>
</tr>
</tbody>
</table>

The kinetic equations are solved simultaneously in MATLAB. The experimental mass loss data is compared to the solid products from the kinetic model and the results are shown in Figure 3.14.
Figure 3.14. Fractional mass loss of E-glass/vinyl/ester at 20°C/min compared to multiple reaction kinetic model

Mass loss results using the refined kinetic parameters from Table 3.4 result in a predicted mass loss that is within 1.0% compared to the actual data throughout the full temperature range. The multiple reaction kinetic model captures the mass loss behavior quite well, particularly the early mass loss as well as the dominant middle reaction. The third reaction is not as well matched as the first and second. This is likely due to the reaction scheme not successfully summarizing the actual decomposition behavior at the high temperatures.

*Heat of Decomposition*

The multiple reaction kinetic parameters are used to define a kinetic model and are combined with the STA data in MATLAB to represent the energy balance. Details on the evolved gas compounds and amounts used to determine the mixture specific heat are tabulated in Appendix A. Results of the optimization scheme to determine the heat of decomposition using the multiple reaction kinetic parameters are shown in Figure 3.15.
Figure 3.15. E-glass/vinyl-ester experimental and predicted heat flows for 20°C/min using multiple reaction scheme

The results shown in Figure 3.15 indicate an improved fit between the experimental data and the model. Compared to the data, the multiple reaction model indicates a fit that has an average of 3.0% difference between the data and the model across the entire temperature range. The heats of decomposition values determined for each reaction of the multiple reaction kinetic model are shown in Table 3.5. The peak heat flow of the model aligns well with the experimental data, and the heat flow is well matched at higher temperature.

Table 3.5. Heat of Decomposition Values for each reaction

<table>
<thead>
<tr>
<th>First Reaction</th>
<th>Second Reaction</th>
<th>Third Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>-870 kJ/kg</td>
<td>-910 kJ/kg</td>
<td>-2700 kJ/kg</td>
</tr>
</tbody>
</table>

Overall, the multiple reaction model matches the data quite well throughout most of the reaction. The peak well is aligned, and the model generally replicates the beginning and end tail behaviors. Concerning the heat flow, the behavior at the high temperature end is better approximated by the multiple reactions rather than the single kinetic reaction; however, the heat of decomposition value for the third reaction is quite high. This is may be due to the reaction scheme not successfully summarizing the actual decomposition behavior at the higher temperatures.
Figure 3.16. Global and multiple reaction models compared to experimental mass loss data for E-glass/vinyl-ester at all heating rates

A heat of decomposition value was determined previously in Chapter 2 by using the experimental data directly from the STA. In this section, the energy analysis was refined to include a single kinetic reaction as well as multiple kinetic reactions. The single reaction and multiple reaction models are compared to the experimental data for all heating rates in Figure 3.16. The data points are shown as the dots, single reaction as the dashed line, and multiple reaction model as the solid line. Looking more closely at the first drop of the mass loss shoulder, the multiple reaction model is a better approximation of the data compared to the global reaction model.
The two heat flow models, the refined global reaction and the refined multiple reaction model, and the heat flow model from Chapter 2 based on the data are compared to the experimental data for the heating rate of 20°C/min in Figure 3.17. The data is a blue line, the model from Chapter 2 is green, the single reaction model is red, and the cyan line is the multiple reaction model. Looking at all the results compared to the data, the multiple reaction model is the best match at the higher temperature range compared to the other models.

For both the global single reaction and the multiple reaction models, the error of the models with respect to the heat flow data is considered. The percent error is calculated at each temperature, and a mean absolute percent error is determined for each model.
The results of the error analysis for the single reaction and multiple reaction models are shown in Figure 3.18. The mean absolute error percentage for single reaction model is 3.5% and for the multiple reaction model is 3.0%. From this plot, error is reduced by incorporating the multiple reaction scheme. This is particularly notable in the temperature range of 500 – 600 K as well as the 800 – 900 K range.

**Conclusion**

An improvement was made to the mass loss prediction by incorporating multiple reactions into the kinetic model. The single reaction kinetic model can be combined with experimental data from an STA and used to effectively determine the heat of decomposition. By creating a kinetic model, insight is gained into the degradation mechanism. In addition, thermal scenarios other than the testing set up can now predicted by the kinetic model. Incorporating a single reaction into an energy balance was computationally straightforward. Results for predicting heat flow are good; however, materials that decompose with more complex behavior would likely suffer from oversimplification and the results may not be as meaningful.

The multiple reaction kinetic model is able to better simulate the mass loss as well as the heat flow experienced by the sample during the decomposition. Error in modeling the heat flow behavior was reduced by using multiple reactions. By considering something like the energy plot of the sample, the energetics of the decomposition can be examined and a multiple kinetic
reaction model devised to suit both the kinetic and energetic behaviors. The downside of this is that multiple reactions may be computationally expensive to implement.

Most significantly, both reaction schemes benefited from the mass loss differential analysis. For energetic predictions, creating a kinetic model based on the mass loss data will have limited success in replicating the heat flow unless the mass loss differential is also considered.

In summary, this methodology can be readily extended to describe more complex mass loss behavior and more complex reaction mechanisms. In this analysis, all of the evolved gas products are considered to be the same mixture of products. Employing a mass spectrometer/gas analyzer and directly measuring the gas products exiting the sample material, and potentially isolating the products in each reaction region, would improve results.
References


Nomenclature

<table>
<thead>
<tr>
<th>SYMBOL</th>
<th>DESCRIPTION</th>
<th>UNITS</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A$</td>
<td>area</td>
<td>$m^2$</td>
</tr>
<tr>
<td>$d$</td>
<td>diameter</td>
<td>$m$</td>
</tr>
<tr>
<td>$g$</td>
<td>gravitational force, 9.81</td>
<td>$m^2/s$</td>
</tr>
<tr>
<td>$m$</td>
<td>solid material mass</td>
<td>$kg$</td>
</tr>
<tr>
<td>$\dot{m}_f$</td>
<td>mass flow rate of fluidizing gas</td>
<td>$kg/s$</td>
</tr>
<tr>
<td>$t$</td>
<td>time</td>
<td>$s$</td>
</tr>
<tr>
<td>$T$</td>
<td>absolute temperature</td>
<td>$K$</td>
</tr>
<tr>
<td>$T_{ref}$</td>
<td>reference temperature, 273</td>
<td>$K$</td>
</tr>
<tr>
<td>$U$</td>
<td>superficial velocity</td>
<td>$m/s$</td>
</tr>
<tr>
<td>$V$</td>
<td>volume</td>
<td>$m^3$</td>
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</table>

**Greek**

<table>
<thead>
<tr>
<th>SYMBOL</th>
<th>DESCRIPTION</th>
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<tbody>
<tr>
<td>$\Delta$</td>
<td>change in the following parameter</td>
<td>--</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>void fraction</td>
<td>--</td>
</tr>
<tr>
<td>$\mu$</td>
<td>viscosity of fluidizing medium</td>
<td>$N/s/m^2$</td>
</tr>
<tr>
<td>$\rho$</td>
<td>density</td>
<td>$kg/m^3$</td>
</tr>
<tr>
<td>$\phi$</td>
<td>sphericity</td>
<td>--</td>
</tr>
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</table>

**Subscripts**

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<th>DESCRIPTION</th>
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<tbody>
<tr>
<td>$b$</td>
<td>bulk</td>
</tr>
<tr>
<td>$f$</td>
<td>fluidizing gas</td>
</tr>
<tr>
<td>$m$</td>
<td>mean</td>
</tr>
<tr>
<td>$mf$</td>
<td>minimum fluidization</td>
</tr>
<tr>
<td>$p$</td>
<td>particle</td>
</tr>
</tbody>
</table>
Abbreviations

FBB – Fluidized Bubbling Bed
MFC – Mass Flow Controller
CHAPTER 4 - Lab Scale Fluidized Bubbling Bed

Motivation

Gasification, which is a method to sublime solid fuels (fossil fuels, biomass and other wastes) into either a combustible gas or a synthesis gas for subsequent utilization, offers the potential both for clean power and chemicals production. Presently, information on operational parameters, particularly at a large scale is lacking. This disconnect is cost prohibitive and is preventing wide-scale commercial application of this technology (Michener [1]).

Aside from knowledge of the kinetics and energetics associated with the fuel, modeling and experimenting with gasification requires understanding the impact of other physical parameters. This includes understanding how fuel size, shape, and density impact the flow in the bed. Knowledge in these areas will aid in modeling and proving out commercial scale fluidized beds.

Fluidized beds are commonly characterized by their minimum fluidization velocity, pressure drop across the fluidized bed, and the flow characteristics observed during fluidization. Material characterization is critical to isolating influencing parameters that might affect fluidization behavior.

Geldart [5] has done extensive work on classifying solid particles into categories for fluidization performance. The two parameters identified by Geldart that are central to predicting fluidization behavior are density and diameter. From the classifications, Geldart was able to generalize solid particle behavior such as mixing and segregating, two important considerations for achieving effective gasification of solid fuels.

Empirical models have also been developed to predict the minimum fluidization velocity for a fluidized bed based on the characterization of the particles. Leva [7] developed an empirical relationship as a function of average particle diameter and density and also includes the density and viscosity properties of the fluidizing gas. Kunii and Levenspiel [9] go a step further and also incorporates particle sphericity and bed voidage.

Several attempts have been made to successfully predict fluidization behavior scaled to fluidizing bed dimensions. Ramirez, Martinez, and Petro [2] presented a methodology to scale a fluidized bed to gasify rice husks mixed with sand. The fluidized bed apparatus design is centered around the characteristics of both particle types although they have very different physical characteristics and utilizes several relationships from Kunii and Levenspiel [9].

However, other factors not addressed by the empirical relationships may be affecting the particle hydrodynamic behavior. Franka, Drake, and Heindel [8] ran fluidization experiments with two different sized fluidized beds, one at 10.2 cm internal diameter and another at 15.2 cm. Glass beads, walnut shells, and corncob particles were fluidized individually in each bed. The observed minimum fluidization velocities for each material decreased with a decrease in bed diameter.
Cui and Grace [12] presented a review of predicting fluidization characteristics particularly for biomass. Biomass has the difficulty of having unusual properties and non-uniformities in its physical characteristics. Cui and Grace suggested incorporating a minimum fluidization velocity theoretical prediction based on average effective mixture density and diameter of the particles.

However, theoretical values are not able to replicate experimental results. Abdullah, Husain, and Yin Pong [4] designed a fluidized bed and experimented with several bed materials including sawdust, rice husk, peanut shell, coconut shell, palm fiber, coal and bottom ash. Particle characteristics for each material spanned a range of values, and an attempt was made to use arithmetic mean values of the particle parameters to predict the theoretical minimum fluidization velocity using empirical relationships. It was reported that only one material had an experimental fluidization velocity that coincided with the theoretical values.

The purpose of this research is to investigate the impact of particle density and diameter on the minimum fluidization velocity. In addition, pressure drops across a bed are investigated for correlation to varying bed mass values. Results from the bed mass investigation are then used to estimate the hydrodynamic behavior for a binary mixture of particles. Minimum fluidization velocities are predicted by mass-driven and particle-centric models and compared to actual results.
Experimental Description

A lab scale cold flow fluidized bubbling bed (FBB) apparatus, shown in Figure 4.1, was used to elicit the hydrodynamic response of bed media during testing. The FBB is an apparatus that can subject bed media to various fluidizing flow rates up to 500 SLPM. The resulting data collected from the apparatus includes pressure drop across the bed material, fluidizing mass flow rate, inline gage pressure and gas temperature, and temperature readings at the inlet and outlet of the apparatus all as functions of time.

Figure 4.1. Fluidized bubbling bed apparatus at right (fluidization chamber top, plenum space bottom), left is the distribution plate with mesh screen cover

Design of the fluidized bed apparatus is based on the collection of equations from Ramirez, Martinez, and Petro [2]. The design is also similar to fluidized bed used by Franka, Drake, and Heindel [8]. The apparatus consists of a plenum space, distribution plate, and fluidization chamber.

The plenum space is constructed of a 7.62 cm thick clear cast acrylic cylinder that measures 10.4 cm internal diameter and 15.25 cm in height. Air was injected into the base of the apparatus through the inlet plate by a 1.9 cm diameter air inlet fitting. The plenum space has a tapped hole for connection to a pressure transducer. The plenum space at the base distributes the jetting fluidizing gas for improved uniform flow. Flanges attached to the plenum space are bolted to the table. The plenum space was filled with glass spheres to aid in diffusing the flow before it reaches the distribution plate. In order to diminish electro-static effects on the
fluidizing material, a sponge with absorbed water was placed in the plenum space to increase humidity during operation.

Directly above the plenum space is the distribution plate. In this apparatus, the distribution plate was an acrylic disc 1.778 cm thick with 2mm diameter holes drilled in a pattern across the distribution plate so that there is a hole every 2.4 cm$^2$. The distribution plate design was based on design guides from Santos [3]. This is done to distribute the fluidizing gas uniformly into the actual fluidization chamber. To prevent bed material from clogging the distribution plate, a 44-mesh screen with 0.04 cm openings was attached to the distribution plate. A rubber gasket was placed between the distribution plate and plenum flange and a second rubber gasket was placed between the distribution plate and fluidization tube flange. The composite was bolted through to create a tight seal.

The fluidization chamber sits above the distribution plate. The fluidization chamber was constructed of a 7.62 cm thick clear cast acrylic cylinder that measures 10.4 cm internal diameter and 76 cm in height. The fluidization chamber has two tapped holes for connection to a pressure transducer. Only one hole was used for the pressure measurements, located at 68 cm above the distribution plate. Bed media was loaded from the top into the fluidization chamber. The chamber was open to the atmosphere; however, another 44-mesh screen was attached to a ring and bolted to the top fluidization chamber flange to prevent bed material from elutriating out of the top of the chamber.

This apparatus is similar in design to another configuration used in research by Franka, Heindel, and Battaglia [6]; however, air flowed through a piccolo type tube pipe prior to entering the plenum space in order to reduce the jetting effects. Also, the distribution plate used in that research had 1 mm diameter holes and the internal diameter of the chamber was 9.5 cm.

Also, Franka, Drake, and Heindel [8] also used another similar apparatus. In that configuration, air injection into the plenum space was the same as used here, along with the use of glass spheres, but the distribution plate had 1 mm diameter holes. In addition, air and material were capable of being injected at side ports in the fluidization chamber.

*Instrumentation and Data Acquisition*

Data is measured during testing by several instruments. The mass flow controller (MFC) is an Alicat Scientific MCR-500SLPM 16 Series mass and volumetric flow controller with accuracy calibration to +/- 0.4% of reading + 0.2% of full scale. The MFC provides controlled flow into the apparatus from 0 to 500 SLPM. The operator sets the MFC flow rate locally. Aside from the mass flow rate, the MFC also measures inline absolute pressure of the flow and temperature of the fluidizing gas. The MFC can be set to provide controlled flow for various gases, but is connected to a compressed air source for this experimental set up.
A Setra DPT-2640-010D-A pressure transducer was used to measure the pressure drop across the bed. The Setra pressure transducer is rated for 0 to 2480 Pa and has an accuracy of 0.25% of the full scale. The high-pressure line measurement is read from the plenum space and the low-pressure line from above the height of the bed material. Tygon tubing is used to connect the apparatus to the pressure transducer. The pressure transducer is powered by an external DC power source supplying 10 Volts excitation to the instrument.

Three thermocouples measure temperature values during testing. All thermocouples are 24 gauge bare-bead K-Type thermocouples with glass braiding. An inconel-sheathed thermocouple measures the temperature of the fluidizing gas as it exits the mass flow controller. Another thermocouple measures the fluidizing gas temperature as it exits the fluidization chamber. Last, a thermocouple measures the ambient environment temperature. All testing was done in an ambient temperature environment, approximately 21°C.

All instrumentation data is collected through a National Instruments Data Acquisition System. An SCXI-1001 12 slot chassis houses an SCXI-1600 Controller module in the first slot followed by an SCXI-1100 module paired with an SCXI-1300 General Purpose terminal block. All instrumentation data is recorded via the SCXI-1300 as voltage signals. The signal-processing program for data acquisition was created using National Instruments LabView 8.6.

A scale was attached to the side of the fluidization chamber to capture the bed height of fluidized materials during testing. Several bed height data points were collected during each test. All data points for bed height are tabulated in Appendix B.

A high definition video camera is set up to capture fluidized bed behavior during testing. The video camera captures bed height and expansion as well as bubble formation characteristics.
Baseline Test

A baseline test must be performed using the apparatus with the desired distribution plate installed. Without the baseline test, the instrumentation will only provide qualitative results regarding the hydrodynamics.

The baseline test establishes the pressure drop across the apparatus without any bed material loaded into the fluidization chamber. The baseline test is performed in the same manner as the bed media will be tested. It is important that the test conditions are identical. The mass flow rate is ramped to a high flow rate, presumably above the minimum fluidization velocity for any bed materials tested, and allowed to stabilize. Once the pressure is stable, the mass flow rate is decreased by small increments and allowed to stabilize again. This is repeated until a zero flow rate is attained. The pressure drops are recorded as a function of the mass flow rate of the fluidizing gas. It is important to start at the higher flow rate and decrease toward zero so that any hysteresis as a result of flow regime change can be avoided. The baseline pressure measurements are subtracted from the sample measurements to determine the actual pressure drop for the sample only.

Sample Description

Two bed media samples were investigated in this study – one ceramic material and one glass material. All bed materials were prepared for testing in the same manner. Bed material was sorted into a narrow diameter range by passing the material through a series of sieves. Enough material of a single diameter range was sorted to fill a volume equal to one diameter cross section by one diameter height based on the dimensions of the fluidization chamber. Particle characterization is provided in the results section.

Zircar Zirconia Alumina (ceramic) Hollow Balls evaluated in this study were sintered ceramic spheres. The ceramic spheres were manufactured for thermal insulation purposes and are meant to flow cleanly into confined spaces. The spheres were white and composed of 99% ceramic. This material was separated into two different diameter ranges. One set of ceramic spheres was separated into a diameter range of 1000 to 1120 µm. The same ceramic spheres were also separated into a diameter range of 500 to 600 µm.

Potters Industries Oil Drilling Coarse Grade glass beads used in this study were solid glass spheres. The glass spheres were manufactured to act as tiny ball bearings to reduce friction for oil drilling mud applications. The glass spheres were transparent, solid soda Lime glass free of pits and excess air bubbles. The glass spheres were also separated into a diameter range of 500 to 600 µm.

Test Matrix

A series of experiments were performed to explore the effects of particle size, density, and binary mixture on the fluidized bed characteristics. Bed characteristics included minimum fluidization velocity, pressure drop across the bed, and particle fluidization behavior. Bed
materials were fluidized as both a single, homogeneous material as well as binary mixtures of the materials above.

A total of 10 tests were performed on the particles. Ceramic particles of diameter range 1000 – 1120 µm were fluidized in four tests performed at 25, 50, 75, and 100% of the total mass equivalent to fill one diameter in height. Ceramic and glass particles of diameter range 500 – 600 µm were both fluidized in two tests for each particle. Tests were performed at 50 and 100% of the total mass equivalent to fill one diameter in height. Two binary tests were also performed. One test combined 50% mass of the ceramic particles of diameter range 1000 – 1120 µm and 50% mass of the ceramic particles of diameter range 500 – 600 µm. Another test combined 50% mass of the ceramic particles of diameter range 500 – 600 µm and 50% mass of the glass particles of diameter range 500 – 600 µm. The tests are summarized in Table 4.1.

<table>
<thead>
<tr>
<th></th>
<th>Ceramic 1000 – 1120 µm</th>
<th>Ceramic 500 – 600 µm</th>
<th>Glass 500 – 600 µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uniform bed</td>
<td>x</td>
<td></td>
<td></td>
</tr>
<tr>
<td>50, 75, and 100% mass</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Uniform bed</td>
<td></td>
<td>x</td>
<td></td>
</tr>
<tr>
<td>50 and 100% mass</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Uniform bed</td>
<td></td>
<td></td>
<td>x</td>
</tr>
<tr>
<td>50 and 100% mass</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Binary bed</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Binary bed</td>
<td></td>
<td>x</td>
<td></td>
</tr>
</tbody>
</table>

The minimum fluidization velocity is a fundamental parameter in fluidization hydrodynamics. During fluidization, the pressure drop across a bed will increase with the gas
velocity until it reaches a theoretical constant pressure drop. The minimum velocity that corresponds to the constant pressure is termed the minimum fluidization velocity.

The velocity measurements for the fluidized beds are based on the theoretical gas velocity experienced in an empty fluidization chamber, also known as the superficial velocity. The theoretical velocity is based on the mass flow rate and density of the gas along with the cross-sectional area of the chamber:

\[ U = \frac{\dot{m}}{\rho \cdot A} \]  

Equation 4.1

Several empirical models have theorized how to predict the minimum fluidization velocity for material in a fluidized bed. Design of the fluidized bed apparatus used in this research is based on the collection of design equations for a pilot scale fluidized bed from Ramirez, Martinez, and Petro [2]. The expression used in that paper to determine the minimum fluidization velocity was developed by Kunii and Levenspiel [9]:

\[ U_{mf} = \frac{\frac{d^2}{150} \cdot (\rho_p - \rho_f) \cdot g \cdot \varepsilon \cdot \phi^2}{1 - \varepsilon} \]  

Equation 4.2

This expression depends on particle diameter, density and sphericity. Also, void space from the bulk bed of particles is included. An estimate for determining the void space is related to the solid particle and bulk packing densities of the material (Cheremisinoff and Cheremisinoff [10]):

\[ \varepsilon = 1 - \frac{\rho_b}{\rho_p} \]  

Equation 4.3

Furthermore, properties of the fluidizing gas such as density and viscosity are also included. This comprehensive relationship requires particles to be well characterized.

Another empirical relationship developed by Leva [7] is commonly used to predict the minimum fluidization velocity:

\[ U_{mf} = \frac{0.0093 \cdot d_m^{1.82} \cdot (\rho_p - \rho_f)^{0.94}}{\mu_f^{0.88} \cdot \rho_f^{0.066}} \]  

Equation 4.4

This expression depends on mean particle diameter and density as well as fluidizing gas properties such as density and viscosity.

A third common empirical relationship developed by Gidaspow [13] also used to predict minimum fluidization velocity is:
\[ U_{mf} = \frac{d^2_p \left( \rho_p - \rho_f \right) g}{1650 \mu_f} , \quad \text{Re}_{mf} < 20 \] 

Equation 4.5

This expression was developed from Stokes Law and depends on mean particle diameter and density as well as fluidizing gas properties such as density and viscosity.

There also exists a theoretical pressure drop based on the physical weight of the bed over the cross-sectional area. When the weight per area of the bed is equal to the pressure drop, shown in Equation 4.6, it is theorized that the bed weight is fully supported by the mass flow of the fluidizing gas, and all the particles should be fluidized (Geldart [5]). When the pressure drop reaches this theoretical value, this correlates to the theoretical minimum fluidization velocity:

\[ \Delta P = \frac{Mg}{A} \] 

Equation 4.6

Results and Analysis

The hydrodynamic behaviors of ceramic and glass particles are presented in this section. Particles are classified into Geldart particle groups based on diameter and particle density. Data measured in the FBB consists of differential pressure values as a function of superficial velocity. First, same particle bed media is fluidized in various mass increments. The minimum fluidization velocities are determined graphically from the data. The graphical results are then compared to the minimum fluidization velocities determined by empirical relationships. The results are also compared to the theoretical pressure drop based on the weight of the bed over cross-sectional area.

Then, binary mixtures of particles are fluidized, and the minimum fluidization velocities are determined graphically from the data. The associated uniform particle data results are combined and compared to the binary data results. In addition, binary results are also compared to the theoretical pressure drop based on the weight of the bed over cross-sectional area.

Particle Classifications

Ceramic and glass particles were sieved and separated into narrow diameter ranges. For the ceramic particles, information was not provided by the manufacturer concerning wall thickness and individual particle density, only ceramic material density in general and a range of bulk densities. For the particles, taking an average mass for 100 particles and dividing by the average diameter determined individual particle densities.

The maximum volume of material tested in each case was a volume equal to 1 diameter in height by 1 diameter in cross-sectional area. Packing densities, also termed bulk densities, were determined by separating particles into increments of 25% of the total volume and then
weighing the samples. Once the bulk and particle densities were determined, voidage was estimated using these two properties. Results for all properties are listed in Table 4.2.

<table>
<thead>
<tr>
<th>Diameter range (µm)</th>
<th>Ceramic 1000-1120</th>
<th>Ceramic 500-600</th>
<th>Glass 500-600</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density of average diameter (gm/cm³)</td>
<td>0.709</td>
<td>1.079</td>
<td>2.5</td>
</tr>
<tr>
<td>Geldart Classification</td>
<td>B</td>
<td>B</td>
<td>B</td>
</tr>
<tr>
<td>Packed Density (gm/cm³)</td>
<td>0.668</td>
<td>0.767</td>
<td>1.464</td>
</tr>
<tr>
<td>Voidage, ε</td>
<td>0.0578</td>
<td>0.2892</td>
<td>0.4347</td>
</tr>
</tbody>
</table>

Table 4.2. Hydrodynamic properties of bed media

Voidage values for the ceramic 1000-1120 µm are very low. During testing, it was noticed that there were a significant number of broken spheres present in this particle range that could not be removed, and this increased the packing density, whereas particle densities were determined by using intact spheres. As a result, this leads to a very small bed voidage value.

Voidage values for the ceramic 500-600 µm and glass 500-600 µm are not close to one another despite having the same diameter. Similar to the ceramic 1000-1120 µm, some broken spheres were present in the ceramic 500-600 µm although not as many as was observed in the ceramic 1000-1120 µm. Also, the hollow ceramic spheres can be compressed more easily than the solid glass particles. Compared to the glass particles, ceramic particles were more likely to have been affected by the sieving process. As for the glass 500-600 µm particles, very few broken spheres were observed. The difference in voidage values between the two materials is likely due to the amount of possible non-spherical material in the bed.

Using the values presented in Table 4.2, the materials can all be classified into their associated Geldart particle ranges. All materials used for experimentation are Geldart B particles. The ranges where all the particles exist in terms of diameter and density are highlighted in Figure 4.3.
According to Geldart [5], particles in the Geldart B classification region are generalized by not being subject to interparticle forces. Gas bubbles for this material begin to form as soon as the minimum fluidization velocity is exceeded. The bubbles also easily coalesce and grow rapidly as they traverse through the bed height. Gas that enters into the bed media is observed as bubbles, and they typically rise faster than the superficial, or empty tube, gas velocity.

**Pressure Drop and Minimum Fluidization**

The baseline test establishes the pressure drop across the apparatus without any bed material loaded into the fluidization chamber. The results of the baseline test for the acrylic distribution plate are shown in Figure 4.4.
Figure 4.4. Baseline pressure drop curve as a function of velocity for the acrylic distribution plate used throughout experimentation.

The distribution plate was tested over a velocity range from 0 to 60 cm/s. In this velocity range, the Reynolds numbers indicate that the flow transitions from developing flow to laminar flow, then transitions to turbulent at the maximum velocity. This change in flow regime likely accounts for the non-linear relationship of the baseline pressure drop curve.

After the baseline test was performed, the fluidization chamber was loaded with the particles of interest and the fluidization test was performed. Pressure drop values measured during testing represent a summation of the pressure drops across distribution plate and chamber as well as across the material. Fluidized ceramic 500 – 600 µm raw data measurements are shown plotted with the plate data in Figure 4.5.
Figure 4.5. Raw test data for Ceramic 500 – 600 µm shown with plate data as a function of velocity.

The pressure drop data associated with the fluidized bed media is the difference between the fluidized bed raw data and the baseline measurements. By subtracting the baseline values, the result is the pressure drop curve associated with the bed as shown in Figure 4.6.

Figure 4.6. Pressure drop curve for Ceramic 500 – 600 µm as a function of velocity.

This curve is used to determine the minimum fluidization velocity by identifying at what velocity the pressure drop reaches a constant value. From the plot in Figure 4.6, the pressure drop increases from 0 to a maximum of 640 Pa and then remains constant. The minimum velocity at which this pressure drop is reached is interpreted as the minimum fluidization velocity.
A method suggested by Geldart [11] was employed to graphically determine the minimum fluidization velocity. As shown in Figure 4.7, a linear relationship between velocity and pressure is established at the lower velocities and the pressure drop becomes constant at the higher velocities.

![Graph showing pressure drop curve for Ceramic 500 – 600 µm]

**Figure 4.7.** Pressure drop curve for Ceramic 500 – 600 µm as a function of velocity, minimum fluidization velocity determined graphically

A trend line was created to capture the linear behavior at the lower velocity values. The constant pressure line was determined by taking the average pressure at the higher velocities. A straight line for the maximum pressure drop and a curve of the linear relationship were extended until they intersected with one another, shown in Figure 4.7 by dotted lines. The velocity that corresponds to the intersection is interpreted as the minimum fluidization velocity for the bed. This graphical method was used to determine the minimum fluidization velocity for all pressure drop curves.

**Single Particle Fluidization**

Partial bed load tests were performed on each material at each diameter range. Detailed testing was performed on the ceramic 1000-1120 µm particles. Bed mass tests were run at 50, 75, and 100% of the total mass equivalent to a volume equal to 1 diameter in height by 1 diameter in cross-sectional area. Results are shown in Figure 4.8.
Figure 4.8. Pressure drop vs. gas velocity for Ceramic 1000-1120 µm particles

For the Ceramic 1000 – 1120 µm, it is difficult to discern from the plot where minimum fluidization might be occurring for all bed mass values. Using graphical analysis of the data, the minimum fluidization velocity is graphically estimated to be 27 cm/s for 100%.

For 75 and 100% mass, the differential pressure does not level off but continues to grow. For 50%, the pressure drop appears to level off at 40 cm/s. At the lower masses, it is possible that there was not enough travel distance through the material for the jetting air to diffuse properly and fluidize the bed. It is also possible that full fluidization was not achieved during the Ceramic 1000 – 1120 µm lower bed mass testing. Due to the limits of the pressure transducer used in this test set up, mass flow rates above 50 cm/s superficial velocity exceeded the upper limit pressure drop measurable by the instrumentation.

The shape of the pressure drop curve appears to weaken with decrease in bed mass. Also, although sifting was performed on the Ceramic 1000 – 1120 µm to isolate the diameter range, there were a significant number of broken spheres present in this particle range that could not be removed. That may have an impact on the ability to fluidize the media uniformly.

Testing was performed on the ceramic 500-600 µm particles and glass 500-600 µm particles at 50 and 100% of the total mass equivalent to a volume equal to 1 diameter in height by 1 diameter in cross-sectional area. Results are shown in Figure 4.9 and Figure 4.10 respectively.
For the Ceramic 500 – 600 µm, pressure drop curves are much more clear. The minimum fluidization velocity is graphically determined to be 19.5 cm/s. The average pressure drop after minimum fluidization is 631.5 Pa for 100% and 282.8 Pa for 50%. Similar to the larger ceramic particles, the shape of the pressure drop curve appears to weaken with a decrease in bed mass.

Figure 4.10. Pressure drop vs. gas velocity for Glass 500-600 µm particles
For the Ceramic 500 – 600 µm, pressure drop curves are the most distinct out of all the uniform particle data. The minimum fluidization velocity is graphically determined to be 22 cm/s. The average pressure drop after minimum fluidization is 1320 Pa for 100% and 570 Pa for 50%. Similar to the ceramic particles, the shape of the pressure drop curve appears to weaken slightly with a decrease in bed mass. For the 50% mass, the pressure drop appears to decline slightly after minimum fluidization is reached.

**Minimum Fluidization Empirical Models**

Theoretical values are determined for the minimum fluidization velocity and compared to the graphical results. For the Kunii and Levenspiel equation, sphericity values were assumed to be 0.9 for all materials. The results are summarized in Table 4.3.

<table>
<thead>
<tr>
<th>Diameter range (µm)</th>
<th>Ceramic</th>
<th>Ceramic</th>
<th>Glass</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphical (cm/s)</td>
<td>27</td>
<td>19.5</td>
<td>22</td>
</tr>
<tr>
<td>Kunii and Levenspiel (cm/s)</td>
<td>0.046</td>
<td>3.215</td>
<td>26.699</td>
</tr>
<tr>
<td>Leva (cm/s)</td>
<td>25.114</td>
<td>11.298</td>
<td>24.904</td>
</tr>
<tr>
<td>Gidaspow (cm/s)</td>
<td>25.991</td>
<td>10.655</td>
<td>24.703</td>
</tr>
</tbody>
</table>

The theoretical models predict minimum fluidization velocities that are not close to one another in value. The Kunii and Levenspiel model does not predict the graphical value well. This may be due to the inclusion of the bed void space, which is a function of the packing density and particle density. As previously stated there were a significant number of broken spheres present in this particle range that could not be removed, and this may inflate the packing density which in turn leads to a very small bed voidage value. On the other hand, the Leva model predicts within 7% and Gidaspow within 3% of the graphical value.

In an attempt to account for small fragments that are not spherical, the bed mass is decreased by 5% and a new packing density is considered along with a new voidage value. The minimum fluidization velocity is calculated using the new mass values. The Kunii and Levenspiel model predicts 0.297 cm/s. While this increases the calculated value of the fluidization velocity, it is still does not predict the graphical value well. In fact, the mass of the
bed must be decreased to 38% to get minimum fluidization results that are close to the graphical results.

The ceramic 500-600 µm theoretical predictions are not close to one another in value. The Kunii and Levenspiel model does not predict the graphical value well (within 84%). The Leva and Gidaspow models have a better prediction within 46% for both models. The glass 500-600 µm theoretical predictions are close to one another and are better predictions for the graphical value. The Kunii and Levenspiel model predicts the graphical result within 21% and the Leva and Gidaspow models predict within 13%.

Mass-Based Theoretical Pressure Drop

Theoretical values are determined for the pressure drop across the bed after the minimum fluidization velocity has been achieved based on the mass of the bed material and are compared to the graphical results. Graphical results for the Ceramic 1000 – 1120 µm are based on the average values of the pressure drop above 30 cm/s. The results are summarized in Table 4.4. It is possible that full fluidization was not achieved during the Ceramic 1000 – 1120 µm lower bed mass testing.

Table 4.4. Theoretical fully fluidized pressure drops compared to graphical results for Ceramic 1000 – 1120 µm

<table>
<thead>
<tr>
<th></th>
<th>50%</th>
<th>75%</th>
<th>100%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphical (Pa)</td>
<td>143.4</td>
<td>275.6</td>
<td>465</td>
</tr>
<tr>
<td>Theoretical (Pa)</td>
<td>357.1</td>
<td>527.5</td>
<td>695.1</td>
</tr>
</tbody>
</table>

The same theoretical calculations were determined for Ceramic 500 – 600 µm and Glass 500 – 600 µm. The results are summarized in Table 4.5. The theoretical values for the Ceramic 500 – 600 µm predict the graphical results better than the larger diameter ceramic. The theoretical results predict the Ceramic 500 – 600 µm graphical values within 41% for the half mass and 25% for the full mass. The theoretical values for the Glass 500 – 600 µm predict the graphical results the best out of all three materials. The theoretical results predict the Glass 500 – 600 µm is within 35% for the half mass and 14% for the full mass.

Other factors such as a boundary layer at the wall, non-uniformities in the distribution plate, and stagnant regions in between distribution plate holes may contribute to a lower observed pressure drop compared to the theoretical calculations.
Table 4.5. Theoretical fully fluidized pressure drops compared to graphical results for Ceramic 500 – 600 µm and Glass 500 – 600 µm

<table>
<thead>
<tr>
<th></th>
<th>50%</th>
<th>100%</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Ceramic 500 – 600 µm</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Graphical (Pa)</td>
<td>282.8</td>
<td>631.5</td>
</tr>
<tr>
<td>Theoretical (Pa)</td>
<td>398.9</td>
<td>790.5</td>
</tr>
<tr>
<td><strong>Glass 500 – 600 µm</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Graphical (Pa)</td>
<td>568.8</td>
<td>1318.3</td>
</tr>
<tr>
<td>Theoretical (Pa)</td>
<td>770.7</td>
<td>1508.6</td>
</tr>
</tbody>
</table>

Graphically determined minimum fluidization velocities and pressure drops for each of the fully fluidized beds are summarized in Table 4.6.

Table 4.6. Uniform fluidized bed pressure and velocity results for all tests

<table>
<thead>
<tr>
<th></th>
<th>Ceramic</th>
<th>Ceramic</th>
<th>Glass</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diameter range (µm)</td>
<td>1000-1120</td>
<td>500-600</td>
<td>500-600</td>
</tr>
<tr>
<td>Graphical Minimum Fluidization Velocity (cm/s)</td>
<td>27</td>
<td>19.5</td>
<td>22</td>
</tr>
<tr>
<td>Graphical Pressure Drop, 50% (Pa)</td>
<td>143.4</td>
<td>282.8</td>
<td>568.8</td>
</tr>
<tr>
<td>Graphical Pressure Drop, 75% (Pa)</td>
<td>275.6</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Graphical Pressure Drop, 100% (Pa)</td>
<td>465</td>
<td>631.5</td>
<td>1318.3</td>
</tr>
</tbody>
</table>
Two additional tests were performed using the particles. The total mass used in both tests was equivalent to a volume equal to 1 diameter in height by 1 diameter in cross-sectional area. A binary mixture of 50% of the Ceramic 1000-1120 µm particles was mixed with 50% of the Ceramic 500-600 µm particles and the mixture was fluidized. Hydrodynamic behavior is estimated based on combining the single particle 50% mass results from both the Ceramic particles 500-600 µm and 1000-1120 µm obtained previously. The results of the binary test are shown in Figure 4.11. In addition, results for the binary behavior are estimated based on a superposition of the uniform particle behaviors using Equation 4.6.

![Graphical representation of binary mixture fluidization](image)

**Figure 4.11.** Mixture of Ceramic particles 500-600 µm and 1000-1120 µm

For the Ceramic mix, it is again difficult to discern from the plot where minimum fluidization might be occurring. A linear relationship between the pressure drop and the velocity is observed from 0 to 13 cm/s. This was not observed in the uniform Ceramic 1000-1120 µm behavior. The pressure drop appears to level off after 40 cm/s. A graphical method can be employed to join the linear pressure slope to the constant value. The point of intersection between these two lines represents the minimum fluidization velocity. This corresponds to a minimum fluidization velocity of 20 cm/s. Pressure drop across the fully fluidized bed is estimated to be 526 Pa based on the constant pressure values observed at the higher superficial velocity. The estimated model using Equation 4.6 predicts the binary behavior with an average of 20% error. The general shape is well predicted, particularly the slight drop downward at around 32 cm/s.

Another binary mixture of 50% of the Ceramic 500-600 µm particles mixed with 50% of the Glass 500-600 µm particles was also tested. Again, hydrodynamic behavior is estimated based on combining the single particle 50% mass results from both the Ceramic and glass particles at 500-600 µm obtained previously. The results of the binary test are shown in Figure 4.12 along with the composite estimated results.
Figure 4.12. Mixture of Ceramic and Glass particles 500-600 µm

For the 500 – 600 µm mixture, the pressure drop curves are quite distinct. The individual particle data had very distinct pressure drop curves, and that same behavior is replicated in the composite. From the graph, the minimum fluidization velocity is approximately 21.5 cm/s. Pressure drop across the fully fluidized bed is taken as the average pressure drop after the fluidization velocity and equals 963.6 Pa. The estimated model predicts the binary behavior with an average of 7.5% error. The general shape is well predicted, particularly the slight drop downward at around 33 cm/s and the slight pressure drop after the minimum fluidization velocity was achieved.

Overall, the estimated results based on a superposition of the uniform particle behaviors does well to predict the general hydrodynamic response of the binary mixtures. The general shapes of both pressure drop curves are predicted; however the composite estimates under predict the actual pressure drop values compared to the results. This is likely because of particle interactions that are not accounted for by the uniform particle results such as separation.

Mass-Based Theoretical Pressure Drop

Theoretical values were determined for the pressure drop across the bed after the minimum fluidization velocity has been achieved based on the mass of the bed material and compared to the graphical results. The results are presented in Table 4.7.
Table 4.7. Theoretical fully fluidized pressure drops compared to graphical results for binary mixtures

<table>
<thead>
<tr>
<th></th>
<th>Ceramic Mix</th>
<th>500-600 µm Mix</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphical (Pa)</td>
<td>526</td>
<td>963.6</td>
</tr>
<tr>
<td>Theoretical (Pa)</td>
<td>742.9</td>
<td>1185.5</td>
</tr>
</tbody>
</table>

The calculated values predict the Ceramic Mix graphical results within 41% and the 500-600 µm results within 23%.

Other factors such as a boundary layer at the wall, non-uniformities in the distribution plate, and stagnant regions in between distribution plate holes may contribute to a lower observed pressure drop compared to the calculated approach.

Discussion

Beds of uniform particles of varying diameters and densities were fluidized in this study and minimum fluidization velocities were investigated for each particle type. Graphical analysis was employed and compared to theoretical empirical models. Pressure drops for fluidized beds were also investigated. Graphical analysis was also employed and compared to theoretical models based on the mass of the bed.

Graphical analysis was initially used to determine the minimum fluidization velocity for a bed of uniform particles. For the Ceramic 1000 – 1120 µm, it was difficult to discern from the plot where minimum fluidization might be occurring for all bed mass values. Using graphical analysis of the data, the minimum fluidization velocity is graphically estimated to be 27 cm/s for 100%; however, at the lower mass, it is possible that there was not enough travel distance through the material for the jetting air to diffuse properly and fluidize the bed. It is also possible that full fluidization was not achieved during the Ceramic 1000 – 1120 µm lower bed mass testing. Due to the limits of the pressure transducer used in this test set up, mass flow rates above 50 cm/s superficial velocity exceeded the upper limit pressure drop measurable by the instrumentation. There were also a significant number of broken spheres present in this particle range that could not be removed, and this may have affected ability of the bed to fluidize.

For the Ceramic and Glass 500 – 600 µm, pressure drop curves were very distinct. Also, very few non-spherical particles were observed in the bed during testing. Glass 500 – 600 µm material of similar density has been fluidized in other research for beds of similar size. The results are compared in Table 4.8.
Table 4.8. Comparison of Glass spheres 500-600 µm diameter Minimum Fluidization values

<table>
<thead>
<tr>
<th>Results</th>
<th>Glass 500-600 µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Results from this investigation</td>
<td>22 (cm/s)</td>
</tr>
<tr>
<td>Franka, Heindel, Battaglia 2007 [6]</td>
<td>19.9 (cm/s)</td>
</tr>
<tr>
<td>Franka, Drake, Heindel 2008 [8]</td>
<td>21.7 +/- 0.5 (cm/s)</td>
</tr>
</tbody>
</table>

As previously stated, the apparatus configuration used in research by Franka, Heindel, and Battaglia [6] is slightly different than the apparatus used in this investigation. Air flowed through a piccolo type tube pipe prior to entering the plenum space in order to reduce the jetting effects. Also, the distribution plate used in that research had 1 mm diameter holes and the internal diameter of the chamber was 9.5 cm. Also, Franka, Drake, and Heindel [8] also used another similar apparatus; however, their distribution plate had 1 mm diameter holes and, air and material were capable of being injected at side ports in the fluidization chamber. The difference in reported fluidization velocities are likely due to geometric and operational differences amongst the apparatuses. The results reported here are within 13.4% of the other reported values.

Empirical models were also used to develop theoretical values for the minimum fluidization velocity and compared to the graphical results. For both of these particle diameter and density ranges, the density is the mathematically dominant contributing factor in calculating the minimum fluidization velocity for the theoretical models when all other factors remain constant.

Kunii and Levenspiel: \( U_{mf} \propto d_p^2 \cdot \rho_p \)

Leva: \( U_{mf} \propto d_m^{1.82} \cdot \rho_p^{0.94} \)

Gidaspow: \( U_{mf} \propto d_p^2 \cdot \rho_p \)

The theoretical models appear better suited for predicting the hydrodynamic behavior of particles that have a higher density.

Pressure drop values were graphically determined for fully fluidized beds. It was generally observed that the shape of the pressure drop curves for all particles appeared to weaken with a decrease in bed mass. In addition, the pressure drops seemed to scale linearly with the amount of mass in the bed. Graphical results for the Ceramic 1000 – 1120 µm are based on the average values of the pressure drop above 30 cm/s. It is possible that full fluidization was not achieved during the Ceramic 1000 – 1120 µm lower bed mass testing. The graphical results for
the Ceramic and Glass 500-600 µm beds had much more distinct pressure drop curves that better aligned with the idealized hydrodynamic behavior of a fully fluidized bed.

Theoretical values were determined for the pressure drop across the bed after the minimum fluidization velocity has been achieved based on the mass of the bed material and were compared to the graphical results using Equation 4.6. All mass driven results overpredicted the graphical results for the pressure drop of the fully fluidized bed. Factors such as a boundary layer at the wall, non-uniformities in the distribution plate, and stagnant regions in between distribution plate holes may have contributed to a lower observed graphical pressure drop compared to the theoretical calculations.

Beds of binary mixtures of particles of varying diameters and densities were fluidized in this study and minimum fluidization velocities were investigated for each mixture. Graphical analysis was employed to determine the minimum fluidization velocity. Also graphical analysis was used to determine the pressure drops for the fully fluidized beds and the results were compared to a theoretical model based on the mass of the bed.

A bed of 50% Ceramic 500-600 µm and 50% Ceramic 1000 – 1120 µm was mixed together and fluidized. The materials were initially loaded into the fluidization chamber in separate layers as shown in Figure 4.13.

Figure 4.13. Glass and ceramic particles (500 – 600 µm) initially loaded as layers in the fluidization chamber

It was difficult to discern from the plot where minimum fluidization might be occurring. A graphical method was employed to determine the minimum fluidization velocity. Another binary mixture of 50% of the Ceramic 500-600 µm particles mixed with 50% of the Glass 500-600 µm particles was also tested. Just like the individual particles, the resulting pressure drops yielded a more distinct pressure drop curve that better aligned with the idealized hydrodynamic behavior of a fully fluidized bed.
A noticeable separation of materials occurred during the testing of the 500 - 600 µm mixture. Photos shown in Figure 4.14 depict the evolution of the separation.

![Figure 4.14. Binary mixture of glass and ceramic particles (500 - 600 µm) shown at superficial velocities of (a) 40 cm/s, (b) 35 cm/s, and (c) 23.5 cm/s](image)

Initially, the bed was fluidized at a high superficial velocity, and the mixture appeared to be homogeneous as shown in Figure 4.14 (a). As the mass flow rate was decreased, the lower density ceramic particles began to separate and a noticeable stratum formed at the bed surface as shown in Figure 4.14 (b). As the mass flow rate continued to decrease, the stratum also continued to increase. Eventually, a large stratum of ceramic particle accumulated at the bed surface, and while the ceramic particles appeared to continue bubbling, there was no observable movement below the ceramic stratum in the glass region as shown in Figure 4.14 (c). From the graphical results of the uniform beds, the ceramic minimum fluidization velocity is 21 cm/s and 23 cm/s for the glass. As the mass flow rate is decreased, the particles may be separating as a result of different hydrodynamic responses.

A notable observation is the existence of a minimum homogeneous mixture velocity that is greater than the minimum fluidization velocity of either particle. It is also evident from the pictures in Figure 4.14 that a stagnant layer has formed at the wall in between distribution plate holes at the perimeter of the fluidization chamber. This is seen as the undulating layer of particles along the wall at the base. Also, a layer of the glass particles is also seen in that stagnant region. A layer of the glass particles was added to the chamber first and they remained stagnant throughout the test even at high superficial velocities. This is likely a result of the distribution plate not able to uniformly distribute air at distances close to the plate and confirms the existence of stagnant regions in between the holes of the distribution plate.

The estimated mass model using Equation 4.6 was used to predict the binary behavior based on the superposition of the individual particle results and compared to the binary mixture. In both cases, the general shapes of the pressure drop curves were well predicted, however the mass-based superposition results under-predicted the measured pressure drop curves. This is
likely because of particle interactions that are not accounted for by the uniform particle results such as separation.

In addition, pressure drop values were graphically determined for fully fluidized beds of the binary mixtures. Theoretical values were determined for the pressure drop across the bed after the minimum fluidization velocity has been achieved based on the mass of the bed material and were compared to the graphical results using Equation 4.6. All mass driven results over-predicted the graphical results for the pressure drop of the fully fluidized bed. Factors such as a boundary layer at the wall, non-uniformities in the distribution plate, and stagnant regions in between distribution plate holes may have contributed to a lower observed graphical pressure drop compared to the theoretical calculations.

**Conclusion**

The focus of this research was to investigate the impact of particle density and diameter on the minimum fluidization velocity. In addition, pressure drops across a bed were investigated for correlation to varying bed mass values. Empirical models as well as a mass-based model were used to predict the minimum fluidization velocity and pressure drop of a fully fluidized bed. Results from the bed mass investigation were then used to estimate the hydrodynamic behavior for a binary mixture of particles.

Not all materials fluidized uniformly. The Ceramic and Glass 500 – 600 µm diameter particle responses more closely resembled idealized fluidized bed cases, where as the Ceramic 1000 – 1120 µm diameter results were difficult to discern graphically. The inclusion of a significant number of broken spheres present in this particle range may have affected the ability of the bed to fluidize. Previously reported minimum fluidization velocity values for similar Glass 500 – 600 µm diameter particles fluidized under similar conditions correspond well to the results from this research.

Empirical models were also used to develop theoretical values for the minimum fluidization velocity and compared to the graphical results. The theoretical models appear better suited for predicting the hydrodynamic behavior of particles that have a higher density.

It was generally observed that the shape of the pressure drop curves for all particles appeared to weaken with a decrease in bed mass. Also, the pressure drops seemed to scale linearly with the amount of mass in the bed. Theoretical values were determined for the pressure drop across the bed after the minimum fluidization velocity has been achieved based on the mass of the bed material. All mass driven results over-predicted the graphical results, and factors such as a boundary layer at the wall, non-uniformities in the distribution plate, and stagnant regions in between distribution plate holes may have contributed to a lower observed graphical pressure drop compared to the theoretical calculations.

Beds of binary mixtures of particles were combined from the previously tested uniform particles and fluidized. Graphical analysis was used to determine the minimum fluidization velocity and pressure drops for the fully fluidized beds. The results were compared to a theoretical models based on the mass of the bed.
A bed of 50% Ceramic 500-600 µm and 50% Ceramic 1000 – 1120 µm was mixed together and fluidized as well as a binary mixture of 50% of the Ceramic 500-600 µm particles mixed with 50% of the Glass 500-600 µm particles. The resulting pressure drops of the binary mixtures were similar to the behaviors observed for the individual particles. Just like the individual particles, the pressure drop curve for the mixture of Ceramic particles was difficult to discern, but the addition of the Ceramic 500-600 µm did reshape the pressure drop curve closer to the idealized hydrodynamic behavior of a fully fluidized bed. The 500 - 600 µm particle mixture yielded a more distinct pressure drop curve just like the individual particles’ behavior.

A noticeable separation of materials occurred during the testing of the 500 - 600 µm mixture at flow rates above the minimum fluidization velocity. As the mass flow rate was decreased, the particles separated, likely as a result of different hydrodynamic responses for each particle. A notable observation is the existence of a minimum homogeneous mixture velocity that is greater than the minimum fluidization velocity of either particle. In addition, a layer of the glass particles at the distribution plate remained stagnant throughout the test even at high superficial velocities. The binary mixture of different colored particles allowed this phenomenon to be readily observed. This behavior was likely a result of the distribution plate not able to uniformly distribute air at distances close to the plate and confirms the existence of stagnant regions at the distribution plate.

The estimated mass model was used to predict the binary behavior based on the superposition of the individual particle results and compared to the binary mixture. In both cases, the general shapes of the pressure drop curves were well predicted, however the mass-based superposition results under-predicted the measured pressure drop curves. This is likely because of particle interactions that are not accounted for by the uniform particle results such as separation. Again, factors such as a boundary layer at the wall, non-uniformities in the distribution plate, and stagnant regions in between distribution plate holes may have contributed to a lower observed graphical pressure drop compared to the theoretical calculations.

It should be noted that the ceramic particles diameter ranges were separated from a body of particles that contained a large range of diameter values, 400 – 1250 µm in diameter, and particle handling may have contributed to the introduction and creation of more non-spherical particles. One recommendation would be to begin with materials that were already separated by a process that involved less handling.

The use of X-Ray computed topography to perform a volume analysis on individual particles would improve the particle characterization. The volume analysis performed on a particle would reveal actual diameter, density, sphericity, and individual porosity of the particle. Also, an accumulation of particles can be investigated to determine actual void space between particles.

A recommendation to address the non-uniformities and stagnant regions in the distribution plate would be to consider using a porous sintered metal plate as the distribution plate. This would provide uniform flow into the bed and minimize any stagnant regions.
References


Appendix A - Evolved Gas Products

Species and mass fraction values used to determine the mixture specific heat capacity of the evolved gas products during decomposition.

E-Glass/Vinyl-Ester

Table A. 1 – Major species evolved from thermal degradation of E-Glass/Vinyl-Ester, trace elements not included (Southwest Research Institute [8])

<table>
<thead>
<tr>
<th>Species</th>
<th>Mass Fraction, y</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bromomethane</td>
<td>0.0151</td>
</tr>
<tr>
<td>Chloromethane</td>
<td>0.0017</td>
</tr>
<tr>
<td>Acetone</td>
<td>0.3360</td>
</tr>
<tr>
<td>Butanone</td>
<td>0.0177</td>
</tr>
<tr>
<td>Benzene</td>
<td>0.0889</td>
</tr>
<tr>
<td>Dibromomethane</td>
<td>0.0041</td>
</tr>
<tr>
<td>Toluene</td>
<td>0.1143</td>
</tr>
<tr>
<td>Hexanone</td>
<td>0.0479</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>0.0254</td>
</tr>
<tr>
<td>m/p-Xylene</td>
<td>0.0030</td>
</tr>
<tr>
<td>o-Xylene</td>
<td>0.0024</td>
</tr>
<tr>
<td>Styrene</td>
<td>0.2326</td>
</tr>
<tr>
<td>Isopropylbenzene</td>
<td>0.0207</td>
</tr>
<tr>
<td>n-Propylbenzene</td>
<td>0.0043</td>
</tr>
<tr>
<td>alpha-Methylstyrene</td>
<td>0.0081</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>0.0010</td>
</tr>
<tr>
<td>Methane, dimethoxy</td>
<td>0.0004</td>
</tr>
<tr>
<td>Octane</td>
<td>0.0004</td>
</tr>
<tr>
<td>Propenal</td>
<td>0.0199</td>
</tr>
<tr>
<td>Propen-1-ol</td>
<td>0.0042</td>
</tr>
<tr>
<td>Bromopropene</td>
<td>0.0085</td>
</tr>
<tr>
<td>Acetic acid</td>
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</tr>
<tr>
<td>Tetrahydrofuran</td>
<td>0.0021</td>
</tr>
<tr>
<td>Nonane</td>
<td>0.0030</td>
</tr>
<tr>
<td>Heptane</td>
<td>0.0021</td>
</tr>
</tbody>
</table>

PMMA

Table A. 2. Major species evolved from thermal degradation of PMMA (Arisawa and Brill [11])

<table>
<thead>
<tr>
<th>Species</th>
<th>Mass Fraction, y</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methylmethacrylate</td>
<td>0.90</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>0.10</td>
</tr>
</tbody>
</table>
### Balsa Wood

Table A. 3. Major species evolved from thermal degradation of balsa wood used for red oak, trace elements not included (Southwest Research Institute [8])

<table>
<thead>
<tr>
<th>Species</th>
<th>Mass Fraction, ( y )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>0.502172008</td>
</tr>
<tr>
<td>Benzene</td>
<td>0.076206113</td>
</tr>
<tr>
<td>Toluene</td>
<td>0.129219061</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>0.052150863</td>
</tr>
<tr>
<td>Styrene</td>
<td>0.154317379</td>
</tr>
</tbody>
</table>
Appendix B - Bed Height Data

Bed height data was also collected during testing at specific velocity intervals. The results are tabulated below for each test.

Uniform Bed Results

*Ceramic 1000-1120 µm diameter particles*

Table B. 1. Ceramic 1000-1120 µm diameter particles, 50% mass

<table>
<thead>
<tr>
<th>Superficial Velocity</th>
<th>Bed height</th>
</tr>
</thead>
<tbody>
<tr>
<td>Static</td>
<td>5.0 cm</td>
</tr>
<tr>
<td>20 cm/s</td>
<td>5.0 cm</td>
</tr>
<tr>
<td>30 cm/s</td>
<td>5.25 cm</td>
</tr>
<tr>
<td>40 cm/s</td>
<td>5.5 cm</td>
</tr>
<tr>
<td>50 cm/s</td>
<td>5.5 cm</td>
</tr>
</tbody>
</table>

Table B. 2. Ceramic 1000-1120 µm diameter particles, 75% mass

<table>
<thead>
<tr>
<th>Superficial Velocity</th>
<th>Bed height</th>
</tr>
</thead>
<tbody>
<tr>
<td>Static</td>
<td>7.75 cm</td>
</tr>
<tr>
<td>20 cm/s</td>
<td>7.75 cm</td>
</tr>
<tr>
<td>30 cm/s</td>
<td>8.0 cm</td>
</tr>
<tr>
<td>40 cm/s</td>
<td>8.5 cm</td>
</tr>
<tr>
<td>50 cm/s</td>
<td>9.0 cm</td>
</tr>
</tbody>
</table>
Table B. 3. Ceramic 1000-1120 μm diameter particles, 100% mass

<table>
<thead>
<tr>
<th>Superficial Velocity</th>
<th>Bed height</th>
</tr>
</thead>
<tbody>
<tr>
<td>Static</td>
<td>11.6 cm</td>
</tr>
<tr>
<td>20 cm/s</td>
<td>11.6 cm</td>
</tr>
<tr>
<td>30 cm/s</td>
<td>12.0 cm</td>
</tr>
<tr>
<td>40 cm/s</td>
<td>12.75 cm</td>
</tr>
<tr>
<td>50 cm/s</td>
<td>13.0 cm</td>
</tr>
</tbody>
</table>
### Ceramic 500 – 600 µm diameter particles

Table B. 4. Ceramic 500-600 µm diameter particles, 50% mass

<table>
<thead>
<tr>
<th>Superficial Velocity</th>
<th>Bed height</th>
</tr>
</thead>
<tbody>
<tr>
<td>Static</td>
<td>5.5 cm</td>
</tr>
<tr>
<td>20 cm/s</td>
<td>5.5 cm</td>
</tr>
<tr>
<td>30 cm/s</td>
<td>6.0 cm</td>
</tr>
<tr>
<td>40 cm/s</td>
<td>6.0 cm</td>
</tr>
<tr>
<td>50 cm/s</td>
<td>6.75 cm</td>
</tr>
<tr>
<td>60 cm/s</td>
<td>7.0 cm</td>
</tr>
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Table B. 5. Ceramic 500-600 µm diameter particles, 100% mass

<table>
<thead>
<tr>
<th>Superficial Velocity</th>
<th>Bed height</th>
</tr>
</thead>
<tbody>
<tr>
<td>Static</td>
<td>11.5 cm</td>
</tr>
<tr>
<td>20 cm/s</td>
<td>11.5 cm</td>
</tr>
<tr>
<td>30 cm/s</td>
<td>12.5 cm</td>
</tr>
<tr>
<td>40 cm/s</td>
<td>12.75 cm</td>
</tr>
<tr>
<td>50 cm/s</td>
<td>13 cm</td>
</tr>
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</table>
Glass 500 – 600 µm diameter particles

Table B. 6. Glass 500-600 µm diameter particles, 50% mass

<table>
<thead>
<tr>
<th>Superficial Velocity</th>
<th>Bed height</th>
</tr>
</thead>
<tbody>
<tr>
<td>Static</td>
<td>5.0 cm</td>
</tr>
<tr>
<td>20 cm/s</td>
<td>5.0 cm</td>
</tr>
<tr>
<td>30 cm/s</td>
<td>5.1 cm</td>
</tr>
<tr>
<td>40 cm/s</td>
<td>5.5 cm</td>
</tr>
<tr>
<td>50 cm/s</td>
<td>5.75 cm</td>
</tr>
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</table>

Table B. 7. Glass 500-600 µm diameter particles, 100% mass

<table>
<thead>
<tr>
<th>Superficial Velocity</th>
<th>Bed height</th>
</tr>
</thead>
<tbody>
<tr>
<td>Static</td>
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</tr>
<tr>
<td>20 cm/s</td>
<td>10.0 cm</td>
</tr>
<tr>
<td>30 cm/s</td>
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<tr>
<td>40 cm/s</td>
<td>11.5 cm</td>
</tr>
<tr>
<td>50 cm/s</td>
<td>12.5 cm</td>
</tr>
</tbody>
</table>
## Binary Mixture Bed Results

Table B. 8. Mixture of ceramic 1000-1120 and 500-600 µm diameter particles

<table>
<thead>
<tr>
<th>Superficial Velocity</th>
<th>Bed height</th>
</tr>
</thead>
<tbody>
<tr>
<td>Static</td>
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</tr>
<tr>
<td>20 cm/s</td>
<td>10.5 cm</td>
</tr>
<tr>
<td>30 cm/s</td>
<td>11.5 cm</td>
</tr>
<tr>
<td>40 cm/s</td>
<td>12.0 cm</td>
</tr>
<tr>
<td>50 cm/s</td>
<td>12.75 cm</td>
</tr>
</tbody>
</table>

Table B. 9. Mixture of ceramic and glass 500-600 µm diameter particles

<table>
<thead>
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<th>Superficial Velocity</th>
<th>Bed height</th>
</tr>
</thead>
<tbody>
<tr>
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</tr>
<tr>
<td>20 cm/s</td>
<td>10.5</td>
</tr>
<tr>
<td>30 cm/s</td>
<td>11.5</td>
</tr>
<tr>
<td>40 cm/s</td>
<td>12.0</td>
</tr>
<tr>
<td>50 cm/s</td>
<td>13.0</td>
</tr>
</tbody>
</table>