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An Investigation of Biochar Removal Systems for Pyrolysis Reactors

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An Investigation of Biochar Removal Systems for Pyrolysis Reactors

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Abstract

Fluidized bed biomass pyrolysis is a process that is becoming popular for the conversion of agricultural, municipal and forestry residues into liquid bio-oils, solid biochar and gaseous products. Bio-oil vapors leave the reactor vessel with the produced gases. Also produced however, is a low density biochar particles which accumulate in the bed. Though some fine biochar particles can be elutriated, a significant amount remains in the bed. Accumulation of biochar leads to poor process stability and defluidization of the bed. Moreover, biochar may have negative effects on the pyrolysis reactions. In the current implementation of a mobile pyrolysis unit, the biochar is removed intermittently from the fluidized bed by stopping biomass feeding, and reducing the fluidization velocity to promote segregation, allowing subsequent removal of the biochar layer with a vacuum line.

The initial of objective of this thesis was the optimization and quantification of the performance of the batch biochar removal process. The second objective was to develop a new, continuous biochar removal system.

A batch process using particle separation through density and removal with overflow ports during fluidization, was used to quantify the amount of disruption to fluidization from different loadings and sizes of biochar, therefore determining the feasibility of a batch removal. The main problem encountered with the batch removal was the inconsistent bed composition throughout the removal process, which can reduce the yield of valuable liquid product. The knowledge acquired during the optimization of the batch process was used to design a novel continuous system. The novel continuous system operated at steady state and allowed for high purity biochar removal, and was more than capable of continuously removing the biochar generated in a practical pyrolysis process. This novel system has been included for use in a full-scale pyrolysis unit, since it will allow the unit to run continuously while controlling the concentration of biochar within the pyrolysis reactor.

Keywords: biochar, pyrolysis, particle separation, particle removal, fluidized bed

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Co-Authorship

Chapter 2

Article Title: Batch Removal of Biochar In a Fluidized Bed Using Particle Segregation and Overflow Ports

Authors: Craig Mara, Lorenzo Ferrante, Cedric Briens, Franco Berruti

Article Status: To Be Submitted

Contributions: All experimental work was completed by Craig Mara, experimental method was developed by Craig Mara, Lorenzo Ferrante, Cedric Briens, Franco Berruti, all data analysis was completed by Craig Mara

Chapter 3

Article Title: Optimization of a Continuous Separation System for Removal of Non-Fluidizable Biochar using a Novel Fluidized Bed

Authors: Craig Mara, Lorenzo Ferrante, Cedric Briens, Franco Berruti

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Contributions: All experimental work was completed by Craig Mara, experimental method was developed by Craig Mara, Lorenzo Ferrante, Cedric Briens, Franco Berruti, all data analysis was completed by Craig Mara

Chapter 4

Article Title: Effect of biochar Size on Continuous Removal Performance using a Novel Fluidized Bed

Authors: Craig Mara, Lorenzo Ferrante, Cedric Briens, Franco Berruti

Article Status: To Be Submitted

Contributions: All experimental work was completed by Craig Mara, experimental method was developed by Craig Mara, Lorenzo Ferrante, Cedric Briens, Franco Berruti, all data analysis was completed by Craig Mara

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LIST OF ABBREVIATIONS, & NOMENCLATURE

List of Abbreviations

DDG- Dried distillers grain

LCA- life cycle analysis

HHV- higher heating value

Nomenclature

A_{bed}-cross sectional area of fluidized bed (m^2)

$A_{bed,pyrolysis}$- cross sectional bed area of pyrolysis unit (m^2)

A_{bp}- free area below separation plate (m^2)

A_{sep}- cross sectional area of separation zone (m^2)

A_{wm}- cross sectional area of well mixed zone (m^2)

Ar- Archimedes Number, $\frac{{d_p}^3 \rho_g (\rho_p - \rho_g) g}{{\mu_g}^2}$

$\bar{d}$- mean particle size in binary mixture (μm)

d_f- particle size of fluid component (μm)

d_p- particle diameter (μm)

d_{pk}- particle size of packed component in bed (μm)

d_{psm}-Sauter mean diameter

$F_{biochar}$- feedrate of biochar (g/min) g- acceleration due to gravity, 9.8 m/s^2

H_{bed}-height of fluidized bed (cm)

L_{bp}- free length below separation plate (cm)

N_f- number fraction of fluid component in binary mixture

P_h- height of plate above bottom of bed (cm)

$Re_{p,mf}$- particle Reynolds number at minimum fluidization, $\frac{d_p U_{mf} \rho_g}{\mu_g}$

t- time (seconds)

U_b- minimum fluidization gas velocity of larger component in bed (m/s)

U_f-minimum fluidization gas velocity of fluid in single component bed (m/s)

U_{mf}- minimum fluidization gas velocity of pure sand (m/s)

$U_{mf,m}$-minimum fluidization gas velocity of binary mixture (m/s)

U_{pk}-minimum fluidization gas velocity of packed component in single component bed (ms)

U_s- minimum fluidization gas velocity of smaller component in bed (m/s)

V_f- volume fraction of fluid component in binary mixture

U_{rem}-superficial gas velocity, batch biochar removal step (m/s)

U_{seg}- superficial gas velocity, batch biochar segregation step (m/s)

U_{sep}-superficial gas velocity in separation zone (m/s)

U_{wm}- superficial gas velocity in well mixed zone (m/s)

X_b-mass fraction of large particle in binary mixture

$\bar{\rho}$- mean density of particles in binary mixture (kg/m^3)

ρ_b- bulk density (kg/m^3)

ρ_f- fluidization gas density (kg/m^3)

ρ_p- particle density (kg/m^3)

ρ_{pk}- particle density of packed component in bed (kg/m^3)

μ- viscosity of fluidization gas (Pa.s)

CHAPTER 1

1. INTRODUCTION

1.1 Present Thesis Work

The work presented in this thesis describes the development of a novel biochar removal system for the pyrolysis of biomass in a fluidized bed reactor. The stages included design, construction, testing, and optimization of both a batch and continuous system to remove biochar from a fluidized bed of inert sand. The thesis uses the Integrated Article format.

The current chapter discusses the purpose and need of the research by introducing biomass pyrolysis and biochar, particle segregation of binary mixtures in a fluidized bed, and particle removal from fluidized beds.

1.2 Pyrolysis and Biochar

Due to the increasing global demand for energy, and a shift from reliance on fossil fuels, different technologies must be developed to use natural resources and distribute energy more effectively between producer and consumer. Fluidized bed pyrolysis, which can utilize a broad selection of low value residual or waste products ranging from corn stover and husk, switch grass, grape skins and seeds, recycled polyethylene, and other organic materials of limited use, converts this feedstock to liquid bio-oil, combustible gases, and a solid biochar (Bridgwater et al.,1999). Fluidized beds are used since they provide uniform mixing of feedstock with heat carrier inert solids, and good transfer of heat and mass. A typical fluidized bed pyrolysis setup can be seen in Figure 1.1.

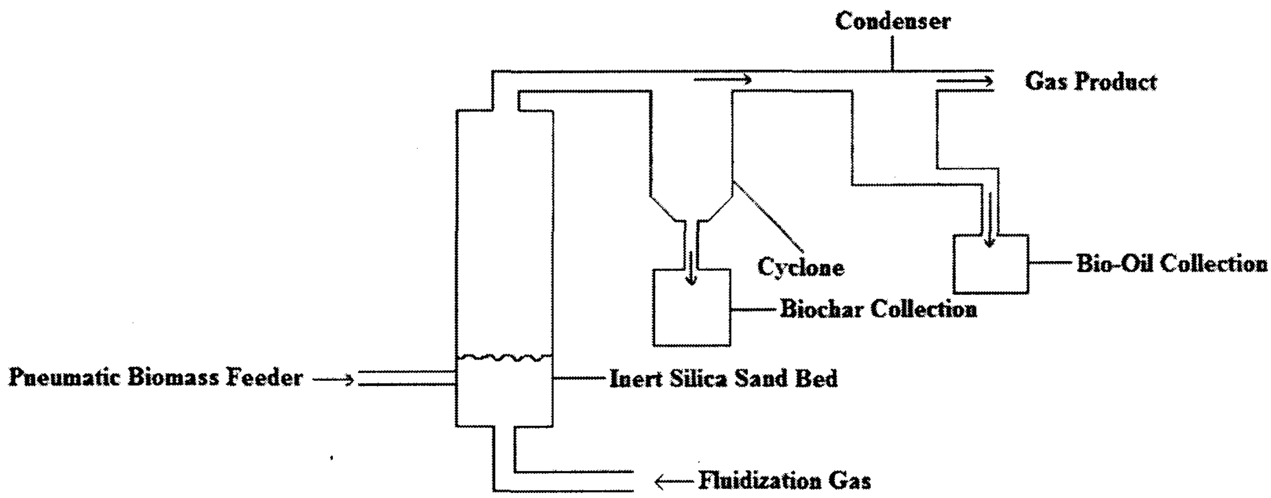

Figure 1.1-Typical fluidized bed pyrolysis unit (Adapted from Xu et al., 2009)

Pyrolysis reactors are made of stainless steel to withstand the relatively high reaction temperatures, ranging from 450 to 600 °C. The product yields of pyrolysis in a fluidized bed have been investigated for several feedstocks by numerous researchers, and are expressed as bio oil, biochar, and gas yields. The bio-oil vapors, are condensed after passing through a cyclone to remove fine biochar particles, and condensed to a liquid.

Typically, bio-oil is the most sought after product due to potential applications as a bio-fuel or as a source of valuable chemicals. These applications are becoming more apparent with continued improvement of pyrolysis and research in fuel upgrading. The chemical composition of bio-oil varies with the composition of the original biomass and the pyrolysis conditions, but generally shares the same building blocks such as water, hydroxyaldehydes, hydroxyketones, sugars, carboxylic acids, and phenolics (Silia et al., 1998). The bio-oil has a higher energy density than the original biomass, especially on a volumetric basis, which eases transportation costs (Mok et al., 1980). Further processing of the bio-oil can lead to different applications, such as the production of chemicals, pharmaceuticals, and food additives. If attaining maximum yields of bio-oil is the goal, this fixes a certain set of operating conditions. In general, the highest yields of bio-oil occur at high temperatures (450-550°C), short gas residence times (2-5 s), and with a fine biomass, as small as possible (Bridgwater & Peacocke, 2000).

Biochar and combustible gases are also pyrolysis products. The combustible gases which consist of H_2, CO, CO_2, and CH_4, can be used to provide additional heat to the process or used as the fluidization gas, making the process more sustainable. Biochar can be elutriated if fine enough, but the majority generally accumulates in the reactor, eventually leading to process shutdowns for combustion of the biochar periodically with air.

Fluidized beds offer good mixing and heat transfer, which is ideal for pyrolysis as the characteristics of biomass are much different from that of conventional feeds used in reactors such as coal, gases, or oils; biomass particles are much more difficult to handle, feed and process due to their shape, density, and cohesiveness. Changing the physical properties of biomass can be accomplished with pretreatments such as grinding, drying, or torrefaction, which has been shown to influence the yields of pyrolysis products. Feedstocks that have been used in fluidized bed pyrolysis range from unprocessed woody biomass particles with a diameter of up to50 mm, to processed and dried grape skins and other grassy materials with a diameter of 0.21 mm or finer (Di Blasi and Branca, 2001) (Xu et al., 2009). Some of these feeds can be seen in Figure 1.2.

Figure 1.2- Typical biomass used for pyrolysis. A) corn meal B) grape skins C) hemp seeds D) woody biomass

Feeds with higher moisture contents show increased yields of biochar, and lower yields of liquid product (Demirbas, 2005). Yields of biochar are generally minimized as process temperature increases. Several types of biomass that are processed during fluidized bed pyrolysis can be seen in Figure 1.2. Furthermore, biomass used in pyrolysis is often residual matter, which means that drying is required to reduce moisture contents to an appropriate level, which is typically 10-15 wt % (Kersten et al, 2005). Increasing the residence time of biomass in the reactor or lowering temperature of the reactor increases biochar yields as the process will become closer to slow pyrolysis or torrefaction, as seen in Figure 1.3 (Demirbas, 2005) (Xu et al., 2009). Biochar is generally expected to be about the same size as the biomass fed or smaller.

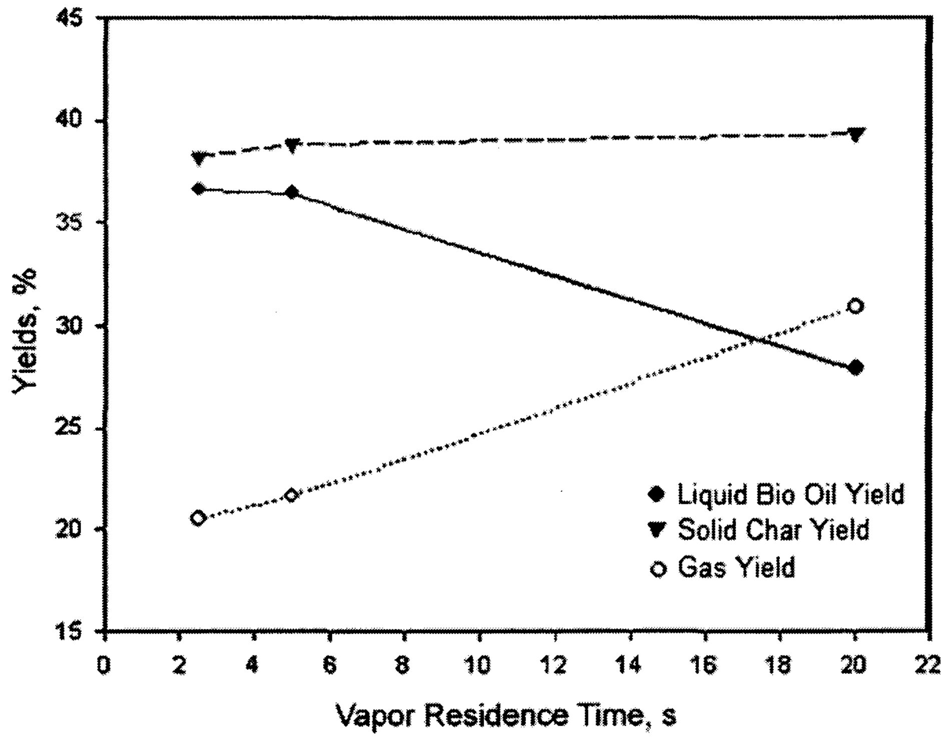

Figure 1.3-Effect of residence time on pyrolysis yields (Adapted from Xu et al., 2009)

Though there are no systematic studies on the size of the biochar particles that remain in the bed, practical experience in the ICFAR laboratories indicates that most of the biochar particles are around the same size as the biomass that is fed to the reactor or slightly smaller, which means they are usually too large to be elutriated. There is also a fraction of elutriable fine biochar that is produced by attrition during fluidization.

The presence of biochar particles in a sand fluidized bed makes the bed a binary mixture, and brings several issues to the process. Primarily, biochar negatively impacts the heat transfer characteristics of the bed and acts as catalyst for secondary cracking reactions that cause higher gas and biochar yields. Biochar accumulating in the reactor will likely lead to worsened properties and yields of products; if the fluidization quality decreases due to excessive biochar it should be expected that the yields of biochar will be higher. If the engineers operating the process wish to synthesize more biochar than bio-oil it may be important to allow some biochar buildup in the bed. Very fine biochar will not drastically affect the fluidization characteristics, as these biochar particles are ejected through the bed through elutriation as they are very small and have a low terminal velocity. On the other hand, larger biochar particles (0.65-1.35 mm) in concentrations of 5-15% (wt biochar/wt sand) in the bed will affect the fluidization. As high superficial gas velocities are used to keep gas residence times low, many fluidized bed pyrolysis processes can tolerate concentrations of biochar in the bed.

Since biochar accumulation in the pyrolysis bed will cause process instability, it is important to develop a technique that will allow continuous removal of biochar, while also minimizing the amount of sand removed from the bed. Excessive sand losses would mean that the sand would have to be reheated and recirculated to the reactor, causing energy losses. The ideal solution should be easy to implement, low in cost, easy to operate, capable of processing biochars from different feedstocks, and simple to optimize.

1.3 Particle Segregation of Binary Mixtures in Fluidized Beds

In fluidized bed pyrolysis, the reactor bed is a binary mixture with regards to hydrodynamics and solids activity, since any biochar that is not elutriated remains in the bed with inert silica sand, fluidization agent particles. An effective way of separating two types of particles within a fluidized bed is through particle segregation at low superficial gas velocities, close to the minimum fluidization velocity of the mixture ($U_{mf,m}$). Depending on process requirements, mixing or particle segregation can be the desired outcome; during the normal operation of the pyrolysis reactor, good solids mixing is desired to ensure that rapid heating of biomass particles, while recovering biochar requires significantly reduced mixing to promote particle segregation. Other than pyrolysis, binary mixtures can occur during catalytic cracking or coal combustion in fluidized beds.

Binary mixtures have been studied extensively, with large volumes of literature published. The amount of work on particle segregation is large since each binary mixture is unique, and must be studied to determine the exact behavior of the mixture. Initial studies on particle segregation in fluidized beds investigated the phenomena and defined terminology to describe the mixture; the term *jetsam* refers to the particles that remain close to the bottom of the bed during fluidization, while the term *flotsam* refers to the lower density particles that migrate to the surface of the fluidized bed. Most commonly, the *flotsam* particles are smaller in size, and the *jetsam* particles are larger, though this is not a necessary condition. *Flotsam* particles are brought to the bed surface by gas bubbles; the *jetsam* particles sink back to the bottom due to gravity and through the emulsion phase created by voids of bubbles, while the *flotsam* particles accumulate near the surface (Rowe et. al, 1972). Gibilaro & Rowe (1972) modeled the axial solids concentration in the fluidized bed at steady state, relating the concentration to particle properties and the superficial gas velocity. Segregation and mixing compete, with segregation predominating at lowered gas velocities.

With binary mixtures, there are many different scenarios that can occur depending on the ratio of densities and sizes. In fluidized bed pyrolysis, and in the studies presented in this thesis, the biochar that remains in the bed during the reaction is larger than the sand and much lighter in density; the biochar constitutes *flotsam* particles and the silica sand the *jetsam* particles. Often in studies that present correlations, the binary mixtures are described by density and diameter ratios between the *jetsam* and *flotsam* particle. The extent of segregation for a binary mixture at a given condition is quantified with a mixing index, which is different depending on the axial location within the bed. The mixing index can be calculated in a number of different ways, but it always relies on bed concentrations at varying heights in the system. For example, Kramer's mixing index is given as,

$$M = \frac{\sigma_0^2 - \sigma^2}{\sigma_0^2 - \sigma_r^2} \tag{1}$$

where σ^2_o is the variance of the jetsam concentration at a completed segregated state, σ^2_r, is the variance of the random mixture at a completely mixed state, and σ^2 is defined as the variance at the tested conditions, which is determined by:

$$\delta = \sqrt{\sum_{i=1}^{n} \frac{(c_{bi} - \bar{c})^2}{n-1}} \tag{2}$$

where $\bar{c}$ is the average mass concentration, m_i is a given mass amount of the jetsam in the sample cell, m_t is the total mass of the sample cell, $c_{bi}= m_i/m_t$, and n is the total sample number of sample cells. This means the mixing index is zero at a completely segregated state (Zhang et al., 2009) (Gyenis, 1999). Marzocchella et al., 2000 do not use statistical methods in calculating their mixing index, but rather absolute concentrations at different heights in the bed.

Segregation behavior can be altered by changing particle properties, fluidization conditions, or implementing bed internals. Density ratio has been shown to have a greater impact than the size ratio (Goldschmidt et al., 2003). Radial segregation in binary mixtures also occurs; at high fluidization velocities, concentrations of *jetsam* particles are higher near the walls of the fluidized bed, while at lower gas velocities, *jetsam* concentrations are higher near the middle of the bed (Joseph et al., 2007). Using sieve-like baffles in the bed maximize the segregation potential. The baffles break up larger bubbles, which are responsible for a mixing mechanism, into smaller bubbles that are still capable of bringing *flotsam* particles to the bed surface. More bubbles result in a greater number of wakes for particles to travel upwards. (Bosma & Hoffman, 2003) (Hartholt et al., 1997).

CFD modeling has been generally unsuccessful in accurately quantifying segregation rates and mixing indexes (Cooper & Coronella, 2005). There are currently no models derived from first principles since the interactions during particle segregation, primarily gravity, drag force, gas-phase turbulence, and particle collisions are too complex to model. CFD studies show the drag force to be the dominant force during particle segregation. (van Wachem et al., 2001).

Particle segregation studies relating to pyrolysis are limited and focus on cold models involving biomass activity; there has been no work focusing on biochar and sand mixtures. Previous segregation studies relating to pyrolysis have examined the segregation tendency of cotton stock biomass and its effect on the mixing quality by determining the mixing index at different bed loadings and superficially gas velocities (Zhang et al., 2009). The goal of these studies was to identify the minimum amount of gas to avoid segregation of the biomass and sand.

Other cold studies relating to pyrolysis have attempted to predict the minimum fluidization gas velocity of the mixture ($U_{mf,m}$), to overcome segregation of the biomass and help define the gas flow required for complete fluidization. Correlations predicting the $U_{mf,m}$ are fitted to experimental data, and are specific to a sand/biomass mixture, which is dependent on the loading, particle sizes and shape of both components, and particle densities. Selected correlations for predicting $U_{mf,m}$, can be seen in Table 1.

Table 1-Correlations for predicting minimum fluidization velocity of mixtures

Reference	Correlation for $U_{mf,m}$	Additional Equations
Rowe and Nienow (1976)	$U_{mf,m} = U_s(\frac{U_b}{U_s})^{x_b{}^2}$	-
Chiba et al. (1979)	$U_{mf,m} = U_f\left(\frac{\bar{\rho}}{\rho_f}\right)(\frac{\bar{d}}{d_f})^2$ (completely mixed bed) $U_{mf,m} = \frac{U_f}{\left(1-\frac{U_f}{U_{pk}}\right)x_f + \frac{U_f}{U_{pk}}}$ (completely segregated bed)	$\bar{d} = [N_f d_f{}^3 + (1-N_f)d^3{}_{pk}]^{1/3}$ $N_f = \frac{1}{1+\left({}^1/_{V_f}-1\right)(\frac{d_f}{d_{pk}})^3}$
Noda et al. (1986)	$U_{mf,m} = \frac{(Re_{p,mf})(\mu)}{\overline{d_p}\rho_g}$	$Ar = ARe^2{}_{p,mf} + BRe_{p,mf}$ $Ar = \frac{\overline{(d_p)}^3\rho_g(\overline{\rho_p}-\rho_g)g}{\mu^2}$ $A = 36.2(\frac{d_{pk}\rho_f}{d_f\rho_{pk}})^{-0.196}$ For a completely mixed bed: $B = 1397(\frac{d_{pk}\rho_f}{d_f\rho_{pk}})^{0.296}$ For a partially mixed bed where $\frac{d_{pk}}{d_f} > 3$ and $\frac{\rho_p}{\rho_f} \sim 1$: $B = 6443(\frac{d_{pk}\rho_f}{d_f\rho_{pk}})^{-1.86}$

The correlations are a good first approximation, but will not be used since the pyrolysis fluidization velocity is fixed to attain a desired gas residence time in the reactor, and the goal of this study is not to develop a model for biochar/sand mixtures, but rather practical batch and continuous systems that are adaptable to different types of biochars.

Though the particle segregation studies discussed offer information regarding the mixing index of the mixture and present empirical models, the findings have limited practicality to industrial situations. Primarily, many studies use ideal particles with good fluidization characteristics. This presents an ideal, best case scenario situation that is rarely seen in an industrial setting with a binary mixture that may actually occur in a reactor. Co-products often do not have these good fluidization characteristics, as in the case of the present research, making any correlations based on the study of these ideal particles ill suited for use with non-idea particles potentially found in an actual industrial process. The correlations presented often use parameters such as particle size, minimum fluidization velocity, and sphericity, and the particle properties of reaction co-products are widely unknown and the particles may not even be fluidizable making these correlations completely unusable. Furthermore, the correlations have further limitations as they are often limited to a binary mixture of "large particle" or "small particle" mixtures (Daw & Frazier, 1988). Each mixture requires independent testing since biomass and biochar channels even at high gas flowrates, meaning it does not have a minimum fluidization velocity (Bilbao et al., 1987). Overall, it is difficult to sample the biochar remaining in the bed during pyrolysis, making it difficult to use a correlation that uses well defined particle properties.

Another fundamental limitation of the current research published to-date is that while it quantifies and models the amount of particle segregation for given mixtures, it does not address methods of removing the separated particles, or describe solutions for removal; that is, merely separating the particles from one another to a certain extent only offers part of the solution for a process to remove a solid co-product from a fluidized bed.

The quantification of particle segregation in the biochar and sand bed has not been studied in the traditional way, or in depth since extensive detail regarding the amount of segregation and the hydrodynamics is not the focus of the research; using particle segregation is merely one step of the process being researched. Since most of the biochar sizes in this study will not show any normal fluidization activity when placed in a bed by themselves due to extensive channeling at all gas velocities used, it is important to investigate the extent of possible segregation, as well as to determine if particle segregation is a feasible process for the separation.

Maximizing the thickness of a separated biochar layer from the rest of the bed will be the key goal during segregation studies.

1.4 Existing Biochar Removal Systems in Pyrolysis Reactors

The most common method of particle removal from fluidized bed pyrolysis units is elutriation, which can most effectively be used when fines are present in the bed. In elutriation, high gas velocities are used to selectively remove fines from a bed. The fines are separated from fluidization gas using a cyclone, with the solids collected in a tank, or collected using a filter bag. Elutriation has been implemented for the removal of ash from coal, though a continuous steady state system could not be achieved, as efficiency decreased as more feed was added to the fluidized bed (Liu & Wey, 2005). Elutriation is currently the only system for biochar removal and is the only system that has been implemented in lab-scale fluidized bed pyrolysis units.

On the industrial scale, Dynamotive, BTG and Ensyn use pyrolysis to generate bio-oil. The pyrolysis process that Dynamotive uses is fast fluidized bed pyrolysis, and assumes that the biochar is small enough to be elutriated from the bed and separated from product gases using a cyclone.

BTG uses a modified rotating cone reactor, using sand to transfer heat to biomass feedstock particles. The biochar produced is combusted to recycle heat. ENSYN uses a circulating fluidized bed for pyrolysis, and uses elutriation for biochar removal.

Elutriation alone is not suitable for a complete removal since only relatively small biochar particles or biochar very low in density can be removed from the bed, as the terminal velocity of the elutriable particles must be smaller than the fluidization velocity. The elutriation rate increases as particles become smaller, which means that larger particles cannot be elutriated compared to smaller particles of the same density (Ma et al., 1995). Previous studies report that the cyclone recovers biochar particles greater than 10 μm, and the hot filter captures particles greater than 1 μm. Other studies report removing biochar of larger sizes through elutriation, but do not report the density, only the particle size distribution as seen in Table 2.

Table 2- Size distribution of biochar elutriated adapted from Mullen et al. (2010)

Particle size distribution of bio-char (μm)							
	Mean	Standard Deviation	<10%	<25%	<50%	<75%	<90%
Corn Cob bio-char	708.8	513.3	71.58	265.5	651.3	1043	1479
Corn Stover Biochar	373.6	420.9	30.35	93.69	212.3	477.8	1008

The literature suggests that there is a broad range of biochar sizes created during pyrolysis making cyclone design important when removing elutriated biochar from the product gases. Unless filters are used after the cyclone the bio oil will contain fine biochar, making the bio-oil unusable for combustion since this will cause erosion and plugging in pipelines (Agblevor et al., 1994). Fine particles agglomerate to other coarse particles or with the other type of solids in the bed, usually silica sand, which prevents their removal by elutriation (Baron et al., 1992) (Briens et al., 1992).

Removal of solids can be accomplished by adding equipment designed for particle transport. Vacuum lines or vertical pneumatic transport lines have been used in coal upgrading processes but required a significant amount of external equipment such as a jet pump and pneumatic vertical line, where significant slugging and unstable flow was reported. In addition, the process is batch, requiring six layers to be vacuumed out subsequently, with only a 60% removal rate of the light waste products (Sahan, 1997). Other studies have accomplished removal through segregation to remove heavier purities like large rocks, leaving lighter coal as the product, and discharging the jetsam from the bottom of the bed. This is accomplished with a moving bed dryer during drying of coal; there are no results reported about the process efficiency, and the only separation in the process is removing the very heavy fraction of the coal (Sarunac et al., 2009).

An accumulation of biochar in the fluidized bed shows that relying on biochar elutriation system is not sufficient to allow a pyrolysis unit to be run continuously, since it will not remove all the fines or the larger biochar. Batch systems have several disadvantages compared to a stable continuous system such as shutdowns, reduced yields, energy losses, and inconsistent operating conditions. Furthermore, having an inconsistent concentration of biochar in the reactor due to the accumulation of biochar in the bed, leads to inconsistent fluidization, causing reduced heat and mass transfer. Developing a system that allows the fluidized bubbling bed pyrolysis unit to operate continuously is paramount in making fluidized bed pyrolysis feasible and applicable on a commercial scale; the system must be capable of processing a variety of feeds (operate in the bubbling regime) while also being capable of separating and removing the biochar co-product from the fluidized bed.

1.5 Research Objectives

In the current chapter, the pyrolysis process has been introduced, principles of particle segregation, and the lack of a proper system to remove the biochar co-product from the fluidized bed pyrolysis reactor.

Therefore, based on the current state-of-the-art, it is necessary to develop a biochar removal system that should meet the following specifications:

- Be easy to operate, and important operating parameters should be easy to adjust
- Keep the biochar concentration low in the pyrolysis unit
- Remove minimal amounts of sand

- Operate in batch or preferably in continuous mode.
- The continuous system should be able to operate at steady state; any biochar that is generated in the system should be able to be removed from the system.
- When operating at steady state, the system should allow the removal of an amount of biochar equal to that generated during the pyrolysis process in order to avoid accumulation

The main objective of this study was the development of a practical biochar removal system based on segregation, in order to allow for the use of larger biomass particles than systems based on elutriation.

The first study that has been carried out relates to a batch removal system; the behavior of the binary mixture of biochar and sand has been investigated to determine the segregation tendency of the mixture at various loadings, and with various biochar particle diameters. A batch removal process has been designed, investigated, and optimized. Though the batch system performed poorly, it offered valuable information regarding (a) how biochar negatively influences the fluidization quality due to its non-ideal properties (b) the ideal conditions for the location of overflow ports with respect to bed solids, and (c) a general indication of how bed loading and particle size affects biochar removal conditions.

The second study focused on the development of a novel continuous biochar removal system, in order to improve the biochar removal process investigated in the previous chapter. The necessity, design, optimization, and discussion of the novel system are presented in this chapter.

The final study focused on the effect of biochar size on performance of the continuous removal system, and the operating parameters that must be changed to address this. The objective was to define the allowable range of biomass particle sizes, since the size of the biochar particles is directly related to the size of the original biomass particles.

The optimization of all the process conditions for this novel fluidized bed led to the continuous removal of high purity biochar from a fluidized bed, capable of operating at pyrolysis conditions. The result of this comprehensive study has a significant impact on the design and operation of fluidized bed pyrolysis units, since it represents the first practical solution for biochar removal from a fluidized bed, which does not require fine grinding of the biomass. As a result of the study described in the this thesis, the novel continuous biochar removal system has been adapted and incorporated for use in the next generation mobile pyrolysis units, by Agri-Therm Inc.

References

F. Agblevor, S. Besler, R. Evans, Inorganic compounds in biomass feedstocks their role in char formation and effect on the quality of fast pyrolysis oils. Proceedings pyrolysis oil properties and combustion meeting, National Renewable Energy Laboratory: Golden, Colorado, 1994; Sept 26-28, 1994, Colorado

A. Aho, N. Kumar, K. Eranen, T. Salmi, M. Hupa, D. Murzin, Catalytic pyrolysis of woody biomass in a fluidized bed reactor: Influence of the zeolite structure, Fuel, 87(2008) 2493-2501

A. Azeez, D. Meier, J. Odermatt, T. Willner, Fast Pyrolysis of African and European Lignocellulosic Biomasses Using Py-GC/MS and Fluidized Bed Reactor, Energy Fuels, 24 (2010) 2078-2085

T. Baron, C. Briens, J. Hazlett, M. Bergougnou, P. Galtier, Size distribution of the particles entrained from fluidized beds: Gas humidity effects, Canadian Journal of Chemical Engineering, 70 (1992) 631-635

R. Bilbao, J. Lezaun, J.C Abanades, Fluidization velocities of sand/straw binary mixtures, Powder Technology, 52 (1987), 1-6

J. Bosma, A. Hoffman, On the capacity of continuous powder classification in a gas-fluidized bed with horizontal sieve-like baffles. Powder Technology, 124 (2003) 1-15

A.V. Bridgwater, G. Peacocke, Fast pyrolysis processes for biomass. Renewable Sustainable Energy, 4 (2000) 1–73.

A. V Bridgwater,. Renewable fuels and chemicals by thermal processing of biomass. Chem. Eng. J., 91, (2003) 87–102.

C. Briens, M. Bergougnou, I. Inculet, T. Baron, J. Hazlett, Size distribution of particles entrained from fluidized beds. Electrostatic effects, Powder Technology, 70 (1992) 57-62

BTG, "Fast Pyrolysis"(2000) <http://www.btgworld.com/index.php?id=22&rid=8&r=rd>

C. Daw, G. Frazier, A Quantitative Analysis of Binary Solids Segregation in Large-Particle Gas-Fluidized Beds, Powder Technology, 56 (1988) 165-177

A. Demirbas, Relationship between Initial Moisture Content and the Liquid Yield from Pyrolysis of Sawdust, Energy Sources, 27 (2005) 823-830

C. Di Blasi, C. Branca, Kinetics of primary product formation from wood pyrolysis. Ind. Eng. Chem. Res. 40 (2001) 5547-5556.

Dynamotive, "Fast Pyrolysis" (1999) <www.dynamotive.com>

M.J.V. Goldschmidt, J.M. Link, S.Mellema, J.A.M. Kuipers, Digital image analysis measurements of bed expansion and segregation dynamics in dense gas fluidized beds, Powder Technology, 138 (2003) 135–159.

J.Gyenis, Assessment of mixing mechanism on the basis of concentration on pattern, Chem. Eng. Process, 38 (1999) 665-674

G. Hartholt, R. la Riviere, A. Hoffman, L. Janssen, The influence of perforated baffles on the mixing and segregation of a binary group B mixture in a gas-solid fluidized bed, Powder Technology, 93 (1997), 185-188

G. Joseph, J. Loboreiro, C. Hrenya, A. Stevens, Experimental Segregation Patterns in Bubbling Gas Fluidized Beds, AIChE, 53 (2007) 2804-2813

S. Kersten, X. Wang, W. Prins, W. van Swaaj, Biomass Pyrolysis in a Fluidized Bed Reactor. Part 1: Literature Review and Model Simulations, Ind. Eng. Chem. Res., 44 (2005) 8773-8785

K. Liu, M. Wey, Dynamic purification of coal ash by a gas-solid fluidized bed, Chemosphere, 60 (2005) 1341-1348

A. Marzocchella, P. Salatino, V. Di Pastena, L. Lirer, Transient fluidization and segregation by size difference of binary mixtures of particles, AIChE Journal, 46 (2000) 2175-2182

M. Mastellone, F. Perugini, M. Ponte, U. Arena, Fluidized Bed Pyrolysis of a Recycled Polyethylene, Polymer Degradation and Stability, 76 (2002) 479-487

L.K. Mok, M.A. Bergougnou, H.J. de Lasa, Fast Pyrolysis of biomass for the production of chemicals and fuels from wood, 4th Bioenergy R and D Seminar, Winnipeg, Canada, 1980.

C. Mullen, A. Boateng, N. Goldberg, I. Lima, D. Laird, K. Hicks, Bio-oil and bio-char production from corn cobs and stover by fast pyrolysis, Biomass and Bioenergy, 34 (2010) 67-74

P. Rowe, A. Nienow, A. Agibim, Preliminary quantitative study of particle segregation in gas-fluidized beds-binary systems of nearspherical particles. Trans. Inst. Chem. Eng., 50 (1972) 324–333.

R. Sahan, Coal Cleaning Performance in an Air Fluidized Bed, Energy Sources, 19 (1997) 475-492

N. Sarunac, E. Levy, M. Ness, C. Bullinger, J. Mathews, P. Halleck, A Novel Fluidized Bed Drying and Density Process for Upgrading Low-Rank Coals, International Journal of Coal Preparation and Utilization, 29 (2009) 317-332.

K. Sipila, E.Kuoppala, L. Fagernas, A. Oasmaa, Characterization of biomass-based flash pyrolysis oils. Biomass Bioenergy, 14 (1998) 102– 113.

B. van Wachem, J. Schouten, C. van den Bleek, R. Krishna, J. Sinclair, CFD modeling of gas-fluidized beds with a bimodal particle mixture. AIChE J., 47 (2001) 1292–1302.

F. Zenz, F. Othmer. Fluidization and Fluid–Particle Systems. Reinhold Publishing Corp. (1960).

Q. Zhang, J. Chang, T. Wang, Y. Xu, Review of biomass pyrolysis oil properties and upgrading research. Energy ConVers. Manage. 48 (2007) 87–92.

Y. Zhang, B. Jin, W. Zhong, Experimental investigation on mixing and segregation behavior of biomass particle in fluidized bed, Chemical Engineering and Processing, 48 (2009) 745-754

CHAPTER 2

2. BATCH REMOVAL OF BIOCHAR IN A FLUIDIZED BED USING PARTICLE SEGREGATION AND OVERFLOW PORTS

2.1 Introduction

Improving green technologies at the lab-scale is an essential step in making a process feasible for use at the industrial scale. Pyrolysis, a green technology, is the thermal conversion of biological materials to a bio oil liquid product, combustible gases, and solid biochar, in absence of oxygen (Bridgwater et al., 1999). Solid biochar, a co-product of pyrolysis, can be used as a soil additive or further used in power generation when co-fired with other fuels, making it necessary to isolate from the inert sand that is typically used in pyrolysis fluid bed reactors for enhancing the heat transfer and the mixing; however, a technique to successfully remove the biochar from the fluidized bed has not been studied. The presence of biochar in the bed decreases the fluidization quality, increases the amount of gas needed to fluidize the bed fully, and acts as a catalyst for undesirable secondary cracking reactions which negatively affect the bio-oil yield. As a result, the biochar concentration should be kept minimal, constant levels to achieve process stability.

Particle segregation based on density or size in binary mixtures is an attractive option as it only requires optimization of the superficial gas velocity in the bed to promote the separation. As fluidized beds are usually employed to promote good mixing during reactions, segregation of particles is often seen as something that must be avoided, as the segregation mechanism competes with mixing (Rowe & Nienow, 1976). Both mixing and segregation are caused by the bubbles resulting from the fluidization gas passing through the bed of solids. The lighter *flotsam* particles are lifted in the wake of each bubble and allowed to settle on the surface of the bed while the heavier, *jetsam* particles sink after being lifted to the surface in the wake of the bubble. The particle that forms a layer on the top of the bed is referred to as the *flotsam* while the heavier sinking particle is referred to as the *jetsam* particle. Bubbles form at the distributor at minimum fluidization velocity for Geldart group B powders. The bubbles carry the solid particles in their wake. The *flotsam* particles tend to remain close to the surface while the *jetsam* particles sink to the bottom of the bed. Operating at a higher gas velocity leads to larger, faster moving and larger bubbles in the bed and more turbulent mixing, which prevents particle segregation (Rowe, 1972). Optimal segregation is occurs close to the minimum fluidization of a binary mixture.

Segregation studies typically utilize ideal particles with well defined fluidization characteristics; however biochar displays different physical characteristics depending on the biomass feed and reaction conditions. Its fluidization characteristics are very poor and it tends to channel during fluidization. Though particle segregation has been researched extensively, practical systems for the removal of separated particles from the bed have not been studied, thus creating the need for the current research.

Separation of coal is carried with vacuum lines to remove less dense fractions of coal in batch mode, following segregation (Sahan, 1997).

Elutriation can be used to selectively remove very fine particles from fluidized beds; however, as biochar is not always fine, elutriation cannot be used. Relating to pyrolysis, a biochar removal technique was employed using elutriation, where the biochar particles were removed from the product and fluidization gas using a cyclone to separate particle >10 μm and a subsequent hot filter removed fine particles around 1 μm. This removal system only removes particles elutriated from the bed, not larger particles that may be present during pyrolysis operations (Lee et al., 2005). Biochar removal techniques in fluidized bed pyrolysis must be developed to maximize stability and profitability of the process.

In this current chapter, the performance of a batch biochar removal process in a fluidized bed was investigated. Using a two step batch process consisting of (1) optimizing particle segregation, defined as attaining a maximum biochar layer thickness above the sand, followed by (2) removal through overflow ports. Studying the batch system's inefficiency and behaviors were essential to designing a successful continuous system.

2.2 Experimental

2.2.1 Equipment

A square fluidized bed, 0.2 m in size at the base, was designed and used to carry out the experiments, as shown in Figure 2.1. Based on particle segregation optimization, 3 holes (0.0225 m in diameter) were drilled on one side of the fluidized bed, 0.2 m above the bottom of the bed. 8 kg of sand was used with various types and concentrations of biochar. The flowrate of fluidization gas through a polypropylene porous plate gas distributor was controlled with a sonic nozzle (3 mm in diameter) by an Omega PX181 pressure transducer, and Mastercraft voltmeter.

The air exiting the fluidization column passed through a fabric filter bag (McMaster Carr), which collected any fines elutriated from the bed.

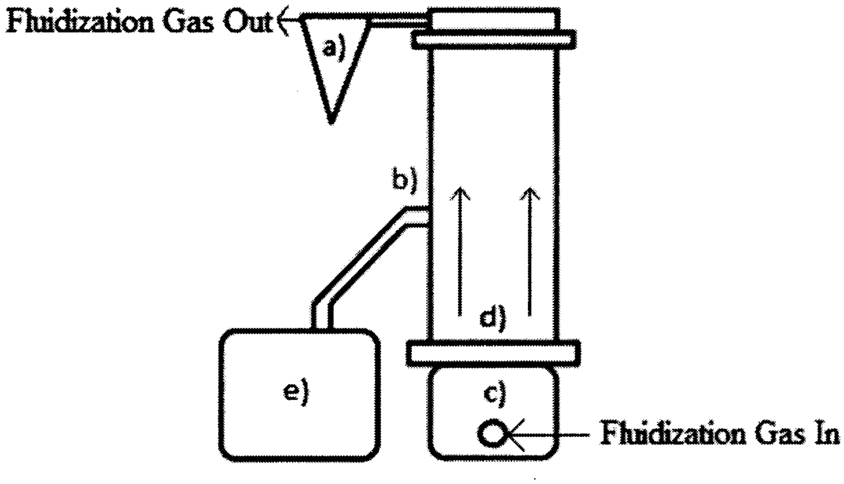

Figure 2.1-Fluidized bed used in batch segregation and removal experiments. a) filter bag, air ouput b) overflow ports c) windbox, air input d) porous plate distributor e) solids collection container

2.2.2 Materials

Biochar obtained from Burt's Greenhouses in Kingston, Ontario, was used for all experiments. Sieving was used to separate the mixture into size cuts with d_{psm}=1.35 mm, d_{psm}=1.15 mm, and d_{psm}=0.65 mm and ρ_b=267 kg/m^3, ρ_b= 252 kg/m^3, and ρ_b=230 kg/m^3 respectively. The particle size distributions of each size cut, determined using sieving, are shown in Figure 2.2. Barco Silica Sand 71 (d_{psm}=0.175 mm, ρ_p=2650 kg/m^3, ρ_b=1675 kg/m^3) was used for all experiments as it is commonly used in fluidized bed pyrolysis. Moisture content of the biochar used in all experiments was constant as tray drying was implemented prior to using the biochar in the bed.

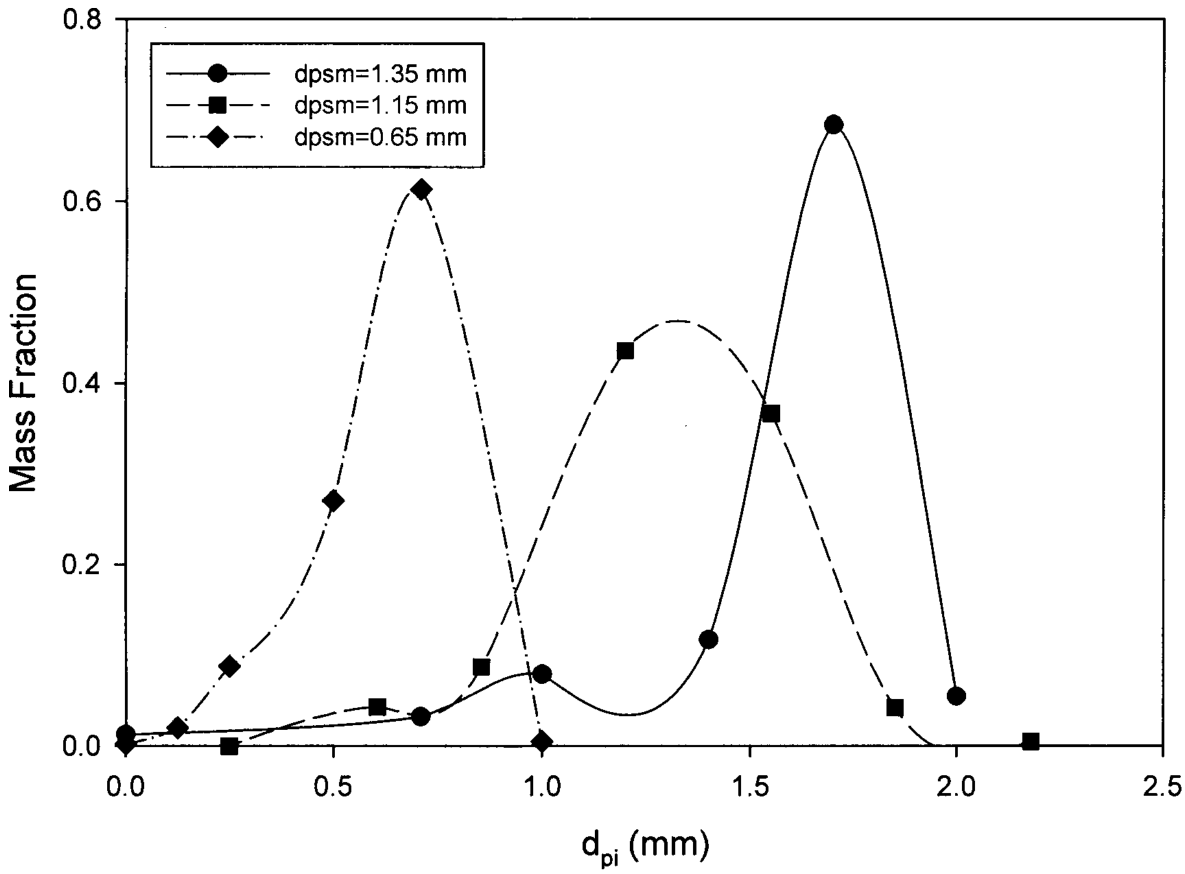

Figure 2.2-Particle size distribution of biochars tested

2.2.3 Experimental Procedure

The bed was loaded with 8 kg of sand. For each experiment, a selected amount of a biochar having a given particle size was introduced to achieve the desired concentration (% wt biochar/% wt sand), then mixed vigorously at a high fluidization velocity to ensure a uniform bed concentration.

Batch segregation was performed to identify the time needed to attain an end point of segregation, defined as the time required for the biochar layer to reach a constant thickness on top of the sand bed. During these experiments, the bed was fluidized at a chosen velocity (U_{seg}) to perform the particle segregation. The biochar layer height above the rest of the bed was measured every 30 seconds for 3 minutes. The bed was then mixed vigorously and the process repeated for other values of U_{seg}.

Following the particle segregation optimization, the biochar removal ports were opened, and the gas velocity changed (U_{rem}), allowing the solids to be removed from the bed. Each 30 seconds, the solids were collected in a container at the side of the bed, and the yield of biochar and sand concentrations were determined through sieving. The equations used to quantify results can be seen below, on a mass basis.

$$Efficiency = \frac{biochar\ removed}{initial\ biochar\ in\ bed} \tag{3}$$

$$Purity = \frac{biochar\ removed}{total\ solids\ removed} \tag{4}$$

2.3 Experimental Results and Discussion

2.3.1 Segregation of the Biochar and Sand Mixture

2.3.1.1 Time Evolution During Biochar Segregation

During this separation process, an end point was identified to determine when particle segregation can be stopped and removal started. The end point in these experiments was identifiable when the biochar layer had reached a maximum thickness. The flotsam particle (biochar) formed a layer above the jetsam particle (silica sand) until a maximum amount of the flotsam particle is separated into the well defined top layer, as seen in Figures 2.3 and 2.4. Experiments were conducted for 3 minutes, though the time required to reach a maximum apparent biochar layer for all conditions was about 2 minutes; all data shown for segregation is at 2 minutes. A qualitative observation of the general effect of gas velocity on the bed solids, and bed expansion is shown in Figure 2.5 for 5% loading and d_{psm}=1.15 mm. This trend is similar for all bed compositions and biochar sizes.

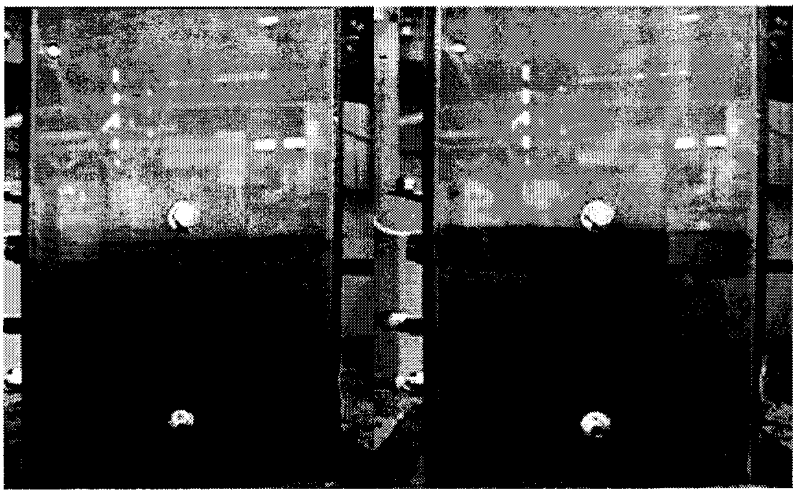

Figure 2.3-A well mixed bed of uniform concentration is shown on left, and a bed that has reached steady state segregation is shown on right, for d_{psm}=0.65mm, 10% loading, U_{seg}=0.064 m/s

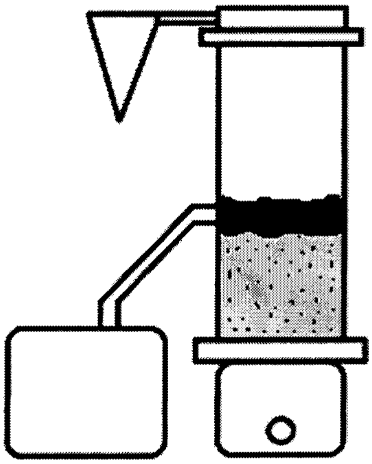

Figure 2.4-Bed depiction of a fully segregated bed

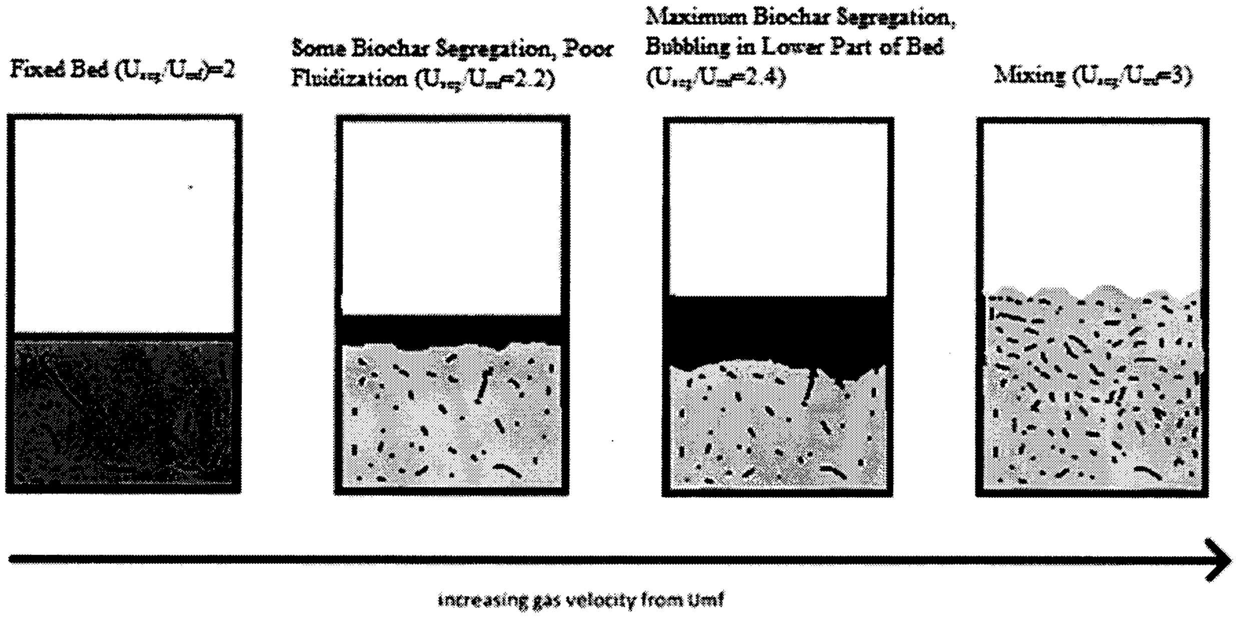

Figure 2.5—Qualitative observation of effect of superficial gas velocity on bed segregation with binary mixture of biochar and sand, with biochar loading=5% and d_{psm}=1.15 mm

2.3.1.2 Effect of Biochar Loading

For biochar segregation to be successful, the amount of gas used was greater than the minimum fluidization velocity of sand (U_{mf}), as shown in Figure 2.6. As the biochar loading increased from 5, to 10, and 15%, the amount of fluidizing gas had to be increased almost linearly to achieve particle segregation, since a smaller fraction of the overall biochar in the bed was segregated. As the concentration of biochar in the bed increased, more gas was required for fluidization and attaining optimal segregation. The higher gas flow led to more bubble activity in the bottom part of the bed where the sand concentration were very high, causing a large amount of sand to be splashed to the surface of the bed. The higher amounts of biochar also lead to some defluidization in the reactor, affecting the well controlled bubble activity that is needed for particle segregation. Smaller biochar loadings inhibit fluidization less, allowing less fluidization gas to be used, resulting in less vigorous mixing. The findings suggest that the presence of biochar in the bed significantly affected the fluidization, and with more biochar in the bed, the fluidization quality worsened and caused less biochar segregation.

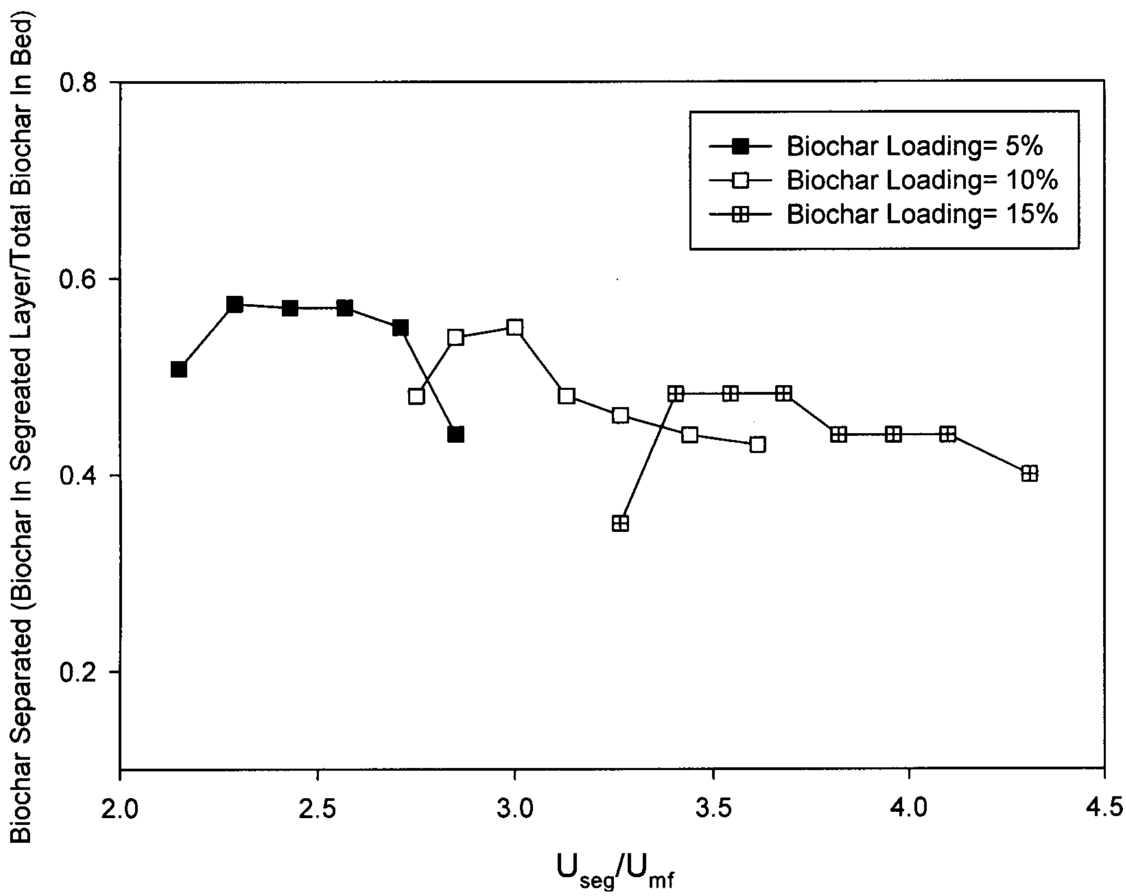

Figure 2.6-Amount of biochar segregation at steady state for different bed compositions, d_{psm}=1.15 mm

2.3.1.3 Effect of Particle Size

Different biochar particle sizes are present in pyrolysis processes depending on the size and properties of the biomass feedstock used, presenting the need for the performance of different sizes of the same biochar to be investigated. Using a10% loading of biochar, the effect of the biochar particle size was investigated, with the results shown in Figure 2.7. The smallest biochar particles inhibited fluidization less than larger biochar particles, but ended up forming a thinner layer. The smaller particles are packed more closely together and have a smaller volume, while the larger particles are packed less closely and have a larger volume. Larger biochar particles allowed for the thickest apparent biochar layer to form on top of the bed, but also required the most gas to segregate successfully. Though the large biochar particles required higher gas velocities to separate, the quality of the segregation improved. This suggests that overloading the bed with biochar was more detrimental than having biochar that was excessively large. The particles segregated most effectively at around minimum fluidization velocity of the mixture, identified with minimum bubbling in the mixture, as some bubbling is required for segregation since the solids move upwards in the wake of each bubble.

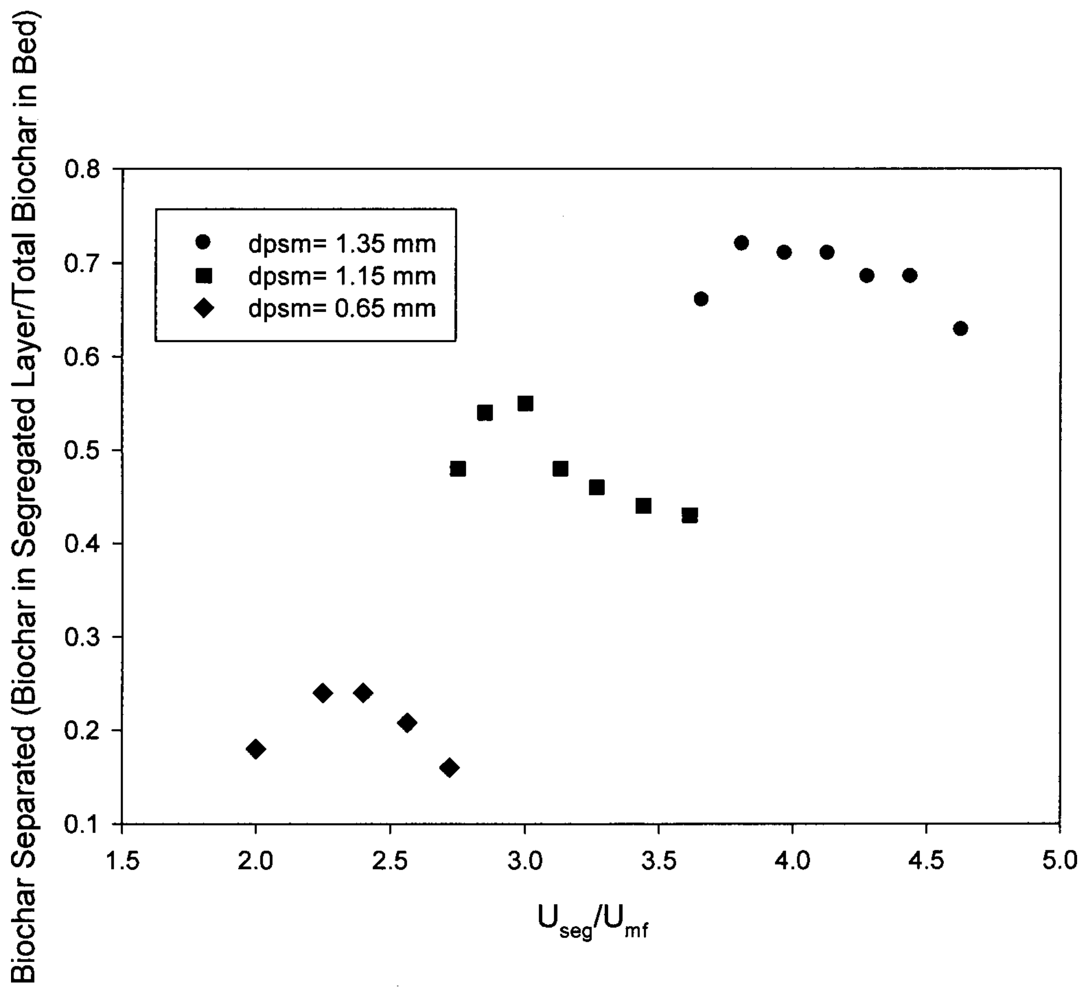

Figure 2.7-Amount of biochar segregation with different biochar particle sizes and 10% loading

2.3.2 Biochar Removal Following Particle Segregation

As described in Section 2.2.3, in each experiment, after a biochar layer was formed through segregation, the superficial gas velocity was adjusted (U_{rem}) and particle removal was performed. The performance of the system was evaluated in terms of efficiency and purity of solids removed.

2.3.2.1 Time Evolution During Biochar Removal

In a batch process, the kinetics of the process are integral in assessing the feasibility; batch processes that can be completed in a shorter amount of time are more desirable as they are less expensive and require less downtime. As time increased, the batch biochar removal process became less efficient, that is less biochar was being removed. Though experiments were conducted for 2 minutes, the removal was most effective during the first thirty seconds. Therefore, the batch process was about 2.5 minutes in length, which included the particle segregation at superficial gas velocity, U_{seg}, followed by the removal of the segregated layer at a different superficial gas velocity, U_{rem}. The solids level of the bed continually decreased until it was close to the bottom of the removal ports and mostly sand was removed, shown in Figure 2.8. One example of batch removal performance- efficiency rates and purity- is shown in Figures 2.9 and 2.10, though all loadings and biochar sizes followed this trend; most of the initial biochar in the bed was removed in the first thirty seconds, then a small amount in the next thirty seconds. The results indicate that removal was most effective during the first thirty seconds, in terms of efficiency and purity.

Figure 2.8- Visual observation of the removal process at 3, 30, 60, 90, and 120 seconds from left to right

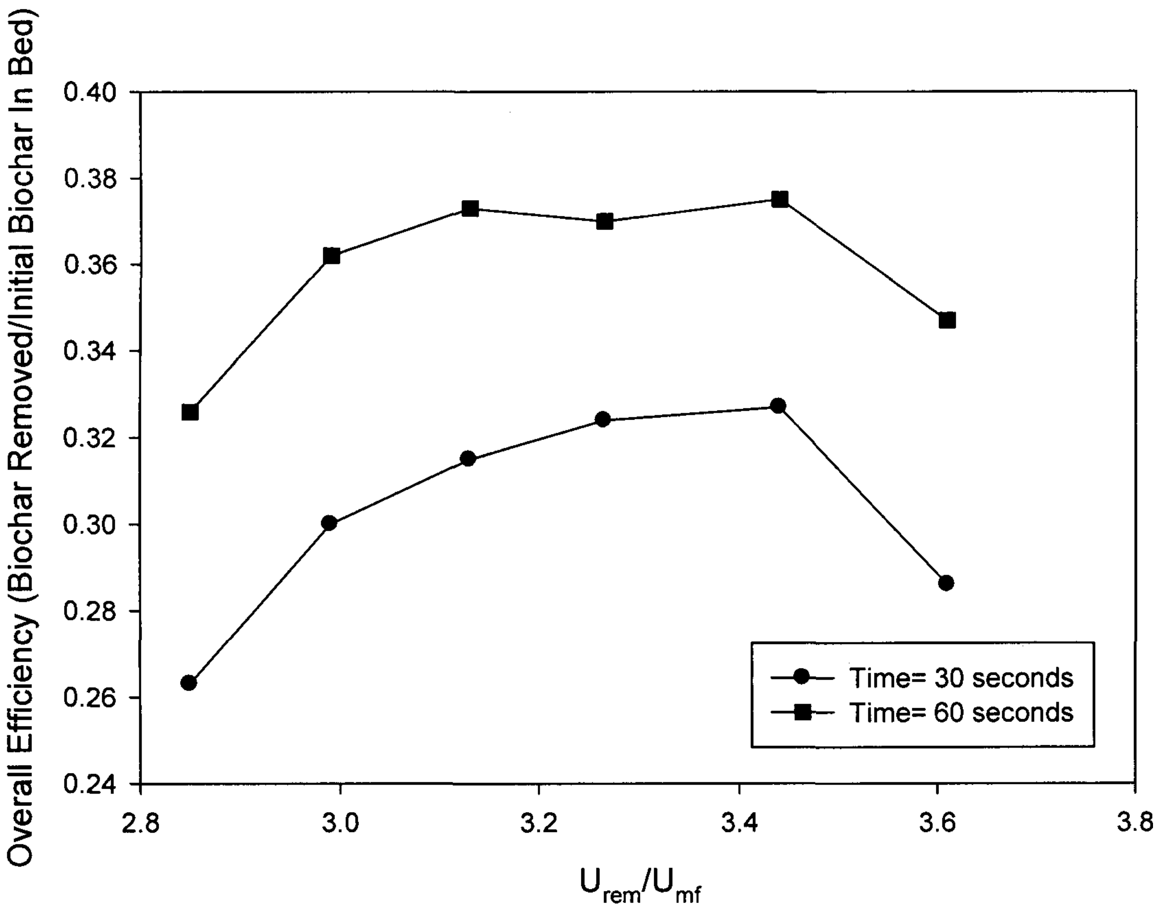

Figure 2.9-Overall Efficiency during the first minute of removal with 10% biochar loading and d_{psm}=1.15 mm

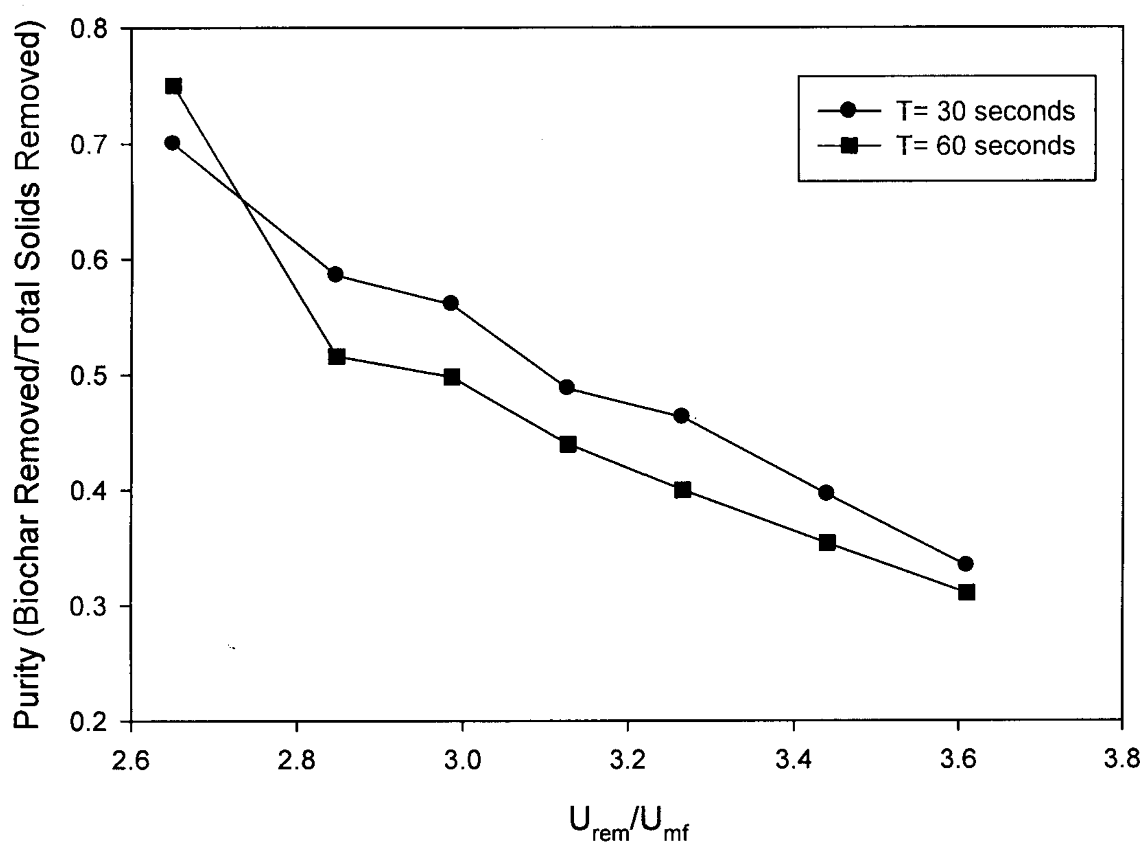

Figure 2.10-Purity during the first minute of removal with 10% biochar loading and d_{psm}=1.15 mm

2.3.2.2 Effect of Biochar Particle Size

Biochar particle size had a large effect on the removal conditions required. Large biochar particles were shown to be the most successfully removed particles in terms of efficiency, though more gas was required, similar to the segregation step. The increased performance during removal of larger particles can be explained through the segregation results, as the largest biochar particles also formed the thickest segregated layer. A larger pressure head built by the larger biochar layer may also have an effect on removal purity and efficiencies. Removal efficiencies at thirty seconds and sixty seconds can be seen in Figures 2.11 and 2.12. Similarly, the smallest biochar particle had the lowest biochar removal yields since these particles created a thinner segregated layer. However, since the largest biochar particles also required more gas for sufficient fluidization, this caused lower purities during removal. Removal purities for each mixture can be seen in Figures 2.11 and 2.12. Higher purities could be attained with the smallest biochar particles since lower gas speeds were required, allowing less sand to reach the surface and be removed through the ports. Though the purity with the smallest particles was increased, the yields were decreased since a smaller amount of biochar segregated. For each particle size, more biochar was removed at higher gas velocities with the purity decreasing due to more sand being removed from the bed. Low purity removal was a result of the changing bed composition, as a higher gas velocity was required at the beginning of removal, but as biochar concentration decreased less gas was required for fluidization.

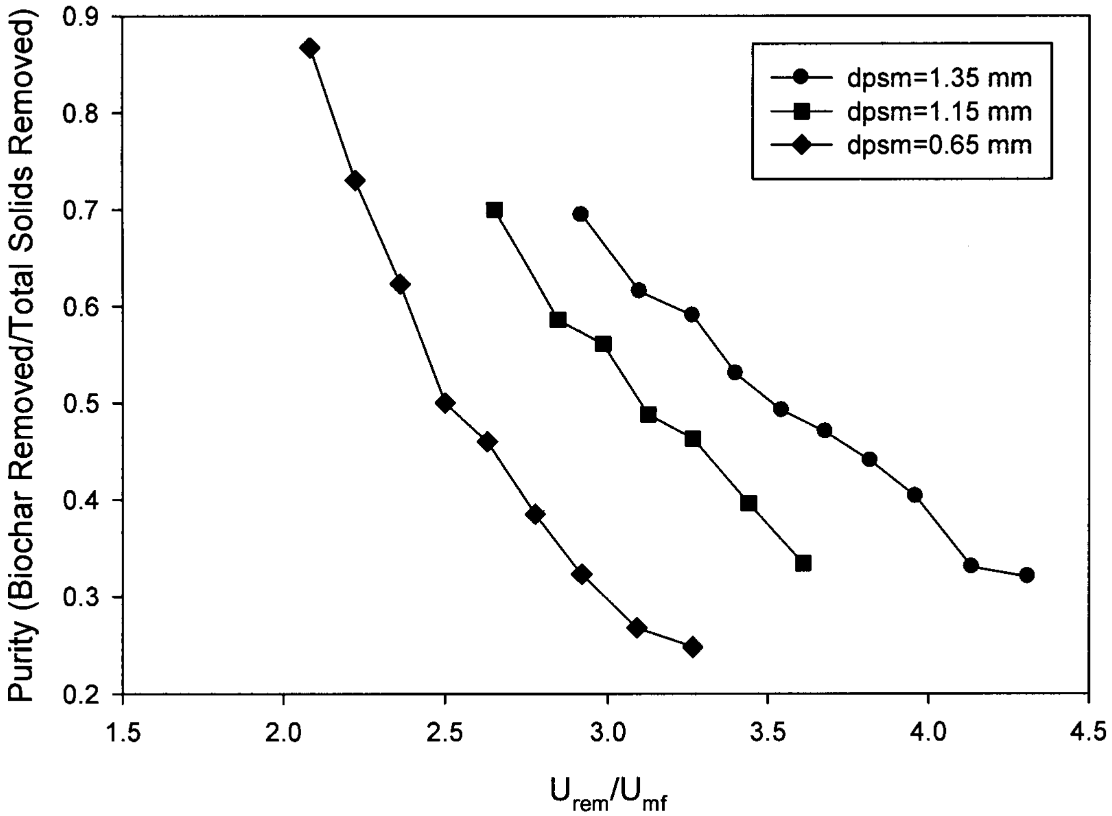

Figure 2.11- Purity after 30 seconds of removal at different removal velocities

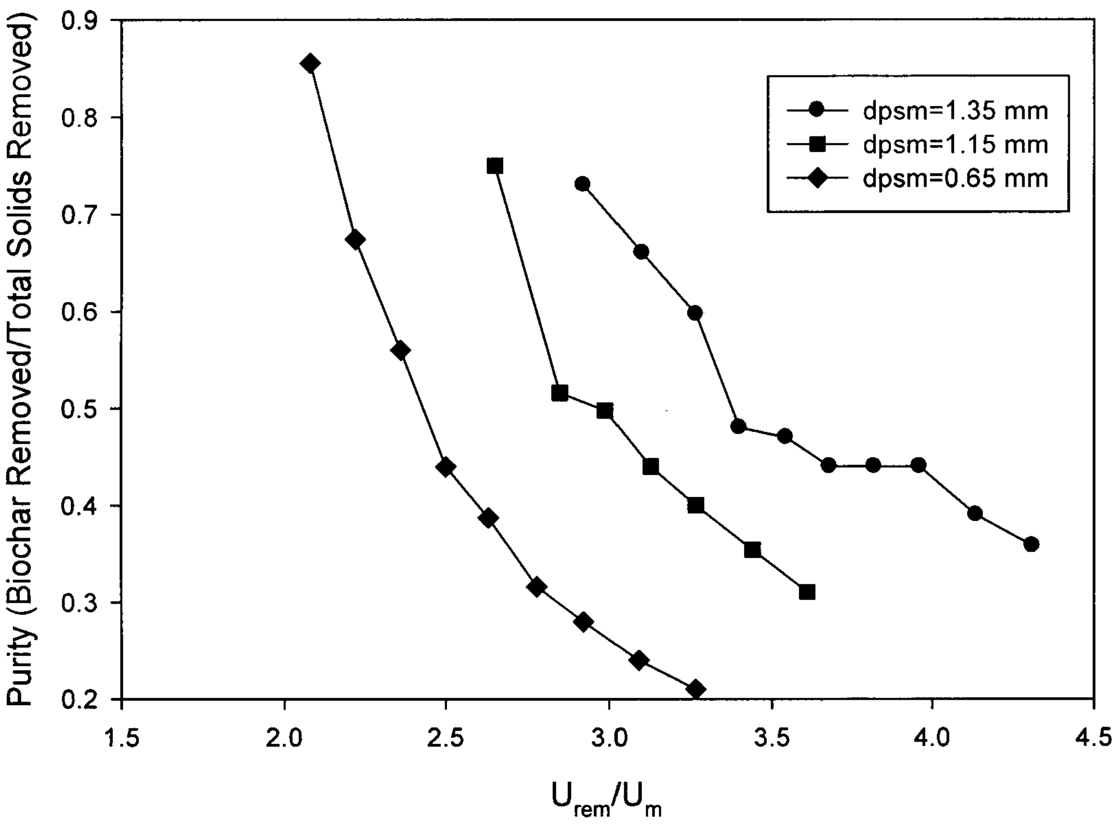

Figure 2.12- Purity after 60 seconds of removal at different removal velocities

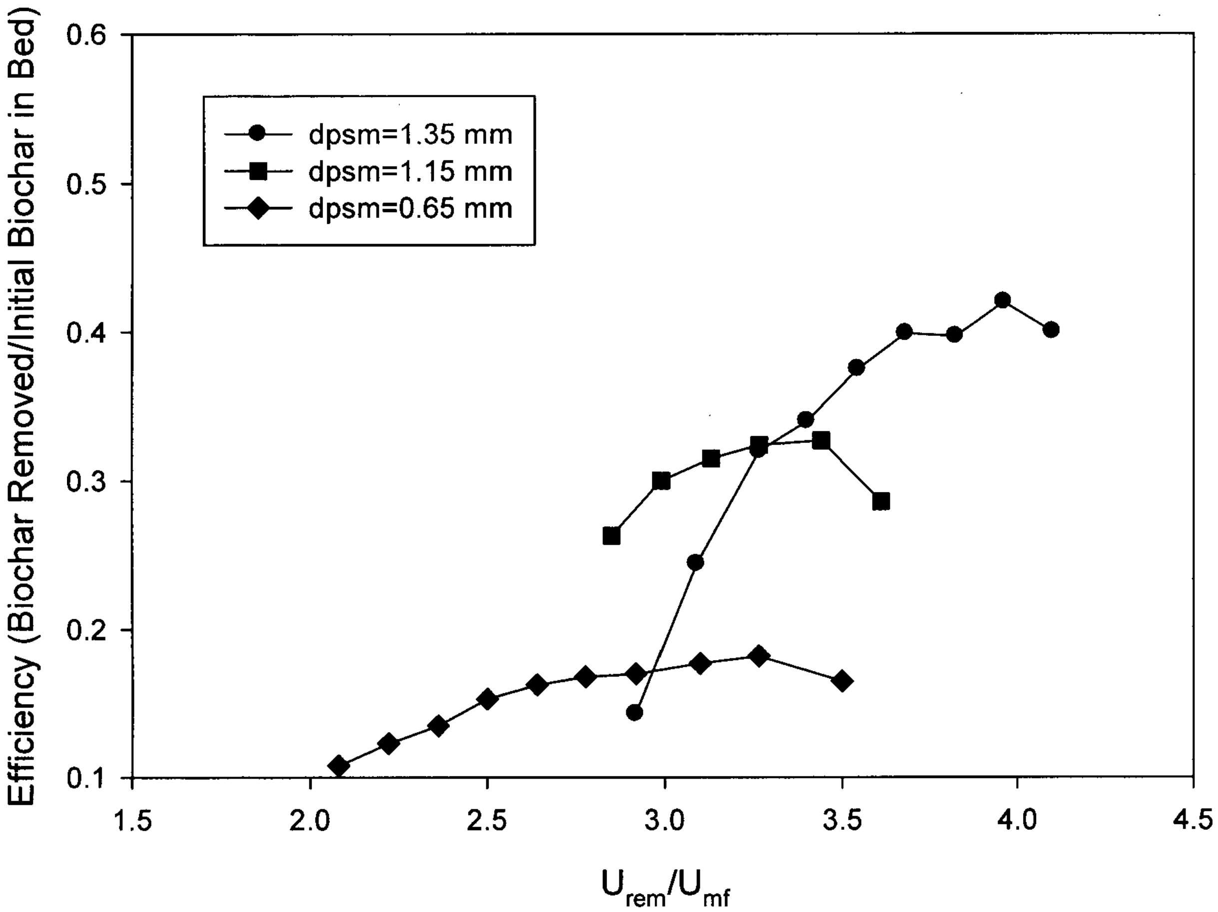

Figure 2.13-Efficiency after 30 seconds of removal at different removal velocities

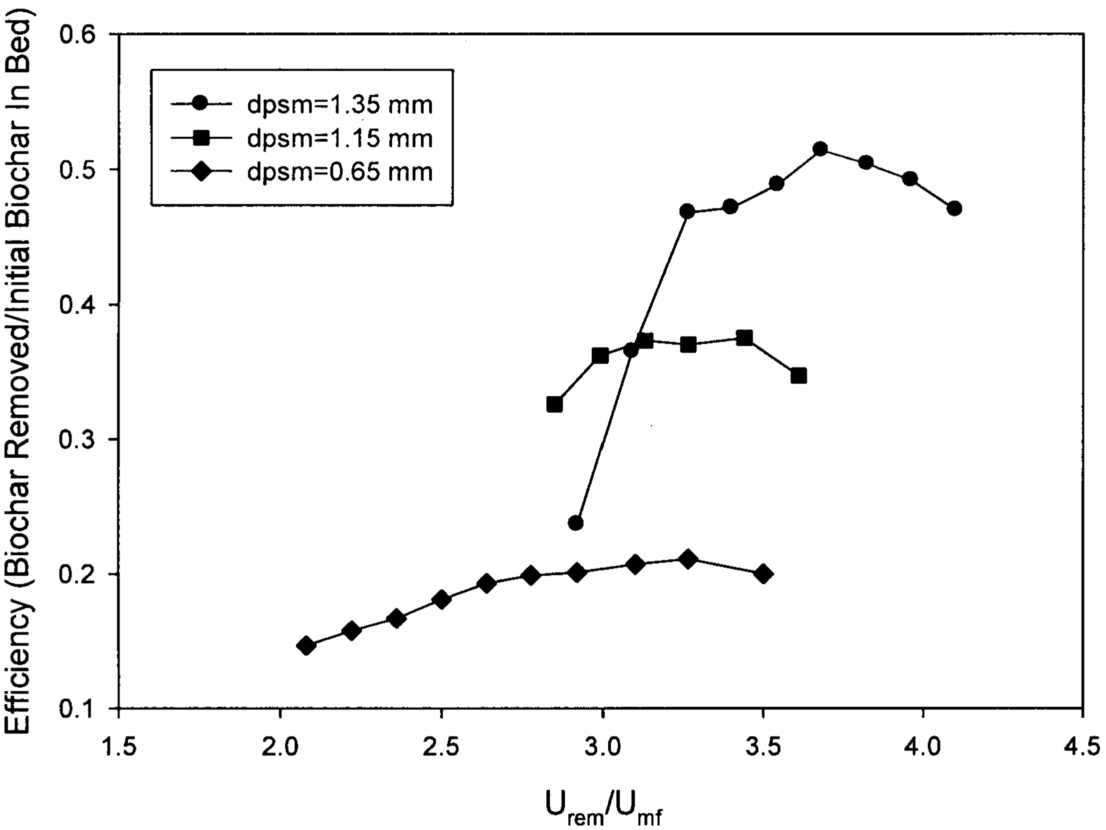

Figure 2.14-Efficiency after 60 seconds of removal at different removal velocities

2.3.2.3 Effect of Biochar Loading

In relation to the pyrolysis process, the biochar loading in the bed is an important design consideration since biochar in the bed at different concentrations affects the quality of fluidization, heat transfer, kinetics, and therefore, the efficiency of the process. The loading of biochar in the fluidized bed was shown be an important variable, which is apparent from the experimental work at the different operating conditions required for removal for different bed compositions. Between 5 and 10% loading of biochar in the bed, the removal efficiency was increased, and decreased for 15% efficiency as seen in Figures 2.17 and 2.18. The decrease in efficiency at 15% can be validated by addressing the segregation results, as it shows a smaller yield of biochar was segregated into a removable layer when the bed is loaded to 15%; with a smaller segregated layer, less biochar will be removed through the ports. Loading the bed with

15% biochar showed poor results due to overall poor fluidization just as in similar studies conducted with binary mixtures with biomass (of similar particle characteristics to biochar tested) and sand, when 15% biomass loading also showed to yield inconsistent results and was considered overloading the bed with the flotsam component (Bilbao et al., 1987). Removal purity results are shown in Figures 2.17 and 2.18. The purities in the first thirty seconds decreased as biochar loading increased. This was a result of more fluidization gas being required during removal, causing more sand to be removed with biochar. Biochar loading of 5% in the bed was the highest purity, as the lower loading inhibits has a much smaller effect on the fluidization, and allowed for lower superficial gas velocities to be used relative to 10% and 15% loadings, making the sand bed less turbulent, and consequently, resulted in less sand loss.

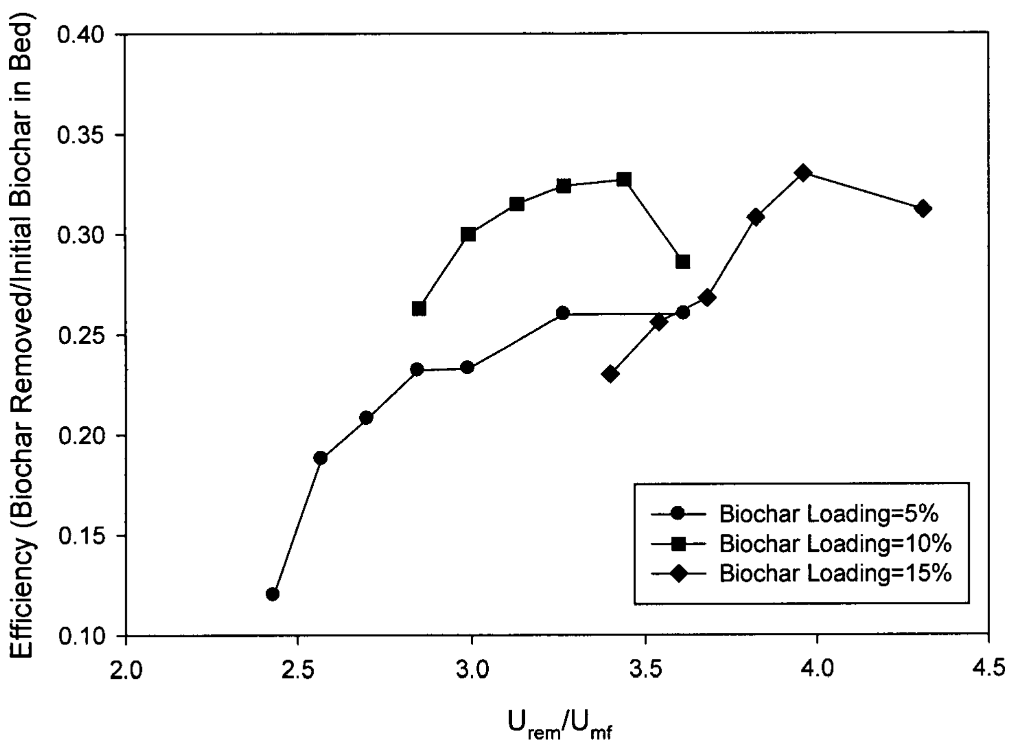

Figure 2.15-Efficiency after 30 seconds of removal at different removal velocities

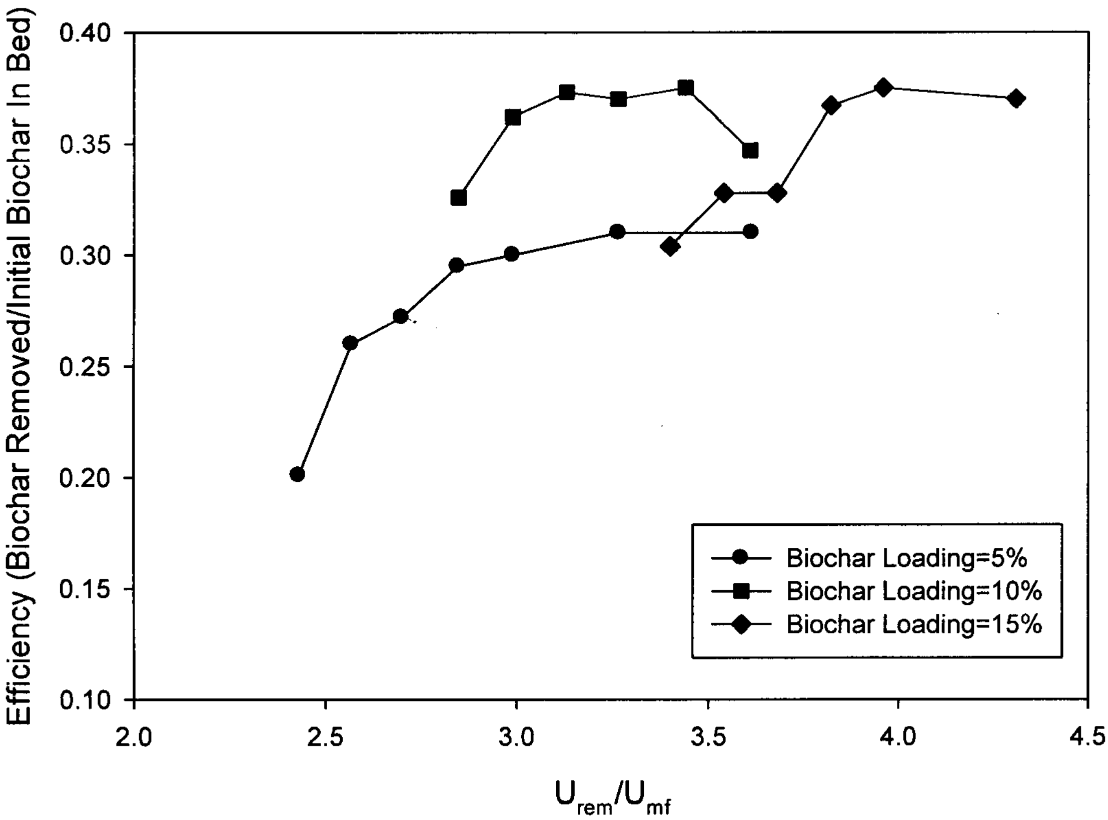

Figure 2.16-Efficiency after 60 seconds of removal at different removal velocities

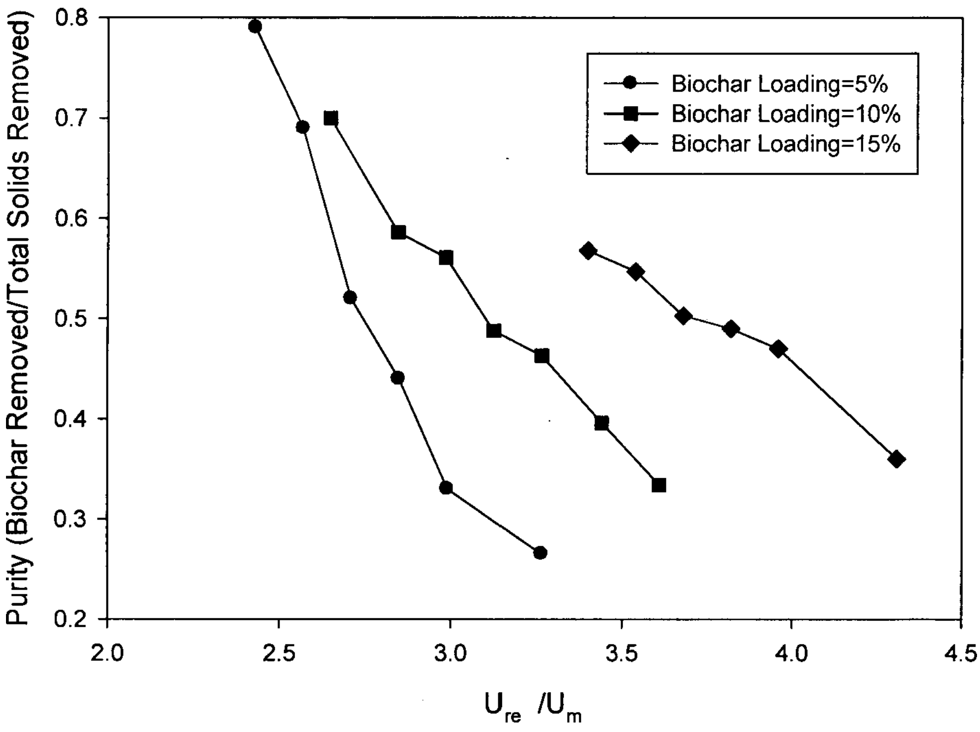

Figure 2.17-Purity after 30 seconds of removal at different removal velocities

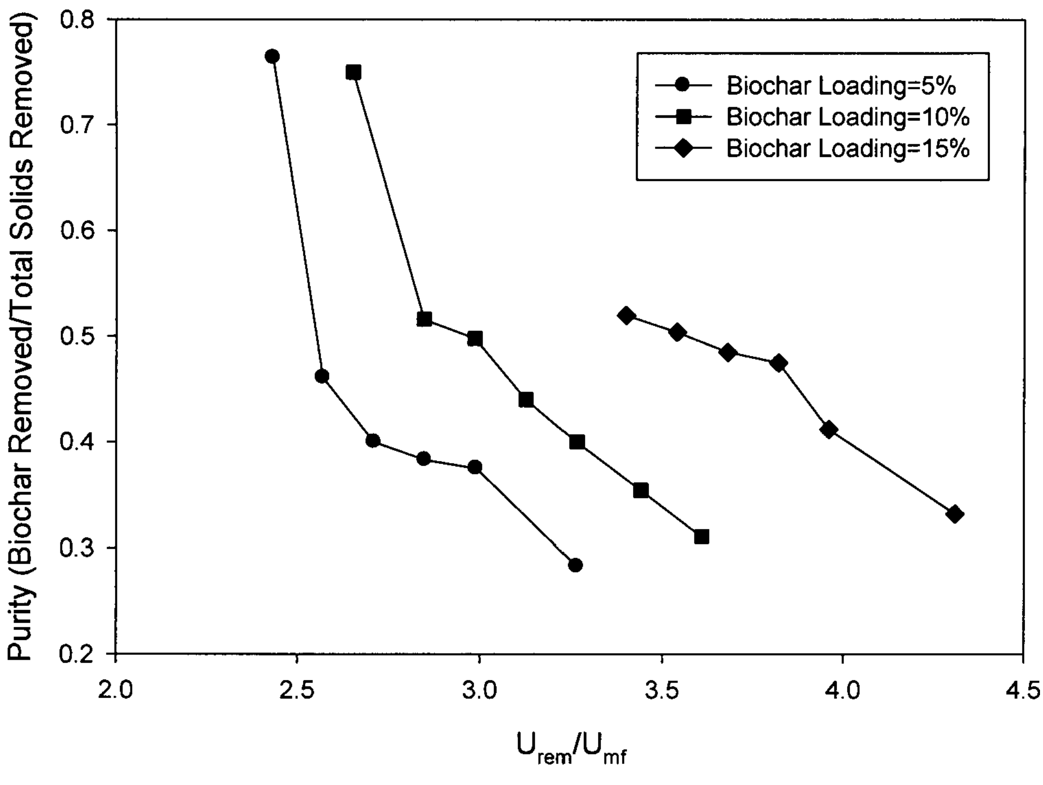

Figure 2.18-Purity after 60 seconds of removal at different removal velocities

2.3.2.4 Axial Port Positioning

Two different axial positions of removal ports were tested, both seen in Figure 2.19, with position (a) being the position used in previous results reported. A third position lower in the bed was not investigated as it would leave to detrimental sand losses. To change the level of the ports with respect to the segregated layer, the amount of sand in the bed was decreased by about 500 g, and a proportional amount of biochar was used to keep the sand to biochar ratio constant. This decrease led to about a 1 cm drop in bed height when position (b) was used. The performance of the system in terms of purity and efficiency after 30 seconds of removal can be seen in Figures 2.20 and 2.21. As expected, the port position (b) yielded a purer product but allowed a smaller amount of biochar to be removed in a two minute period. Placing the removal ports lower along the segregated layer allowed more solids to be removed, both biochar and sand, ultimately causing a lower purity removal, while placing the removal ports higher along the segregated layer offered more selectivity with less sand being removed since there is more distance between the bottom of the biochar layer and the removal ports.

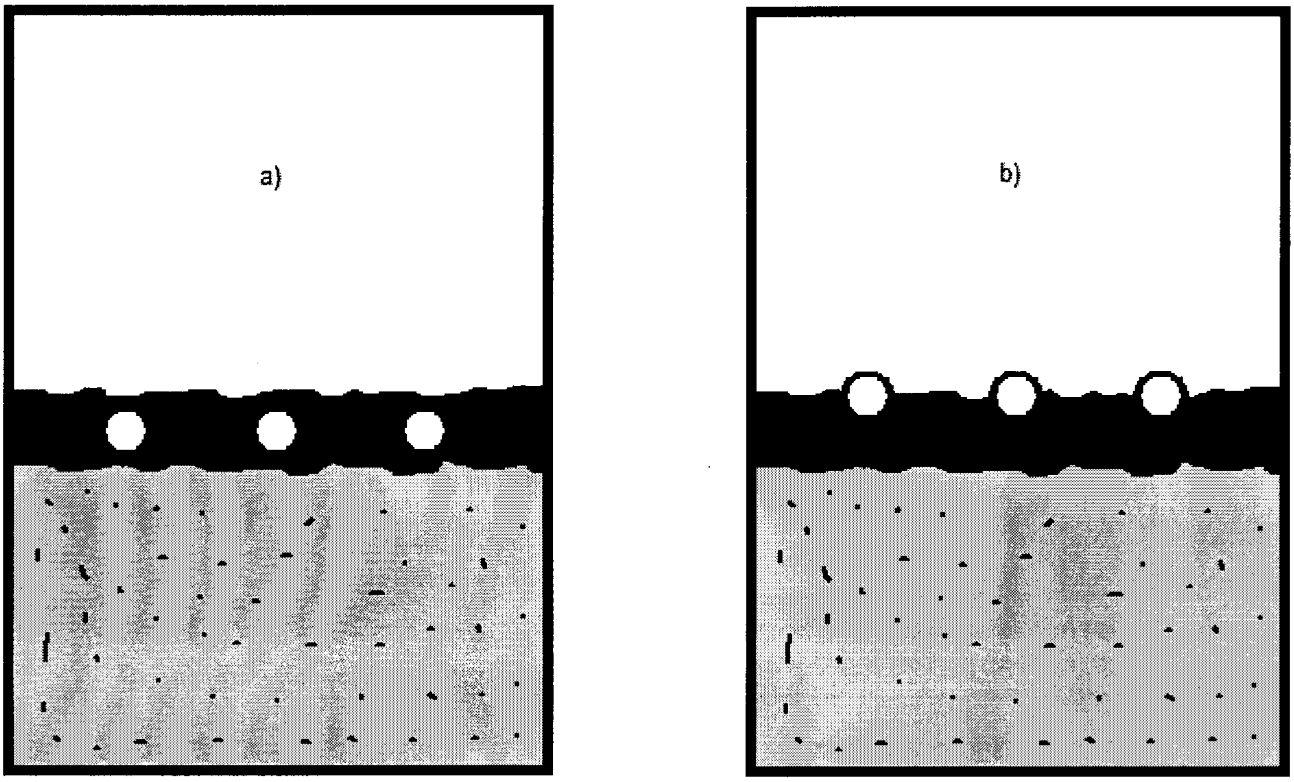

Figure 2.19- Different axial removal positions tested with respect to the biochar layer following segregation. A) ports at bottom of biochar layer, b) ports in middle of biochar layer

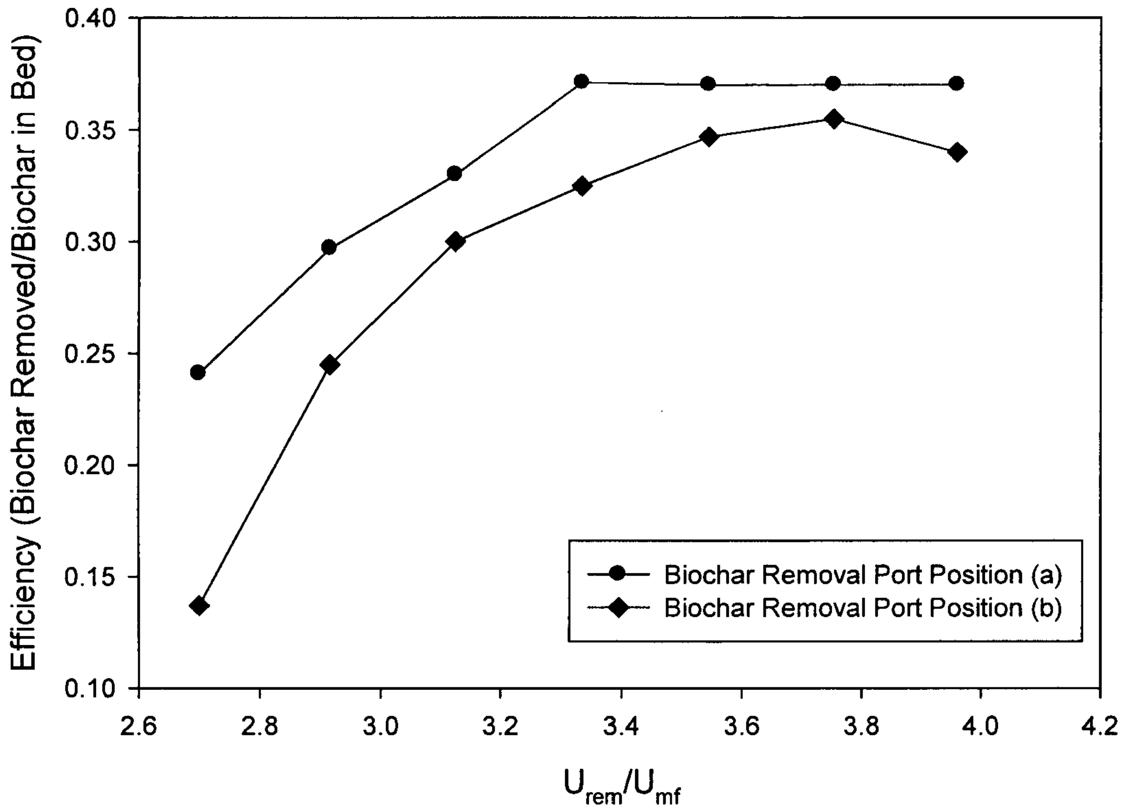

Figure 2.20-Efficiency with two different locations to remove biochar from with 10% biochar loading and d_{psm}=1.15 mm

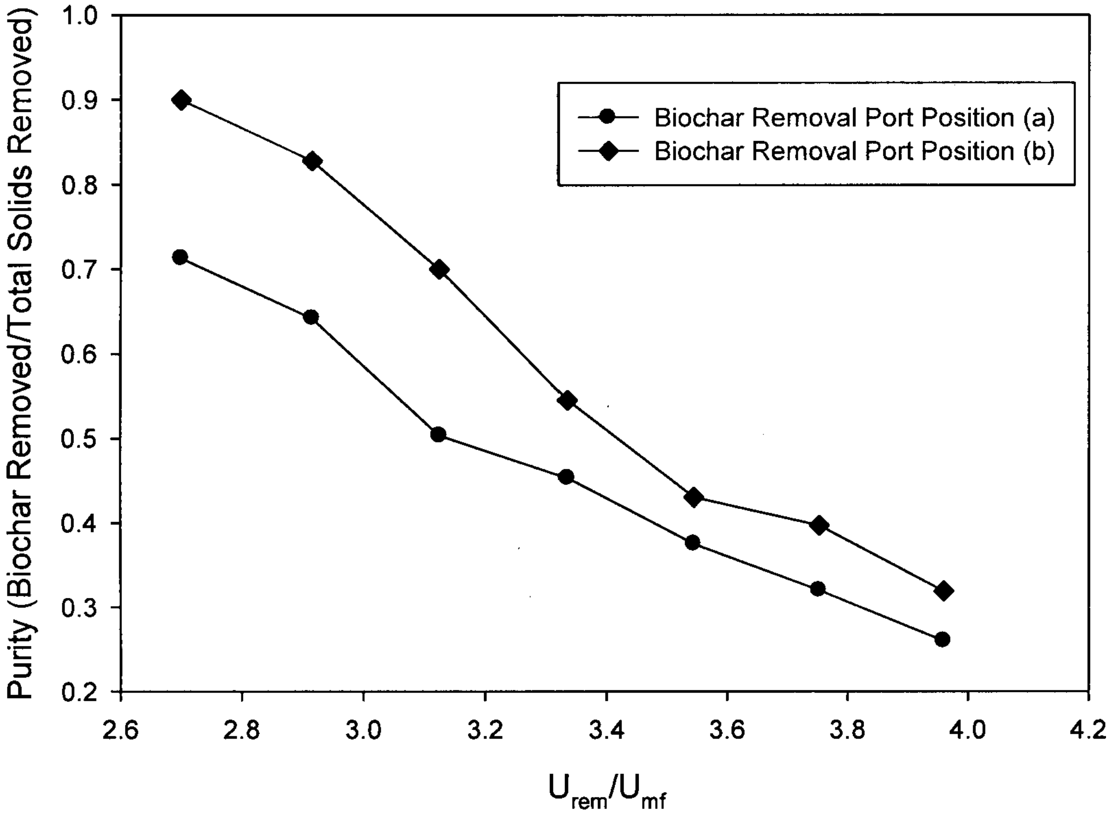

Figure 2.21-Purity with two different locations to remove biochar from with 10% biochar loading and d_{psm}=1.15 mm

2.4 Shortcomings of a Batch System

The batch removal system performed relatively poorly for several reasons. Primarily, the amount and concentration of the solids in the bed constantly changed as the segregated biochar layer was removed through the overflow ports. During removal, some particle segregation continued, which reduced the concentration of biochar in the lower part of the bed. This reduction in biochar caused the bed to display better mixing characteristics, since the binary mixture with lower biochar concentrations did not require as much gas to fluidize, as confirmed through experimental work and past work by other authors regarding the minimum fluidization velocity of a mixture at varying flotsam concentrations (Clarke et al., 2005). Since the amount of solids (primarily biochar) was decreasing, less solids flowed through the overflow ports as time increased. During the first 30 seconds, most of the biochar that was removed from the bed was removed. After that, the majority of solids removed from the fluidized bed was sand, making operating past 30 seconds undesirable.

The inconsistent solids concentration also presented significant issues in the process. During removal, the biochar concentration in the bed decreased, making the bed composition closer to pure sand. Consequently, less gas was required for fluidization, which caused more vigorous bubbling in the bed, and lead to excessive sand losses. The batch system could not operate under stable conditions due to this transient behavior; operating at higher gas velocities removed the most biochar but with lower purities, as depicted in Figure 2.21. On the contrary, operation at lower gas velocities allowed higher purities but lower efficiencies, as depicted in Figure 2.20. Selected results showing this short coming are shown in Table 3. A continuous system would ensure that the amount of solids in the bed stays constant and a constant biochar layer is maintained, thereby increasing the stability and performance of a removal system.

Table 3-Efficiency and purity after 30 seconds for 10% biochar loading and d_{psm}=1.15 mm

U_{rem}/U_{mf}	Efficiency	Purity
2.85	0.26	0.586
3	0.3	0.56
3.14	0.315	0.49
3.27	0.324	0.46
3.44	0.327	0.40

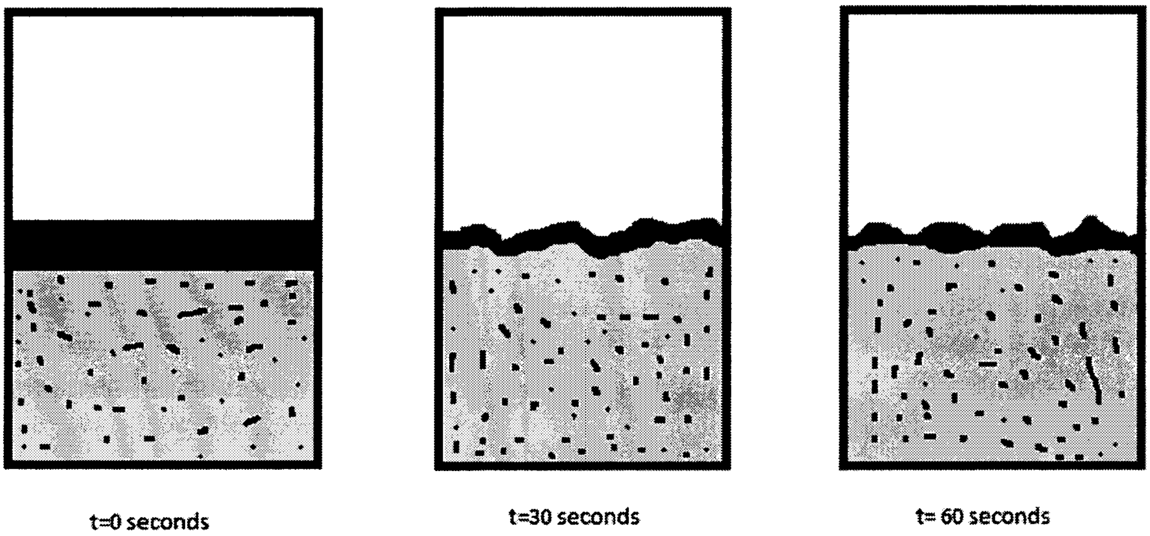

Figure 2.22-Bed depiction of batch removal at a lower U_{rem} value attaining high purity, low efficiency removals.

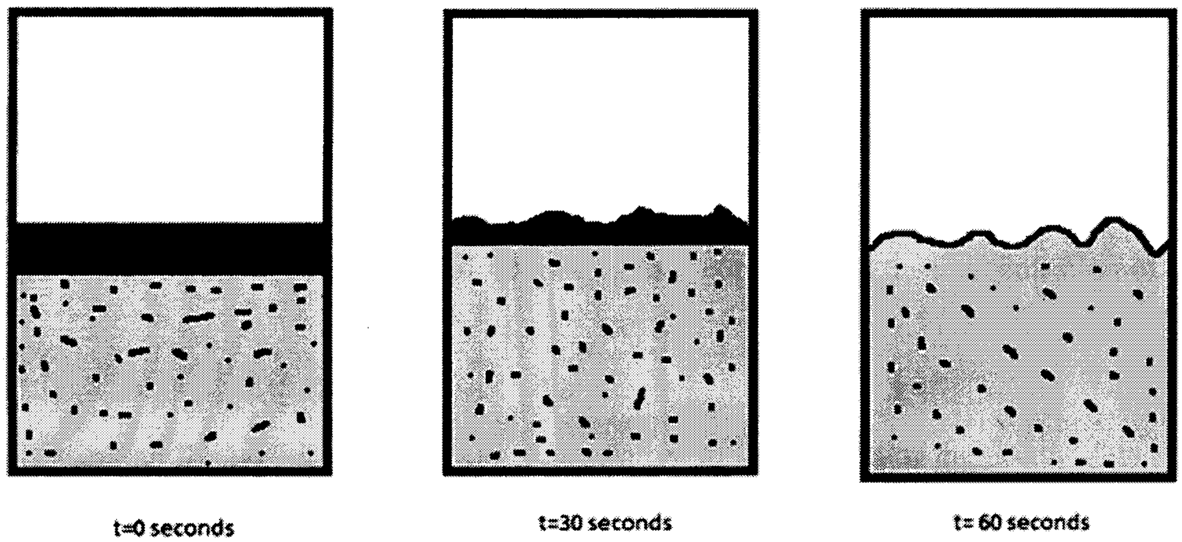

Figure 2.23- Bed depiction of batch removal at high U_{rem} values attaining low purity, higher efficiency removals

2.5 Conclusions

Batch removal of biochar from a sand and biochar mixture was investigated and offered valuable insight regarding the removal method using overflow ports and regarding the impact of biochar on a fluidized bed of sand. The largest biochar particles allowed for higher separation of biochar from sand during segregation while the intermediate size cut provided a moderate size biochar layer. Larger biochar particles required more gas to achieve maximum separation. The smaller biochar particles inhibited fluidization less than the large particles, but allowed less biochar to segregate. Similar trends were seen when attempting removal of the biochar layer, as smaller quantities of biochar were removed with smaller particles, while more biochar was removed when large particles were used. However, more gas was required to allow removal of the largest sized biochar.

As expected, using more fluidization gas during removal for each size cut tested, resulted in a less pure biochar product, but allowed for higher efficiencies in almost every case. The efficiency reached a maximum and then would plateau or decrease as the gas velocity used was increased. Lowered yields of biochar removal at high gas velocities are due to increased mixing and less biochar being able to reach the surface and be evacuated from the bed through the ports. Generally, purity decreased throughout the removal process for all conditions tested as the fluidization regime changed from lightly bubbling to vigorous since the concentration of biochar decreased.

Changing the position of the exit ports relative to the bottom of the accumulated biochar layer affected the process. Raising the position of the removal ports closer to the top of the biochar layer allowed for higher purity removal but with lower efficiencies, with the opposite occurring when the removal ports were lowered.

Depending on the engineer's goals, the results can be used to predict realistic batch removal performance in pyrolysis processes. As a batch system performed poorly due to inconsistent bed concentration and height, a continuous system capable of maintaining a constant biochar concentration in the bed and a constant segregated layer thickness in a pyrolysis unit should provide an overall superior performance.

Acknowledgements

The author expresses gratitude to the Ontario Centre of Excellence (OCE) and Agri-Therm INC. for funding of this project.

Nomenclature

U_{rem}-superficial gas velocity used during biochar removal (m/s)

U_{seg}- superficial gas velocity used during biochar and sand particle segregation (m/s)

U_{mf}- minimum fluidization velocity of sand (m/s)

d_{psm}- sauter mean diameter of biochar(mm)

t- time (seconds)

H_{bed}= height of bed (m)

References

R. Bilbao, J. Lezaun, J.C Abanades, Fluidization velocities of sand/straw binary mixtures, Powder Technology, 52 (1987), 1-6

J. Bosma, A. Hoffman, On the capacity of continuous powder classification in a gas-fluidized bed with horizontal sieve-like baffles. Powder Technology. 134 (2003) 1-15

A. Bridgwater, An overview of fast pyrolysis of biomass. Organic Geochemistry. 30 (1999) 1479-1493.

T. Chou, Y. Uang, Separation of Particles in a Modified Fluidized Bed by a Distributor with Dead-Zone Collector. Industrial Engineering Chemical Process Design Development, 24 (1985) 683-686

K.L Clarke, T. Pugsley, G.A Hill, Fluidization of moist sawdust in binary particle systems in a gas-solid fluidized bed, Chemical Engineering Science, 60 (2005) 6909-6918

M. Guillan, K. Fairouz, S. Mar, F. Monique, L. Jacques, Attrition-free pyrolysis to produce bio-oil and biochar, Biosource Technology, 100 (2009) 6069-6075

G. Hartholt, R. la Riviere, A. Hoffman, L. Janssen, The influence of perforated baffles on the mixing and segregation of a binary group B mixture in a gas-solid fluidized bed, Powder Technology, 93 (1997) 185-188

C. Hulet, C. Briens, F. Berruti, E. Chan, Experimental and analytical study of the solids circulation loop of a compartmented fluidized bed, Powder Technology, 185 (2008) 131-143

P. Rowe, A. Nienow, Particle mixing and segregation in gas fluidised beds.
A review, Powder Technology, 2 (1976) 141-147

P. Rowe, T. Evans, J. Middleton, Transfer of gas between bubbles and dense phase in a two-dimensional fluidized bed, Chemical Engineering Science, 1971

CHAPTER 3

3. OPTIMIZATION OF A CONTINUOUS SEPARATION SYSTEM FOR REMOVAL OF NON-FLUIDIZABLE BIOCHAR USING A NOVEL FLUIDIZED BED

3.1 Introduction

In fluidized bed pyrolysis, a biomass is fed to a fluidized bed of hot sand where it reacts in the absence of oxygen. Pyrolysis products include bio-oil vapor, non condensable vapors, and a solid biochar. The non-condensable gases can be combusted, to provide heat for the endothermic pyrolysis reactions. In many reactors, a significant fraction of the solid biochar product remains in the reactor bed, accumulating during the process. Therefore, the biomass feed then has to be periodically interrupted while biochar is either removed or combusted with air, thus preventing smooth continuous operation of the pyrolysis unit.

Elutriation is currently the main system for biochar removal and is the only system that has been previously used in fluidized bed pyrolysis units, in both lab-scale and industrial scale (Dynamotive). A system that uses elutriation can be seen in Figure 3.1

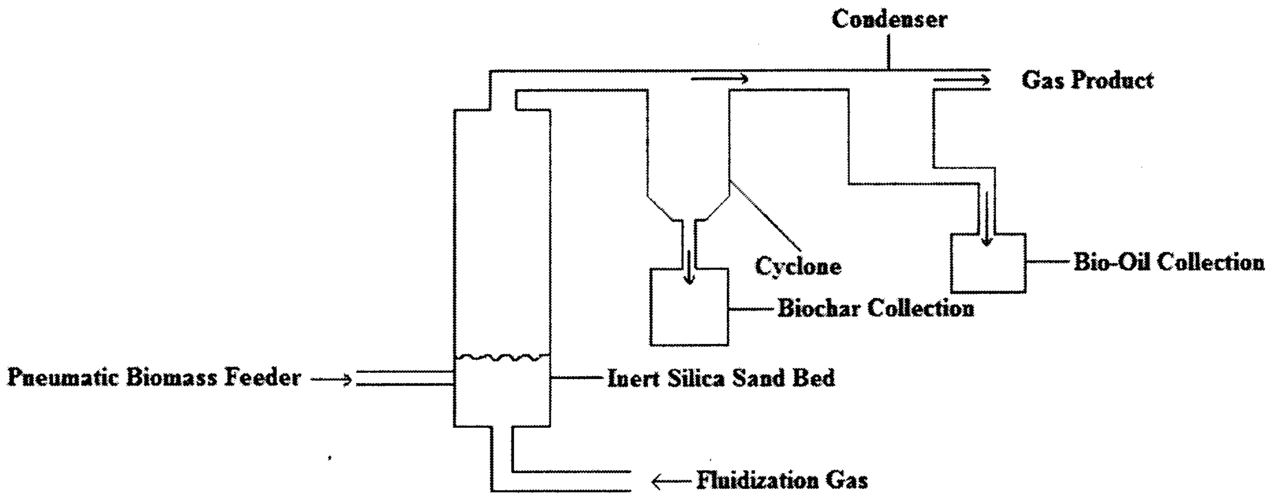

Figure 3.1-Biochar removal system for fluidized bed pyrolysis using cyclone separator (Adapted from Xu et al., 2009)

The result is that there are only two operating alternatives: to grind the biomass very finely, which is expensive, or to tolerate the accumulation of biochar particles in fluidized sand bed, leading to a continuous increase in biochar concentration in the bed, making the process quality difficult to monitor and control. The fine biochar that is elutriated may be difficult to handle due to its small size, similar to a dust. Furthermore, at high gas velocities, unreacted biomass and attrited sand are also elutriated with the biochar, requiring additional purification of the elutriated solids as well as decreased feedstock conversion (Jung et al., 2008) (Mastellone et al., 2002) (Azeez et al., 2009)

A removal system improves the process, while also increasing profitability as biochar has been shown to be valuable for several applications; opposite to older views of biochar being considered a low value waste product. Proposed uses of biochar include amending soils, with the added advantage of carbon sequestration, and substituting for coke in metallurgy and for coal in power plants. The carbon in high temperature biochar is stable and does not provide nutrient to soil, thus providing a carbon sequestration opportunity, while the porous structure of the biochar improves soil structure, water retention and nutrient availability while lowering soil acidity, and reducing toxicity from metals in the soil (Winsley, 2007). Using biochar in soil can allow for increased crop yields per unit of fertilizer, making the land more valuable since it is capable of growing more food, an important aspect as land shortage is becoming a global crisis. In addition, there are reductions in erosion, runoff, and lost nutrients (Gaunt & Lehmann, 2008).

The use of biochar as a substitute fuel for coal has shown the overall net carbon emissions to be negative as biochar is made from renewable resources, has a high mass energy content, and can be easily ground to smaller sizes for use in pulverized coal plants. Studies found that using biochar in coal plants presents advantages over directly feeding biomass (Abdullah & Wu, 2009). Biochar, however, has a relatively low density, which means that its transportation costs are higher than those for coal, although they are lower than for raw biomass; quantifying the auxiliary services and energy requirements has been approximated with life cycle analysis (LCA). LCA approximates the lifetime of the biochar from source generation to its end point and attempts to determine the amount of energy to gain or lose by the generation and utilization of the biochar. Just as with any fuel, there are many steps before it can be used efficiently in a reactor, such as harvesting (or generation of the feedstock in the case of biochar), drying, cutting, size separation, and transportation (Vignes, 2001). Similar studies have shown that in the use of biochar for carbon sequestration, renewable energy generation, use as a soil amendment, and biomass waste management, net energy generation was positive, emissions were negatives, while also allowing financial benefits. However, transportation of the original biomass and of the biochar product results in a large source of emissions that is difficult to overcome (Roberts et al., 2010).

Different types of pyrolysis employing different biomass feedstocks creates biochar with different properties such as BET surface area, moisture, fixed carbon, and HHV, but density remains relatively similar, which is important in particle separation by fluidization (Brewer et al., 2009).

The yield of biochar typically ranges from 10 to 50 wt%, depending on the biomass and the pyrolysis conditions, so biochar accumulation can be rapid (Xu et al., 2011). If the main objective of the pyrolysis reaction is the production of biochar, continuous biochar removal is required to prevent a rapid deterioration of the fluidization quality that would result from a high concentration of biochar in the sand bed. There are currently no studies that have measured the amount of elutriable biochar and the amount that remains in the bed.

In Chapter 2, batch biochar removal with a conventional fluidized bed was investigated using a two step process of particle segregation, then removal through overflow ports. The overall performance of this batch system was poor, but highlighted many important insights about the behavior of the binary mixture, as well as information important for the design of the novel continuous system. With a conventional batch system, the purity and removal efficiency were very low. The efficiency, defined as the mass ratio of removed biochar to the biochar initially in the bed, reached a maximum of 51%, with an associated purity of only 22%, which means that the removed material contained 78% sand. A maximum purity of 90% could be reached, but the efficiency was then only 14% (Mara et al., 2011). These numbers are unacceptable in a real process, but this batch system generated valuable knowledge about the mechanism and quantification of biochar-sand segregation with subsequent removal.

The relatively poor performance of the batch system could be explained with visual observations as well as by the quantification of the process efficiency and purity of the removed biochar. At the start of the removal process, nearly pure biochar could be extracted, while at the end, nearly pure sand would be exiting the removal ports. The bed level also dropped below the overflow ports, leaving much of the biochar accumulated in the bed following a batch process (Mara et al., 2011). This justifies the need of developing a continuous removal process, where the biochar concentration would be maintained at a constant level and the bed maintained at a constant height, while also having practical advantages.

Similar to the previous study, the continuous removal system utilized particle segregation using low fluidization velocities as the main separation technique, as it was shown to effectively segregate the binary mixture. Advantages of particle separation in fluidized beds include having good separation based on different densities, low gas velocities that prevent particle attrition, and using less gas than other separation processes such as wind sifting (Bosma & Hoffman, 2002).

The term *jetsam* describes the heavy component that sinks to the bottom of the bed, and *flotsam* describes the component that rises to the bed surface. In this study, biochar is the *flotsam* and silica sand is the *jetsam.* All previous studies have reported that the best particle segregation occurs close to the minimum fluidization velocity of the mixture, with minor bubbling (Rowe et al., 1972). Limited bubbling must occur for successful particle segregation since particles travel upwards in their wake; when the particles reach the surface the flotsam particles stay near the surface of the bed and the jetsam particles sink again to the bulk of the bed. More intense bubbling causes mixing, and results in an almost uniform bed composition, which is undesirable for particle separation (Gibilaro & Rowe, 1974).

An empirical approach is commonly taken to normalize particle segregation results by using a 'mixing index'. With the mixing index, the concentration of *jetsam* or *flotsam* in each section of the bed can be determined by taking a sample and determining the overall composition (Rowe et al., 1972). The mixing index can be predicted in a density driven system if both particles species are monosized, spherical, and fluidizable (Nienow et al., 1978). Although the proposed study does not focus on quantifying particle segregation within the bed, these correlations could potentially help identify the best operating conditions for the planned process. The correlations are largely built on segregation of ideal binary mixtures, using well defined particle properties as the inputs, making them inappropriate for actual processes where the particles are not ideal, and have relatively undocumented particle properties.

Internals can be used to promote segregation though adding baffles to a continuous biochar removal system for pyrolysis would have severe limitations since different feedstocks create biochar of different sizes of biochar and different baffles would be required for each feedstock. There has been limited work that is similar to the presented study. A study used a distribution plate with a non uniform positioning of holes, designed to allow solids circulation of large wood chips; one plate had uniform holes, the second had more holes in the centre, and the third plate had most holes around the perimeter of the plate. The application was for improving air drying, and authors found they could circulate wafers between two sides of the bed. This study focused on radial mixing rather than particle segregation, and did not separate and remove the particles that they were studying (Laytner et. al, 1995).

The objective of the present study was, therefore, the development of a new, simple, and novel system for the continuous removal of biochar from a bubbling bed pyrolysis reactor. This system should be simple to build and operate, provide biochar with a low level of sand contamination, maintain a constant biochar concentration in the pyrolysis bed, and be easily adjustable to handle different types of biochar. The majority of previous particle separation studies used ideal model particles to analyze particle separation dynamics required for modeling; this study uses real biochar so that its results can be directly applicable to practical pyrolysis reactors. In addition, previous studies often used two particles that were easily fluidizable; the biochar used in this study does not fluidize at any gas velocity, but rather channels as a cohesive powder, creating a worst case scenario situation.

In the current chapter, steady state biochar separation and removal from a fluidized bed of sand particles was investigated using a novel fluidized bed system. Using optimal process conditions, a steady state removal purity of 93% was achieved. The continuous system showed a vast improvement in stability and performance compared to the batch system.

3.2 Experimental

3.2.1 Equipment

Bubbling bed pyrolysis units operate under vigorous bubbling conditions to provide good mixing of the biomass particles with hot sand particles, high heat transfer rates and low vapor residence times. Biochar segregation, on the contrary, requires gently bubbling conditions occurring at much lower superficial gas velocities, just above the minimum fluidization velocity of the binary mixture. A schematic of the novel fluidized bed designed and built for this research project is shown in Figures 3.2. Different gas velocities in each compartment are achieved with 2 types of gas distributors; a porous plate and sparger pipes. The porous plate provided minimum fluidization to the entire bed, while sparger pipes supplied additional air to the part of the bed where vigorous bubbling and good mixing are desired to simulate the reactor zone of a fluidized bed pyrolysis unit. Five sparger pipes (0.127 m in diameter, 0.002 m holes, 12 holes per tube) are located at the bottom of the bed; flow through each sparger pipe was enabled or disabled through the use of ball valves. Gas flow through each distributor was independently controlled with calibrated sonic nozzles using pressure regulators and Omega PX181 pressure transducers connected to Mastercraft voltmeters.

The bed also incorporated a simple internal baffle, which was a movable vertical plate partially submerged in the bed, and acted as a partial divider between the two compartments (i.e between the well mixed "reaction" zone and the separation zone). Biochar that freely circulated underneath the plate from the well mixed part of the bed to the separation zone was then brought to the surface of the separation zone of the bed due to the lower gas velocity. The plate also prevented back-mixing from the separation zone to the well mixed zone, and prevented larger bubbles from the well mixed zone migrating to the separation zone.

Similar to the batch study, removal ports were positioned to allow for solids removal, with the position located based on findings from Chapter 2. The ports, 0.0254 m in diameter, were located close to the top of the segregated biochar layer, thus optimizing purity. (Mara et al., 2010). The removed biochar was collected in a bucket at the side of the fluidized bed. Biochar removal port flows were disabled or enabled through use of ball valves, and were placed 0.25 m above the bottom of the bed; positioning was determined through preliminary experiments.

Biochar was fed each 30 seconds to the vigorously bubbling zone through a lock system made of two ball valves connected in series beneath a solids hopper. It was discharged through a transparent plastic tube, located approximately 0.1 m above the bed height of the well mixed side, to ensure that all the biochar entered the vigorously bubbling zone. The continuous biochar feedrate, per unit of reactor of reactor cross-sectional area, was set at a level that is typical of the biochar that is generated in bubbling bed pyrolysis units. The square base of the column was 0.2m, making it larger than most fluidized beds used in lab-scale pyrolysis processes.

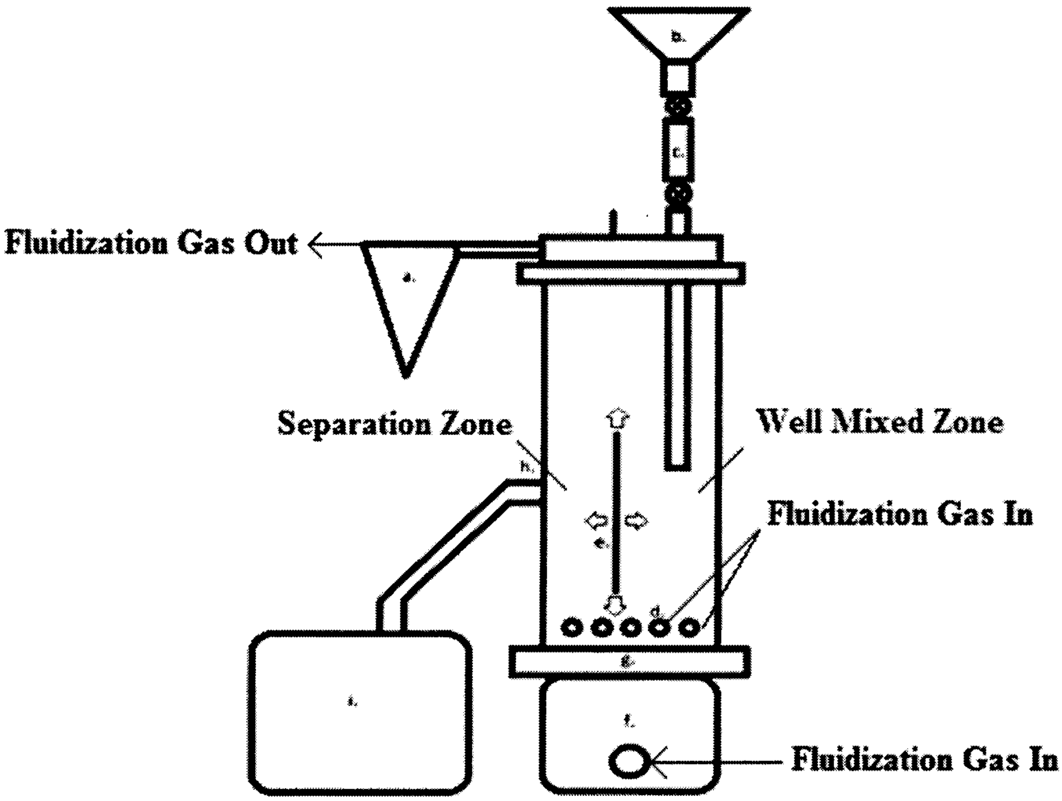

Figure 3.2-Schematic of the novel fluidized bed used for continuous biochar separation. A) filter bag, b) solids hopper, c) biochar feed system, d) sparger distributor e) movable vertical plate f) windbox g) porous plate distributor h) biochar removal ports (3) (0.025 m diameter i) biochar collection

3.2.2 Materials

Biochar obtained from Burt's Greenhouses in Kingston, Ontario, was used in these experiments as an approximation of the biochar created during fluidized bed pyrolysis experiments, since it was available in large volumes. Bulk quantities of the biochar were purchased and then separated into distinct size cut ranges using sieving. The particle size distribution of the tested biochar can be seen in Figure 3.3 and the bulk density (ρ_b) was 252 kg/m^3. The biochar was made from chipped wood through a partial combustion process, shown in Figure 3.4. Barco silica sand 71 (d_{psm}=175 μm, ρ_b=1650 kg/m^3, ρ_p=2750 kg/m^3, U_{mf}=0.025 m/s, Geldart Group B). Data from Dynamotive shows pyrolytic biochar to have a bulk density of 250 kg/m^3, and can deviate depending on particle size, with smaller particles having a lower bulk density and larger biochar having a greater bulk density (Dynamotive, 2009). Particle density is not reported. A magnified image showing the biochar particles used can be seen in Figure 3.5, which emphasizes the jagged shape characteristic of non-fluidizable materials. The biochar showed significant channeling at high gas velocities.

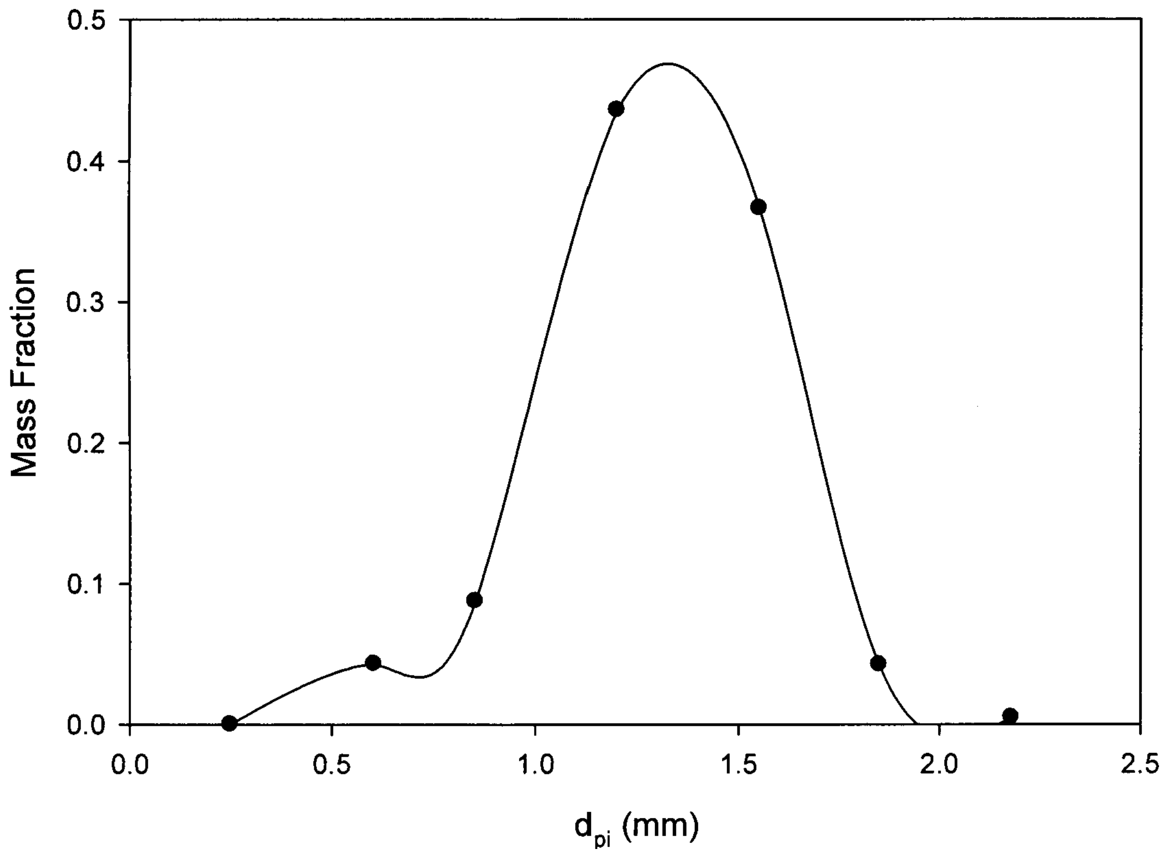

Figure 3.3-Particle size distribution of biochar in the bed during testing

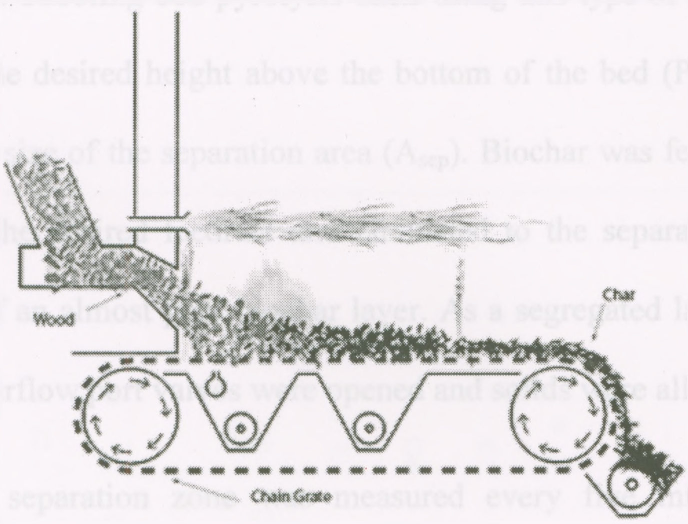

Figure 3.4-Equipment and method used by Burt's Greenhouses to synthesize biochar (adapted from Burt's Greenhouses)

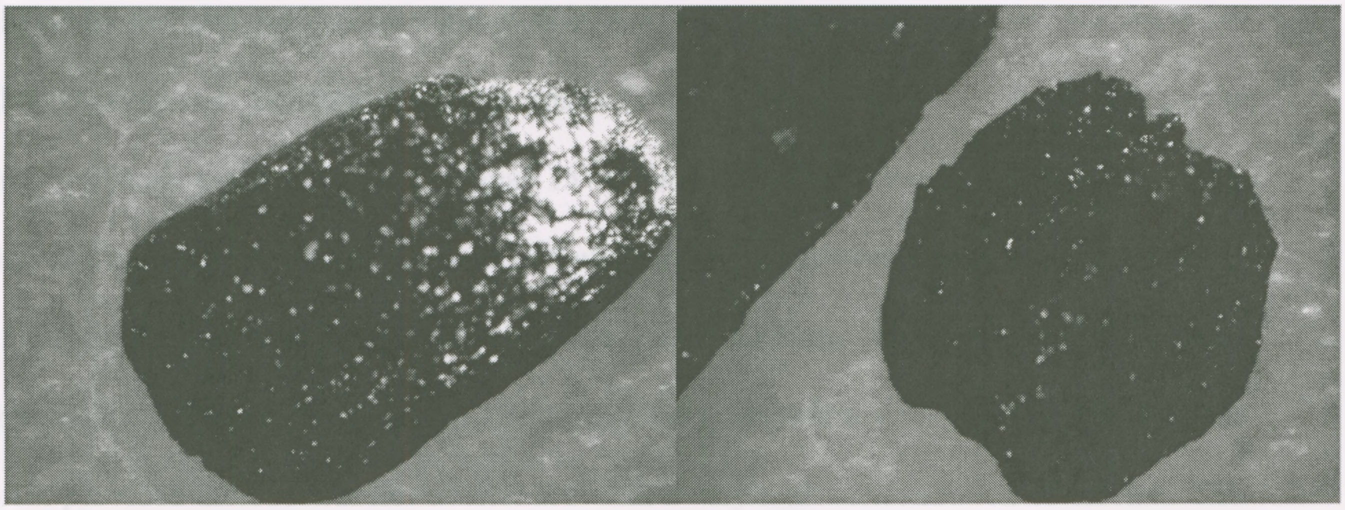

Figure 3.5-Microscopic images of biochar used in this project at 60x magnification

3.2.3 Experimental Procedure

The experiments were carried out at room temperature and atmospheric pressure. The bed was loaded with 8 kg of sand (0.1675 m; 0.15-0.20 m sand height is common in actual pyrolysis pilot plants) and then fluidized with air. The gas flowrate injected through the porous plate was set to deliver the desired velocity (U_{sep}) and supplementary air was then provided to the well mixed zone such that it was kept at the same velocity (U_{wm}=0.16 m/s) for each experiment, which is a typical value for bubbling bed pyrolysis units using this type of sand ($6.4U_{mf}$) . The plate location was set at the desired height above the bottom of the bed (P_h) , and the desired lateral location, setting the size of the separation area (A_{sep}). Biochar was fed to the well mixed zone each 30 seconds at the desired feedrate and circulated to the separation zone, where it accumulated in the form of an almost pure biochar layer. As a segregated layer accumulated in the separation zone, the overflow port valves were opened and solids were allowed to flow out.

The output from the separation zone was measured every five minutes, after which fluidization was temporarily ceased. The purity of the removed solids, defined as the mass fraction of biochar in these solids, was determined using sieving. Any removed sand was reintroduced to the well mixed zone and fluidization was resumed. Steady state was achieved once the flowrate of removed biochar equaled the biomass feedrate. Reported purity measurements were averaged over the final 15 minutes (3 points) during a steady state run. Replicates are considered as the presented results are averaged over steady state conditions. Figure 3.6 shows that different initial concentrations of biochar in the bed resulted in the same purity removal of 93%, at steady state. The results were, therefore, independent of the initial conditions, provided the bed was not overloaded with a very high concentration of biochar. The stability of the steady state as seen in Figure 3.6, was apparent under all operating conditions tested. All experiments were completed with good fluidization present in both zones in the fluidized bed, based on visual observations. The bed height at the beginning of each experiment was about 0.25 m, measured by removing the partition plate, and was at the same value after each experiment.

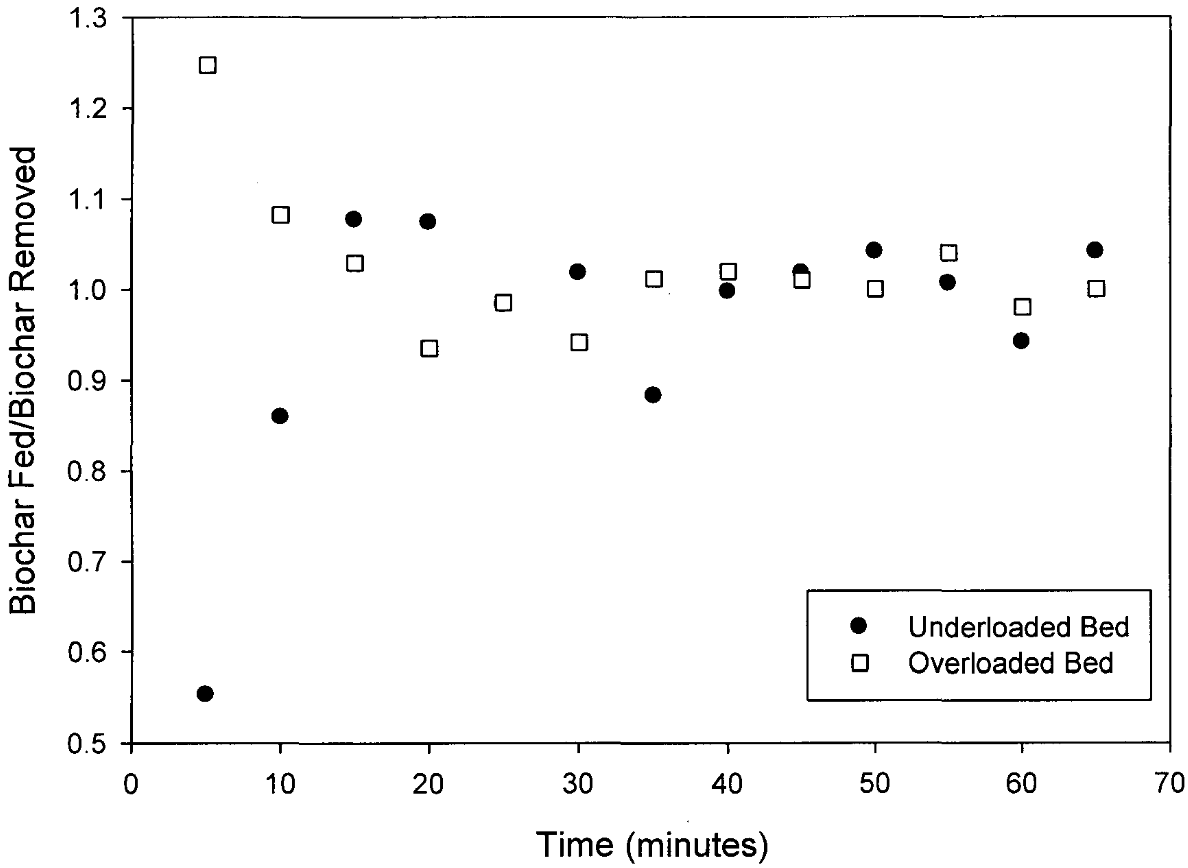

Figure 3.6- Experiments completed with different initial bed compositions. U_{sep}=0.09 m/s, U_{wm}=0.16 m/s, P_h=18 cm, $F_{biochar}$=0.034 kg/min, Purity= 93%. Overloaded Bed=2.2 kg biochar, 8kg sand. Underloaded Bed=1.8 kg biochar, 8kg sand

3.3 Experimental Results and Discussion

3.3.1 General Operation during Steady State Biochar Removal

Figure 3.7 shows a qualitative depiction of the two sides of the bed at steady state. Due to the different gas velocities and the presence and location of the vertical partition plate in the bed, a density difference in the two sections of the bed was apparent, which resulted in different bed heights. With an initial bed height of 0.25 m, during steady state operations the bed height in each zone changed due to the higher concentration of low density biochar in the separation zone.

At steady state, the bed height in the well mixed zone decreased to 0.24 m, while the bed height in the separation zone increased to about 0.30 m, i.e. the height of the removal holes. The height difference phenomena was an inherent characteristic of this system that made it operate efficiently. This change in height resulted in less sand reaching the surface and allowed for a thicker biochar layer to be formed, which meant higher purity biochar could be removed through the removal ports, as biochar higher in the layer was more pure than the biochar closer to the sand/biochar boundary; this was observed in a preliminary batch study (Mara et al., 2011). The biochar layer was about 0.05 m thick at steady state.

Steady state conditions were not possible under certain operating conditions, due to overloading of the bed with the non-fluidizable biochar. In cases where there was too much biochar fed to the system, initially the bed performed normally, but the fluidization rapidly degraded as the biochar concentration increased, leading to defluidization before steady state could be achieved. An example where steady state removal was unsuccessful is shown in Figure 3.8, where the feedrate of 0.041 kg/min was shown to be too high. Efficiency after the process had 'stabilized' to 80% removal, meaning that only 80% of the biochar fed to the fluidized bed was being removed and 20% of the biochar fed was accumulating in the bed. Adjusting operating parameters did not allow for reliable state steady separation with a feedrate of 0.41kg/min, meaning this represents overcapacity.

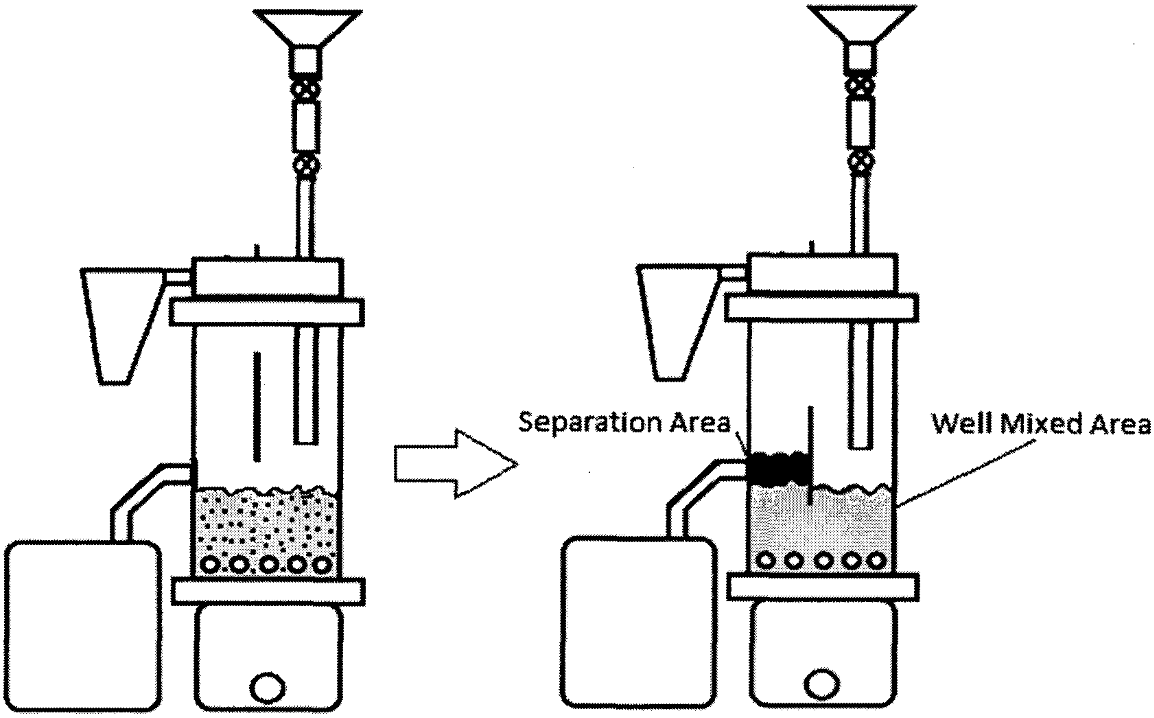

Figure 3.7- System depiction before and during steady state removal

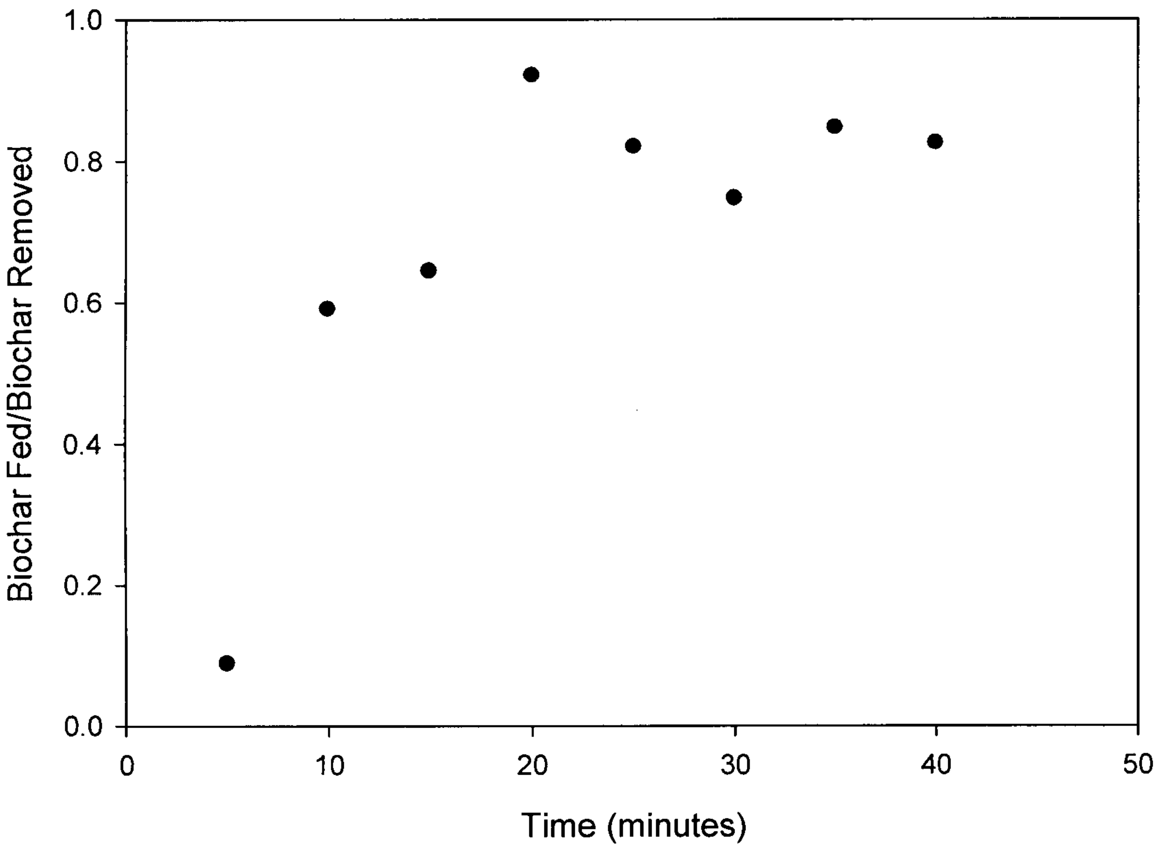

Figure 3.8- Attempted biochar removal at 0.041 kg/min, U_{sep}=0.09 m/s, U_{wm}=0.16m/s, H_p=0.18 m, A_{sep}/A_{bed}=0.38

3.3.2 Effect of Separation Zone Gas Velocity On Purity

As superficial gas velocity dictates whether particle segregation or mixing will dominate, the performance of the system was dependent on the amount of gas used in the separation zone. Figure 3.9 shows that, since biochar particles were large and would not fluidize by themselves, the optimum gas velocity was much larger than the minimum fluidization velocity of the sand. The highest purity of the removed biochar (93%) was achieved with a ratio of the velocity in the separation zone to the minimum fluidization velocity of pure sand of 3.6. At lower fluidization velocities, the mixture did not fluidize consistently in the separation zone, and formed large, inconsistent bubbles due to pressure build-ups, which resulted in a large amount of sand splashing above the surface to be removed with the biochar. At higher gas velocities, the separation zone was too vigorously mixed, and more bubbles splashed the surface, carrying both biochar and sand, allowing large amounts of sand to exit the bed with the removed biochar. Overall, the separation zone needed to be fluidized at a velocity high enough to achieve consistent fluidization but low enough to minimize mixing with gas bubbles. These findings were consistent with literature findings obtained with ideal binary systems, where both particle types were fluidizable; the optimal superficial gas velocity was close to the incipient fluidization gas velocity of the mixture (Rowe et al., 1974).

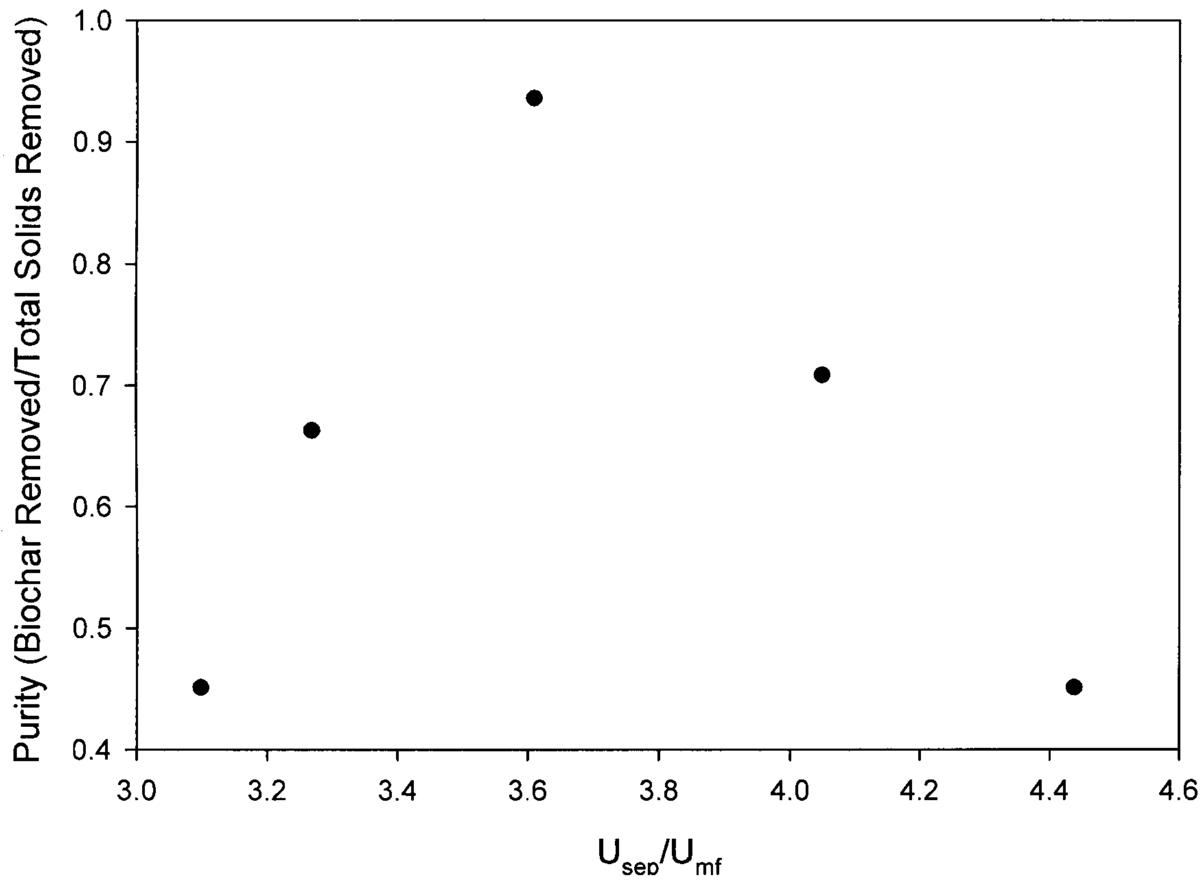

Figure 3.9- Effect of gas velocity in separation zone on purity of removed biochar. U_{wm}=0.16 m/s, P_h=0.18 m, $F_{biochar}$=0.034 kg/min, A_{sep}/A_{bed}=0.38

3.3.3 Effect of Plate Height (P_h) on Purity

The vertical position of the plate height relative to the bottom of the bed (P_h) had a profound effect on system operation. Figure 3.10 shows that increasing the plate height increased the purity of the removed biochar. A constraint, however, was that the plate submersion should be enough to allow a biochar layer to form in the separation zone. Figure 3.10 shows process failure when the P_h value was increased to over 0.22 m, or 0.03 m submerged in the bed before the continual removal process was initiated. The P_h value used was dependent on the solids height in the bed; for example, if the bed is 10 kg of sand, instead of 8 kg as used in this study, optimization would be required to determine the optimal P_h value for that system. As more sand was not added during these experiments, this meant that biochar made up for the solids difference, leading to overloading of the bed and the inability to achieve steady state at the operating conditions tested, leading to an immeasurable purity, or a purity of 0. Having the plate too close to the bed surface did not provide a solid surface does not allow for particle segregation as the bed become overloaded. Most of the biochar that was brought to the surface of the separation zone to be easily recirculated to the well mixed zone, causing an accumulation of biochar in the well mixed zone and decreased fluidization quality over the relevant conditions tested. Experiments indicated that the purity could be maximized by submerging the separation plate 0.05 to 0.07 m in the initial bed of 0.25 m as seen on the left diagram in Figure 3.7.

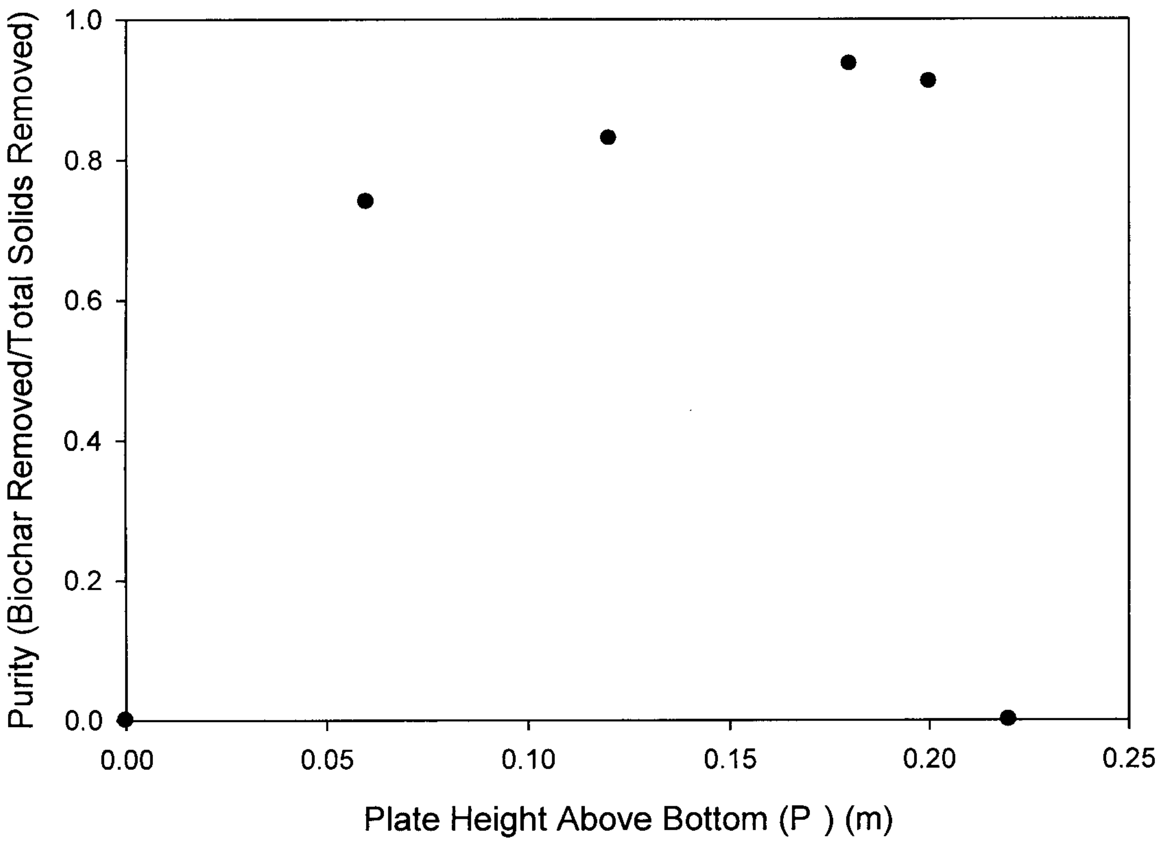

Figure 3.10- Effect of plate height on purity of biochar removed, U_{sep}=0.09 m/s, U_{wm}=0.16 m/s, $F_{biochar}$=0.034 kg/min, A_{sep}/A_{bed}=0.38

3.3.4 Effect of the Gas Velocity in the Vigorously Bubbling Zone (U_{wm}) On Purity

The separation process had to be able to perform over a wide range of gas velocities in the vigorously bubbling or well-mixed zone. For example, in pyrolysis processes, the vigorously bubbling zone will be the reactor zone and its fluidization velocity will be set to optimize mixing, mass and heat transfer, and short gas residence times. Figure 3.11 shows that the purity of the recovered biochar was high when operating under vigorously bubbling conditions, with the gas velocity U_{wm} larger than 0.16 m/s, i.e. with a ratio of gas velocity to minimum fluidization velocity of the sand larger than 6.4. When U_{wm} was too low, a small biochar layer was formed in the well-mixed zone, indicating that the segregation mechanism were dominant over the mixing mechanism. Increasing U_{wm} above 0.16 m/s had a minimal effect on the purity of the removed biochar, showing the flexibility of the system. The well mixed zone must be vigorously bubbling for this process to work, to allow circulation of biochar particles to the separation zone.

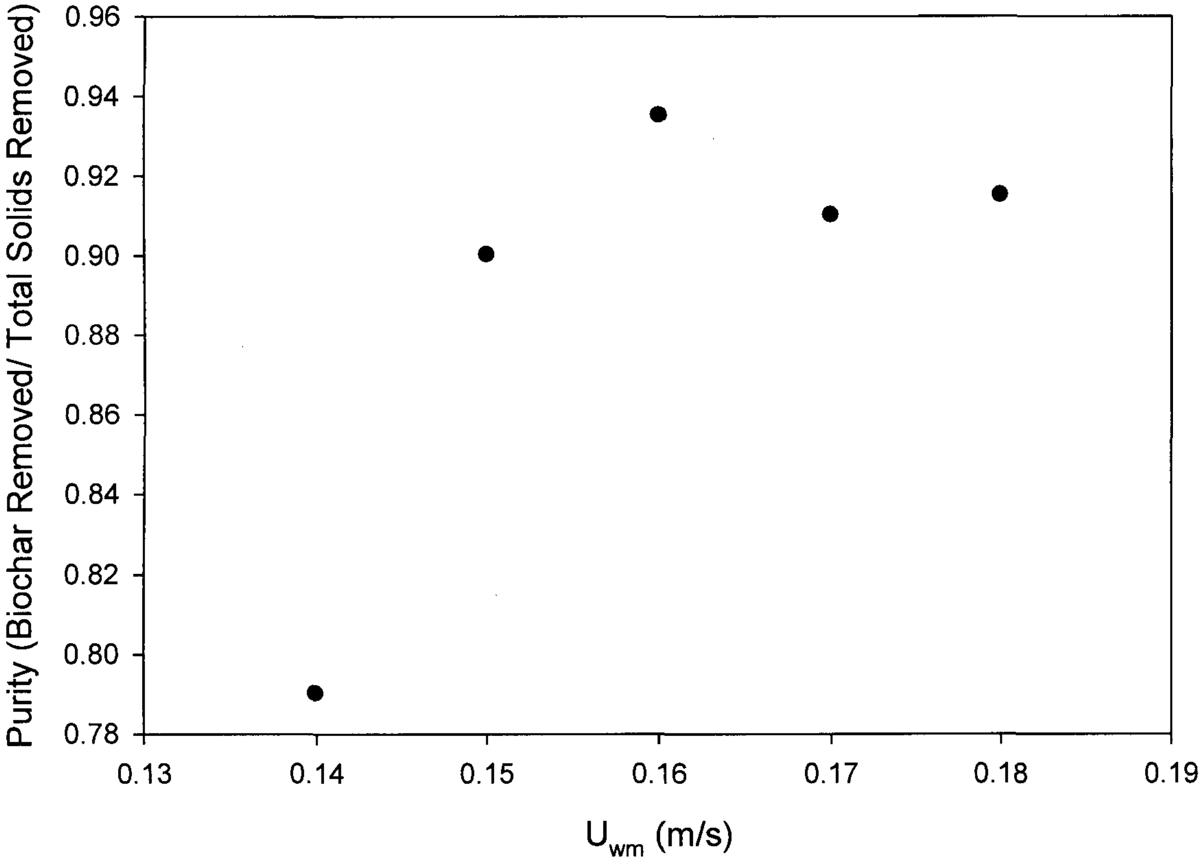

Figure 3.11-Effect of gas velocity in well mixed zone on purity of biochar removed, U_{sep}=0.09 m/s, P_h= 0.18 m, $F_{biochar}$= 0.034 kg/min, A_{sep}/A_{bed}=0.38

3.3.5 Effect of Biochar Feedrate and Separation Zone Size on Purity and Steady State

A range of biochar feedrates were tested. They were based on, first, typical biomass feedrates per unit of reactor volume and, second, on typical biochar yields for a variety of feedstocks (Xu et al., 2011). Figure 3.12 shows that the new biochar separation system performed very well over this range of feedrates with 38% of the bed being used as the biochar separation zone, and achieved similar purities at all feed rates. Going to much lower feedrates would create problems as the biochar later at the surface of the separation zone would become too small, which would make it difficult to extract pure biochar and would not be a relevant biochar generation rate in a pyrolysis setup. It was not possible to operate the system properly at biochar feedrates greater than 0.041 kg/min, suggesting this represented overcapacity. Though this system offered continuous, high purity removal of solid waste co-products with minimal addition of internals, additional area had to be provided for the separation zone. By placing the vertical plate at different locations along the width of the bed, separation zones of various sizes were tested. Figure 3.12 shows the results obtained with different cross-sectional separation areas. Reducing the separation area by 1/2 multiplied sand losses by a factor of about 2.5, leading to worse purities. Figure 3.12 also shows operation with the reduced separation area was less robust: the biochar purity was more sensitive to small variations in operating parameters such as the biochar feedrate.

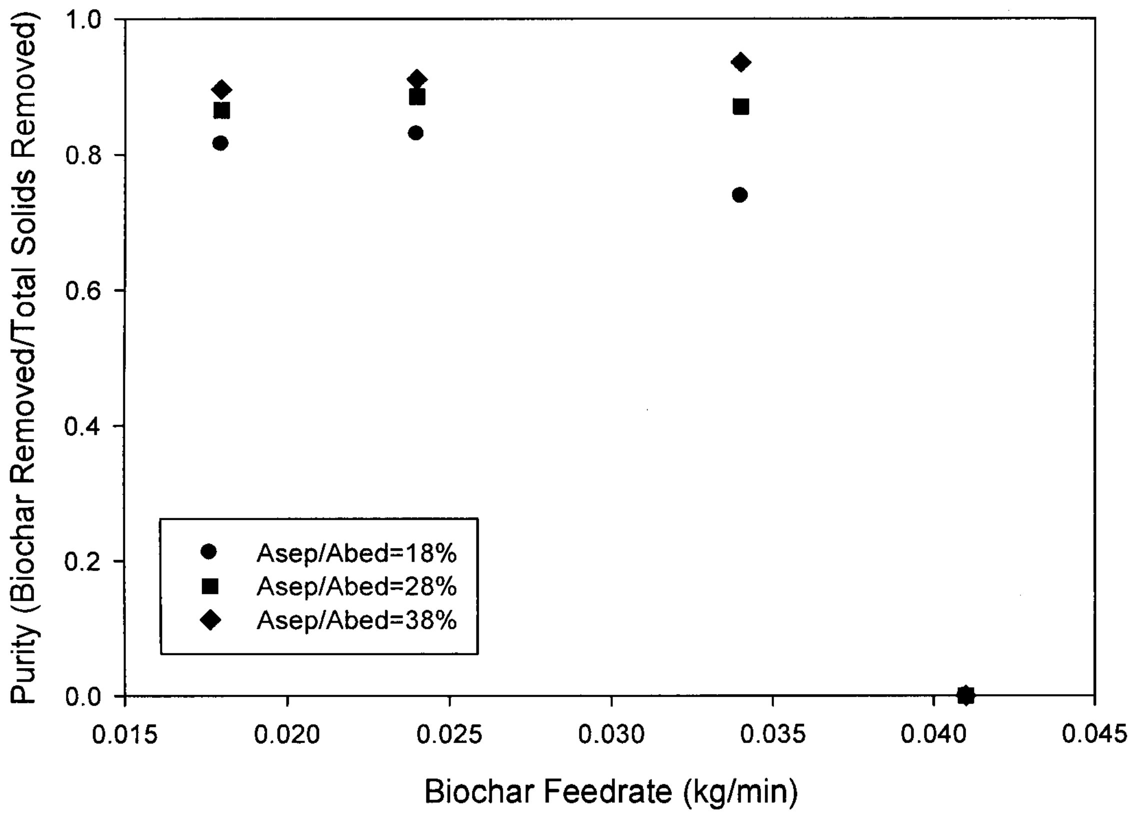

Figure 3.12-Effect of biochar feedrate on purity of removal using a using different size separation zone, V_{sep}=0.09 m/s, V_{wm}=0.16 m/s, P_h=0.18 m

3.3.6 Effect of Modified Separation Plate on Purity

Previously, the effect of changing the vertical height of the plate above the bottom of the bed (P_h) has been addressed, but the effect of changing the cross sectional area below the plate by changing the open horizontal length beneath the plate (L_{bp}). Figure 3.13 shows how the cross sectional area was decreased by attaching additional steel plates to the bottom, which allowed for the performance of the system to be investigated with a reduced A_{bp}. This may lead to relevant considerations when approaching reactor design geometry. Using this plate allowed for slightly lower purity during steady state conditions and the results can be seen in Figure 3.14, with an A_{bp} of 100% being the unmodified corresponding to a 100% free area. The loss of free space for biochar movement to the separation zone seemed to have a negative effect on the operation of the system, perhaps causing increased residence time of biochar in the well mixed part of the bed and caused lower concentrations of biochar in the separation zone. However, the prongs of the plates may also caused break up of larger bubbles from the sparger tubes in the bubbling zone of the bed, which allowed less gas to be used to reach an optimal purity for each plate. From the results, it appears that changing the L_{bp} and the P_h parameter have a similar negative effect on purity.

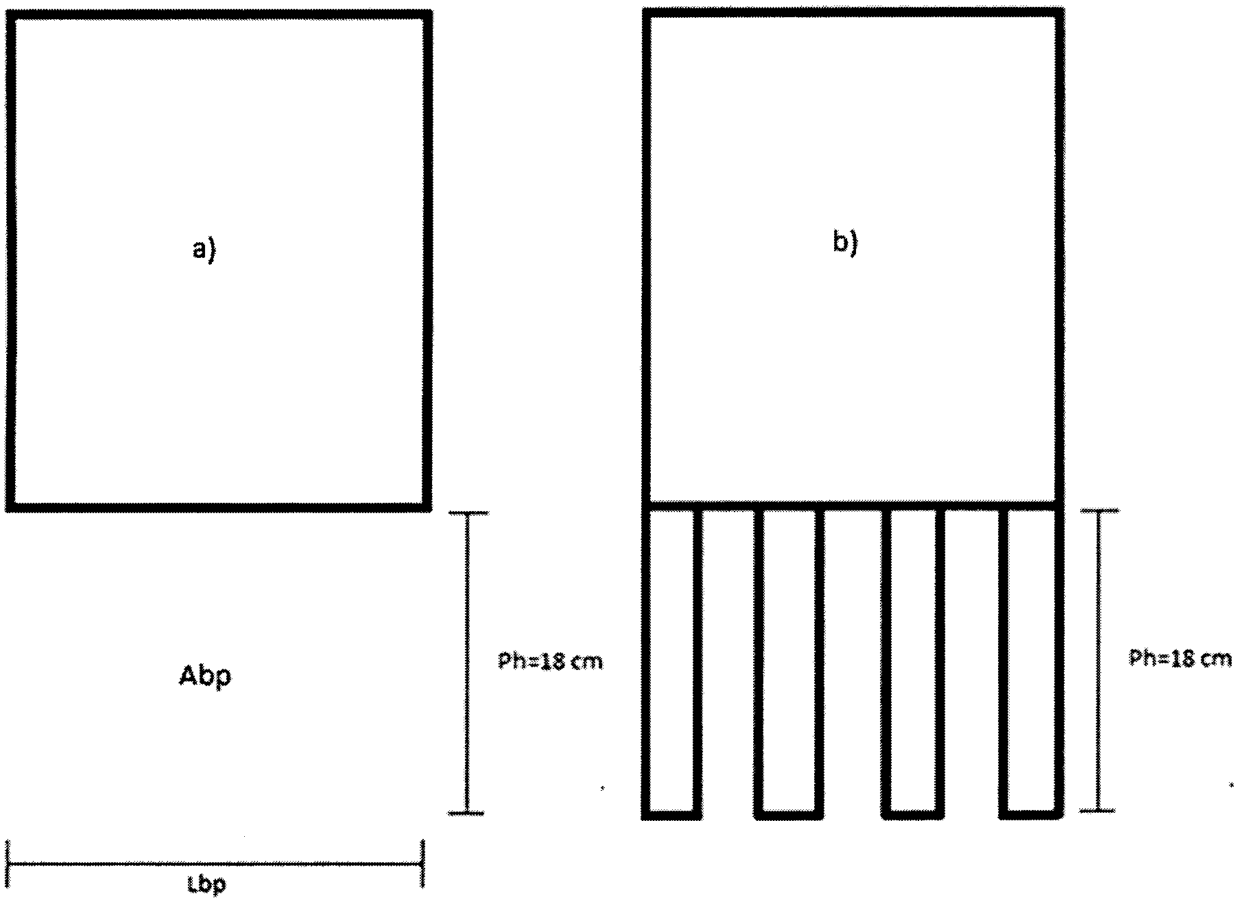

Figure 3.13- Separation plates investigated. a) standard plate b) plate that reduces A_{bp}

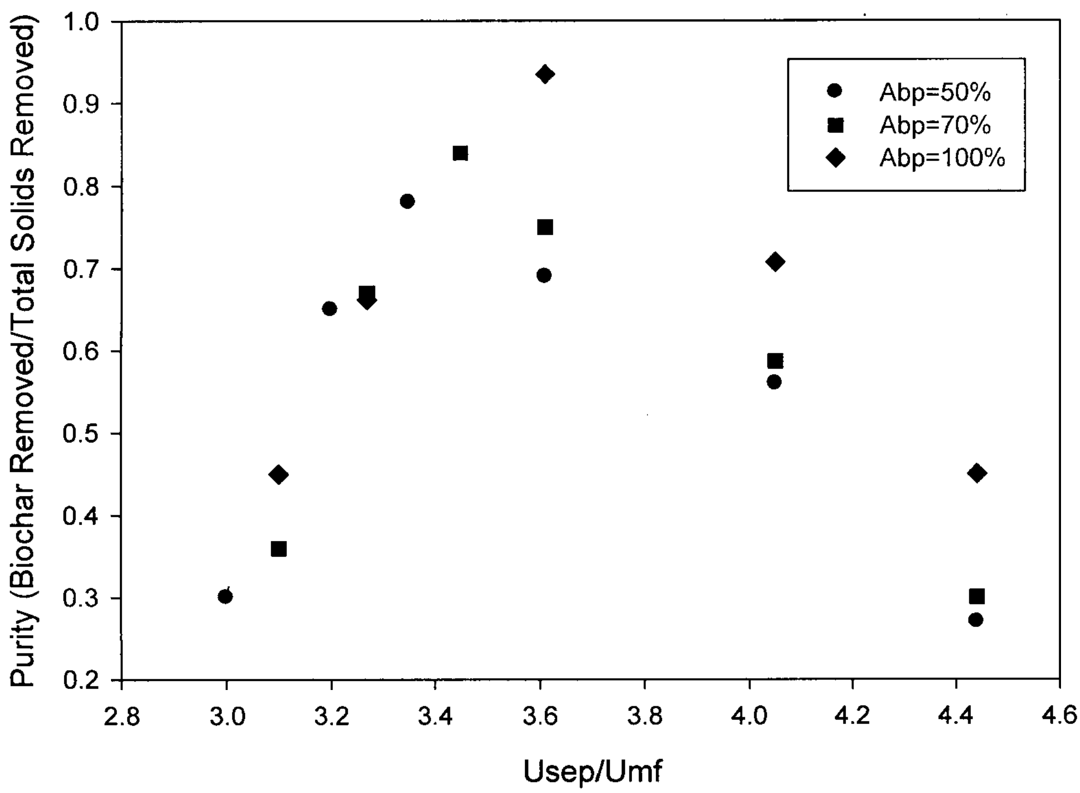

Figure 3.14-Conditions tested for plates with different free areas

3.3.7 General Stability of Steady State Removal at Different Operating Conditions

The process stability was studied by taking solids measurements every 5 minutes during steady state operation. All results presented were obtained under stable conditions, aside from the conditions of note that led to accumulation of biochar in the system. Having a biochar removal system operating at steady state has numerous benefits that would help maximize system stability, profitability, and use of resources. System stability was maximized since the system continually removes the biochar, instead of having a batch system where normal operation must be interrupted to remove the biochar.

Compared to a batch system, the new system offered radically improved purity, system stability, and removal capability since the bed height, and biochar concentrations remained stable during the removal process. Using a batch system would introduce shutdowns, cause energy losses, and lower yields over time. Removing the biochar is a better option than burning it with air, as biomass feeding must be stopped. Energy for the process can be attained from other sources that are of lower monetary value than biochar, making it negligent to burn a high value co product. Since the biochar removed was of high purity, a very low amount of sand from the reactor was removed with the biochar product, meaning there would be minimal heat additions when placing the sand back in the reactor.

The additional design considerations for this system were simple and effective. The biochar removal ports were simple in design, and the removal required no additional equipment to remove the biochar from the fluidized beds, unlike vertical vacuum systems that have been previously been used (Hulet et. al, 2008). The main disadvantage of implementing this removal system is that 38% of the reactor was occupied by the removal section. This reduces the overall capacity that the reactor can process, which may be a problem for some engineers who wish to process as much biomass as possible. However, batch operation to remove biochar from the bed showed not to be a feasible option, making the reduction in reactor capacity a necessity for enabling continuous biochar removal.

3.3.8 Improvements from Batch System

The batch system operated poorly due to the constantly changing solids amount and concentration within the fluidized bed. Following a segregation process at a superficial gas velocity (U_{seg}) for 2 minutes to reach an end point for particle separation, the superficial gas velocity is then adjusted (U_{rem}) and overflow ports opened, which allowed the segregated biochar layer to flow from the fluidized bed.

Inherent to the process, the level of bed solids always decreased, so the process only operated efficiently close to the beginning of the time scale, at which time the bed solids dropped close to the bottom of the overflow ports. Simultaneously, the solids concentration in the bed was constantly changing, with the biochar concentration dropping, meaning the fluidization quality had shifted from limited bubbling, to a vigorous bubbling that was not ideal for particle segregation or removal. The continuous system avoided this problem as the system operates at steady state, which maintained a constant bed concentration and height.

3.3.9 Scale-Up Considerations

It is possible approximately scale-up of this system based on size and volume of the experimental lab-scale fluidized bed and the desired fluidized bed pyrolysis unit. In the lab scale system, 2.04 kg/h of d_{psm}= 1.15 mm of biochar could be removed, with bed properties of 8 kg of sand, and a cross-sectional area of the well mixed zone of A_{WM}=0.015376m^2 (i.e. allocating 38% of the bed area for biochar removal).

A standard lab scale pyrolysis unit has 1.5 kg of sand, a cross sectional area of the reactor or well mixed zone of 0.00456 m^2 and processes 1 kg/h of biomass, generating about 0.15 kg/hr of biochar (Xu et al., 2009). Based on the well-mixed zone areas, the reactor has an area 3.37 times smaller than the cold model used in this study. The cold model separation unit can process 13.6 times the feedrate of the actual pyrolysis unit, meaning it is more than capable of removing the proportional amount of biochar that is generated in an actual pyrolysis unit, based on sizing. The calculation process can be seen in Table 4.

Table 4-Scale up based on reactor area and product generation

Fluidized Bed Unit	Cross Sectional Area (m^2)	Biochar Generation (kg/hr)	Biomass Processing Capability (kg/hr)	Area Ratio ($A_{WM}/A_{bed,pyrolysis}$)	Required Feed Ratio	Actual Feed Ratio
Lab-scale pyrolysis unit	0.00456	0.15	1	3.37	3.37	**13.6**
Novel Biochar Removal System	0.0154	2.04	13.6			

3.4 Conclusions

In the current study, a novel fluidized bed system for the continuous removal of biochar was developed, designed, and optimized. The intended application for this is pyrolysis, as the system allowed for vigorous bubbling conditions required for pyrolysis conditions (U_{wm}), while also allowing for biochar removal by implementing favorable particle segregation conditions at a decreased gas velocity (U_{rem}); the only additional internal was a vertical plate which was paramount in allowing particle segregation and offering some partition between the part of the bed that was well mixed and the part that allows particle segregation. Following optimization, the novel continuous system was shown capable of high purity biochar removal at rates consistent with real biochar generation rates found in pyrolysis. Inherent to the continuous system, process stability was maximized, which would lead to increased profitability and energy requirements if implemented in a pyrolysis unit.

Considering the flaws and performance of the batch system described in Chapter 2, the new system offered radically improved purity, system stability, and removal capability due to consistent bed level heights and consistent biochar concentrations in the fluidized bed. Similar to the batch system, the superficial gas velocity was essential in optimizing purity of the removed solids, allowing the best purity at $3.6U_{mf}$. The height of the vertical plate above the bottom (P_h) proved to be important, as placement allowed for accumulation of the biochar layer in the separation zone, and also helped prevent bubbles from the well mixed zone disturb the accumulated biochar layer. Having the plate submerged in the bed minimally caused the system to fail due to a lack of biochar segregation in the separation zone, eventually causing overloading of the bed and subsequent defluidization. Operating the well mixed zone at various high gas flowrates that are used in pyrolysis processes, had almost no effect on the removal performance, making this system flexible to pyrolysis processes that use different superficial gas velocities or residence times in reactors.

The system was shown to work over a range of many feedrates (0.018-0.034 kg/min) that are proportional to biochar generation rates present in pyrolysis units, based on proportional area scaling. The removal process requires segmenting part of the fluidized bed to operate at lower gas velocities to promote particle segregation and removal, and decreasing the $A_{sep}/A_{WM}<38\%$ showed decreased performance. Overall, optimization of the system allowed biochar removal from the fluidized bed system with purity higher than 93%.

Acknowledgements

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Nomenclature

A_{bed}-area of fluidized bed (m^2)

$A_{bed,pyrolysis}$- bed area of a pyrolysis unit (m^2)

A_{bp}- free area below separation plate (m^2)

A_{sep}- area of separation zone (m^2)

A_{wm}- area of well mixed zone (m^2)

d_p- particle diameter (μm)

d_{psm}-sauter mean diameter

$F_{biochar}$- feedrate of biochar (g/min)

H_{bed}-height of fluidized bed (cm)

L_{bp}- free length below separation plate (cm)

P_h- height of plate above bottom of bed (cm)

U_{mf}- minimum fluidization gas velocity of pure sand (m/s)

U_{rem}-superficial gas velocity used during batch biochar removal step (m/s)

U_{seg}- superficial gas velocity used during batch biochar segregation step (m/s)

U_{sep}-superficial gas velocity in separation zone (m/s)

U_{wm}- superficial gas velocity in well mixed zone (m/s)

ρ_b-bulk density (kg/m^3)

ρ_p- particle density (kg/m^3)

References

H. Abdullah, H. Wu, Biochar as a Fuel: 1. Properties and Grindability of Biochars Produced from the Pyrolysis of Mallee Wood under Slow-Heating Conditions, Energy & Fuels. 23 (2009) 4174-4181

R. Bedmutha, L. Ferrante, C. Briens, F. Berruti, I. Inculet. Single and two-stage electrostatic demisters for biomass pyrolysis application. Chemical Engineering and Processing: Process Intensification, 48 (2009) 1112-1120.

J.C Bosma, A.C Hoffman, On the capacity of continuous powder classification in a gas-fluidized bed with horizontal sieve-like baffles, Powder Technology. 134 (2003) 1-15

J. Gaunt, J. Lehmann, Energy Balance and Emissions Associated with Biochar Sequestration and Pyrolysis Bioenergy Production, Environmental Science Technology. 42 (2008) 4152-4156

L.G. Gibilaro, P.N. Rowe, A model for a segregating gas fluidized bed, Chemical Engineering Science. 29 (1974) 1403–1412

C. Hulet, C. Briens, F. Berruti, E. Chan, Experimental and analytical study of the solids circulation loop of a compartmented fluidized bed, Powder Technology, 185 (2008) 131-143

S.H Jung, B.S Kang, J.S Kim, Production of bio-oil from rice straw and bamboo sawdust under various reaction conditions in a fast pyrolysis plant equipped with a fluidized bed and a biochar separation system. Journal of Analytical and Applied Pyrolysis. 82 (2008) 240-247

F. Laytner, J. Grace, N. Epstein. K.L Pinder. Mobility of wood wafers in a gas-fluidized bed, Fluidization. 8 (1995) 93-102

C. Mara, L. Ferrante, C. Briens, F. Berruti, Optimization of a Batch Separation System For Removal of Biochar from a Fluidized Bed, To Be Submitted (2011).

A. Nienow, P. Rowe, L. Cheung, A Quantitative Analysis of the Mixing of Two Segregation Powders of Different Density in a Gas Fluidized Bed, Powdery Technology, 20 (1978) 89-97

K. Roberts, B. Gloy, S. Joseph, N. Scott, J. Lehmann, Life Cycle Assessment of Biochar Systems Estimating the Energetic, Economic, and Climate Change Potential, Environmental Science Technology. 44 (2010) 827-833

P.N. Rowe, A.W. Nienow, A.J. Agbim, A preliminary quantitative study of particle segregation in gas fluidised beds—binary systems of near-spherical particles, Trans. Inst. Chem. Eng. 50 (1972) 324– 333.

R. Vignes, Use limited life-cycle analysis for environmental decision-making, Chemical Engineering Progress, 97 (2001) 40-55

P. Winsley, Biochar and bioenergy production for climate change mitigation, New Zealand Science Review, 64 (2007).

R. Xu, L. Ferrante, C. Briens, F. Berruti, Flash pyrolysis of grape residues into biofuel in a bubbling fluid bed, Journal of Analytical and Applied Pyrolysis, 86 (2009) 58-65

R. Xu, L. Ferrante, K. Hall, C. Briens, F. Berruti, Thermal Self-Sustainability of Biochar Production by Pyrolysis, Journal of Analytical and Applied Pyrolysis, In Press, (2011)

CHAPTER 4

4. EFFECT OF BIOCHAR SIZE ON CONTINUOUS REMOVAL PERFORMANCE USING A NOVEL FLUIDIZED BED

4.1 Introduction

As described in the previous chapters, fluidized bed pyrolysis generates bio-oil vapors, non condensable gases, and a solid biochar product. A fraction of the smallest biochar can be elutriated, though there has been no method or attempts of efficiently retrieving biochar that remains in the fluidized bed mixed with the hot sand. Other methods of addressing biochar accumulation have limited fluidized bed pyrolysis to a batch process, as described in Chapter 2.

Continuous biochar removal systems have been limited to elutriation, though other authors have shown that large amounts of biochar often remain in the bed following fast pyrolysis, making the performance of this elutriation system questionable (Jung et al., 2008) (Xu et al., 2009). Elutriable biochar particles must be very small, which is accomplished through costly size reduction of the feed, or using large amounts of gas during fluidization to promote attrition; each of these techniques requires additional resources, reducing the overall profitability of the process.

Previously, the authors developed a novel fluidized bed capable of continuously removing biochar through particle segregation while also allowing high gas flows necessary for vigorous mixing in bubbling bed pyrolysis (Chapter 3). The system continuously removed biochar (d_{psm}=1.15 mm and ρ_b= 252 kg/m^3) at with a purity of 93% following optimization. The operating parameters that required optimization in this system included the superficial gas velocities in the separation zone well mixed bubbling area, the height of plate above the distributor, biochar feed rate, and size of separation zone.

Optimization of the fluidization velocity in the separation zone maximized steady state purity. The gas velocity in the well mixed zone had little effect on biochar purity did not show major changes in biochar purity. Locating the separation plate properly was essential in optimizing biochar removal; bringing the bottom of the plate too close the gas distributor decreased the purity of the removed biochar as the biochar did not circulate to the separation zone as readily, while locating it too close to the bed surface led to back mixing of the biochar from the separation zone, decreasing purity. An optimum biochar feedrate was also apparent; increasing the feedrate beyond this value decreased the biochar purity and quickly reached unsustainable values above which the bed could not be operated, while reducing the feedrate showed minimal effects on purity.

As this system showed potential for various pyrolysis conditions or other processes that create solid wastes in fluidized beds, the system required further testing of biochar of different sizes. The operating parameters and feedstock properties have an impact on the properties of the biochar generated in the pyrolysis process. Though the biochar density can also deviate due to feedstock and reaction conditions, this study focuses on applications where biomass is ground to different sizes prior to its use to generate biochar in a pyrolysis unit.

There is a broad range of biochar particle characteristics, and the tested biochar falls within this range. As other particle separators, such as cyclones, filters, or sieves must undergo significant design changes when particle sizes change, it must be ensured that this novel separator was adaptable to biochar size. As reported in Chapter 2, the biochar particle size impacted the operation of the batch separator significantly, and the performance of the novel, continuous system with different sized biochars had to be investigated.

In the current chapter, using the fluidized bed previously developed (Chapter 3), additional biochar particle sizes were tested for continuous removal performance, with the objective of confirming the performance of the novel fluidized bed and of better understanding its flexibility.

4.2 Experimental

4.2.1 Equipment

The equipment used for these tests was the same as previously developed by authors (Chapter 3) and can be seen in Figures 4.1 and 4.2. The design relied on three aspects: a low velocity zone that allowed biochar segregation and separation from the sand, a high velocity, well mixed, bubbling zone that ensured the vigorous solids mixing that is necessary biomass pyrolysis, and a vertical plate that reduced back mixing and allowed biochar accumulation in the separation zone. A porous plate provided a low fluidization velocity and additional gas was supplied to the well mixed bubbling zone by a maximum of five sparger tubes. The gas flow through both the porous plate distributor and the sparger distributor were regulated with separate calibrated sonic nozzles, and Omega PX181 pressure transducers connected to a Mastercraft voltmeter measured the pressure upstream of these nozzles.

The vertical plate provided a boundary between the separation zone and the well mixed bubbling zone, and also allowed biochar to accumulate by reducing biochar back mixing to the well mixed zone. Biochar was continuously removed through overflow ports in the side of the fluidized bed, 0.0254 m in diameter, and 0.30 m above the bottom of the bed.

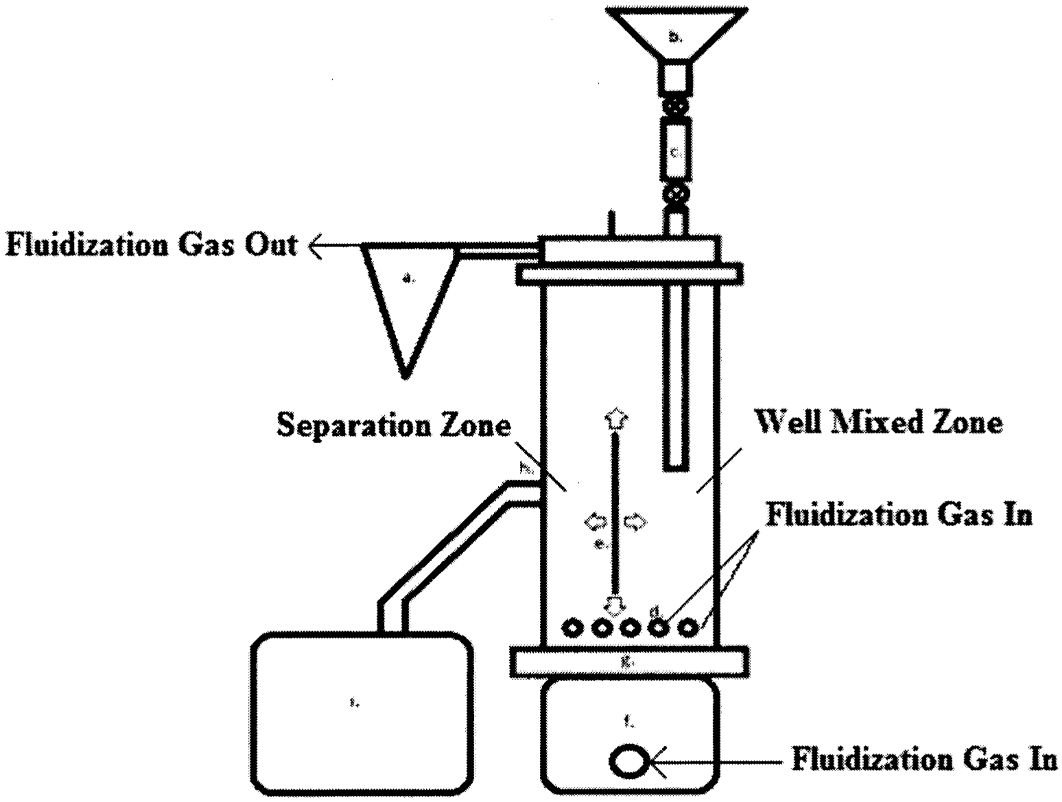

Figure 4.1-Schematic of the novel fluidized bed used for continuous biochar separation, side view. A) filter bag, b) solids hopper, c) biochar feed system, d) sparger distributor e) movable vertical plate f) windbox g) porous plate distributor h) biochar removal ports (3) (0.0254 m in diameter, 0.30 m above base), i) solids collection storage

4.2.2 Materials

As in the previous study, biochar from Burt's Greenhouses in Kingston, Ontario, was sieved into various size cuts to approximate biochar generated during fluidized bed pyrolysis. The particle size distribution of the biochars tested can be seen in Figure 4.2. The jagged particle structure that is partly responsible for poor fluidization properties, can be seen in the microscopic pictures of Figures 4.3 and 4.4. Silica sand (d_{psm}=175 um, ρ_b= 1650 kg/m^3, ρ_p=2750 kg/m^3, U_{mf}=0.025 m/s) was used as for the main bed particles. The sand properties are such that it was a Geldart group B powder.

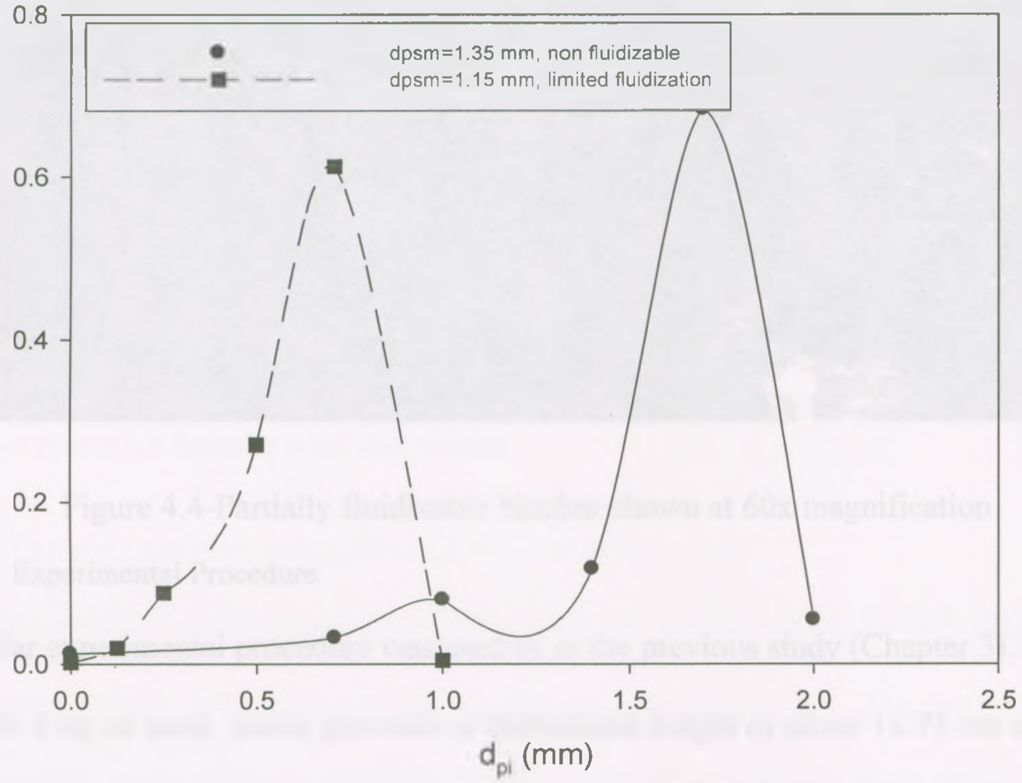

Figure 4.2- Particle size distribution of biochars tested

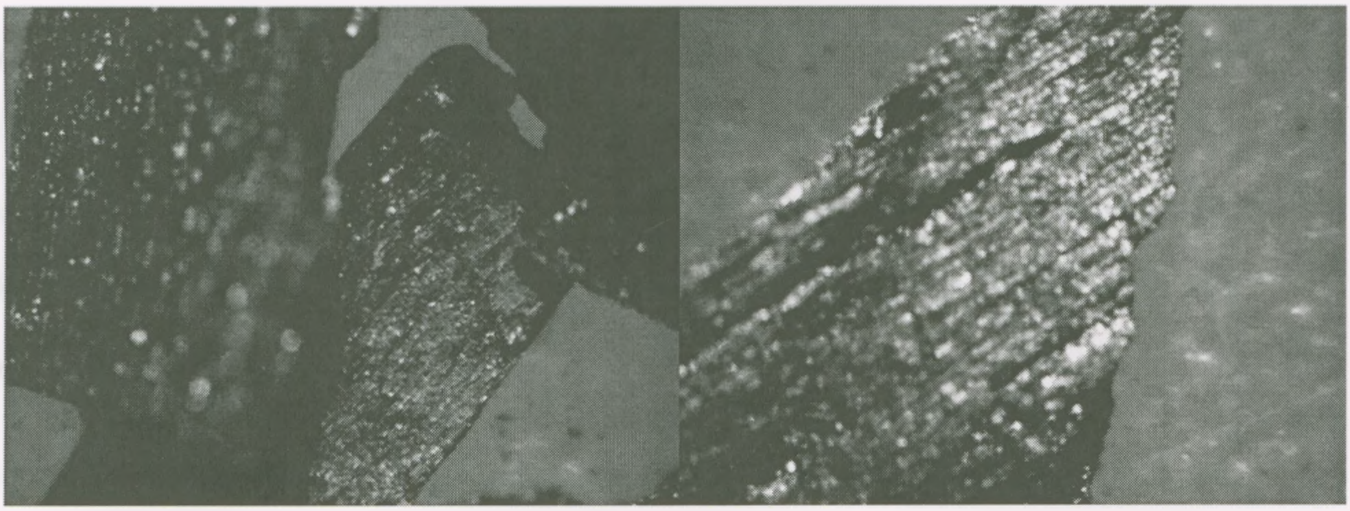

Figure 4.3- Large non-fluidizable biochar shown at 60x magnification

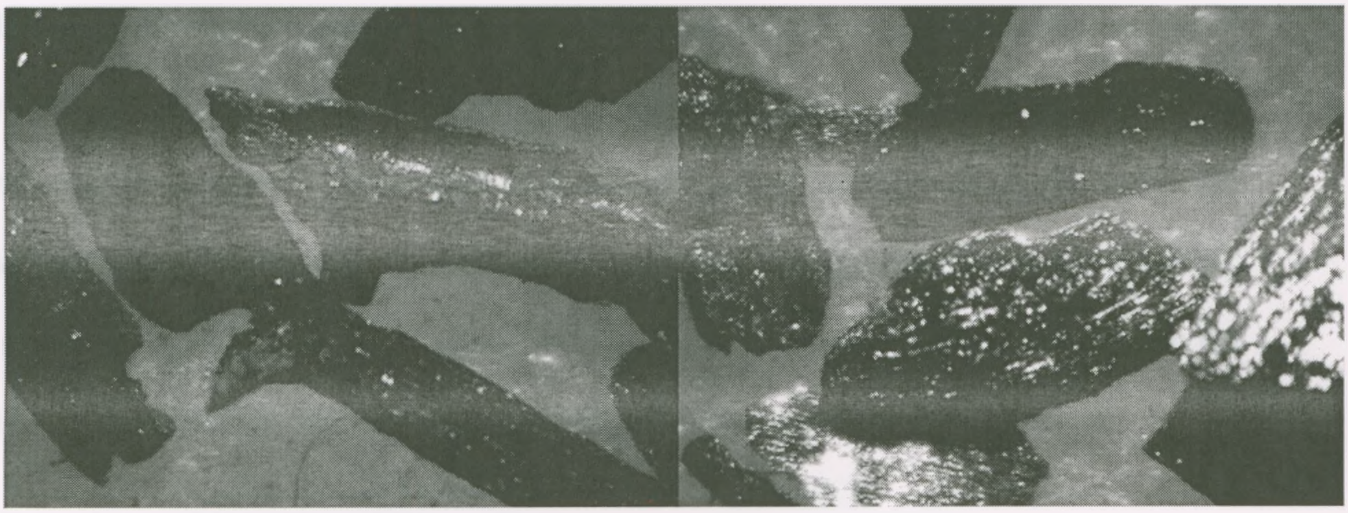

Figure 4.4-Partially fluidizable biochar shown at 60x magnification

4.2.3 Experimental Procedure

A similar experimental procedure was used as in the previous study (Chapter 3). The bed was loaded with 8 kg of sand, which provided a defluidized height of about 16.75 cm and was then fluidized with air. The porous plate was fluidized at the desired gas velocity and then supplementary air was provided to the well mixed part of the bed such that it is kept at the same velocity (U_{wm}=0.16 m/s) for each experiment. Experiments with the large, non-fluidizable biochar required larger gas flows in the well mixed, bubbling section due to its particle size; U_{wm} was increased to 0.22m/s in these cases. This is supported by findings from the proceeding study (Chapter 3) where it was shown that good mixing and vigorous bubbling was required in the well mixed zone for the removal process to work.

The plate location was also set at this time at the desired height above the bottom of the bed, and the desired lateral location. Biochar was continuously fed to the well mixed part of the bed once every 30 seconds and circulated to the separation zone, where it was allowed to segregate and accumulate. Once a segregated layer had accumulated in the separation zone, the overflow port valves were opened and solids were allowed to flow out, with the quantity and concentration of solids evaluated every 5 minutes. The purity of the removed solids, defined as the amount of biochar divided the total amount of solids, was determined using sieving. Reported purity measurements are averaged over the final 15 minutes (3 points) during a steady state run. The removed sand was placed back in the well mixed side of the bed and fluidization was resumed. Steady state was achieved once the amount of biochar removed from the system was equal to the amount fed to the system in that time period, at which time the experiments are stopped.

4.3 Experimental Results and Discussion

4.3.1 General Operation during Steady State Biochar Removal

As in the previous study presented in Chapter 3, the two zones of the bed reached different heights during steady state removal, as can be seen in Figure 4.5. The two zones became different heights due to the accumulation of biochar in the separation area, and a biochar layer forming above the biochar and sand mixture. As in the previous study, steady state was not possible for certain operating conditions that have not been reported, as when the feedrate was too high, which caused accumulation. For the small, partially fluidizable biochar, the bed height of biochar and sand mixture was 0.26 m. The height of the separation area at these conditions was about 0.30 m and the well mixed zone was about 0.24 m. For the large non-fluidizable biochar, the bed was 0.25 m mixed, similar to the previous study by the authors, with solid heights of 0.30 m for the separation area, and 0.24 m for the well mixed area.

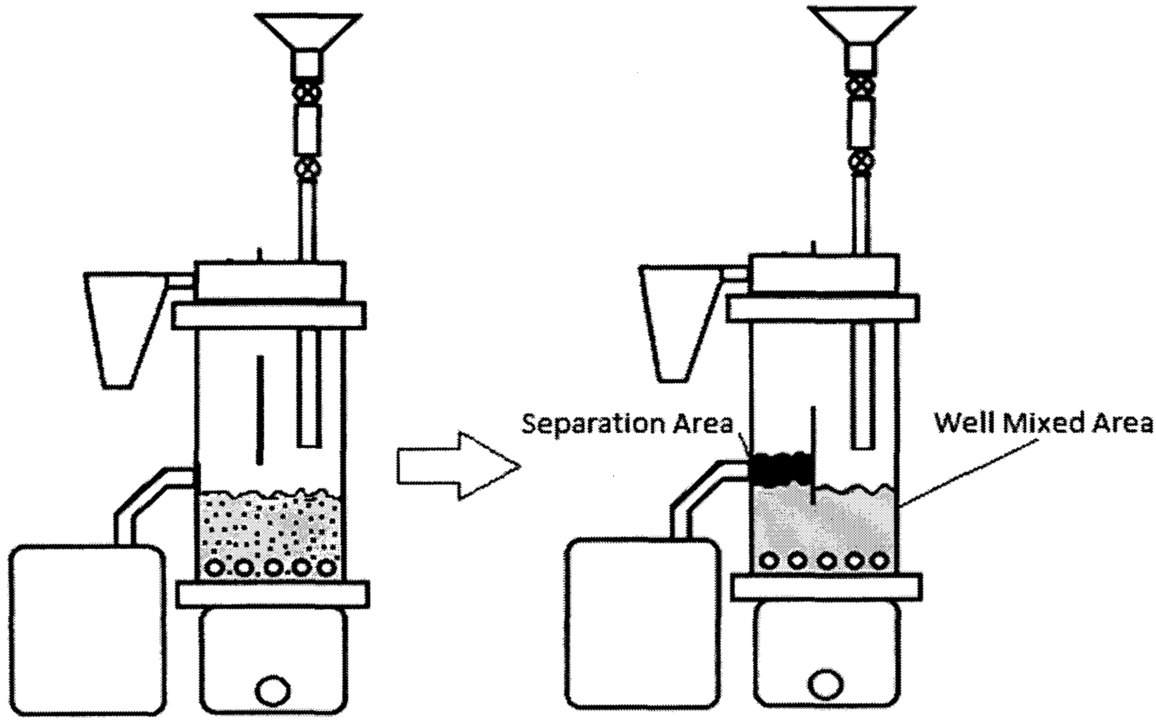

Figure 4.5-Depiction of novel fluidized bed before and during steady state biochar removal

4.3.2 Partially Fluidizable Biochar

The performance of biochar removal at steady state can be seen in Figure 4.6. About half as much gas was required for steady state biochar removal, than the larger biochar tested. Using less gas means that the resource demand was less, which would increase the profitability of the overall process. Not only did using less gas decrease the resource demand but it also ensured that less sand was being removed from the reactor with the biochar. The separation velocity, as expected, was close to the minimum fluidization of the mixture, but high enough to allow for small bubbles to promote particle segregation, which allowed for high purity removal.

Further increasing the gas velocity in the separation zone led to decreased purity, as there was more intense particle mixing in the separation zone, which caused the ejection of more sand throught the biochar ports.

The range of acceptable biochar feedrates was also determined, as shown in Figure 4.7. Biochar feedrates of 0.036, 0.041 g/min provided a biochar purity of 96%, while flowrates higher than 46 g/min caused biochar accumulation in the bed and process failure. The smaller biochar was more readily segregated from the sand, and this was apparent as the capacity was larger than in Chapter 3. Similarly, decreasing the feedrate had minimal effect on the performance of the system. Overall, using smaller biochar allowed less gas to be used for successful removal, than the biochar used in Chapter 3.

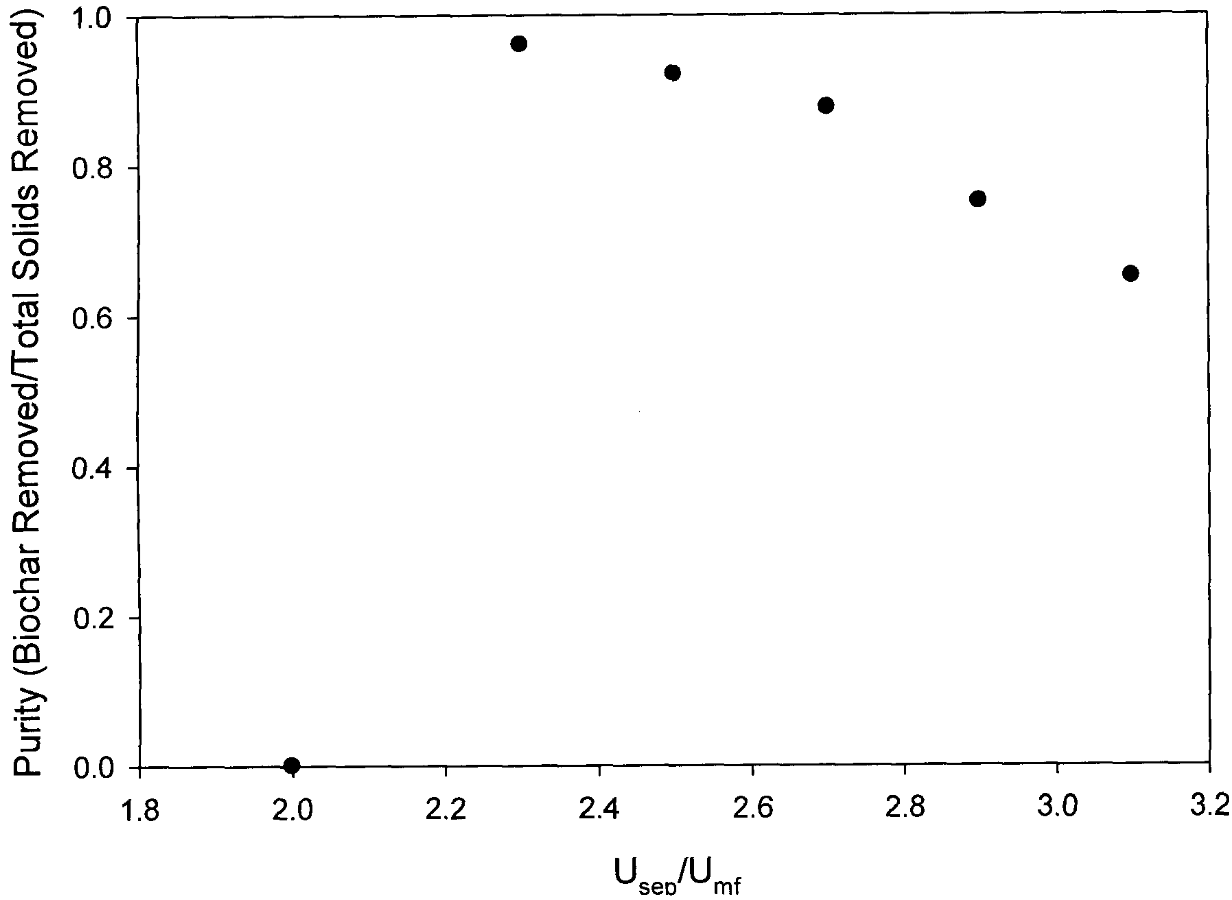

Figure 4.6-Effect of gas velocity on purity of removed fluidizable biochar. U_{wm}=0.16 m/s, P_h=0.18 m, $F_{biochar}$= 0.036 kg/min, A_{sep}/A_{bed}=0.38

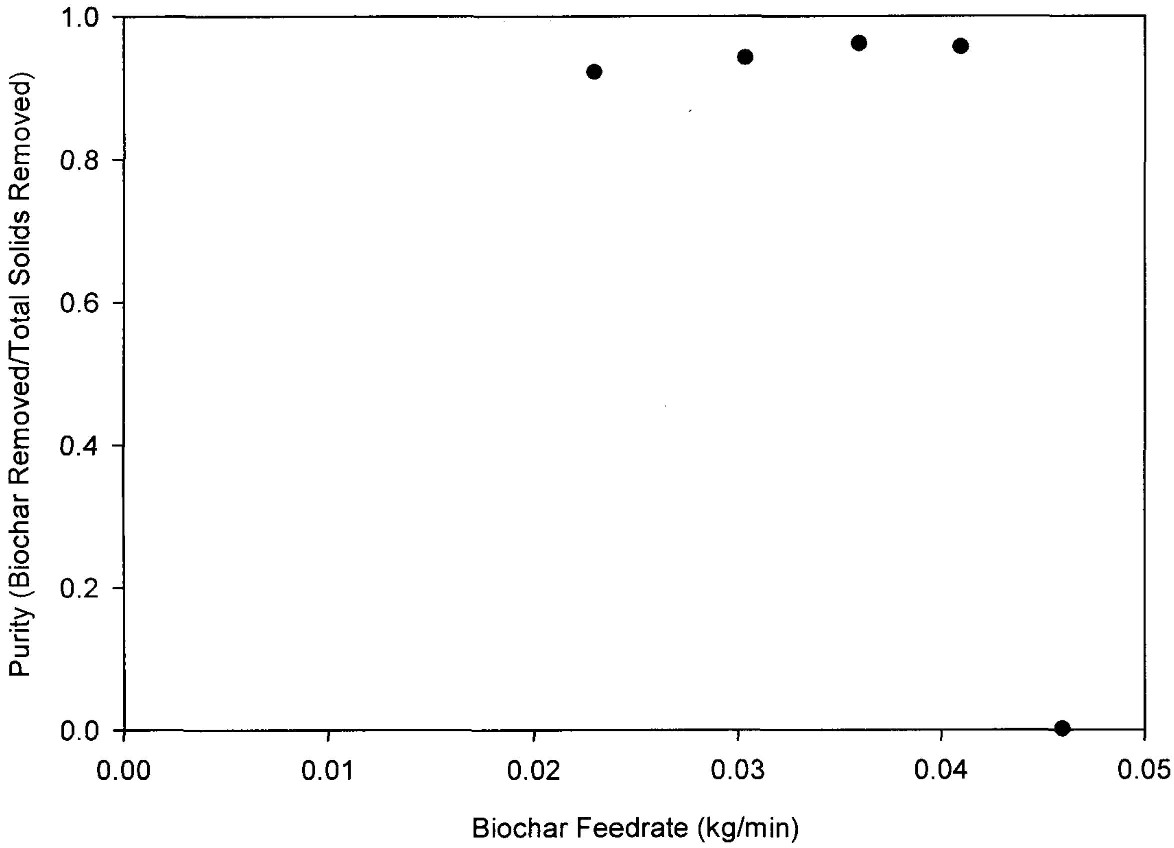

Figure 4.7-Effect of biochar feedrate on purity of removed biochar, U_{sep}= 0.0575 m/s, U_{wm}=0.16 m/s, P_h=0.18 m, A_{sep}/A_{bed}=0.38

4.3.3 Non-Fluidizable Biochar

The larger biochar allowed for steady state removal as seen in Figure 4.8, after adjustments in operating parameters. Additional gas was provided in the well mixed zone since the large biochar required more gas for good mixing with sand; operating at the base U_{wm}=0.16 m/s provided insufficient mixing and resulted in accumulation of biochar in the well mixed zone; U_{wm}=0.22 m/s had to be used. The system worked well, achieving 95.5% biochar removal purity, following optimization of the fluidization velocity in the separation zone, U_{sep}. Figure 4.9 shows that the range of dimensionless fluidization velocities in the separation zone (U_{sep}/U_{mf}) that allowed for good separation is larger than for the smaller biochar.

Similar to the biochar utilized in Chapter 3, a biochar feedrate of 0.041 kg/min caused the system to fail due to accumulation of biochar in the separation zone. Figure 4.9 shows the system performed well for feedrates between 0.022 and 0.034 kg/min.

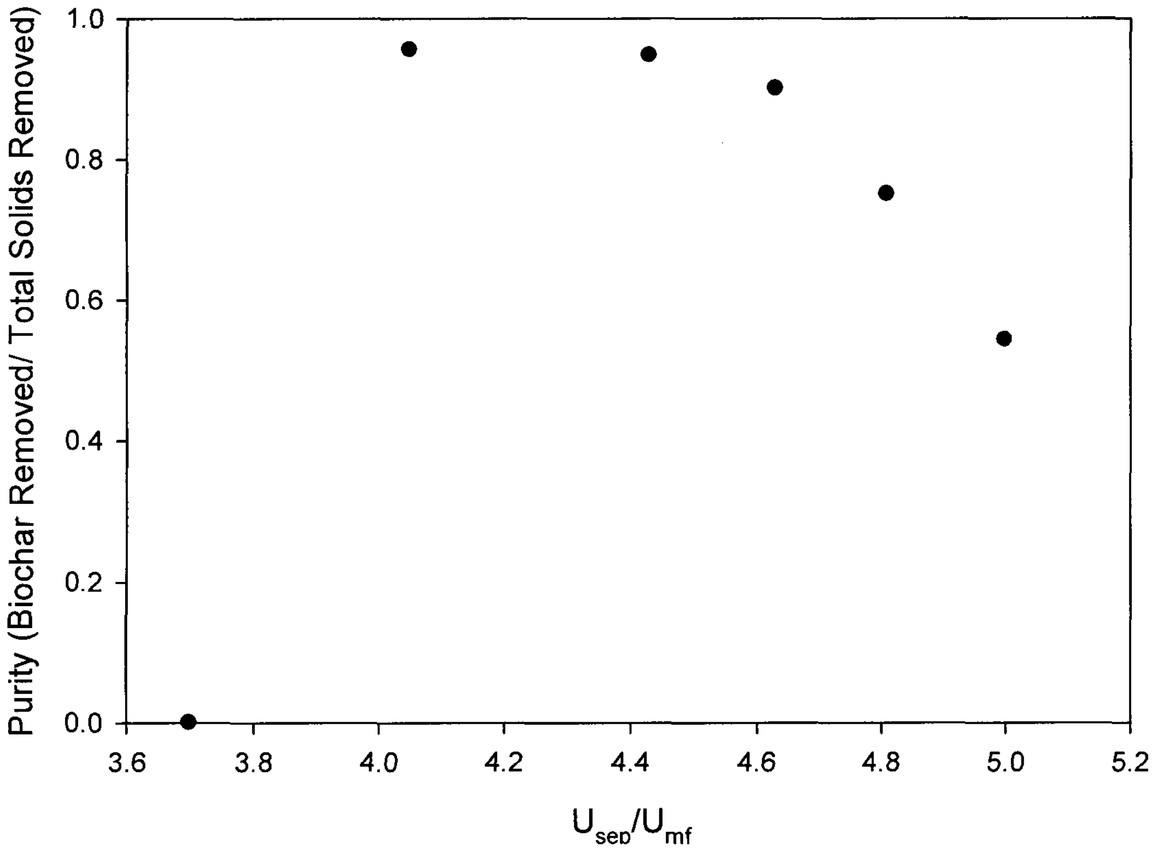

Figure 4.8- Effect of gas velocity on purity of removed fluidizable biochar. U_{wm}=0.22 m/s, P_h=0.18 m, $F_{biochar}$= 0.034 kg/min, A_{sep}/A_{bed}=0.38

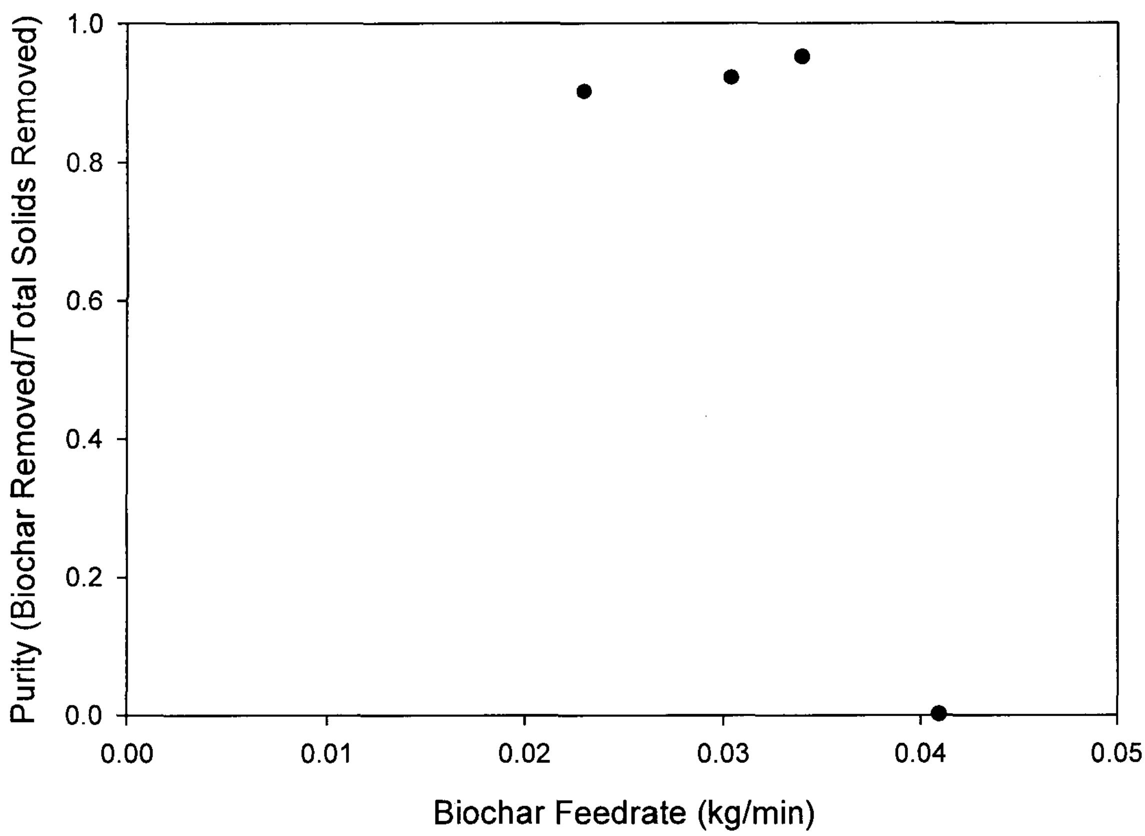

Figure 4.9- Effect of feedrate on purity of removed biochar. U_{sep}= 0.101 m/s ,U_{wm}=0.22 m/s, P_h=0.18 m, A_{sep}/A_{bed}=0.38

4.3.4 General Stability of Steady State Removal at Different Operating Conditions

Though both biochars allowed reach steady state removal conditions, for which the flowrates of added and removed biochar were equal, there would be fluctuations in the performance under some operating conditions. The fluctuations when operating under poor operating conditions, usually at too high of a biochar feedrate or using insufficient gas in the separation zone, were more apparent; the bed failed to stabilize and operated more unpredictably. Poor stabilization manifested itself in an obvious way; the system removed more biochar than fed in one 5 minute period, but in the next 5 minute period removed less than was fed. These instabilities in biochar output led to lower purity. In addition, based on visual observations, the packing of the separated biochar influenced the purity of removed biochar. Tighter biochar packing or a biochar layer that was thicker allowed less sand bubbles from the bottom of the bed to be splashed to the surface, and thus higher purities.

4.3.5 Performance of Other Materials

Biomass and heavy ideal particles were investigated to determine if the system would work for heavier or more cohesive particles. Different particles that were investigated included dried distillers grain, sawdust, and spherical polyethylene beads, with particle properties shown in Table 5. Over a wide range of conditions, particle segregation was too poor to allow separation using this technique. However, the failure to separate the heavy biomass particles was a positive aspect of this process, as removal of unreacted biomass would be undesired and would lead to lower yields due to smaller conversions. The inability of biomass to be separated and removed from the bed improved the functionality of the bed, since it insured unreacted biomass will not be removed with the biochar. Though sawdust had a similar density and size to biochar, it was very cohesive and did not allow for good particle segregation.

Table 5-Materials tested that caused system failure

Material	ρ_b (kg/m^3)	d_{psm} (μm)
DDG	572	1282.25
PET Beads	820	1200
Sawdust	200	150

4.3.6 Scale-Up Considerations

It is possible to do an approximate scale-up of this system based on size and volume of the experimental laboratory-scale fluidized bed utilized in this project and a fluidized bed pyrolysis unit. In this system, 2.46 kg/h of d_{psm}=0.65 mm or 2.04 kg/h of d_{psm}= 1.35 mm of biochar could be removed, with bed properties of 8 kg of sand, and a cross-sectional area of the well mixed zone of A_{WM}=0.015376m^2 (i.e. allocating 38% of the bed area for biochar removal). Based on a high temperature pyrolysis yield of 15 wt% biochar/wt biomass from dried distillers grain (DDG), a pyrolysis reactor of the same size could process 16.4 kg/hr of biomass that would create small biochar, or if the feed created large biochar 14.4 kg/hr of biomass.

A standard lab scale pyrolysis unit has 1.5 kg of sand, a cross sectional area of the reactor or well mixed zone of 0.00456 m^2 and processes 1 kg/h of biomass, generating 0.15 kg/hr of biochar (Xu et al., 2009). Based on the well-mixed zone areas, the reactor has an area 3.37 times smaller than the cold model used in this study. Since the cold model can process 16.4 kg/hr of biomass or 14.4 kg/hr of biomass this is about 16.4 and 13.6 times the feedrate of the actual pyrolysis unit meaning the novel system is more than capable of removing the amount of biochar that is generated in an actual pyrolysis unit, based on sizing. The calculation process is shown also be seen in Tables 6 and7.

Table 6-Scaling considerations for processing d_{psm}=0.65 mm biochar

Fluidized Bed Unit	Cross Sectional Area (m^2)	Biochar Generation (kg/hr)	Biomass Processing Capability (kg/hr)	Area Ratio ($A_{WM}/A_{bed,pyrolysis}$)	Required Feed Ratio	Actual Feed Ratio
Lab-scale pyrolysis unit	0.00456	0.15	1	3.37	3.37	**16.4**
Novel Biochar Removal System	0.0154	2.46	16.4			

Table 7-Scaling considerations for processing d_{psm}=1.35 mm biochar

Fluidized Bed Unit	Cross Sectional Area (m^2)	Biochar Generation (kg/hr)	Biomass Processing Capability (kg/hr)	Area Ratio ($A_{WM}/A_{bed,pyrolysis}$)	Required Feed Ratio	Actual Feed Ratio
Lab-scale pyrolysis unit	0.00456	0.15	1	3.37	3.37	**13.6**
Novel Biochar Removal System	0.0154	2.04	13.6			

4.3.7 Expected Practical Limitations to the System

As with every system, there are limitations to the operation; this novel system is not capable of separating all types of binary mixtures in a fluidized bed. The body of literature on particle segregation can be considered a good guide to what type of particles can be separated using this system. Logically, binary mixtures that segregate more easily, and form thicker layers during particle segregation will offer the best continuous removal results, as this allows less sand to splash to the surface from bubbles in the lower part of the bed. Smaller particles of the same particle type can also be considered to perform marginally better as shown in the results and use less fluidization gas, while larger particles will still perform well but require more fluidization gas for separation.

4.3.8 Expected Effect of Heat on Removal System

Following implementation of the developed equipment and process in an actual unit, further fine adjustments will have to be made due to the increase to the actual reaction temperatures of approximately 500 °C. The fluidization gas properties change with increased temperature, the gas viscosity will increase and density will decrease. The increased viscosity leads to changes in the fluidization characteristics.

Recent studies on temperature effects on bed hydrodynamics shows Group B powder mixing increases when holding the superficial gas velocity constant, from 25 to 300 °C due to increasing bubble size. However, at temperatures higher than 300 °C, bubbles decreased in size (Sanaei et al., 2010). Other literature supports this trend for Group B powders, reporting decreases in minimum fluidization as system temperature increased (Formisani et al., 1997) (Radmanesh et al., 2005). A decrease in bubble size due to the temperature increase may help to decrease mixing, since large bubbles are the primary cause for mixing in fluidized beds (Kunii & Levenspiel, 1991). The change in gas viscosity as a result of temperature, at 1 atm, is shown in Table 8.

Table 8-Effect of temperature on gases related to pyrolysis

	Dynamic Viscosity, μ_g ($x10^{-5}$)	
Gas Species	25 °C	500 °C
Air	1.86	3.64
Carbon Monoxide	1.50	3.34
Carbon Dioxide	1.50	3.34
Hydrogen	0.89	1.62
Methane	1.04	2.35

Pyrolysis occurs at approximately 500 °C, much different than the standard conditions used during optimization of the removal system. The increase in temperature will cause a decrease in the minimum fluidization velocity of the mixture as the gas viscosity will increase; this will require additional optimization of the superficial gas velocity in the separation zone. Using the optimal gas flows at the standard conditions, or the gas velocities reported in these studies will result in vigorous bubbling and cause low purity removal.

4.4 Conclusions

Following initial optimization of a novel system for the continuous separation and removal of biochar from a fluidized bed, 2 additional biochars of different sizes and bulk densities were tested and removed at high purity. Operating parameters were optimized to attain 96% purity biochar removal for the partially fluidizable biochar and 95.5% for the non-fluidizable biochar. As expected, decreasing the biochar particle size reduced the gas velocity required in the separation zone for optimal removal. In addition, using smaller biochar allowed for higher biochar feedrates to be used in the system.

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Nomenclature

A_{bed}-cross sectional area of fluidized bed (m^2)

$A_{bed,pyrolysis}$- cross sectional bed area of a pyrolysis unit (m^2)

A_{sep}- cross sectional area of separation zone (m^2)

A_{wm}- cross sectional area of well mixed zone (m^2)

d_p- particle diameter (μm)

d_{psm}-sauter mean diameter

$F_{biochar}$- feedrate of biochar (g/min)

H_{bed}-height of fluidized bed (cm)

P_h- height of plate above bottom of bed (cm)

U_{mf}- minimum fluidization gas velocity of pure sand (m/s)

U_{rem}-superficial gas velocity used during batch biochar removal step (m/s)

U_{seg}- superficial gas velocity used during batch biochar segregation step (m/s)

U_{sep}-superficial gas velocity in separation zone (m/s)

U_{wm}- superficial gas velocity in well mixed zone (m/s)

ρ_b-bulk density (kg/m^3)

ρ_p- particle density (kg/m^3)

References

H. Abdullah, H. Wu, Biochar as a Fuel: 1. Properties and Grindability of Biochars Produced from the Pyrolysis of Mallee Wood under Slow-Heating Conditions, Energy & Fuels. 23 (2009) 4174-4181

R. Bedmutha, L. Ferrante, C. Briens, F. Berruti, I. Inculet. Single and two-stage electrostatic demisters for biomass pyrolysis application. Chemical Engineering and Processing: Process Intensification, 48 (2009) 1112-1120.

A. Boateng, C. Mullen, N. Goldberg, K. Hicks, T. Devine, I. Lima, J. McMurtrey. Bioenergy and Biochar from the Straw of High-Biomass Soybean Lines via Fast Pyrolysis, Environmental Progress & Sustainable Energy, 29 (2010) 175-183

J.C Bosma, A.C Hoffman, On the capacity of continuous powder classification in a gas-fluidized bed with horizontal sieve-like baffles, Powder Technology. 134 (2003) 1-15

C. Brewer, K. Schmidt-Rohr, J. Satrio, R. Brown, Characterization of Biochar from Fast Pyrolysis and Gasification Systems, Environmental Progress & Sustainable Energy, 28 (2009) 386-396

B. Formisiani,R R. Girimonte, L. Mancuso, Analysis of the Fluidization Process of Particle Beds at High Temperature, Chem. Eng. Sci., 53 (1997) 951-961

L.G. Gibilaro, P.N. Rowe, A model for a segregating gas fluidized bed, Chemical Engineering Science. 29 (1974) 1403–1412.

J. Gaunt, J. Lehmann, Energy Balance and Emissions Associated with Biochar Sequestration and Pyrolysis Bioenergy Production, Environmental Science Technology. 42 (2008) 4152-4156

S.H Jung, B.S Kang, J.S Kim, Production of bio-oil from rice straw and bamboo sawdust under various

D. Kunii, O. Levenspiel, Fluidization Engineering, 2nd ed., Butterworth-Heinemann, Boston, MA (1991)

F. Laytner, J. Grace, N. Epstein. K.L Pinder. Mobility of wood wafers in a gas-fluidized bed, Fluidization. 8 (1995) 93-102

K. Lee, B. Kang, Y. Park, J. Kim, Influence of Reaction Temperature, Pretreatment, and a Char Removal System on the Production of Bio-oil from Rice Straw by Fast Pyrolysis, Using a Fluidized Bed, Energy & Fuels, 19 (2005) 2179-2184

C. Mullen, A. Boateng, K. Hicks, N. Goldberg, R. Moreau, Analysis and Comparison of Bio-Oil Produces by Fast Pyrolysis from Three Barley Biomass/Byproduct Streams, Energy Fuels, 24 (2010) 699-706

D. Ozcimen, F. Karasmanoglu, Production and biocharacterization of bio-oil and biochar from rapeseed cake, Renewable Energy, 29 (2004) 779-787

R. Radmanesh, R. Mabrouk, J. Chaouki, C. Guy, Effect of Temperature on Solids Mixing in a Bubbling Fluidized Bed Reactor, International Journal of Chemical Reactor Engineering, 3 (2005) 1-14

K. Roberts, B. Gloy, S. Joseph, N. Scott, J. Lehmann, Life Cycle Assessment of Biochar Systems Estimating the Energetic, Economic, and Climate Change Potential, Environmental Science Technology. 44 (2010) 827-833

P.N. Rowe, A.W. Nienow, A.J. Agbim, A preliminary quantitative study of particle segregation in gas fluidised beds—binary systems of near-spherical particles, Trans. Inst. Chem. Eng. 50 (1972) 324– 333

S. Sanaei, N. Mostoufi, R. Radmanesh, R. Sotudeh-Gharebagh, C. Guy, J. Chaouki, Hydrodynamic Characteristics of Gas-Solid Fluidization at High Temperature, The Canadian Journal of Chemical Engineering, 88 (2010) 1-11

M.E. Sanchez, E. Lindao, D. Margaleff, O. Martinez, A. Moran, Pyrolysis of agricultural residues from rape and sunflowers: Production and biocharacterization of bio-fuels and biochar soil management, Journal of Analytical and Applied Pyrolysis, 85 (2009) 142-144

P. Winsley, Biochar and bioenergy production for climate change mitigation, New Zealand Science Review, 6 4 (2007) 5-10

Chapter 5

5. Conclusions and Recommendations

This chapter discusses the main conclusions and the impact of the work described in this thesis, as well as recommendations for related future work.

5.1 Conclusions

During fluidized bed pyrolysis, a solid biochar co-product is generated with bio-oil vapors, and combustible gases. Previous to the work described in this thesis, methods of removing biochar limited the pyrolysis process to a batch process; feeding of biomass was temporarily ceased and air was used to combust the biochar in the bed. Combusting the biochar is wasteful since it is a high value co-product that can be used for soil amendment, carbon sequestration, or as an alternative to coke in metallurgical applications or to coal in power generation. Elutriation techniques have been used, but this technique can only remove the smallest biochar particles, creating a difficult to handle biochar product and leaving significant amounts of biochar in the pyrolysis bed. Biochar accumulation in the fluidized reaction bed also creates process instability.

First, a batch process was developed to attempt removal of the biochar product, which resulted in an overall poor performance, but verified that particle segregation during fluidization was a valid separation technique and would offer better results if the system could be converted to a continuous process.

A novel continuous system was then designed, tested, and optimized to allow for high purity removal at biochar generation rates higher than in a real pyrolysis reactor. Since biochar size deviates significantly from one feedstock to another, smaller and larger sizes of biochar were also tested in the novel system, and following a similar optimization, an even higher purity was attained during the continuous removal. The results were very encouraging and a similar system has been adapted for use in an industrial pyrolysis unit, and will undergo optimization during further research.

5.2 Recommendations for Future Work

1. The continuous biochar removal system should be adapted for a circular system since many pyrolysis units are circular.
2. Additional solids should be tested such as smaller biochar or larger sands since some pyrolysis units may use larger sand for different heat or mass transfer characteristics. The author is confident that finer biochar would fully work following optimization of process variables. Finer biochar should also be tested since it is negligent to assume elutriation operates at 100% efficiency.
3. Testing different geometry plates that will create a gradient in gas velocities, which may allow for different particle segregation patterns to be observed
4. Determining the biochar loading in each side of the bed, since concentrations may affect heat transfer. New, noninvasive methods to detect biochar concentrations should also be investigated such as capacitance or conductance.
5. Modeling the particle transfer throughout the bed using tracer particles, taking measurements of residence time of individual tracer particles, may help validate the model
6. Additional biochar related studies must be completed to fully optimize sustainable, continuous fluidized bed pyrolysis. Using a heated unit, beds of different biochar and sand concentrations should be studied to determine how heat transfer is disrupted through the presence of biochar. This data and the findings of the study detailed in

recommendation 4, will determine if the loading of biochar in the bed using this novel separation system will cause drops in the yield of various product, or cause detrimental effects to the process.