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Human Fecal Biochar Briquettes from the Sol-Char Toilet for Use as a Solid Fuel in the Developing World

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HUMAN FECAL BIOCHAR BRIQUETTES FROM THE SOL-CHAR

TOILET FOR USE AS A SOLID FUEL IN THE DEVELOPING WORLD

by

BARBARA JEANNE WARD

B.S., North Carolina State University, 2009

A thesis submitted to the Faculty of the Graduate School of the

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This thesis entitled:

Human Fecal Biochar Briquettes from the Sol-Char Toilet
for use as a Solid Fuel in the Developing World

written by Barbara Jeanne Ward

has been approved for the Department of Civil, Environmental,
and Architectural Engineering

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The final copy of this thesis has been examined by the signatories, and we find that both the

content and the form meet acceptable presentation standards of scholarly work in the above

mentioned discipline.

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Human Fecal Biochar Briquettes from the Sol-Char Toilet for use as a Solid Fuel in the Developing World

Thesis directed by Professor Lupita D. Montoya

Abstract

A team at the University of Colorado at Boulder is working with the Bill & Melinda Gates Foundation to develop a novel technical solution for 2.5 billion people in the developing world with no access to basic sanitation. The university's Sol-Char toilet uses concentrated sunlight to convert human fecal sludge into biochar, which has potential as a value-added product. The feasibility of using feces-derived biochar as a solid fuel for heating and cooking is assessed, considering energy content and elemental analysis of biochars made under different reactor conditions, ease of briquetting, and durability of biochar briquettes. Fecal biochars made at 300°C were similar in energy content to wood biochars and bituminous coal, possessing a higher heating value of 25.6 MJ/kg, while fecal chars made at 750°C were significantly lower in energy content at 13.8 MJ/kg. Chars derived from simulant feces favored by other Bill & Melinda Gates Foundation sanitation research projects were found to differ significantly from fecal char in their energy content and briquetting characteristics. A frequently used correlation between elemental composition of chars and their higher heating values was adapted to be more applicable to feces-derived chars based on a review of fecal char literature and experimental results. Fecal chars made at low temperatures and briquetted with molasses and lime binders yielded briquettes of comparable strength and energy content to commercial charcoal briquettes, suggesting that briquettes made from human feces could be a significant contribution to the sanitation value chain.

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1 Introduction

The developing world faces dual crises of rapid urban expansion and escalating energy demand. As former rural inhabitants flock to cities looking for jobs and better quality of life, urban infrastructure is unable to keep pace with population increase. It is estimated that urban areas in developing countries have less than 10% sewer coverage[1], leaving 2.5 billion people – 40% of the world's population - without access to adequate sanitation facilities[2]. Many of the aforementioned 2.5 billion use standard pit latrines, others share public toilet blocks, and still more defecate in the open. The slums of the developing world's megacities are littered with "flying toilets" – plastic bags full of human excrement that are launched over fences, deposited on railroad tracks and in drainage rivers in an attempt to separate people from their waste. Even when waste is collected (emptied from pit latrines with buckets and shovels or pumped from septic tanks with trucks) the majority of the collected fecal sludge is not processed to make it safe for disposal, but is dumped back into the environment untreated.[3] The Bill & Melinda Gates Foundation estimates that 2.1 billion people use toilets connected to septic systems or other collection tanks that empty raw sewage into surface waters or open drains.[4] All of the uncollected and unprocessed waste is not only an environmental and public health quandary, but is also an untapped resource.

A second crisis of the developing world looms in the background. An estimated 90% of the population of developing nations suffers from insufficient access to reliable energy supplies.[5] Energy scarcity disproportionately affects the poorest households – across Africa and India, the poorest economic bracket can spend up to 25% of their total income on fuel. In comparison, the most economically disadvantaged group of people in the United States spends only 1% of yearly income on energy. [6]   In addition to the financial burden of energy, the over-

collection of firewood and the production of wood charcoal contribute to ecological deterioration causing deforestation, increased erosion, and higher levels of air pollution. For the more than 3 billion people that rely on solid fuels like biomass and coal for cooking, heating, and water boiling[7], a practical supplementary energy source should come in a solid form that works with existing cooking and heating methods. This thesis evaluated a potential alternative for solving both crises of the developing world: the use of processed human waste as a solid fuel energy source.

In an effort to address the issue of unprocessed waste and limited sanitation access, the Bill & Melinda Gates Foundation challenged researchers to reinvent the toilet. The University of Colorado (CU) and a group of other universities and research institutes received funding to develop a new toilet design that does not depend on an existing sewer, piped water, or energy infrastructure, and can process human waste and transform it into a useful resource at a limited cost to the user. CU's Sol-Char toilet uses concentrated sunlight to process fecal sludge at high-temperature and low oxygen conditions and transforms it into useful and pathogen-free biochar. The reactor uses pyrolysis, the thermal decomposition of organic matter in the absence of oxygen, to reduce the fecal feedstock into biochar and high-energy gas. The biochar byproduct of pyrolysis contains inorganic materials, carbonized residue of organic components, and potentially unconverted organic solids. Pyrolysis gas usually contains CO_2, CO, CH_4, H_2, C_2H_6, and C_2H_4.[8] Pyrolysis was chosen because it offers relatively quick, high-temperature pathogen destruction, and reduces waste volume by 90%. Collection and use of biogas and use of biochar as a nutrient source for agricultural use is also being investigated as a value-chain for toilet byproducts; however, this thesis focused on the feasibility of biochar as a solid fuel.

Previous studies have examined the pyrolysis of human feces, but not with the goal of using the resulting biochar as a fuel source. NASA investigated pyrolysis of simulated human fecal matter for waste volume reduction and reclamation on the space station[9], but did not study pyrolysis products of real human feces and also did not aim to use biochar as a fuel, but as a means of temporary carbon sequestration. Recent studies have examined use of biochar created from animal manure as a fuel, performing ultimate and proximate analyses on manure-derived biochars and determining higher heating values (HHVs).[10-13] Animal manure biochars pyrolyzed at low temperatures, especially with higher energy content biomass added, were found to have heating values between high and low rank coals.[10] No previous studies have investigated the use of fecal biochar (animal or human) as a domestic heating and cooking fuel source. Most studies have focused on industrial use of biochar as fuel – e.g. grinding biochar and feeding it back into the pyrolysis reactor to heat the process.[13] Because of the industrial application of most fecal biochar, there has previously been no interest in studying its briquetting properties. Briquettes of Sol-Char biochar can be used as a solid fuel in the developing world, as a charcoal alternative, without making any adjustments to existing cooking practices. Researchers have looked into the briquetting of coal particulates (coal fines) and wood char particles to make charcoal briquettes. Taulbee et al. identified a range of cost-effective binders for pulverized coal[14], and Atlun et al. examined the effect of different binders on combustion kinetics[15]. Demirbas and Stevenson et al. discuss effective and sustainable briquetting of coal for use in the developing world.[16, 17]

The overall objective of this study is to evaluate the feasibility of using human fecal biochar briquettes as a solid fuel for domestic heating and cooking. The performance of the biochar in the categories of energy content, and ease of use were considered. Energy content

was evaluated by determining the higher heating values (HHVs) of fecal chars and finding the optimal pyrolysis reactor conditions to maximize energy content of char. Char energy and elemental composition were compared to those of simulant fecal char and to other solid fuels and calculated HHVs were verified with a pre-existing model. The existing model was then modified using data from the literature and from performed experiments to yield a better correlation for feces-derived biochars. Fecal char ease of use was determined by evaluating different binder formulations and evaluating briquette strength and durability.

2 Background

2.1 Introduction to Pyrolysis

Pyrolysis is the thermochemical conversion of an organic feedstock into biochar, bio-oil, and syngas under oxygen-limited conditions. The process of pyrolysis can be classified into two distinct methods: (1) traditional slow pyrolysis, which happens on the timescale of hours to days, and (2) fast "flash" pyrolysis, which incorporates rapid ramp rates and residence times of seconds to minutes.[18] Slow pyrolysis favors the production of char and has been used for centuries in the traditional production of charcoal fuels. Typical yields from slow pyrolysis are about 35% biochar, 30% bio-oil, and 35% syngas on a mass basis.[19] Syngas produced from slow pyrolysis of manure ranges from 40% to 77% methane[10], indicating that slow pyrolysis reactors should also incorporate gas capture for better energy resource utilization. Fast or "flash" pyrolysis at moderate temperatures (400 - 600°C) is optimized for bio-oil production and produces 50-70% bio-oil, 10-30% biochar, and 15-20% syngas[20]. Optimal syngas production takes place in fast pyrolysis gasification reactors, which operate at temperatures between 800 and 1200°C and produce virtually no biochar or bio-oil.[20] Peak temperature and ramp rate impact not only the yield of biochar, but also the qualities of char produced. Generally, slower heating

rates produce higher char yields and more physically robust char pieces, while faster pyrolysis reduces char mass yields and leads to a more brittle and crumbly char product.[21] The effects of peak temperature and biomass feedstock on biochar product properties relevant to its use as fuel will be discussed in more depth in the following sections.

2.1.1 Peak Temperature Effect on Biochar Properties

More species volatilize as peak pyrolysis temperature increases. Because of increased conversion to gas at higher peak temperatures, overall mass yields of biochar decrease with peak temperature increase.[11, 22-28]

Elemental analysis of biochars made from wood or cellulosic feedstocks at different peak temperatures generally indicate an increasing percentage of elemental carbon by mass, increasing percent ash, and decreasing hydrogen and oxygen in the char with increased peak temperatures.[23, 24, 27] Feedstocks with high initial mineral contents, such as manure, have much higher inorganic concentrations than wood or crop wastes, and as a result exhibit much higher ash contents as biochars. Partly due to increased ash concentrations, biochars made from manure exhibit decreasing relative carbon concentrations,[11, 27] as ash mass comes to dominate biochar at higher pyrolysis temperatures.

While pyrolysis of woods, nut shells, and cellulosic biomass shows trends of increasing char energy content with rising peak pyrolysis temperature,[23-26] the only published study on the effect of temperature on HHV, the energy density in MJ/kg of fuel, of manure biochar shows opposite trends.[11] Cantrell et al. showed that energy per mass of livestock and poultry manure biochars decreases with increasing pyrolysis temperature. Cantrell's study saw an increase from feedstock HHV to HHV of biochar at 350°C, but then showed biochar made at 700°C to have a

lower HHV than even the raw feedstock. The proposed explanation for this behavior was that the expulsion of lower energy value volatiles along with the rearrangement of the carbon structure at lower pyrolysis temperatures elevates the HHV, but that at higher pyrolysis temperatures, a disintegration of the carbon structure takes place, reducing the HHV. Other studies of biochars from unconventional non-cellulosic feedstocks with high ash contents show similar trends of decreasing HHV with increased pyrolysis temperature.[26]

2.1.2 Biomass Feedstock Effect on Biochar Properties

The final structural properties, elemental composition, and energy content of biochar are ultimately dependent on the initial makeup of its biomass feedstock. Important biochar properties relevant to its use as a solid fuel, such as fuel chemistry, ability to be pulverized, bulk density, energy density, and particle shape are all dependent on the biomass from which char is derived.[28] Some of the most important fuel qualities of biochar and their dependence on feedstock are shown in Table 1. The energy density or HHV of biochar depends on feedstock, as the energy content of the char is directly dependent on the original energy content and molecular structure of the feedstock material. The ash content of the fuel is crucial when evaluating its appropriate use. High ash contents in chars lead to sintering, deposition, fouling, and corrosion of furnaces and are the major obstacle for biomass combustion technologies.[29] The elemental molecular ratios O:C and H:C are important to the evaluation of a solid fuel because they are good indicators of how much CO_2, smoke, and water vapor will be produced during the fuel's combustion. Low O:C and H:C ratios are preferred for more efficient, clean combustion.[29, 30]

Table 1: Biochar fuel properties affected by feedstock type

Biochar Feedstock	Biochar Properties				References
	HHV (MJ/kg)	ASH (%)	H:C	O:C	
Wood	32-35	0.7-1.3	0.03-0.7	0.01-0.35	[26, 29, 31]
Bagasse	17	5-20	0.13-0.15	0.99-1.07	[32-34]
Manure	13.4	20-60	0.2-1.5	0.05-0.62	[11, 32, 33]
Activated sludge	4.7-7.2	40-50	0.5-1.5	11.2-12.4	[32, 33, 35]

2.2 Introduction to Briquetting

2.2.1 Agglomeration Forces

The durability and strength of a char briquette depend on the strengths of the intermolecular interactions holding the char particles together. Rumpf and Pietsch et al. classified the forces acting in tabled and briquetted materials into 5 interaction types: (1) solid bridges, (2) adhesion and cohesion forces, (3) surface tension and capillary pressure, (4) attraction forces between solids, and (5) mechanical interlocking bonds.[36, 37]
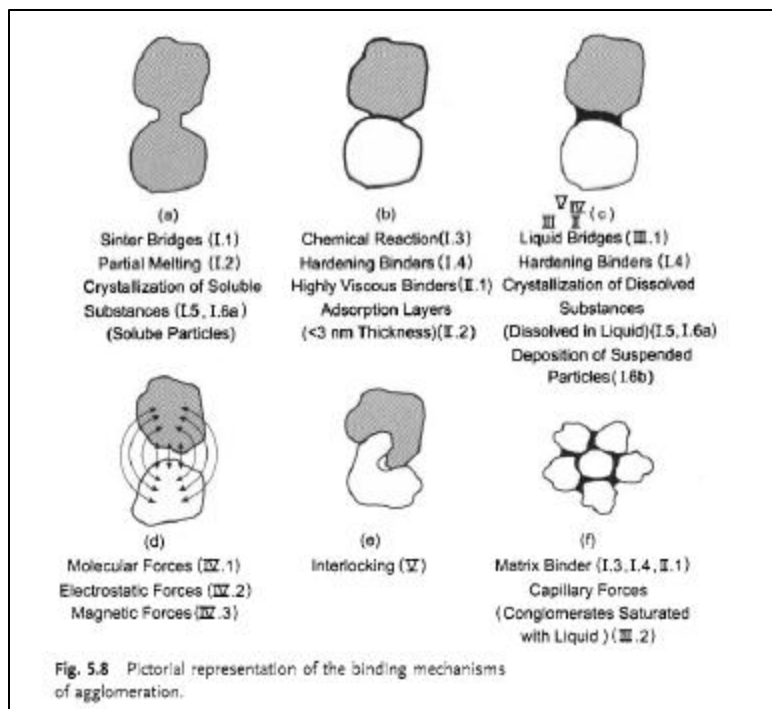
Figure 1: Representation of particle agglomeration mechanisms, courtesy of Pietsch et al.[37]

Solid bridges can form due to sintering of particles if brought close to their melting point by partial melting at roughness points due to friction or increased pressure, or due to chemical reactions or the addition of hardening binders that fill interstitial voids between particles. Crystallization of dissolved or suspended colloidal particles by evaporation of liquids can also form solid crystal bridges between particles.[37]

Adhesion and cohesion forces will dominate especially with the use of viscous binders (molasses, tar, pitch). Adhesion forces at the binder-particle interface and cohesive forces within the binder act to hold particles together. Thin adsorptive layers with a thickness less than 3nm can act to increase contact area by adding deformed, rough surfaces at particle contact points. This addition of contact area increases adhesive and cohesive force strength.[37]

Surface tension and capillary pressure are important binding mechanisms when water is used in the binding process. Liquid bridges form at coordinate points between particles, and are often the precursors to solid bridges. Liquid-filled pore volumes also act using negative capillary pressure to hold particles together in an agglomerate.[37]

Attraction between solid particles is caused by electrostatic, intermolecular, and magnetic forces. Intermolecular adhesive forces can be extremely strong at very close distances, but quickly lose strength over larger spaces between coordination points. High adhesion forces are most possible between smaller particles with low surface roughness. Van-der-Waals forces, electrostatic attraction, hydrogen bridges, and magnetic attraction all act on particles at very small distances.[37]

Interlocking bonds occur when particles twist or entangle during agglomeration. Sometimes in order to encourage better binding strength, fibrous additives are included in the particle material to facilitate this type of force. Interlocking bonds can also occur when plastic and rigid materials are mixed and pelletized at high pressures. The more elastic particles will flow around and envelope the more rigid materials.[37]

2.2.2 Binders

In cases when the interactions between particles cannot be strengthened enough by compression or heat addition alone, the addition of binders to the fuel mix is necessary to form a robust briquette. Binders can act either as bridge type additives or matrix forming additives. The bridge or film-forming binders are fluids that coat particles and form coordination points between them using bridging forces to stabilize the agglomerate. Water is a good example of a bridge type binder. Matrix forming binders fill most of the available interstitial volume between

particles and usually undergo chemical reactions or hardening processes to bind particles. Cement is a common matrix-forming binder.[37]

Common additives used to bind coal and char dust into briquettes include molasses, carboxyl methylcellulose (CMC), starch, lime, cement, heavy crude oil, clay, and polyvinyl acetate.[14] Some binders are high in energy content and add to the overall energy within a briquette, like polyvinyl acetate, heavy crude oils and tars. Starches and molasses tend to have lower energy content than the fuel particles they are holding together and can decrease the energy of a charcoal briquette. Low-to-no energy binders, like lime and cement, will add no energy at all to a briquette.[15] Waste products from some industries have also been used with some success as binders. Sawdust, brewery waste, paper mill waste,[38], cotton plant residues[39], molasses[14, 15, 17, 40], and fish waste[41] have all been used as binders for coal fine and biomass briquettes.

2.2.3 Parameters Affecting Briquette Usability

The effectiveness of a binder in creating a briquette that is strong enough to be used to cook with can be measured by evaluating several parameters. The four physical properties that have been identified as most valuable for a useable fuel briquette are the abilities to resist crushing, impact, abrasion and water penetration.[42] Other than binder configuration and concentration, briquette durability is affected by moisture content of the char, particle size of the char, briquetting pressure, and cure time.[14]

Moisture content in the feed material is important for briquette durability. Water facilitates adhesion by increasing the contact area between particles.[43] For char and coal fines, a moisture content of around 30% is optimal for briquetting.[44, 45] Water addition also aids in

the homogenous dispersion of powdered binders; however, when water content is too high, some of it is squeezed out during briquetting compression, carrying away dissolved binders and making binding less effective.[14]

Particle size has a large effect on briquette durability. Finer particles usually make a more durable briquette[44], as they are able to get closer together and form more high strength intermolecular bonds[37]. Recommended particle size for a durable pellet is between 0.5 and 0.8 mm in diameter.[44] Larger particles can act as a nucleus for fractures in a briquette.[46]

Briquetting pressure is important when the feed or binder used contains starch, protein, or lignin. Under pressure, these materials will squeeze around to envelope particles and facilitate inter-particle bonding.[44] Pressures from 1,000 psi to 80,000 psi have been successfully applied to briquette coal fines.[17] Application of high briquetting pressure is limited without mechanized industrial equipment, and much of the developing world relies upon hand presses for briquetting. The average hand press can deliver about 1400 psi of briquetting pressure.[39]

Cure time has also been found to impact briquette durability. In general, 7 days is enough for any binder to set and reach full effectiveness.[14] For a variety of binders including guar gum, wheat starch, and lignosulfonate + lime, compressive and shatter strengths of briquettes dramatically improved with age from 1 to 7 days.[14]

3 Materials and Methods

3.1 Sample Collection

Char samples tested in this research were derived from real human feces and a simulant feces developed by Wignarajah et al. [47] for NASA's human waste processing trials for use on the space station. CU received approval to collect and process real human waste for this study. Simulant feces was also tested and served as a basis for comparison with other BMGF Reinvent the Toilet teams' results. This step was necessary since many BMGF teams were not able to access or use real human fecal matter in their experiments. Real fecal matter was collected from the student population at CU Boulder and stored in a freezer for a maximum period of two weeks prior to pyrolysis. Simulant feces was produced using recipe #2 from Wignarajah et al.'s publication, shown in Table 2.

Table 2: Components of NASA #2 Simulant Feces from Wignarajah et al.[47]

Component	% dry weight	Material used
E.coli	30	Nutritional yeast*
Cellulose	15	Cotton balls
Polyethylene glycol	20	Polyethylene glycol
Psyllium	5	Psyllium
Peanut oil	20	Peanut oil
Miso	5	Miso
Inorganics	5	Calcium Phosphate**
Dried coarsely ground vegetable matter	50 mg	Did not add this component

*Nutritional yeast was selected to represent the E. coli bacterial component of simulant feces because of its relatively low cost and its similar molecular content.

**Calcium Phosphate was chosen to represent the inorganic (ash) portion of simulant feces because it is the most abundant salt in human feces.[48]

3.2 Char Manufacturing

Since the prototype solar-powered reactor was still under development at time of experiments, fecal biochar was manufactured in a simulation pyrolysis chamber (Thermo Scientific Lindberg Blue M heavy duty box furnace). Internal temperature of the feces was monitored with a thermocouple and temperature data logger to obtain reliable temperature measurements. Ramp rate was not programmed in to the oven for pyrolysis of the chars tested. Instead, the oven was set to pyrolysis temperatures of 300, 450, and 750°C and the temperature increase rates of the feces were recorded. Once fecal internal temperature reached the target temperature, the sample was held at that temperature for 2 hours. A note should be made that at the 300°C temperature point, char made from the NASA #2 simulant was pyrolyzed at a slightly lower set point than real fecal matter char. The simulant feces contained 15wt% polyethylene glycol, which auto-ignites at 305°C. Care was taken not to allow the internal temperature of the simulant char to rise above 300°C. Pyrolysis runs at 450°C and 750°C were performed by Ryan Mahoney and Tesfa Yacob, and runs at 300°C were carried out with the assistance of Barbara Ward. Biochar samples produced and tested are listed in Table 3.

Table 3: List of analysis performed on each char type

Pyrolysis Conditions	Feedstock	Analysis Performed
300°C	Human feces	Elemental analysis, Energy content, briquetting
	NASA #2 simulant	Elemental analysis, Energy content
450°C	Human feces	Elemental analysis, Energy content
	NASA #2 simulant	Elemental analysis, Energy content
750°C	Human feces	Elemental analysis, Energy content
	NASA #2 simulant	Elemental analysis, Energy content

3.3 Elemental Analysis

Elemental analysis was performed on char samples at the North Carolina State University Environmental and Agricultural Testing Service laboratory. Samples were analyzed on a 2400 CHN Elemental Analyzer (Perkin Elmer Inc., Waltham, MA). The analyzer works by combusting the sample at a high temperature under oxygen presence. The resultant gases are sent through several stages to clean the sample of unwanted gases and to convert all the forms of C to CO_2, N to NO_2 and H_2 to H_2O. The gas emissions are then mixed and sent through a separation column, which allows the different gases to come out at different times, similar to a gas chromatograph. The gases are then passed by a detector, which determines the relative amounts of gases produced. This information is then used to calculate the mass percentage of carbon, hydrogen, nitrogen, and ash in the char sample. Mass percent of oxygen is determined by subtraction. Elemental composition is reported on a dry basis.

3.4 Oxygen Bomb Calorimetry

The higher heating value of biochar was determined using a Parr oxygen bomb calorimeter and following ASTM D2015 procedures with several modifications.[49] The heat capacity of the calorimeter setup was determined using 3 replicate runs of benzoic acid calorimeter standard (Fisher Scientific) with known heat of combustion using the following equation:

$$C_p = (H_{benz}g + e)/\Delta T$$

Where C_p is the heat capacity of the calorimeter system, H_{benz} is heat of combustion of benzoic acid (6318 cal/g), g is the mass of the benzoic acid sample, e is the correction for combustion of the fuse wire, and ΔT is the temperature rise in the calorimeter.

Biochar was combusted in the oxygen bomb calorimeter using 0.7-1.0g pellets and a bomb pressurized with 30 atm oxygen and 1mL of DI water inside the bomb to ensure that water vapor emitted during combustion did not condense. Two liters (2L) of DI water were added to the calorimeter boss for each run. Higher heating values of biochar, binders, and biochar-binder combinations were determined using the experimentally determined C_p with the following equation:

$$HHV = (C_p \Delta T - e)/g$$

Where HHV is the higher heating value of the sample, ΔT is the temperature rise in the calorimeter, e is the correction for the combustion of the fuse wire, and g is the mass of the biochar or binder sample.

Fecal biochar samples pyrolyzed at 300°C, 450°C, and 750°C, simulant biochar samples pyrolyzed at 300°C and 750°C, and molasses and lime binders were tested to determine energy content. Three replicate calorimeter runs were performed for each char and binder sample, and an average value with standard error is reported here. In the cases of high, medium, and low temperature fecal biochar and high temperature simulant char, molasses and lime binders were needed to facilitate the formation of a stable pellet. In the case where binders were necessary to make the pellets, the following equation was used to determine absolute higher heating value of the char (without added binder):

$$HHV_{char} = (HHV_{sample} - x_{molasses}HHV_{molasses})/x_{char}$$

Where HHV_{char} is the gross calorific value of the biochar, HHV_{sample} is the gross calorific value of the biochar pellet bound with molasses and lime, $x_{molasses}$ is the weight fraction of molasses in

the pellet, $HHV_{molasses}$ is the gross calorific value of molasses, and x_{char} is the weight fraction of char in the pellet.

3.5 Calculating LHV

Lower heating value (LHV) is similar to HHV in that it is a measure of energy density of a fuel (measured in MJ/kg fuel). HHV calculations assume that the latent heat of vaporization of water in the fuel is not lost by the formation of steam, but is recovered by the return of the steam to liquid water form. Although this makes HHV easier to calculate in a calorimeter where all moisture within the fuel stays in liquid form, during combustion in a cooking scenario energy lost from the vaporization of water in fuel is not recovered within the duration of cooking. LHV takes into account the latent heat of vaporization of moisture in the fuel, and subtracts it from the total HHV to estimate a heating value that more closely approximates the energy the char briquettes will actually deliver when combusted as fuel. Latent heat of vaporization for each sample was calculated by determining the moisture content of the sample using ASTM D2961[50]. This method involved weighing char samples at room temperature, then heating the samples in a clamshell furnace to 107°C for 1.5 hours, and then taking their weights every 30 minutes until weights recorded after two consecutive measurements were consistent to 0.05% of the original mass of the sample. Once moisture content was determined, the % moisture in a mass of sample was multiplied by the latent heat of water (2.257 MJ/kg water) to determine the total amount of energy per mass of fuel lost to vaporization of water.

$$latent\ ht\ vap\ sample\ \left(\frac{MJ}{kg}\right) = \%\ moisture\ sample \cdot 2.257\left(\frac{MJ}{kg\ water}\right)$$

Once the latent heat of vaporization of the sample was determined, it was subtracted from the experimentally determined HHV to calculate LHV.

$$LHV\left(\frac{MJ}{kg}\right) = HHV\left(\frac{MJ}{kg}\right) - latent\ ht\ vap\ sample\left(\frac{MJ}{kg}\right)$$

HHV is preferentially used as a benchmark for the energy content of solid fuels in most of the literature cited in this thesis [10, 11, 51, 52], so results will be given in terms of HHV; however, LHV of the chars will also be addressed in Section 4.2.4.1.

3.6 Briquetting

Biochar briquettes were manufactured using a 1.25 inch diameter stainless steel die and a Carver Model C pneumatic laboratory press. Briquettes were about 3 inches in height, and contained about 15g of char or a char-binder combination, and had a briquette volume of 3.7 cubic inches.

Several different binders were tested. Starch and a molasses + lime combination were selected as potential binders based on their likely availability in many parts of the developing world.[17] Table 4 shows the types of binders and the weight ratios tested in this study.

Table 4: Binder ratios tests for briquetting char

Binder Type	Binder Ratio (by weight)
Starch	5% corn starch, 150°C
	3% corn starch, 7% wheat starch, 350°C
Molasses and Lime	10% and 3.5%
	20% and 7%

The molasses + lime binding process is simpler than starch binding, as it requires no heating of the briquette or briquetting material. In both cases, char was first finely ground with

mortar and pestle to obtain a smaller and more uniform particle size. For binding with molasses + lime, lime and char were thoroughly dry mixed together in a large mixing bowl followed by the addition of molasses. After mixing for approximately 5 minutes, briquettes were made with a die and press and set aside to cure. For briquetting with starch, the procedure from Henley et al. was adapted for bench-scale use.[53] Corn starch and wheat starch were first dry mixed with char powder, then water was added slowly to the mixture at a ratio of 6:1 water to binder weight. The paste was mixed until homogeneous and then briquetted in press. Briquettes were subsequently heated in an oxygen limited clamshell oven in order to break down the starch binders and encourage bonds to form in a process called calcination. Briquettes were held at a temperature of 150°C for 15 hours and then ramped up to hold at 350°C for 2 hours. The 5% cornstarch bound briquettes followed the same procedure as the starch-bound briquettes, except the calcination period was excluded. Cornstarch briquettes were heated in a clamshell oven at 115°C for 15 hours to drive off water but then were ramped back to room temperature and allowed to cool.

In order to simulate briquetting pressures likely achieved by hand presses used in much of the developing world, a pressure of 1400 psi was applied to the die, based on estimates from Coates et al. which assigns 1400 psi as the average pressure applied by a hand operated briquette press.[39]

3.7 Briquette Durability Testing

Briquette durability for several different binders and binder-char ratios was determined using standardized briquette strength tests proposed by Taulbee et al. and Richards.[14, 42] Shatter strength and compressive strength tests were performed after briquettes were allowed to cure for 4 days. Shatter strength was measured by repeatedly dropping briquettes from a height

of 2 feet onto an epoxy resin laboratory countertop. The number of repeated drops until the briquette broke apart was recorded, as well as the number of pieces generated during the test. The Impact Resistance Index (IRI) was calculated via Richards' methods:

$$IRI = \frac{100 * Average\ number\ of\ drops}{Average\ number\ of\ pieces}$$

Four repeat tests were performed for each briquette configuration to calculate IRI.

The compressive strength of the briquettes was tested using methods adapted from Taulbee et al.[14] and Richards.[42] To measure compressive strength, a briquette was placed between two plastic disks on the pneumatic laboratory press and pressure was applied until the briquette fractured or crumbled. The following equation from Richards was used to calculate compressive stress limit:

$$Stress = \frac{load\ at\ fracture}{cross\ sectional\ area\ of\ plane\ of\ fracture}$$

Four repeat tests were performed for each briquette configuration to calculate average compressive strength.

3.8 Statistical Analysis

Mean values of HHV and briquette strength metrics were calculated based on all trials performed. Three replicate runs for each calorimeter sample and four replicate trials for each briquette strength test were performed. Standard error of the mean for HHV measurements and

briquette strength testing trials was calculated with a 95% confidence interval using the following equation:

$$SE_{\bar{x}} = \frac{s}{\sqrt{n}}$$

Where $SE_{\bar{x}}$ is the standard error of the mean, s is the standard deviation of the sample, and n is the number of replicate trials performed. The standard deviation of the sample was calculated using the Microsoft Excel function *stdev.s*.

The student's t-test was used to determine standard error at a 95% confidence interval using the following equation:

$$\mu_0 = \bar{x} \pm (t * SE_{\bar{x}})$$

Where μ_0 is the true value that the data is approximating, $\bar{x}$ is the mean value of the data set, and t is the t value of the data set at 95% confidence interval. The t value was calculated using the Microsoft Excel function *T.INV.2T(probability, sample size)*.

In the case of calculation of briquette Impact Resistance Index (IRI), standard error within a 95% confidence limit was calculated for 'number of drops until fracture' and for 'number of pieces generated', and the following equation was used to determine the cumulative propagation of error in the IRI:

$$\frac{SE_{IRI}}{IRI} = \frac{SE_{avg \# drops}}{avg \# drops} + \frac{SE_{avg \# pieces}}{avg \# pieces}$$

Where SE_{IRI} is the standard error of the IRI value, $SE_{avg \# drops}$ is the standard error calculated for the average number of drops until fracture, and $SE_{avg \# pieces}$ is the standard error of the average number of pieces generated when the briquette was dropped.

4 Results and Discussion

4.1 Energy Content

The following sections contain comparisons of energy content and elemental composition of fecal and simulant char and determinations of best pyrolysis temperatures for maximum energy content. Experimental HHV data was fit to a published model for verification, and suggested improvements to the model are presented for predicting HHVs of fecal chars.

4.1.1 Effect of Pyrolysis Temperature on HHV of Char

Table 5 shows measured HHVs and elemental composition for human fecal chars, simulant chars, and molasses binder with a comparison to raw human feces and raw simulant feces HHV. Char produced from low temperature pyrolysis of human feces was found to have a higher HHV than char produced at high temperatures. Human fecal char pyrolyzed at 300°C for 2 hours was almost twice as high in energy content as fecal char pyrolyzed at 750°C for the same duration (Figure 2). This trend was also followed by the NASA #2 simulant char, which had a 1.5 times higher energy content when treated with 300°C pyrolysis conditions compared to 750°C settings.

Table 5: HHVs and elemental analysis of fecal and simulant chars, HHVs of binder and raw feces. Elemental composition is reported on a dry basis. Error presented for the HHV is within a 95% confidence interval of the mean. Elemental analysis was not performed on molasses or either of the raw fecal feedstocks.

Char Type		% ASH	%C	%H	%N	%O	HHV (MJ/kg)
Feedstock	Pyrolysis Temp (°C)						
Human Feces	300	20.0	58.23	6.10	5.19	10.47	25.57 ± 0.08
Human Feces	450	37.1	50.67	1.90	4.76	5.56	17.91 ± 0.40

Human Feces	750	50.0	42.03	0.44	2.44	5.09	13.83 ± 0.48
Simulant Feces	300	8.3	64.05	7.48	3.10	17.06	29.53 ± 0.75
Simulant Feces	450	20.0	57.67	1.91	5.25	15.17	--
Simulant Feces	750	38.3	56.17	0.38	2.72	2.43	18.92 ± 1.30
Molasses Binder	--	--	--	--	--	--	12.92 ± 0.11
Human Feces, pre-pyrolysis	--	--	--	--	--	--	19.21 – 19.65[54]
Simulant Feces, Pre-pyrolysis	--	--	--	--	--	--	18.8[55]
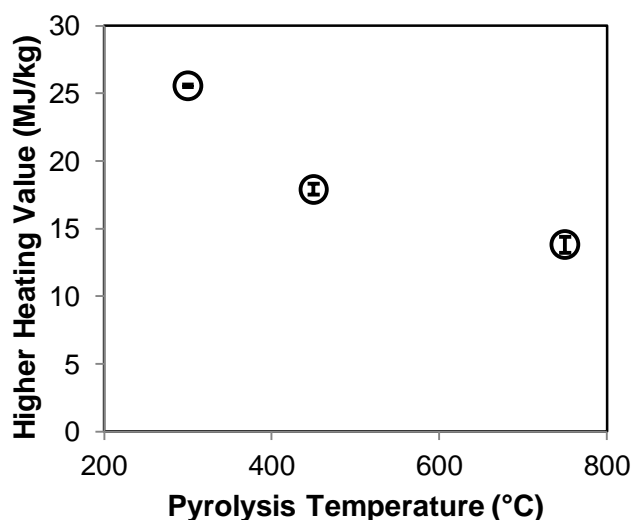
Figure 2: Effect of pyrolysis temperature on HHV of fecal biochar – significant decrease in energy content of biochar as temperature increases. Error bars indicate standard error at a 95% confidence interval.

Decreasing HHV with increased pyrolysis temperature is a trend that is rarely observed with biochar production from conventional feedstocks. Only in the cases of non-cellulosic, high ash content feedstocks e.g. animal manure[11] and algae[26] has HHV of biochar been shown to decrease with increasing pyrolysis temperature. Pyrolysis of wood and other cellulosic biomass usually produces higher energy biochars with increasing pyrolysis temperatures.[23-26, 56]

Figure 3 shows the energy content versus pyrolysis temperature for two different feedstocks: human fecal char and hazelnut shell char (nut shell char data courtesy of Demirbas et al. 2010).[24]
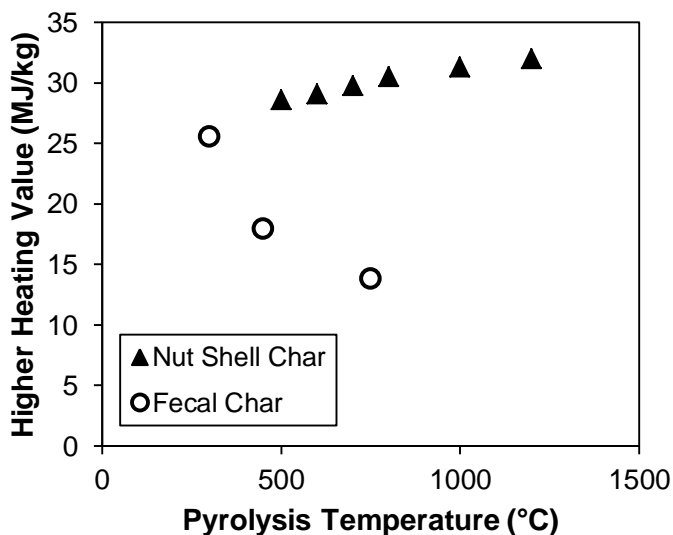
Figure 3: Comparison of trends in HHV for fecal char and hazelnut shell char

4.1.1.1 Explanation of Trend

It is likely that decreasing HHV with increasing temperature is due to the degradation and volatilization of energy-rich mobile aliphatic hydrocarbons as pyrolysis temperatures increase from 300 to 750°C. In most traditional biochar pyrolysis studies, the %C is shown to increase with pyrolysis temperature[23-25, 56] as more volatile compounds are driven off and the remaining lignocellulosic carbon arranges into stable aromatic graphene structures. Because feces is primarily composed of carbohydrates, proteins, and lipids instead of cellulose or lignin[57], it does not form stable, highly aromatic biochar as readily. A much higher percentage of the carbon in feces-derived biochar is in the form of aliphatic hydrocarbons compared to wood

biochar[57, 58]. The alkanes present in fecal biochar are more energy-rich[59], but also less thermally stable than aromatic compounds. The upper thermal stability limit for molecules containing long-chain alkyl groups is 349°C.[60], whereas aromatic carbon remains stable, with only slight deformation in graphene sheets at temperatures upwards of 2000°C [61]. This degradation and volatilization of high-energy aliphatic hydrocarbons in fecal biochar is likely the largest contributing factor in the decrease in char energy content with increased pyrolysis temperature.

It has been suggested that high ash content also contributes to the decrease in HHV with higher pyrolysis temperatures for feedstocks with large quantities of inorganic material[26]. Unlike wood chars, which are usually less than 4% ash[33], fecal char ash content ranges from 20 to 50%, with ash percentage increasing with pyrolysis temperature. Ash % increases as volatile matter is driven off because its non-reactive and incombustible nature allows it to remain in the final biochar product. For human fecal char, however, energy content decreases with increased pyrolysis temperature *even* on an ash-free basis, as shown in Figure 4. While the removal of ash decreases the magnitude of HHV loss at higher pyrolysis temperatures, HHV still maintains its downward trend with increasing temperature, indicating that another mechanism, most likely degradation of energy-rich aliphatic compounds mentioned previously, is responsible for the trend.
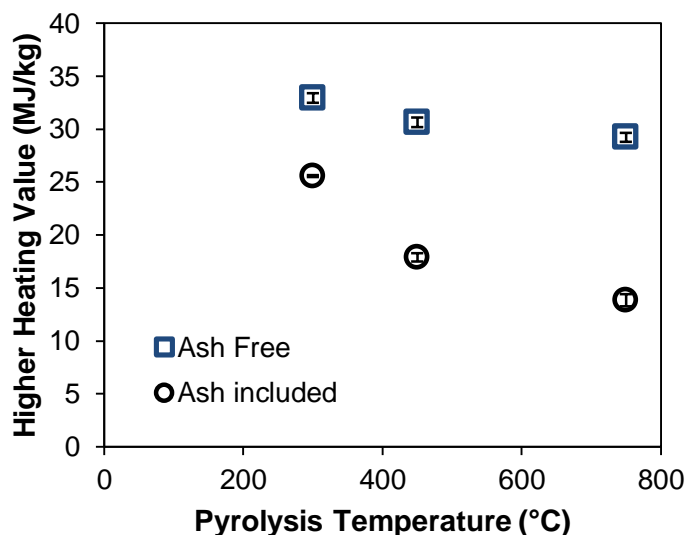
Figure 4: Trend of decreasing HHV with increasing pyrolysis temperature still exhibited even when inorganic ash portion of biochar is not included. Ash free HHV calculated using Channiwala et al. elemental correlation.[33] Error bars for ash-included HHVs represent 95% confidence interval for standard error of experimental results, error bars for ash-free HHVs represent the average absolute error in the Channiwala model ($\pm$1.45%).

4.1.2 Comparison of Simulant and Fecal Chars

Char made from NASA #2 simulant feces was higher in energy content than fecal char at high and low pyrolysis temperatures (Figure 5). These results are of interest to the Bill & Melinda Gates Foundation Reinventing the Toilet Challenge teams, as many collaborating groups do not have access or approval to use human fecal matter, and must instead substitute NASA simulant feces for testing. Results from this study suggest that NASA #2 simulant feces may not be ideal as a model for the energy content of human fecal char. At 300°C, the simulant char was 29.3 MJ/kg, 4 MJ/kg higher in energy content than fecal char, and at 750°C simulant char was 18.9 MJ/kg, 5 MJ/kg higher in energy than fecal char.
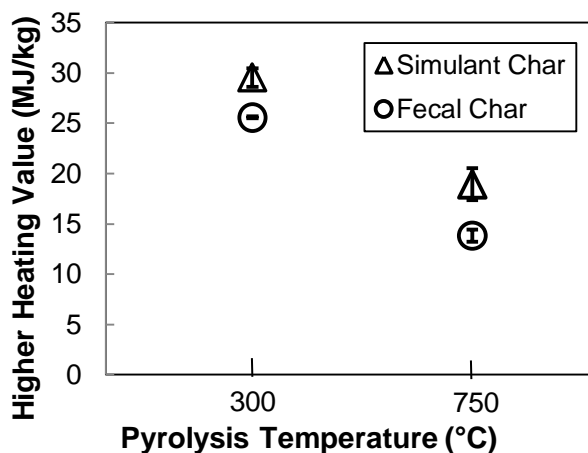
Figure 5: Comparison of HHVs of NASA #2 simulant char and fecal char at high and low pyrolysis temperatures. Simulant char has a significantly larger HHV at both temperatures.

Simulant and real feces start with similar calorific values before charring; estimated HHV of raw NASA simulant is 18.8 MJ/kg[55], while human feces has been measured at 19.4 MJ/kg[54]. This initial similarity in energy content suggests that the difference in HHV is not due to innate differences in energy contained in the raw feedstocks. More likely, the difference in energy content between simulant char and fecal char is due to the difference in % ash of the chars. Feces contains about 18% ash before charring[57], while the NASA simulant recipe calls for only 5 dry% inorganics, contributing to an inaccurately low inorganic mineral composition in the resulting char. Figure 6 shows the differences in % ash between simulant char and fecal char over the range of pyrolysis temperatures investigated here.
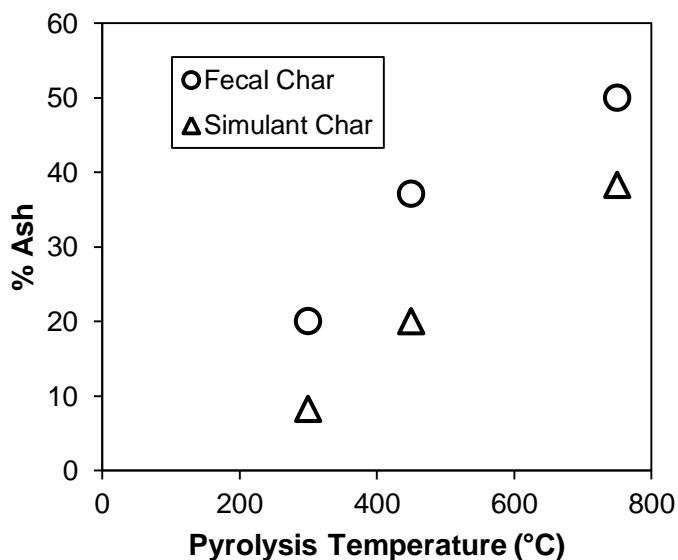
Figure 6: Comparison of % ash in fecal char and simulant char over the range of pyrolysis temperatures tested

Follow-up experiments could be performed to develop a correlation between HHVs of simulant chars and real fecal chars for varied pyrolysis settings to enable the accurate comparison of energy contents. Simulant and feces should be pyrolyzed at 600°C and 900°C, and a simulant pyrolysis run should be performed for 450°C. HHV of the resulting chars should be determined and plotted with existing data to figure out whether there is a consistent correlation between simulant and fecal char energy values over a range of pyrolysis temperatures. The resulting correlation could aid researchers with limited access to real human feces.

In lieu of developing a correlation between pyrolysis behavior of real and simulant chars, a new formulation of simulant feces could be developed to better model the energy content in fecal char. As previously discussed, NASA #2 simulant feces has a significantly lower initial inorganic content than human feces. The amount of calcium phosphate added to the dry simulant

mix should be increased from 5% to 18%, the ash content of human feces measured here and that of animal feces reported elsewhere [57], to determine whether the HHV of the revised simulant char would more closely represent the energy within real fecal chars.

4.1.3 Comparison to Conventional Solid Fuels

Fecal char pyrolyzed at 750°C in this study contained 13.8 MJ/kg energy, which slightly lower than the energy content of low-rank lignite coal, wood, and swine manure biochar pyrolyzed at 700°C.[10, 11] At this low energy content, the char is still comparable to other common solid fuels. High-energy binders could potentially be used to supplement the energy content of a char briquette.

Figure 7 offers a visual comparison of published higher heating values of common solid fuels and illustrates how fecal char energy values compare. Fecal char pyrolyzed at 300°C has a higher heating value of 25.6 MJ/kg, which is comparable in energy content to bituminous coal and wood charcoal.[51, 52] This HHV is quite favorable, and allows for flexibility in briquette manufacturing, such as adding a lower-energy binder for durability. The next section discusses in more depth the necessity of using binders in the manufacture of biochar briquettes. It is important to note, however, that in cases where the binder material has a lower energy content than the char, the addition of the binder will decrease the overall heating value of the briquette. Charcoal briquettes sold commercially should have an HHV of at least 22 MJ/kg as stipulated by the Food and Agriculture Organization of the United Nations (FAO) [62] which is significantly lower than the energy of unbound fecal char. Using this commercial energy content as a benchmark, as much as 10% of a completely incombustible, low-energy binder could be added to make a 300°C char briquette without falling below the acceptable standard briquette energy value.
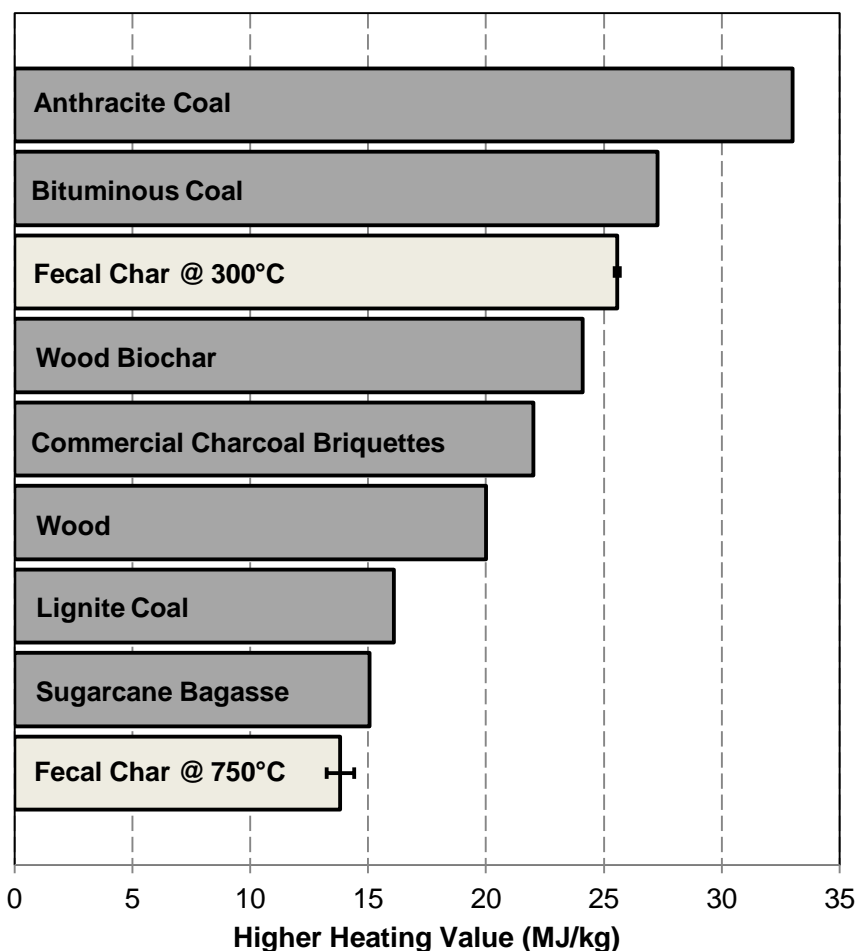
Figure 7: Comparison of HHVs of common solid fuels with fecal char HHVs – at an HHV of 25.6 MJ/kg, fecal char pyrolyzed at 300°C is comparable in energy content to wood biochar and bituminous coal. HHVs of common solid fuels are sourced from the literature as follows: Anthracite and Lignite Coals [10], Bituminous Coal and Sugarcane Bagasse [52], Wood Biochar and Wood [51], Commercial Charcoal Briquettes [42].

4.1.3.1 H:C and O:C Ratios

Briquettes with low H:C and O:C ratios produce less CO_2, water vapor, and smoke when burned, leading to higher combustion efficiency.[28, 30] For biochars of cellulosic origin, H:C and O:C ratios tend to decrease with increased pyrolysis temperature as carbon in the char transitions from aliphatic hydrocarbons into aromatic elemental carbon structures.[28, 30] Wood

chars typically have O:C ratios ranging from 0.01 - 0.35 and H:C ratios from 0.03 to 0.7[28, 31] and coals tend to have O:C ratios of 0.01-0.25 and H:C ratios of 0.4 – 1.0.[63]

Table 6 shows the O:C and H:C ratios for fecal and simulant chars and Figure 8 shows a relationship between these elemental ratios and pyrolysis temperature compared to wood char data. Chars made in the pyrolysis reactor in this study ranged from O:C ratios of 0.09-0.13 (within the range of coals and wood chars), and had H:C ratios of 0.13-1.26 (a much broader span than typical H:C ratios for efficient-burning solid fuels). Simulant chars had measured O:C ratios ranging from 0.03-0.20 and H:C ratios from 0.08-1.40. As with fecal chars, the O:C ratio of the char made from simulant falls within the reported range of coals and wood chars, but the upper range of the measured H:C values are higher than those typically measured for efficient solid fuels. Chars made from human feces and simulant feces showed trends similar to wood chars in that H:C ratios decreased with increased pyrolysis temperature; however, the trends in O:C ratios were not similar to trends seen for other biochars.

Table 6: Elemental molar ratios for fecal and simulant chars over the range of pyrolysis temperatures used in this study

Feedstock	Pyrolysis Temp (°C)	O:C molar	H:C molar
Human Feces	350	0.13	1.26
	450	0.08	0.45
	750	0.09	0.13
NASA #2 Simulant	350	0.20	1.40
	450	0.20	0.40
	750	0.03	0.08
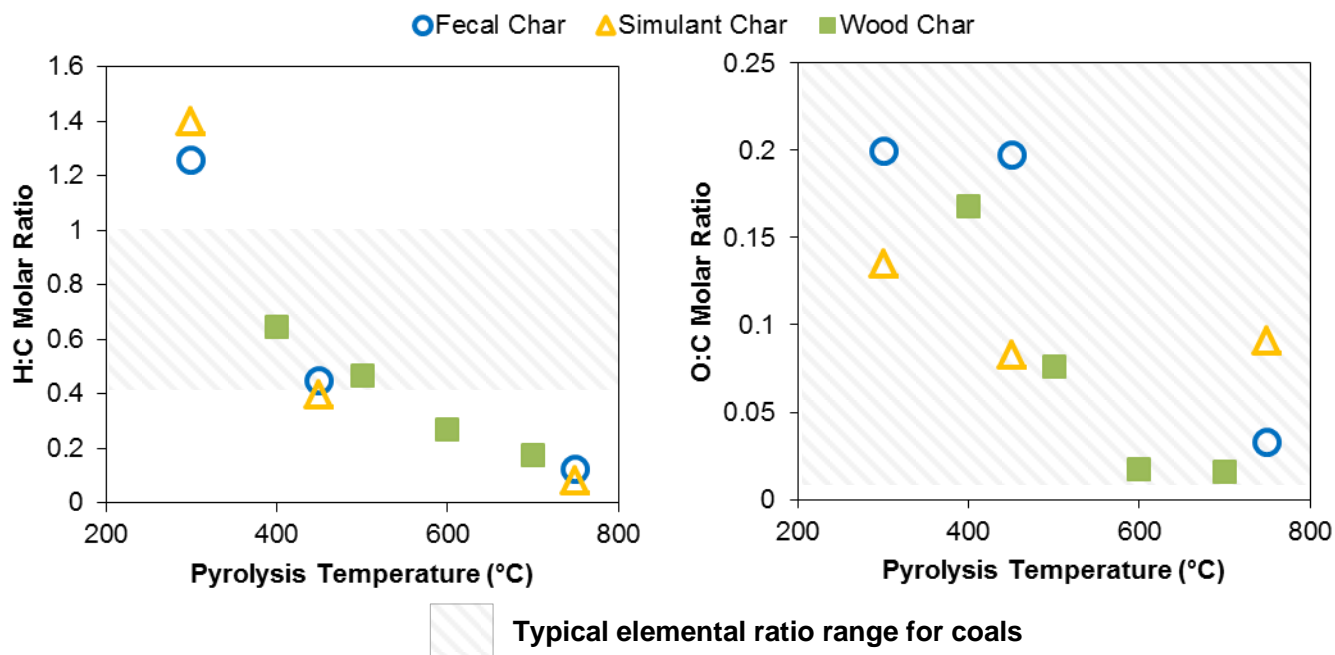
Figure 8: Trends in elemental ratios H:C and O:C over range of pyrolysis temperatures for fecal char and simulant char compared to typical wood char data [31] and typical elemental ratios for coals [53]. H:C ratios for fecal char, simulant char, and wood char follow similar trends with pyrolysis temperature, although only chars made at medium temperature ranges (between 350 and 500°C) fall within the H:C ratio of coals. O:C ratios for all three chars appear to follow different trends with pyrolysis temperature, although all fall within the acceptable elemental ratio of standard coals.

4.1.4 Verification of Empirical Model

The results of the elemental and calorimetry analyses performed on char samples were used to verify the accuracy of a published model that correlates HHV to elemental composition of biofuels. Channiwala et al's correlation has been highly tested and refined and is often used as a substitute for experimental calorimetry analysis. It allows for the accurate determination of HHV from elemental analysis results, which report mass percentages of carbon, hydrogen, oxygen, nitrogen, and ash in the fuel[33, 34, 56]. The Channiwala model was derived and validated using elemental analysis and HHV data for 275 chars, coals, biomass materials, bio-oils, and fuel gases, and the unified correlation is shown here [33]:

$$HHV\ (MJ/kg) = 0.3491C + 1.1783H + 0.1005S - 0.1034O - 0.0151N - 0.0211ASH$$

Where HHV is the higher heating value of the fuel, C is the % dry mass of carbon in the sample, H is the % dry mass of hydrogen in the sample, S is the % dry mass sulfur in the sample, O is the % dry mass oxygen in the sample, N is the % dry mass nitrogen in the sample, and ASH is the % dry mass ash in the sample.

When elemental composition data for fecal and simulant char was substituted into the Channiwala model, the predicted HHVs were well within the standard error of the experimentally measured HHVs. Figure 9 shows the predicted HHVs from the Channiwala model and the HHVs determined in this study. There is a close agreement at the 95% confidence level between predicted and empirically determined HHVs. Figure 10 shows a close linear correlation between the measured HHVs and those predicted by the model.
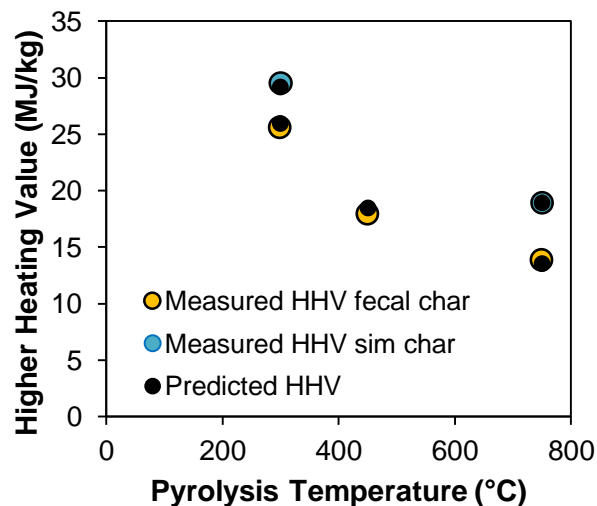
Figure 9: Comparison of HHV prediction from Channiwala et al.[33] based on elemental analysis data and experimentally determined HHVs of simulant and fecal char
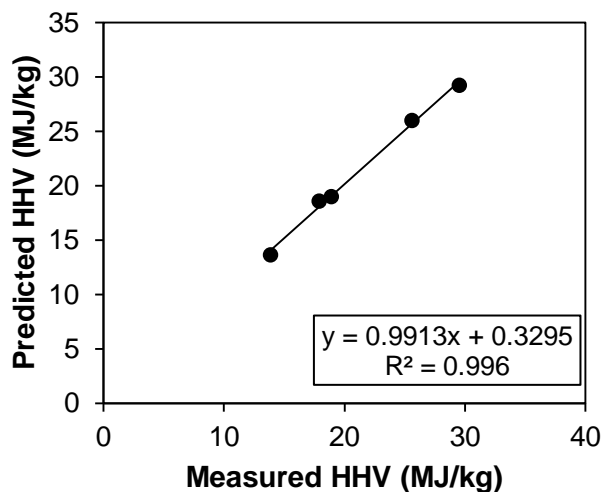
Figure 10: Linear correlation between HHV predicted by elemental data using Channiwala model and experimental HHV

4.1.5 Application of Correlation to Fecal Chars from Literature

Although the Channiwala correlation for predicting HHV appeared to fit well for human fecal char and NASA #2 simulant fecal char, it only employed one feces-derived char in its calculations. It was hypothesized that the model could be improved by using data from chars derived from human feces, animal manure, and sewage sludge. To test this hypothesis, an additional exercise was performed. Elemental content and HHVs of bovine, swine, poultry, and turkey manure chars [11, 64] was gathered from the published literature along with data characterizing sewage sludge chars manufactured via microwave and electric furnace pyrolysis[13, 35], as shown in Table 7.

Table 7: Experimentally determined HHV and elemental analysis data (dry basis) for fecal chars and manure-derived chars, gathered from in-house experiments and the literature.

Char Type	Pyrolysis Temp (°C)	Exper. HHV (MJ/kg)	ASH	C	H	N	S	O	Data Source
Human Fecal Char	300	25.57	20.00	58.23	6.10	5.19	0.06*	10.41	OUR DATA
	450	17.906	37.10	50.67	1.90	4.76	0.06*	5.50	
	750	13.83	50.00	42.03	0.44	2.44	0.06*	5.03	
NASA #2 Simulant Char	300	29.53	8.30	64.05	7.48	3.10	0.06*	17.00	
	750	18.92	38.30	56.17	0.38	2.72	0.06*	2.37	
Dairy Char	350	20.9	24.2	55.8	2.29	2.6	0.11	18.73	[11]
	700	18.97	39.5	56.67	0.94	1.51	0.15	4.13	
Paved-feedlot Char	350	20.39	28.7	53.32	4.05	3.64	0.45	15.7	
	700	17.23	44	52.41	0.91	1.7	0.4	7.2	
Poultry Litter Char	350	19.03	30.7	51.07	3.79	4.45	0.61	15.63	
	700	14.75	46.2	45.91	1.98	2.07	0.63	10.53	
Swine Solids Char	350	21.12	32.5	51.51	4.91	3.54	0.8	11.1	
	700	15.07	52.9	44.06	0.74	2.61	0.85	4.03	
Turkey Litter Char	350	17.28	34.8	49.28	3.6	4.07	0.55	15.4	
	700	14.45	49.9	44.77	0.91	1.94	0.41	5.8	
Animal Waste Char	--	13.4	23.5	35.1	5.3	2.5	0.4	38.7	[64]
Sludge-Manure Mix Char	550	17.14	23.04	40.49	5.46	5.11	0.75	24.77	[13]
Sewage Sludge Char	1040	5.58	82.5	16.17	0.40	0.61	0.33	0.00	[35]
	1040	7.22	74.6	21.31	0.00	1.19	0.41	2.49	
	1040	6.71	78.5	19.78	0.00	0.75	0.43	0.54	
	1040	5.84	83.5	15.64	0.00	0.43	0.43	0.00	
	1040	6.21	80.00	17.62	0.62	0.92	0.40	0.44	

*Wt. % sulfur was not measured by elemental analysis performed at NCSU. %S and additive %O values for human fecal char and NASA #2 simulant char have been adjusted based on literature values for sulfur content of NASA simulant feces [55] and literature demonstrating little change in %S of feces before and after charring[11].

Figure11 shows a comparison of experimental HHVs from the literature and HHVs predicted by

the Channiwala elemental correlation applied to the elemental analysis values from the literature.

The linear regression of the data has been set to a y-intercept of zero in order to graphically show

how close of a 1:1 correlation exists between the Channiwala predicted HHVs and experimentally determined HHVs from the literature. While Channiwala et al. reports a 3% average absolute error and 0% average bias error in its modeling of all fuels, and a 0.951% absolute error and 0.08% bias error in its modeling of chars alone (including wood chars, biomass chars, municipal solid waste chars, and one animal manure char), the use of the Channiwala correlation with exclusively feces/manure-derived chars generates a higher average absolute error of 6.5% and the same bias error of 0.08%. Especially for very low energy chars made from sewage sludge, the Channiwala model is shown to underestimate the HHV.
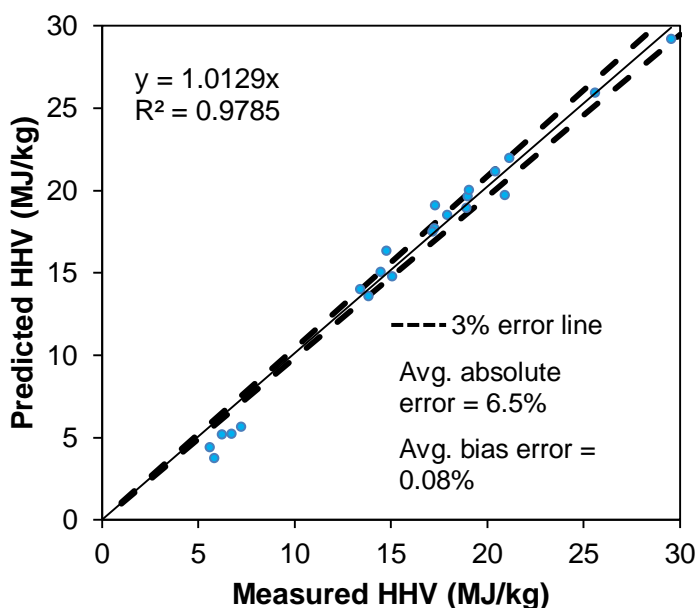
Figure 11: Linear correlation between experimentally determined HHVs of fecal/manure-derived chars from the literature and Channiwala elemental composition model. Channiwala model does not correlate as closely with fecal chars as with other char types, especially for lower energy chars. A 3% error line is shown in order for best visual comparison to Channiwala et al. graphs, which use 3% error lines as benchmarks.

Since the Channiwala et al. elemental correlation did not perform as well as expected with a data set of fecal chars, a least squares regression was performed to determine whether another model

could be found that would better correlate HHV and elemental composition in fecal biochars. Based on the data from the literature, a new correlation was developed:

$$\boldsymbol{HHV}\ (MJ/kg) = 0.3328\boldsymbol{C} + 1.3309\boldsymbol{H} - 1.4187\boldsymbol{S} - 0.1035\boldsymbol{O} - 0.1629\boldsymbol{N} - 0.0077\boldsymbol{ASH}$$

Shown in Figure 12, the revised elemental correlation reduced the average absolute error in the correlation by about half of the Channiwala model error to 4.18%, and reduced the average bias error by about half of the Channiwala model error to -0.04%.
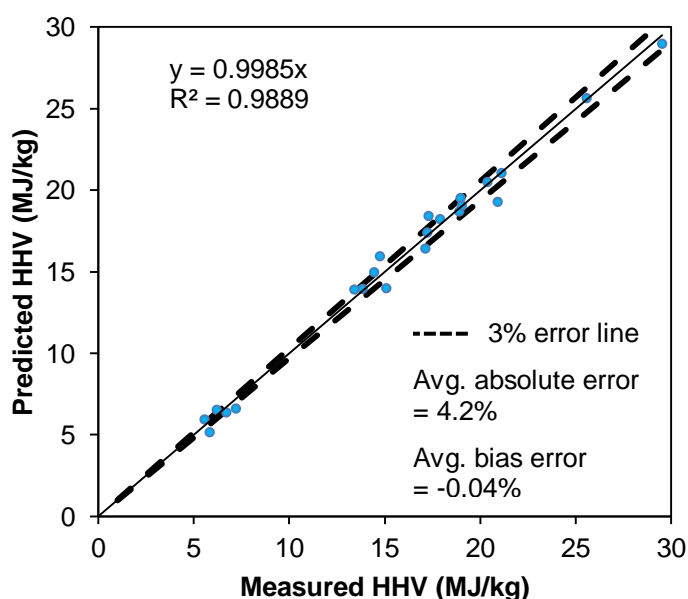
Figure 12: Linear correlation between experimentally determined HHVs of fecal/manure-derived chars from the literature and improved elemental composition model. Note improvements to Channiwala model fit in the lower HHV region.

Consistent with both correlations are the dominant effects of hydrogen and carbon in predicting the HHV of a char. Hydrogen composition has the strongest positive correlation with HHV, followed by carbon content. A significant difference between the two models is that Channiwala et al. shows a slight positive correlation between fuel sulfur content and HHV, whereas the improved model shows a very strong negative correlation between percent sulfur and HHV.

Further research on the topic of feces and manure-derived biochars is recommended, which can yield data needed to improve this model.

4.2 Briquettes

The briquette durability and energy content was assessed for different binders and binder configurations. The compressive strength of most briquette formulations was found to be adequately high, while high amounts of molasses + lime binders showed the best resistance to impact.

4.2.1 Shatter resistance

Shatter resistance, the resistance of a briquette to impact, was tested for starch and molasses + lime binder configurations. Cornstarch binder cured at low temperature was the least effective binder, and briquettes crumbled at touch after drying for 15 hours. Starch binder cured at high temperature produced much stronger briquettes, likely because starch was taken to a temperature high enough to allow it to calcinate and secure interparticle bonds within the briquette. A binder of 20% molasses + 7% lime proved to be the most effective binder at promoting shatter resistance, as shown in Table 8. A large variability in Impact Resistance Index (IRI) was determined for all binder configurations. Other shatter resistance testing in the published literature report standard deviations of 40% for IRI values.[42] Once fecal sample collection and charring efficiency has been improved, larger amounts of char will be available for more replicate briquette strength tests. More replicates of these tests for each binder configuration will reduce the size of the error bars considerably.

Table 8: Impact Resistance Index for briquettes made with different binder configurations

Briquette Binder	Number of Drops	Number of Pieces	IRI
Corn starch with 115°C temp treatment	1	>100	< 1
Wheat and corn starch with 350°C temp treatment	2.75 ± 1.15	3.50 ± 0.69	79 ± 48
10% Molasses + 3.5% Lime	3.75 ±2.05	3.00 ± 0.98	125 ± 109
20% Molasses + 7% Lime	21.67 ± 2.70	3.00 ± 1.30	722 ± 403

An IRI of 50 is considered the lowest acceptable limit of briquette shatter resistance for industrial applications.[41] Figure 13 shows that although mean IRI values for starch with high temperature treatment (10% molasses + 3.5% lime, and 20% molasses + 7% lime) all fall above 50, 20% molasses + 7% lime is the only binder configuration that produces a briquette with a statistically significant IRI greater than 50.
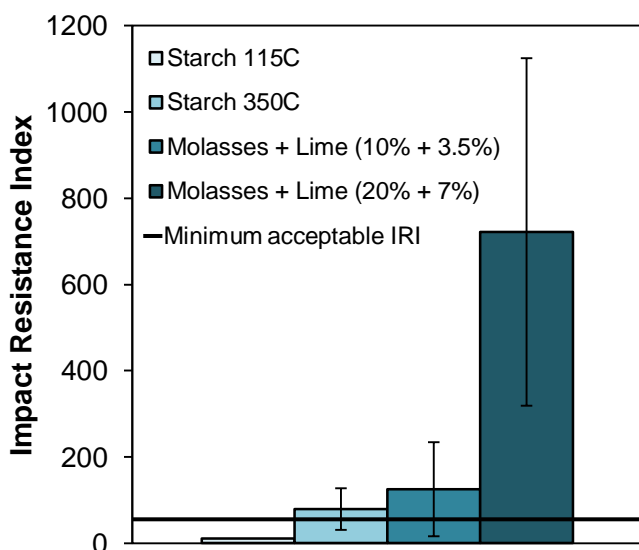
Figure 13: Impact Resistance Index (IRI) for different binder configurations with minimum acceptable IRI of 50 indicated by black line

4.2.2 Compressive strength

While fecal char briquettes proved fairly brittle at most binder configurations when tested for impact resistance, the majority of binder configurations tested yielded briquettes with very high compressive strengths. The upper limit of the pneumatic hand press used to measure compressive strength was 20,000 lb$_f$. All briquettes except for those made with low temperature starch configuration remained unfractured at the upper limit of the press, as shown in Table 9. The minimum compressive strength of a commercial charcoal briquette is 375 kPa[42], which both molasses + lime configurations and the high temperature starch configuration easily exceed.

Table 9: Critical compressive stresses for briquettes made with different binder configurations

Briquette Binder	Critical Compressive Stress (kPa)
Starch with 115°C temp treatment	~0*
Starch with 350°C temp treatment	> 110,000
10% Molasses + 3.5% Lime	> 110,000
20% Molasses + 7% Lime	> 110,000

* Briquettes crumbled to rubble at slightest pressure

The performance of the low-temperature starch was the weakest binding method employed. Since starch binding works via a temperature-activated calcination process that relies on the degradation of starch at a temperature of 300°C [65], the 115°C treatment did not generate the desired results. Molasses + lime binders were expected to perform extremely well, as the hardening reaction that occurs between lime and molasses to create calcium sucrate happens at room temperature, and is not negatively impacted by the presence of oxygen or by temperature changes.[66]

4.2.3 Observations on briquetting

Moisture content appeared to make a large difference in dispersion of binders throughout the mixture. Even briquettes made after the die had been freshly washed and still contained a small amount of moisture on the piston were generally more stable directly after production.

When calcinating starch-bound briquettes, extra caution was necessary to ensure that furnace was not open to the air. During starch binding experiments, a leaking clamshell furnace led to the discovery that briquettes exposed to air during calcination suffer a dramatic decrease in structural integrity. Briquettes exposed to oxygen during calcination turned entirely white and were brittle and ashy, while those still oxygen-limited remained strong and black in color.

While no rigorous quantitative comparison between simulant char and fecal char binding was undertaken, there were some noticeable qualitative differences. Rheological differences in the chars made for significantly different binding characteristics – 300°C and 450°C simulant char was sticky and spongy to the touch, and was unable to be ground finely without immediate agglomeration. This char was able to be briquetted with no added binder, but resulting briquettes were not very strong. It also produced tar when pressed that gummed up the briquette die. Fecal chars, even at the lowest pyrolysis temperatures, were much more brittle and easily ground with mortar and pestle. Because these chars were able to achieve smaller particle sizes, they formed much denser and stronger briquettes with less added binder than the simulant chars required.

Both molasses and starch binders showed advantages and disadvantages during the briquetting process. Molasses + lime binders did not require as lengthy of a manufacturing process as starch binders (30 minutes for the former, up to 15 hours for the latter), and required no heating to set the binder. Molasses + lime briquettes, on the other hand, required a hardening

period of about 3 to 7 days to fully strengthen[14], which limits the immediacy with which they can be used. Molasses also tended to clog the briquette maker, making the piston stick, and requiring frequent washing of the die.   Starch binders were easier to measure accurately and were far less messy to work with, but correctly calcinating the briquettes was tedious and energy intensive. Starch bound briquettes required less overall time to reach maximum strength, as they were fully set after the calcination treatment had been completed.

4.2.4 Binder Impact on Briquette Energies

The energy density of the molasses + lime binder was calculated using oxygen bomb calorimetry. Lime has no internal energy, being completely inorganic and incombustible, and molasses was found to have a HHV of 13 MJ/kg. Figure 14 details the decrease in energy content of briquettes with the addition of molasses + lime binder. Because binders comprised between 13.5% and 27% of the char briquette in the formulations tested, but had a lower HHV than char, the energy content of the briquette decreased as binder was added for stability. Assuming briquettes are made from the highest energy fecal char (pyrolyzed at 300°C) with an energy content of 25.6 MJ/kg, the addition of 10% molasses + 3.5% lime binder will decrease the energy content by 8.45% to 23.4 MJ/kg. Adding the much more durable formulation of 20% molasses + 7% lime binder reduced energy content of the char briquette by 17% to 21.3 MJ/kg. These values are still comparable to the energy contained within a commercial charcoal briquette, which has a HHV of 22.8 MJ/kg[52]. FAO charcoal briquette energy standards state that the minimum HHV for a commercial charcoal briquette should be 22 MJ/kg with binders added, and 25 MJ/kg without binder.[67] Fecal char briquettes fall just beneath the minimum acceptable energy content for commercial briquettes, suggesting that the next step in subsequent research is to determine whether 15% molasses + 5.25% lime binder, which would have an

acceptable energy content, might also pass strength tests for commercial briquettes. Section 4.3 will discuss how well the fecal char briquettes manufactured for this thesis meet other FAO briquetting standards.
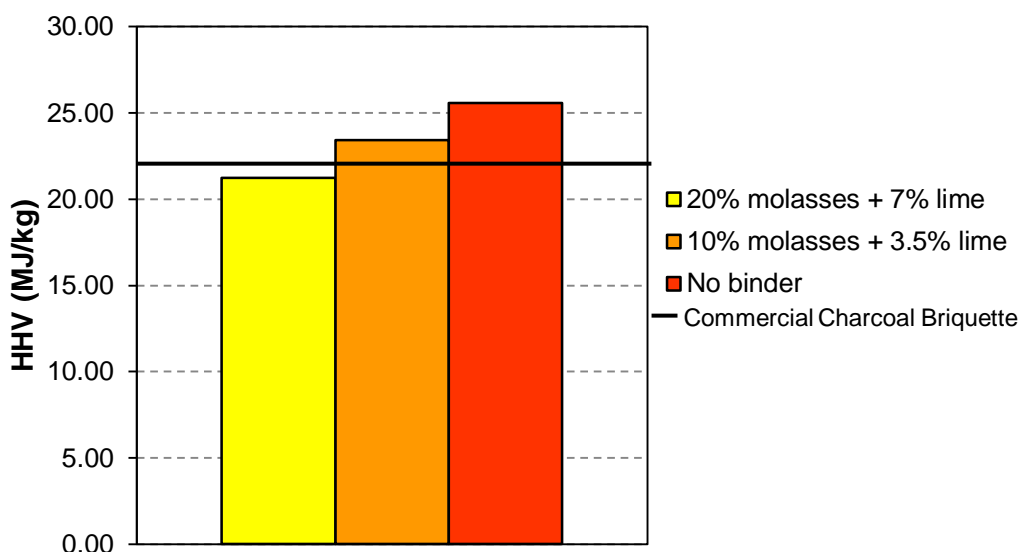
Figure 14: Impact on HHV of fecal char briquette by added binder, comparison to commercial charcoal briquette standard

4.2.4.1 Lower Heating Value Comparison

Lower heating value (LHV) is similar to HHV in that it is a measure of energy density of a fuel (measured in MJ/kg fuel). HHV calculations assume that the latent heat of vaporization of water in the fuel is not lost by the formation of steam, but is recovered by the return of the steam to liquid water form. Although this makes HHV easier to calculate in a calorimeter where all moisture within the fuel stays in liquid form, during combustion in a cooking scenario energy lost from the vaporization of water in fuel is not recovered within the duration of cooking. LHV takes into account the latent heat of vaporization of moisture in the fuel, and subtracts it from the total HHV to estimate a heating value that more closely approximates the energy the char briquettes will actually deliver when combusted for fuel.

The LHVs for unbound 300°C fecal char and 300°C fecal char briquettes made with 20% molasses + 7% lime are displayed in Table 10. As LHV is dependent on the loss of energy from the volatilization of water in the fuel, the higher the moisture content of the fuel, the lower the LHV. Using ASTM D2961[50], percent moisture of fecal char made at 300°C was found to be 0.07% by weight, and moisture content of the char briquetted with 20% molasses + 7% lime after a curing period of 7 days was found to be 0.4%. Using these percent moisture values, the LHVs of fecal char was calculated at 25.41 MJ/kg and the LHV of briquette fecal char was 20.35 MJ/kg.

Table 10: Experimentally determined % moisture and calculated LHVs for 300°C fecal char and 300°C fecal char briquettes made with 20% molasses and 7% lime binder.

Sample Type	% Moisture	HHV (MJ/kg)	LHV (MJ/kg)
Fecal Char	0.07	25.57	25.41
Fecal Char Briquette	0.4	21.25	20.35

Shown in Figure 15, the LHV of briquetted fecal char is 95.8% of its HHV, meaning that moisture content accounts for a loss of about 4.2% of the total available energy within the briquette. Un-briquetted char only displays a 0.6% drop in energy when moisture is taken into account.
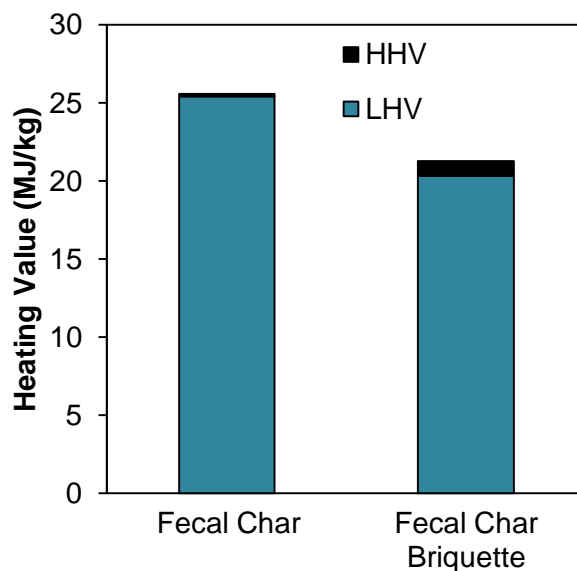
Figure 15: Comparison of HHV and LHV for 300°C fecal char and 300°C fecal char briquettes made with 20% molasses + 7% lime binders. Briquettes, having a higher % moisture, show a larger difference between HHV and LHV.

The addition of moist binders like molasses and water-holding binders like lime increase the moisture content and somewhat lessen the overall available energy of the briquette. It is worthwhile to note that samples were prepared, stored, and tested in Boulder, Colorado, which has an arid climate, and an average humidity of about 67% (daytime) and 35% (nighttime). [68] The moisture content of char and char briquettes likely depend on local relative humidity during storage and also on the specific binder used. Char and briquette moisture content should be measured in the field to determine whether lower LHVs can be expected under different conditions.

4.3 Meeting FAO Briquette Specifications

The Food and Agriculture Organization of the United Nations (FAO) published a manual for managers of industries in developing countries on how to improve the production and

distribution of charcoal.[62] The manual outlines specifications for charcoal briquettes manufactured and distributed for use in stoves designed for the developing world. The specifications detail acceptable levels of ash, moisture, volatiles, binders, and calorific value. Table 11 outlines FAO specifications and details how close the highest performing fecal char briquettes (char made at 300°C with 20% molasses + 7% lime binder) come to meeting briquette content specifications.

Table 11: How fecal char briquettes measure up to FAO briquette specifications

	FAO Specification	Highest Performing Fecal Char Briquettes	Meets Specs? [Y/N]
Ash (wt.%)	25	23.2	Y
Moisture (wt.%)	5	0.4	Y
Volatile Matter (wt.%)	10 - 15	*	*
Binder (wt.%)	10	27	N
HHV (MJ/kg)	22	21.3	N

* Volatile matter of briquettes was not measured as part of analysis suite

Fecal char briquettes fall within FAO ash % specifications, even accounting for the added 7% lime binder, which is assumed to be entirely inorganic in nature, and thus will increase ash content in the briquettes. Briquette moisture content also falls well below the maximum specified % moisture; however, as is discussed previously, briquettes manufactured in a more humid environment may have a significantly larger % moisture and should be tested in the field for moisture compliance. Volatile matter of char briquettes was not measured in the suite of testing performed but should be evaluated in the future for a thorough analysis of briquette performance. It is likely that volatile matter will be high in chars made at lower temperatures, which are thought to contain a substantial amount of hydrocarbons that will degrade and form

volatile compounds when burned. The amount of binder used to create the most durable briquette is more than double the FAO specified limit, and the energy content is about 0.7 MJ/kg lower than the specified limit for briquettes. Both of these shortfalls could be addressed by identifying a more efficient binder that will give briquettes good mechanical properties but at lower binder concentrations.   Even if the new binder were entirely without energy value, at a binder composition of 10 wt.%, the HHV of the improved char briquette would be no less than 23 MJ/kg, which is appreciably higher than the FAO specification.

4. 4 Actual Energy Impact of Briquettes – Haiti Case Study

Assuming the most favorable char and binder combination is used to create briquettes from Sol-Char toilet byproduct fecal char, what percentage of a person's daily cooking energy needs would be met with the addition of fecal char briquettes? The average person outputs 1 ounce (28.3g) of feces per 12 pounds (5.44kg) of body weight.[69]   The average mass of a person is 150 pounds (68 kg).[70]   Thus, one person's average daily fecal output is about 350g. With a conservative char yield of 10% of original feedstock weight, one person's daily waste will be converted to 35g of biochar. Using the LHV to account for moisture content, the usable energy content of the char with binder added to facilitate briquetting will total about 1000 kJ. Using Haiti as an example, it has been determined that over 70% of Haitian people rely on charcoal to meet their daily cooking needs[71]. The energy provided by the charring and briquetting of daily feces would be around 6% of the energy used by one Haitian for cooking every day.

How does this 6% energy savings translate into the real bottom line: reduction of costs? Continuing with the example of a typical Haitian charcoal-user, assume he gains access to a Sol-

Char Toilet and it is completely subsidized and free to the user. Assume also that the cost of briquette binders such as molasses and cassava starch are negligible; rum refineries and cassava crops is high in Haiti and waste molasses and cassava should be obtained for little to no expense.[6] The average Haitian earns $4.50 a day and spends $2.00 a day (44% of his or her income) on charcoal for cooking.[71] Assume that a working Haitian is supporting a family of 5, and all family members are using the Sol-Char toilet. Using briquettes from the Sol-Char Toilet, the average Haitian family could reduce the expense of charcoal for cooking by $0.55 per day, which translates to a savings of 12% of family income. The average Haitian family would save $200/year by supplementing charcoal with fecal char briquettes, which amounts to the cost of about 3 month's supply of charcoal.

5 Conclusions

Biochar produced as a byproduct of pyrolysis of human feces has potential for use as a solid fuel for heating and cooking. In this investigation, the most energy-rich char was produced at a reactor temperature of 300°C, the lowest temperature studied. This result means that a small solar collection array might be sufficient to provide the temperature needed to carry out the pyrolysis process in situ. A smaller solar array would decrease the cost of the Sol-Char toilet.

Simulant feces was found to be a poor proxy for human feces in terms of energy content and briquette characteristics, which points to limitations of the simulant formula presently used. This knowledge may be useful to other Bill & Melinda Gates Foundation teams, especially those who have no access to real human feces for their evaluations.

A modification of the Channiwala correlation between elemental composition and higher heating value was determined appropriate to describe char made from human and simulated

human feces. This correlation will facilitate the work of fecal char researchers by allowing for the calculation of HHV from elemental analysis, rather than the costly and time intensive determination via bomb calorimetry.

With regards to the application of fecal char briquettes in the field, it was found that briquetting with 20% molasses and 7% lime using the pressure of a typical hand press created a durable briquette with energy content comparable to that of commercial charcoal briquettes. The briquette configuration used in this study, however, does not meet standards for commercially distributed charcoal briquettes because of the high quantity of binder needed to create a durable briquette. A variety of locally available binders should be tested once the toilet is deployed in the field to optimize briquette quality and cost.

Possible barriers to the adoption of fecal char as a fuel may include the limited yield of fecal char from a Sol-Char toilet and societal taboos associated with the handling of feces. The fecal char byproduct of pyrolysis studied in this investigation was determined to be energy rich, easily briquetted, and essentially free – potentially making it attractive as a fuel regardless of its ignoble source.

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