Experimental Study of Renewable Energy Implementation in Cement Kilns through Industrial-Scale Downdraft Gasification of Poultry Litter

by

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Abstract

Waste biomass, most notably poultry litter, is a potential source of energy that is widely available and cheap, especially in the southeast. Using poultry litter as an energy source provides a year-round outlet for this waste product. One major energy user that currently utilizes alternative solid fuels is the cement industry. Poultry litter in its raw state, however, is limited in use because of its high chlorine content and relatively large concentration of other unwanted constituents. Downdraft biomass gasification of pelletized poultry litter is a proposed solution to this problem as a means to produce a clean, consistent product gas for injection into the kiln. In this study, this process has been analyzed through experimentation on a pilot-scale 65 Nm^3/hr (Normal m^3/hr at 0˚C, 101.3 kPa) syngas production downdraft gasifier to determine its effectiveness and consistency. The low ash fusion temperature and high alkali content of poultry litter prove to be difficult obstacles to overcome as ash clinker formation is an issue. Experiments with temperature depression via flue gas recirculation as well as experiments employing an additive (limestone) to prevent fusion and aid in chlorine retention in the ash have been carried out. Flue gas recirculation allowed the reduction of the gasifier secondary air oxygen concentration by 40-45%, yielding an approximately 100˚C depression in average temperature. Results have shown that the clinkering is temperature independent, at least within the controllable temperature range. Limestone also has only a slight effect on the fusion when used to coat the pellets. However, limestone addition did display some promise in regards to chlorine capture, as ash analyses showed chlorine concentrations of more than four times greater in the limestone infused ash as compared to raw poultry litter. Experiments were also conducted to explore the effectiveness of mixing limestone with raw poultry litter, the object being to coat more surface area and have a more even mixture. These resulted in the most consistent experiments with no ash clinkering.

Once consistent gasification of raw poultry litter was achieved through a combination of woodchip dilution (60% woodchips:40% poultry litter) and addition of limestone at 5% of the wet poultry litter mass, experiments were performed to determine the capture rates of the contaminants pertinent to cement kilns. Limestone percentage was varied to explore its effect on chlorine retention at three different set points. It was found that limestone percentage, at least within the tested range, had little effect on neither the retention of contaminants nor distribution of contaminants through the gasifier system. On average, 89% of the chlorine was retained in the gasifier char, as was 94% of both the potassium and sodium, and 100% of the phosphorus. A contaminant concentration profile, developed from analyses of char samples from different sections of the gasifier system, showed that 69.1% of the chlorine retained was captured past the gasifier grate and 52.6% was captured in the significantly cooler filter box and heat exchanger sections of the gasifier system. Additionally, peaks in concentration of sulfur and potassium were observed in these same sections. From these results, it was concluded that cooling and filtering the syngas in the range of 60-110˚C obtains the maximum removal of contaminants from the syngas stream.

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List of Abbreviations

Acronyms

CPC	Community Power Corporation
HEX	Heat Exchanger
HHV	Higher Heating Value
LHV	Lower Heating Value
LOI	Loss on Ignition, % mass
MW	Molecular Weight, g/mole
PL	Poultry Litter
WAL	Wyoming Analytical Labs

Symbols

A	Atomic Weight, g/mole
U_i	Uncertainty of i, same units as i
ΔH	Change in Enthalpy, kJ/mole
n	Number of moles
Nm^3/hr	Normal cubic meters per hour, at 0˚C and 101.3 kPa (1 atm)
P	Pressure, Pa
R_U	Universal Gas Constant, $\frac{\mathrm{J}}{\mathrm{mole \cdot K}}$
T	Temperature, K
V	Volume, m^3

Chapter 1

Introduction

1.1 Poultry Litter

Poultry litter is a waste product of the poultry industry that comes from floor-raised birds (primarily broilers) and consists of their manure, bedding material (usually wood shavings), waste feed, and feathers. According to the USDA, over 8 billion broilers (47.7 billion pounds) were produced in the US in 2009, and approximately half of all broiler production was from Alabama, Georgia, Arkansas, and Mississippi alone (1). Using an estimate of .52 lb litter/lb bird recommended by Alabama Cooperative Extension System, that translates to 12.4 million tons of litter produced annually (2). The most common use for this litter is as a soil amendment in farming (3). However, due to high transportation costs most of the litter is applied only to neighboring farmlands leading to nutrient buildup and runoff, most notably of phosphorus, causing excess algae growth, disruption of local ecosystems, and drinking water pollution (3-5). Because of these harmful effects garnered over time, there is much interest in finding other outlets for this waste product.

1.2 Cement Kiln

One proposed alternative use for poultry litter is as a fuel. It has an average higher heating value (HHV) of ~14 MJ/dry kg which is comparable to ~20 MJ/dry kg for wood and about half that of coal (3). A current major waste and alternative solid fuel consumer and potential venue for poultry litter utilization is the cement production industry. Portland cement is manufactured by heating limestone, primarily calcium carbonate ($CaCO_3$), to temperatures up to 1450˚C to form calcium oxide (CaO) as well as calcium silicates and aluminates in a process called calcination (6). These temperatures are achieved by burning large amounts of primarily non-renewable fossil fuels such coal, petroleum coke, gas, or oil in a massive rotating kiln (Figure 1.1).

Figure 1.1: A typical cement production facility, rotating cylindrical kiln circled **(7)**

It is in the cement producer's interest both economically and environmentally to supplement some energy needs with alternative, renewable fuels. Types of alternative fuels vary depending on availability relative to plant location, but some examples include: waste oils, landfill gas, bark, paper, tires, and plastics (8). A good alternative fuel will have sustained availability and be economically beneficial to the cement producer, and in areas such as the southeast and where plants are in close proximity to poultry farms, poultry litter fulfills those requirements well. While these fuel selection requirements are not very discriminating, some further process-specific limitations do exist. The alternative fuel introduced must not adversely affect the kiln functionality or the quality of the cement product, and while the robust nature of the process makes this a generally undemanding requirement, negative effects can be garnered from excess heavy metal, alkali, sulfur, or chlorine content. Chlorides, sulfides, and alkalis become circulating elements in the kiln, volatilizing in hotter portions while condensing in cooler portions, leading to the formation of kiln ring build-ups and subsequent, costly shut-downs (8) (7). Every cement manufacturing facility has its own unique standards to determine the quantity of these deleterious components that is permissible, but the high level of alkalis and chlorine found in poultry litter either prevents or severely limits its substitution rate almost universally. Therefore, in order to gain the distinct economic and environmental advantages presented by poultry litter use, an intermediate step of biomass gasification is presented as a means to extract the chemical energy for use in the cement kiln while limiting the throughput of undesirable elements.

1.3 Gasification

Thermochemical gasification via partial oxidation is a relatively old technology; it has been in existence for over 150 years (9). The overall goal is to convert the solid biomass energy into a gaseous form with minimal loss, usually 10-30%, in order to gain the many advantages which gas possesses over solid fuel (10). A possible secondary goal is to remove unwanted components from the fuel source, such as sulfur, as in coal gasification (9). This is the feature of interest relevant to the implementation of poultry litter energy in the cement kiln. There are many types of gasifiers, each typified by the oxidizer employed; the orientation and flow of products relative to inputs; or the use of fluidized beds versus static, packed fuel beds (9). A commercially available, relatively simple, low-tar production option is a downdraft gasifier. This vertically-oriented setup draws both the oxidizer (air in this case) and the feedstock in through the open top. The consumption of the biomass then occurs along the throat of the gasifier, proceeding to the grate at the bottom where the hot synthesis gas (syngas) exits, ready for use. The gasification process can be broken down into several stages as it progresses from the entry to the exit of the gasifier: thermal decomposition, or pyrolysis, in which the volatiles are driven off producing pyrolysis vapors and tars; char oxidation, in which char remnants from the pyrolysis zone react with remaining oxygen and other gases and are gasified in both endothermic and exothermic reactions; and char reduction, in which remaining carbon content is consumed through primarily endothermic reactions (11) (12). While the exact chemistry of this process is highly complex, there are several principal reactions vital to the formation of the syngas products that are well agreed upon and used commonly when mathematically modeling biomass gasification (11) (13-15):

Heterogeneous Reactions (Solid and gas reactants)

$C + \frac{1}{2}O_2 \rightarrow CO$ $\Delta H = -110.6$ kJ/mol

$C + O_2 \rightarrow CO_2$ $\Delta H = -393.8$ kJ/mol

$C + CO_2 \rightarrow 2CO$ $\Delta H = +172.6$ kJ/mol

$C + H_2O \rightarrow CO + H_2$ $\Delta H = +131.4$ kJ/mol

$C + 2H_2 \rightarrow CH_4$ $\Delta H = -74.9$ kJ/mol

Homogeneous Reactions (Gas reactants)

$CO + H_2O \rightarrow CO_2 + H_2$ $\Delta H = -41.2$ kJ/mol

$CH_4 + H_2O \rightarrow CO + 3H_2$ $\Delta H = +201.9$ kJ/mol

The gas produced with the downdraft, air-oxidation gasifier is ‘low joule’ or ‘low energy’ gas, relative to other methods of gasification or pure pyrolysis, and is best employed in a ‘closely coupled’ arrangement for immediate use to preserve efficiency (9) (10). This arrangement would be ideally suited in preparing potentially harmful fuels, specifically poultry litter, for use in a cement kiln and, therefore, is the focus of the current study.

Chapter 2

Background

2.1 Poultry Litter Composition

Poultry litter is a non-homogeneous mixture of bedding, feathers, excrement, and feed. Because of this, no two samples are exactly alike and, thus, a model or standard definition doesn't exist. Proximate and ultimate analyses, on a dry basis, from different farms are usually relatively similar, but can have as much as a 20-30 average percent difference between parameters (16-18). A comparison of several proximate analyses and ultimate analyses of different litter samples from the literature is presented in Tables 2.1 and 2.2.

Table 2.1: Proximate analyses (% mass, dry basis) of five litter samples from the literature

	Li et al. (17)	**Schaffer** (19)	**Reardon et al. (raw litter sample)** (16)	**Reardon et al. (pelletized sample)** (16)	**Primenergy** (18)	***Average***
Ash	27.96	32.65	21.9	26.5	20.61	**25.9**
Volatile Matter	65.16	53.96	62.7	59.8	45.64	**57.5**
Fixed Carbon	6.88	13.39	15.4	13.7	33.75	**16.6**
Total	100.00	100.00	100.0	100.0	100.00	**100.0**

Table 2.2: Ultimate analyses (% mass, dry basis), chlorine content, and heating value of six litter samples from the literature

	Li et al. (17)	**Schaffer** (19)	**Reardon et al. (raw litter sample)** (16)	**Reardon et al. (pelletized sample)** (16)	**Primenergy** (18)	**Bock** (5)	***Average***
Carbon	28.2	35.03	36.6	33.7	40.89	37.8	**35.4**
Hydrogen	5.0	4.50	4.9	4.5	4.86	5.1	**4.8**
Oxygen	35.0	21.51	32.0	29.3	28.66	31.1	**29.6**
Nitrogen	3.4	4.06	3.9	5.0	4.30	3.8	**4.1**
Sulfur	0.9	1.14	0.78	0.95	0.68	0.4	**0.8**
Ash	27.7	32.65	21.9	26.5	20.61	21.8	**25.2**
Total	100.2	98.89	100.08	99.95	100	100	**99.9**
Chlorine	1.16	1.11	Not reported	Not reported	0.051	1.0	**0.8**
MJ/kg	13.31 (LHV)	Not reported	14.82 (LHV)	13.62 (LHV)	15.99 (HHV)	14.87 (HHV)	**15.43 (HHV)**

It can be seen from the tables that while the samples do compare relatively well to the calculated average, the differences between individual samples may be significant. Differences become even more apparent when comparing the ash analyses of poultry litter samples. There can exist as much as a 40-50 average percent difference between the oxide concentrations of two separate samples. Table 2.3 shows the comparison between five ash component analyses found in the literature and the average of these values.

Table 2.3: Ash analyses (% mass, ignited basis) of five litter samples from the literature

Oxide	**Li et al.** (17)	**Schaffer** (19)	**Primenergy** (18)	**Bock** (5)	**Codling** (20)	***Average***
Al_2O_3	4.9	3.45	0.84	1.9	1.73	**2.6**
CaO	13.5	15.00	23.60	17.3	17.63	**17.4**
Fe_2O_3	2.1	1.14	0.85	1.2	1.03	**1.3**
K_2O	12.2	8.68	20.51	16.3	6.06	**12.7**
MgO	4.6	3.62	7.76	5.0	3.96	**5.0**
Na_2O	5.8	4.58	7.04	9.2	N/A	**6.7**
P_2O_5	15.3	10.90	24.62	24.4	17.39	**18.5**
SO_3	5.8	7.11	6.60	6.7	N/A	**6.6**
SiO_2	35.6	38.40	7.46	8.1	N/A	**22.4**
TiO_2	0.2	N/A	0.07	0.2	N/A	**0.2**
Total	100.0	92.88	99.35	90.3	47.79	**93.4**

While the exact concentration of each element (presented here as their oxide) can be very different for each sample, the species with the highest concentrations tend to be CaO, K_2O, P_2O_5, and SiO_2. The relatively high concentrations of K and P, along with nitrogen, are what make poultry litter an attractive soil amendment. However, the high ratio of P to N and the high water-solubility of the phosphorus-containing compounds is what causes the phosphorus concentrations to build up in the soil over time and run off into watersheds and water supplies (5) (20).

The high variance in poultry litter composition, specifically of the ash components, is due to many variables involved in how the birds are raised and the individual farm's practices. Commercial poultry houses have dirt floors, so some components of litter come from varying amounts of dirt mixed in by humans when cleaning the pens or by the birds themselves (21). This inconsistency between farms most likely accounts for the high variability in silica (SiO_2) content found in the literature. Wood shavings are typically used as bedding in the pens and make up a substantial portion of the litter, and therefore the type of wood used has an effect on the poultry litter composition. The diet of the birds, in the form of unconsumed feed or through their excrement, contributes to the composition as well. A listing of ash components, other elements of interest, and their origins is displayed in Table 2.4. The table was compiled after consulting Carla Price, a nutritionist for Sanderson Farms, but can also apply to other production facilities as well. The broilers' primary diet consists of corn, soy and water and is supplemented with meat meal (ground up chicken parts).

Table 2.4: Origins of poultry litter components relevant to cement kiln implementation. Element % are elemental, not oxide **(21) (22)**

Element	Possible Origin
Al	• In soil • In alum (Aluminum Sulfate), used to keep ammonia levels of litter down • Generally ~0.1-0.7% of wood ash
Ca	• In feed for bone strength • 40g per bird over lifetime, large amount retained • Generally the largest ash component in wood (~20-35%)
K	• High concentration (2-3%) in soy fed to birds • Generally second largest ash component in wood (~5-15%)
Mg	• Fed as a trace mineral • Also in meat meal • Generally the third largest ash component in wood (~3-9%)
Na	• In feed • 10g per bird over lifetime, some retained • Trace element in wood
P	• In feed for bone strength • Generally ~1% of wood ash
S	• Not in the diet • Generally ~1% of wood ash
Si	• In dirt, sand and water • In wood ash
Cl	• Fed as trace mineral • In water, extra added to poultry farm supply if experiencing health issues

2.2 Undesirable Elements in Cement Kilns

The exact alternative fuel standards and composition limits for a given kiln vary depending on the cement plant and are usually trade secrets. However, a few examples have been published and general guidelines are known about which elements in excess are harmful to cement product or the kiln itself. For example, the alternative solid fuels used by the Lafarge Cement Polska group in Poland must meet the following requirements (7):

- Heating value > 14.0 MJ/kg (weekly average)
- Chlorine content < 0.2%
- Sulfur content < 2.5%

Using these values as a general guideline, it can be seen that poultry litter barely satisfies the energy requirement, easily satisfies the sulfur requirement, and fails the requirement for chlorine with an average from the literature of about 1%. Although not included in this list, much attention is also paid to the alkalis in the fuel which become circulating elements in the kiln, alongside sulfur and chlorine. A list of elements found in poultry litter and their effects on the cement manufacturing process can be seen in Table 2.5. It is evident that the elements whose throughput it is most important to reduce are Cl, K, Na, and S.

Table 2.5: List of elements relevant to cement manufacturing that are present in poultry litter and their effects, adapted from Bhatty, 2004 **(23)**

Element	Effects on Cement Production
Chlorine, Cl	• Circulating element • Forms alkali chlorides • Causes ring formation in kiln and blockages • Causes pre-heater buildup
Magnesium, Mg	• Improves burnability of clinker • Goes into aluminate and ferrite phases • In excess may affect concrete behavior
Phosphorus, P	• Reduces negative effects of alkalis on cement strength • In excess can decrease concrete strength
Potassium, K	• Circulating element • Forms chloride and sulfate compounds in kiln
Sodium, Na	• Circulating Element • Forms chloride and sulfate compounds in kiln
Sulfur, S	• Can be a circulating element • Forms alkali sulfates, necessary in removal of alkalis from the kiln • Excess leads to ring formation and blockages

It can be seen that any alternative fuel with concentrations of harmful elements exceeding that of the primary fuel will be restricted in its substitution rate, the elements in question becoming the limiting factor. Conversely, any deleterious components with a lower concentration than in the primary fuel become less important. Comparing samples of coal and petroleum coke used in the Lafarge Roberta cement plant to an average of poultry litter samples from the literature on a mass basis (Table 2.6) and energy basis (Table 2.7) it becomes apparent that sulfur is not a limiting factor and is insignificant next to the concentrations in coal and coke. Making a comparison on an energy basis is pertinent because substitution rates are based on energy content, not mass (7). It was reported by Folta (7) that over a series of five burns, the energy supplied by coal was between 35-60% of the total, coke was 20-37%, and a combination of tires, plastics and alternative fuel was 18-30% of the total kiln energy consumption.

Table 2.6: Comparison of poultry litter composition (% mass, dry) to coal and coke samples used at the Lafarge Roberta plant **(7)**

	Average Litter Composition from Tables 1,2 & 3	**Coal**	**Coke**
Proximate Analysis, % mass, dry			
Ash	25.9	24.9	8.81
volatile matter	57.5	25.4	12.9
Fixed Carbon	16.6	49.7	78.3
Total	100.0	100.0	100.0
Ultimate and Elemental Analysis, % mass, dry			
Carbon	35.4	64.50	78.7
Hydrogen	4.8	3.24	2.7
Oxygen	29.6	2.84	1.81
Nitrogen	4.1	1.02	1.23
Sulfur	0.8	3.47	6.74
Chlorine	0.8	0.059	0.013
Al	0.36	2.98	0.53
Ca	3.22	1.98	1.67
Fe	0.24	1.74	0.42
K	2.73	0.60	0.13
Mg	0.78	0.18	0.07
Na	1.29	0.05	0.02
P	2.09	0.02	0.00
(SO_3 in ash) S	0.68	0.03	0.74
Si	2.71	5.89	1.13
Ti	0.03	0.16	0.03
MJ/kg	15.43 (HHV)	26.45 (HHV)	32.25 (HHV)

Table 2.7: Comparison of poultry litter composition (g/MJ, dry) to coal and coke samples used at the Lafarge Roberta plant **(7)**

	Average Litter Composition from Tables 1,2 & 3	**Coal**	**Coke**
Proximate Analysis, g/MJ dry			
Ash	16.79	9.41	2.73
volatile matter	37.27	9.60	4.00
Fixed Carbon	10.76	18.79	24.28
Total	64.81	37.81	31.01
Ultimate and Elemental Analysis, g/MJ dry			
Carbon	22.94	24.39	24.40
Hydrogen	3.11	1.22	0.84
Oxygen	19.18	1.07	0.56
Nitrogen	2.66	0.39	0.38
Sulfur	0.52	1.31	2.09
Chlorine	0.52	0.022	0.004
Al	0.23	1.13	0.16
Ca	2.09	0.75	0.52
Fe	0.15	0.66	0.13
K	1.77	0.23	0.04
Mg	0.51	0.07	0.02
Na	0.83	0.02	0.01
P	1.36	0.01	0.00
(SO_3 in ash) S	0.44	0.01	0.23
Si	1.76	2.23	0.35
Ti	0.02	0.06	0.01

Having compared the composition of poultry litter to the standard fuels, observed an example of limits, and examined the effects of certain elements on cement kilns, it becomes evident that the most important components to limit introduction into the kiln are Chlorine, Sodium, and Potassium. This study will focus on these elements, but attention will be paid to other components previously mentioned as potentially harmful.

2.3 Chlorine and Alkali Release from Biomass under Gasification and Combustion Conditions

There is little documentation as to the study and quantification of the capture rates of the unwanted constituents of interest to the cement manufacturing process by means of downdraft gasification, especially with regards to poultry litter. However, some work has been done in examining chlorine and alkali release from other types of biomass under similar pyrolytic and gasification conditions. It has been found that in gasification of biomass HCl and KCl are the dominating chlorine-containing species released in the gas and are formed during the pyrolysis and char oxidation phases. Chlorine exists in several forms in biomass but it is believed that a significant portion is present as the salt KCl which is assumed to begin volatilization above its melting point of approximately 750˚C (24). It was found in experiments performed by Bjorkman, et al. that under pyrolysis conditions using N_2, switchgrass retained its chlorine at all temperatures above 400˚C far better than the two types of coal tested (Figure 2.1), an positive initial sign for the retention of this harmful component of poultry litter in the ash.

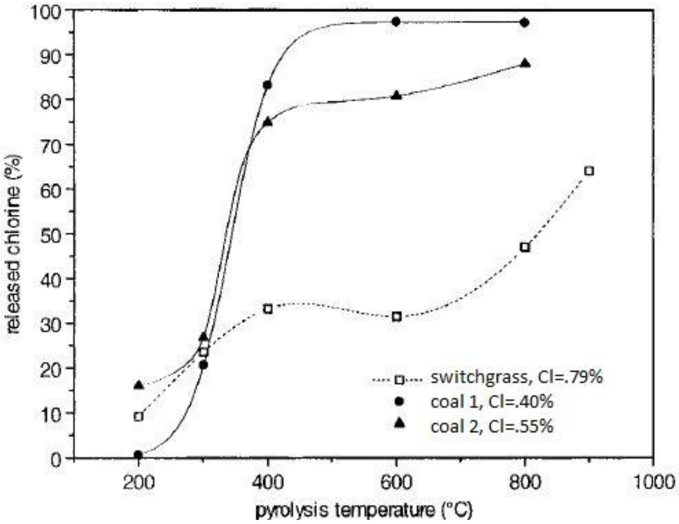

Figure 2.1: % Cl released by switchgrass and coal at varying pyrolysis temperatures **(24)**

It was also found that using CO_2 in place of N_2, the same experiments yielded higher chlorine release at temperatures above 800˚C (24). Additionally, chlorine presence in biomass is known to facilitate the volatility and mobility of many inorganic elements, specifically alkali metals. Chlorine, in fact, has as much effect on the amount of alkali vaporized during combustion as does the alkali concentration (25). It has been found that in combustion of switchgrass, the dominant alkali containing gas species is KCl, followed by either KOH or NaCl at 1100˚C or 800˚C, respectively (26).

In experiments employing an ashing furnace, it was found by Misra, et al. (22) that varying temperatures from 600-1300˚C when combusting wood sees a loss of K and S with increase in temperature but a retention of Na, Mg, P, Mn, Al, Fe, and Ca. K concentration drops off significantly above 800-900˚C, while S decreases, although less severely, above 1000-1100˚C. All results were normalized with respect to Ca which was assumed to be constant. A similar experiment was performed by Adams (4) with poultry litter, the temperature varying from 450-1000˚C. Sulfur was not analyzed and different results were found. K, Na, Mg, Al, Fe, and Mn all decreased with increasing temperature, K the most severe. However, P and Ca were still retained.

2.4 Gasification of Poultry Litter

In the literature, gasification trials using poultry litter have been run in both bench-scale and pilot-scale arrangements with varying degrees of success. In all cases slagging or clinkering (fusion) of the poultry litter during gasification was an issue that had to be addressed (16) (19) (13). It was found by Community Power Corporation (CPC) that using pelletized litter with reduced moisture and limiting the superficial velocity (volume flow rate of gas produced/gasifier cross-sectional area, measured in m/s) of the gasifier provided the best results in a bench-scale downdraft gasifier. This is said to control the temperature at the pyrolysis front, and without these measures, clinker formation was an issue. A pilot scale trial using 12.5% moisture pellets was run for 5 hours, producing 45 Nm^3/hr (Normal m^3/hr at 0˚C, 101.3 kPa) of syngas with a lower heating value of 4.79 MJ/Nm^3. However, no mention was made of the state of the gasifier char remaining upon completion of the run, as to whether fusion occurred or not (16). In another study, using a fixed-bed, counter-current updraft gasifier, in which the fuel entry and syngas exit is at the top and oxidizer entry is at the bottom, it was found that gasifying pure poultry litter resulted in a large agglomeration forming inside the gasifier. However, mixing the poultry litter with a fuel less prone to slagging, cow manure, in a 50:50 weight ratio char fusion was negligible (13).

2.5 Reasons for Clinker Formation and Possible Solutions

The clinkering problems encountered when gasifying poultry litter are attributed the interaction between the alkali metals, chlorine, and silica present in the fuel (24) (25). The root of the problem is thought to be caused by either one or both of two reactions. The first is the formation of alkali silicates from a reaction of alkali metals and silica. Alkali silicates can soften or melt at temperatures as low as 700˚C depending on the composition, and most poultry litter is high in both alkalis (K and Na) and silica (SiO_2). The second is the formation of alkali sulfates from alkali and sulfur (25). As mentioned previously, chlorine aids immensely in the volatilization and transport of alkalis, particularly potassium, conveying them to surfaces where ash deposition occurs (25).

Potential solutions to this problem are co-gasification with other fuels, temperature reduction, and, as suggested by several sources, addition of up to 5% limestone or dolomite (5) (16) (27).

2.6 Limiting the Release of Chlorine and Alkalis

The addition of limestone in a combustion or gasifier environment can promote the capture and sequestration of volatilized chlorine. This aids in both the minimization of ash clinkering as well as potentially limiting the throughput of chlorine in the product gas with consideration to cement kiln usage. It has been proposed that gaseous chlorine is removed through the following path during combustion:

$$CaO(s) + 2HCl(g) \rightarrow CaCl_2(s) + H_2O(g)$$

It has been suggested through thermodynamic modeling that this equation is favored more at lower temperatures (550-700˚C) and when high HCl and low H_2O are present in the flue gas (27). The use of limestone also would be convenient if needed at a cement production facility, as this is one of the primary raw materials employed in cement manufacture.

In the endeavor to mitigate alkali release, it has been shown that simply cooling and filtering the product gas at 400-500˚C (cooler than the melting point of the alkali-containing salts) can have a dramatic effect on the gas alkali concentration (28). This effect can be seen in Figure 2.2 where the alkali concentration (Na + K) in the product gas from a fluidized bed gasifier is plotted relative to temperature for many different solid fuels. The points on the right side of the graph are samples taken before the gas cooler and those on the left from after the gas cooler.

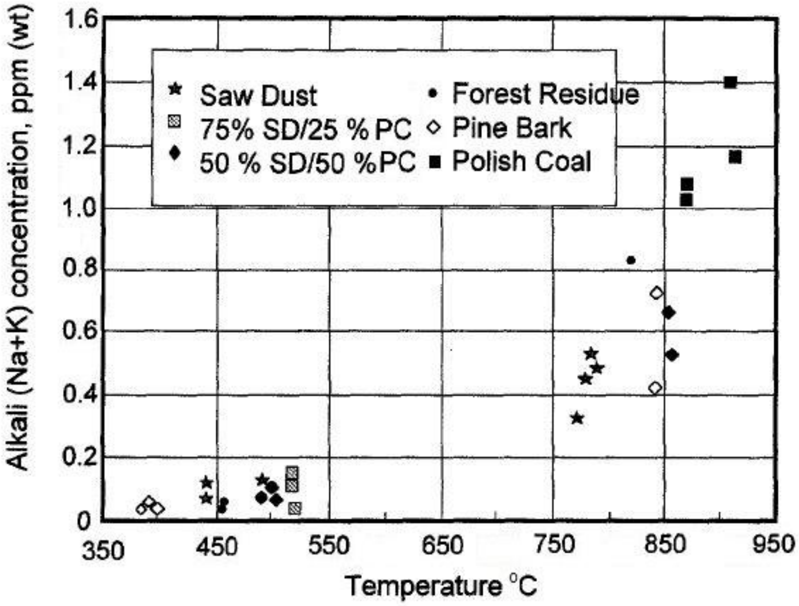

Figure 2.2: Alkali concentration in fluidized bed product gas before and after the gas cooler for various fuels **(28)**

In this study, various experiments were performed initially utilizing methods drawn from the literature as well as methods devised based on known fuel characteristics in an attempt to inhibit the fusion of the poultry litter during gasification in order to consistently gasify it (Sections 3.2.1 and 4.1). Specifically, trials were run experimenting with dilution of the fuel using non-sintering material, attempting to lower the average gasifier temperature using flue gas recirculation, and utilizing limestone as an anti-fusion and potential chlorine-capturing additive. This was done with the end goal of quantifying the alkali, chlorine and other potentially interesting elements released in the gasification of poultry litter, and as such, attention was paid to these properties along the way.

The next set of experiments in this study were performed to actually quantify the contaminant retention and sequestration garnered by the use of a gasifier while extracting the chemical energy from poultry litter.

Chapter 3

Experimental Setup and Procedure

3.1 Experimental Setup

3.1.1 Gasifier

This study was conducted using a Community Power Corporation (CPC) Biomax 25 downdraft, co-current gasifier (Figure 3.1). This unit is fully automated utilizing a Labview interface and designed to gasify 22kg/hr (~50lbs/hr) of dry biomass and produce 65 Nm^3/hr (~2300 std ft^3/hr) of syngas with a nominal energy content of 4.8 MJ/Nm^3 (~130 Btu/Std ft^3). The produced gas is pulled through a shell and tube, air-cooled heat exchanger and dry bag filter and can either be flared or used to run an internal combustion engine to generate up to 25kW of electricity. The heat removed from the syngas by the heat exchanger is used either to dry the feedstock in the storage bins or to heat the control room. A screenshot of the Labview gasifier schematic can be seen in Figure 3.2.

Figure 3.1: CPC mobile gasifier unit parked outside of the Alabama Capitol Building

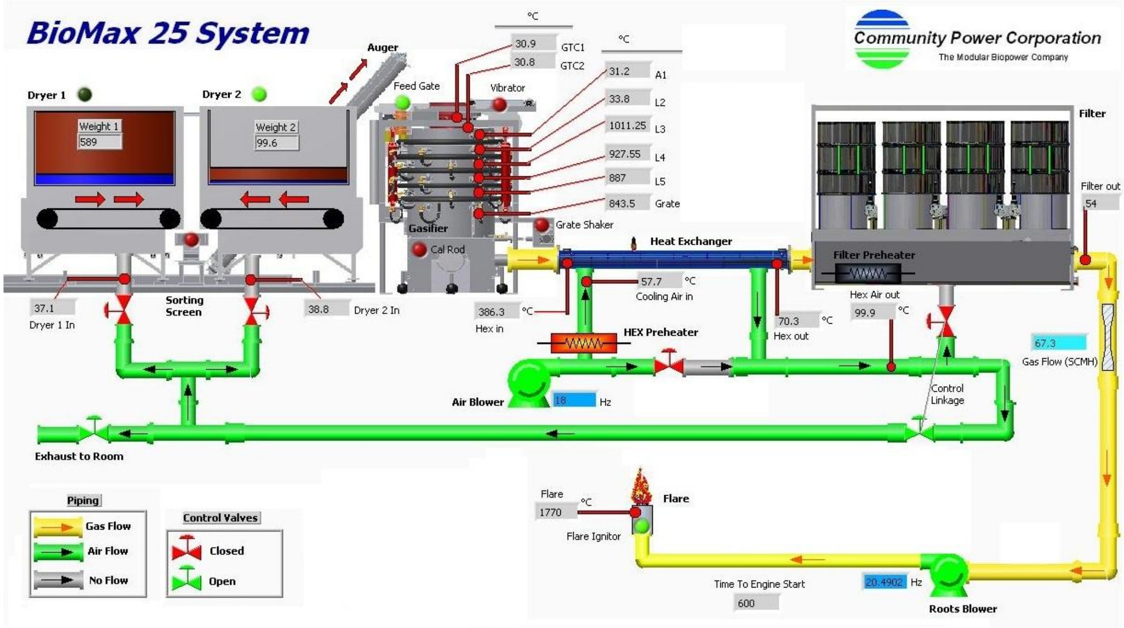

Figure 3.2: Labview schematic of Biomax 25 Gasifier

The gasifier is an open top design, which is where both the primary air and biomass enter. The inside dimensions of the gasifier throat are 130 cm height and 35 cm diameter. The biomass level inside the gasifier is constantly maintained using distance sensors which activate the onboard feed system. Secondary air is injected through five levels of nozzles spaced equally along the height of the gasifier and controlled by proportional valves in order to control the gasifier temperature and syngas composition. The gasifier temperature is monitored using k-type thermocouples (±2.2˚C) at each of the 5 levels, at the grate, and at two locations above the nozzles (Figure 3.3).

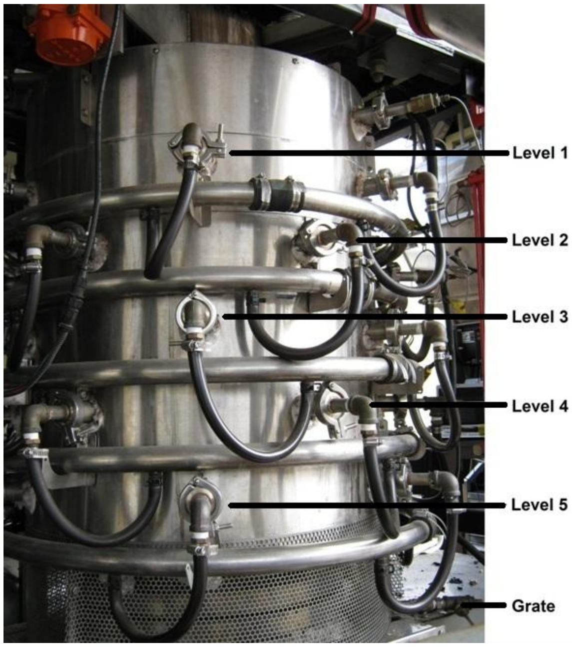

Figure 3.3: Gasifier with secondary air injection levels and grate level labeled

Pressure drop is also measured across the gasifier and across the grate using onboard digital manometers and the oscillation of the grate is varied according to the degree of pressure drop. Syngas flow rate is measured via the onboard venturimeter and corrected to 0˚C, 101.3 kPa (1 atm). All pressures, temperatures, and gas flow rates are recorded by the onboard computer every 10 seconds.

Because the gasifier is fully automated, operating parameters such as temperature are controlled to stay within a desired range. Variations in secondary air amount, grate shaker speed/interval, heat exchanger blower speed, and other controls are made by the onboard computer to keep the gasifier as close to steady-state as possible during operation. An average temperature profile in the gasifier from a standard woodchip-fed run can be seen in Figure 3.4. The temperature profile through the rest of the gasifier during the same run can be seen in Figure 3.5.

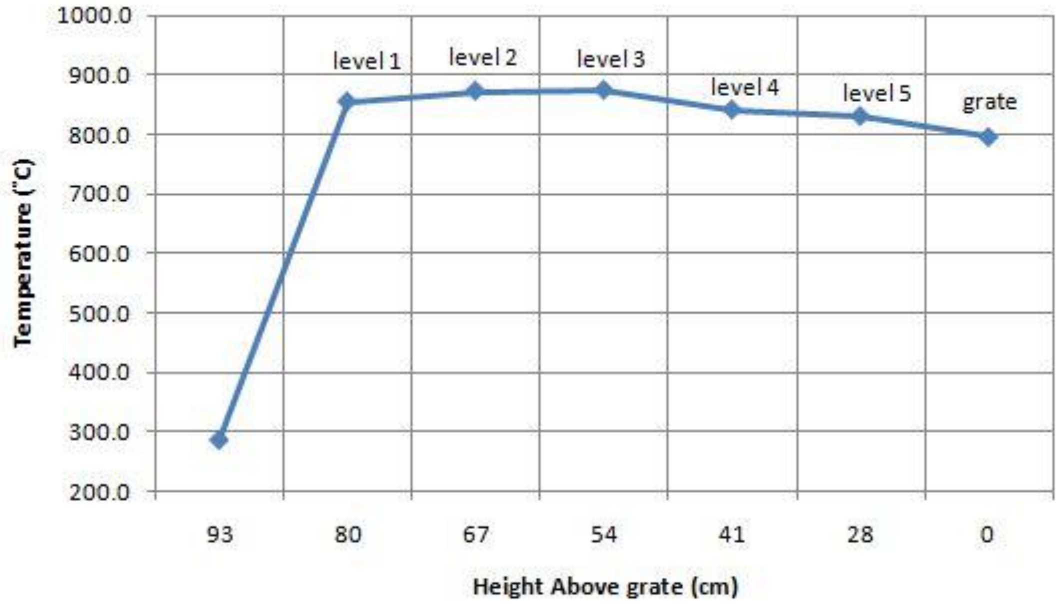

Figure 3.4: Average temperature profile inside the gasifier during a standard woodchip run

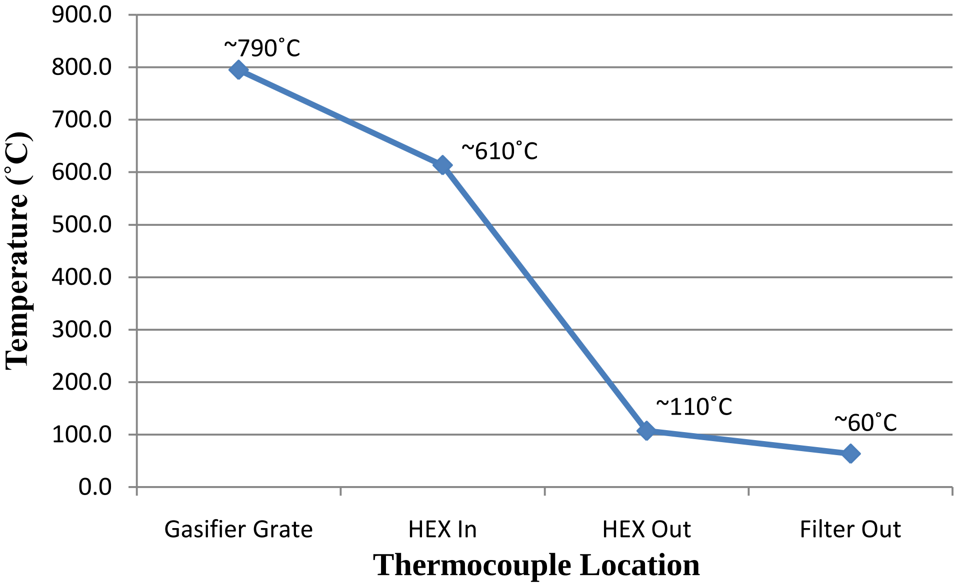

Figure 3.5: Average temperature of the syngas at different locations in the system starting at gasifier exit, proceeding through the heat exchanger (HEX), and finally after the filter

Additionally, syngas composition, and consequently the syngas higher heating value (HHV), are intended to stay within a desired range during steady-state operation. A typical run employing pine chips sees an average dry syngas composition (by volume) and volumetric HHV of approximately:

O_2 [%]	CO [%]	CO_2 [%]	CH_4 [%]	H_2 [%]	HHV [MJ/m^3]
0.5	20	12	1.5	18	5.4

*Syngas over duration of a typical run can be seen in Appendix D, Figure D.1

The O_2 concentration in the syngas is a result of tiny air leaks in the system and is higher if the gasifier differential pressure is elevated. The moisture percentage in the syngas varies with the feedstock moisture and is typically in the range of 5-10% (by volume).

Ash sampled at the end of experiments was collected at several locations in an attempt to capture all of it. Before all experiments, ash was purged from every location using the same methods. Charred woodchips were removed from the top of the gasifier using a Shop-Vac down to around level 4 (see Figure 3.3). Ash remaining in the gasifier was collected by removing bolts and opening the gasifier at a sealed seam 10 cm (4 inches) above the grate (Figure 3.6).

Figure 3.6: Gasifier opened at seam 10cm above the grate

Below the gasifier grate is a round chamber (Figure 3.7) where the heavier ash tends to settle as opposed to becoming entrained and continuing through the pipe (slanted inlet, right side of Figure 3.7) towards the heat exchanger.

Figure 3.7: Chamber below grate, slanted entrance to tube leading to heat exchanger at right. Larger, heavier ash particles settle here

Some ash settles in the bend just before the heat exchanger. This is accessed through a port at the heat exchanger entrance (Figure 3.8).

Figure 3.8: Access port at heat exchanger entrance, Shop-Vac in use

More ash settles in the heat exchanger itself and in the pipe leading from heat exchanger to filter box. This is accessed by removing the pipe bend from the end of the heat exchanger (Figure 3.9, bottom right) and using a Shop-Vac to retrieve ash from the individual tubes in the shell and tube heat exchanger (Figure 3.9, just visible at left inside the heat exchanger exit). The Shop-Vac is also used to remove ash from the pipe leading to the filter box.

Figure 3.9: Heat exchanger exit, tubes visible inside at left. Pipe bend and flexible hose leading to filter box at right.

The rest of the ash is captured in the filter box by the self-cleaning, dry bags. Ash is collected from the filter box using the onboard auger that runs the length of the filter box bottom. The sides of the filter box are v-shaped, funneling ash to the half-pipe containing the auger at bottom.

Figure 3.10: Filter box with doors open. Bags are inverted inside barrels by syngas flow

3.1.2 Gas Analysis

During all experiments the syngas was continuously side-stream sampled and analyzed through a valve located after the heat exchanger and filter box, so the gas was cooled to approximately 60˚C and relatively clean. The sample flow is as shown in Figure 3.11.

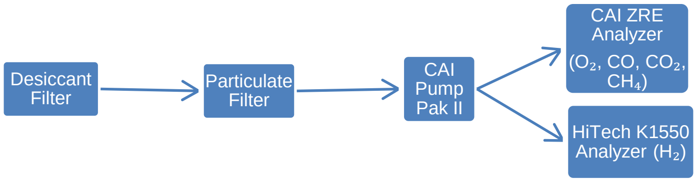

Figure 3.11: Gas analysis flow diagram

The two gas analyzers used were a California Analytical Instruments model ZRE and a HiTech Instruments K1550. The ZRE measured CO (±0.6%), CO_2 (±0.6%), and CH_4 (±0.3%) using Non-Dispersive Infrared (NDIR) method and O_2 (±0.5%) by means of a fuel cell (Figure 3.12, bottom). The K1550 measured H_2 (±2%) using thermal conductivity (Figure 3.12, top right). Gas composition data was recorded every 15 seconds using an Omega OMB-DAQ-56 connected to the analog 4-20mA outputs of the instruments.

Figure 3.12: Gas analyzer train used during experiments. HiTech K1550 top right, California Analytical ZRE bottom, California Analytical Pump Pack II middle

A dew point meter was used in the quantification of contaminant retention experiments (Sections 3.2.2 and 4.2). The meter was a GE DewPro MMR101 (Figure 3.12) that measured percent volume H_2O and was linked to the Omega-DAQ-56 through a 4-20mA loop. The probe was mounted directly in the syngas stream, just before the gas analyzer sampling port.

Figure 3.13: DewPro MMR101 used in contaminant quantification experiments, measures % volume moisture

The ZRE and K1550 analyzers were calibrated less than 1 week before each experiment using both zero and span gases. The DewPro analyzer was received factory-calibrated and requires re-calibration every two years, and thus was not re-calibrated during the study.

3.1.2 Feedstock/Ash Analysis

All biomass and ash analyses were performed by Wyoming Analytical Laboratories (WAL) in accordance with the corresponding ASTM standard except moisture analyses and woodchip char ash analyses performed during the quantification of contaminant retention experiments (Sections 3.2.2 and 4.2). For the analyses that were performed in-house during these experiments, moisture was analyzed according to ASTM Method E 871. Ash was analyzed according to ASTM Method D 1102, with the maximum temperature being 750˚C, as used and suggested by WAL.

3.2 Procedure

3.2.1 Exploration of Poultry Litter Gasification Procedure

The first set of experiments was performed with the goal of consistently gasifying poultry litter. The literature showed this to be either difficult or was ambiguous as to whether poultry litter gasification could actually be sustained. In this study, various experiments were performed utilizing methods drawn from the literature as well as methods devised based on known fuel characteristics in an attempt to inhibit the fusion of the poultry litter during gasification. Specifically, trials were run experimenting with dilution of the fuel using non-sintering material, attempting to lower the average gasifier temperature using flue gas recirculation, and utilizing limestone as an anti-fusion and potential chlorine-capturing additive.

Poultry litter pellets were used for all tests initially (Figure 3.14a). The size and shape of the pellets, coupled with their ease of handling and relative homogeneity, made them a better candidate than raw poultry litter for the type of gasifier and feed system being used. Pellets used were manufactured by Organic Growing Systems, Monticello, MS.

Figure 3.14: a) Poultry litter pellet detail **b)** Raw poultry litter

Later experiments employed the use of raw poultry litter, acquired from the Auburn University Poultry Science Department Research Farm (Figure 3.14b). In cases where poultry litter was diluted with pine woodchips or mixed with limestone, relatively consistent homogeneity in the mixed feedstock was achieved by employing the use of a portable, clean cement mixer.

For all experiments, the gasifier was started using a combination of natural charcoal and pine chips and allowed to come to steady-state operation, taking approximately one half hour, before the feedstock of interest was fed. All feedstocks tested were run for at least three hours so the effects of the fuel being tested would be amplified relative to the woodchips and charcoal used for startup.

In an attempt to lower and control the average gasifier temperature, trials were run using flue gas as a diluent, supplementing the secondary air. Early gasification trials with poultry litter pellets displayed a tendency to hang up on, and adhere to, the secondary air injection nozzles (can be seen in Figure 4.3). In the oxygen deficient environment of the gasifier, the highest reaction rates, and thus the highest temperatures, would be where oxygen is most available. Limiting the local “hot-spots” generated at the secondary air injection sites was seen as a potential solution. The experimental setup consisted of generating and cooling flue gas using an Eccotemp L10 propane water heater and feeding it into the secondary air blower inlet (Figure 3.15). The amount of flue gas generated was controllable by the propane valve and the O_2 and CO_2 content of the secondary air mixture could be measured with a second gas analyzer sampling after the blower. This analyzer was manufactured by NOVA Analytical Systems.

Figure 3.15: Propane water heater used for flue gas generation

3.2.2 Quantification of Contaminant Retention Procedure

These later experiments were executed after consistent gasification of poultry litter was achieved. They were performed with the goal of quantifying the retention of the deleterious components pertinent to the cement kiln in the ash. It was found in the first set of experiments (Section 3.2.1 and 4.1), that in order to gasify the litter consistently, raw poultry litter had to be mixed with approximately 5% powdered limestone (by mass, relative to wet poultry litter, or ~6.5% relative to dry litter) and diluted with pine chips to about 40%. In the Quantification of Contaminant Retention experiments, the limestone ratio functioned as the independent variable and two runs each were performed using 3.71, 5.71, and 7.71 percent lime relative to wet poultry litter mass. These slightly higher percentages were selected to account for the lower moisture content of the poultry litter used in these runs versus that used in the Exploration of Poultry Litter Gasification experiments (sections 3.2.1 and 4.1.4), as well as to allow for rounded-off, easy to work with weights of feedstocks (can be seen in Tables A.3-8). Also, to account for the lower moisture content, all runs were performed with the raw litter diluted by pine chips to a 35:65 ratio (litter:woodchips) instead of the 40:60 ratio used previously. As in section 4.1.4, 200 lbs (90.72 kg) of woodchips were fed into the gasifier following the poultry litter/limestone/woodchip mixture to ensure complete gasification of the fuel of interest. Despite this excess biomass, poultry litter would still be dominant source of the chlorine and alkali components in the resulting gasifier char due to the low ash content of the woodchips. All char produced was collected, sampled, and sent for analysis after every experiment. These analyses were then compared in a mass balance to the composition of the incoming feedstocks to determine the retention rate of contaminants pertinent to cement kilns. Additionally, char from three of the experiments was sampled and analyzed by location from the heat exchanger, filter box, and below the gasifier grate in order to examine the effects of temperature variation on char composition.

Preliminary preparation consisted of acquiring a large amount of raw poultry litter from the Auburn Poultry Science Research Farm from the same pile and mixing well for batch homogeneity. This batch would be used for all runs. A consistent, homogeneous batch of pine woodchips was also delivered and used for all runs. Powdered limestone and natural charcoal were purchased by the bag and are assumed to be consistent in composition from bag to bag. Poultry litter, woodchip, and charcoal samples were taken and sent to Wyoming Analytical to have proximate, ultimate, chlorine, Btu, and ash analyses performed. A sample of limestone was sent to WAL to have an ash analysis performed.

The following setup was consistent between experiments, the only variable being limestone percentage:

- Prior to each experiment, the gasifier system was purged using a Shop-Vac and the onboard auger, as shown in Section 3.1.1.
- The feedstock mixture was prepared using a cement mixer, weights measured with an electronic scale. First all the litter and lime were mixed separately, then added to the woodchips in the following amounts:
    - 130 lbs (58.97 kg) pine woodchips
    - 70 lbs (31.75 kg) raw poultry litter
    - 2.6/4/5.4 lbs (1.17/1.81/2.45 kg) powdered limestone

- 200 lbs (90.72 kg) of woodchips were weighed, to be fed after the poultry litter mixture in order for the litter to fully gasify
- The gasifier was filled to level 1 with charcoal from a bag, the weight taken before and after, and the difference recorded as the charcoal weight
- The gasifier was filled the rest of the way with woodchips, the weight recorded
    - Woodchips were kept at ready to be fed as the gasifier warmed up until the poultry litter mixture was fed
- Representative samples were collected and analyzed for moisture content, according to ASTM E 871:
    - Charcoal
    - Warm-up Woodchips
    - Poultry Litter
    - Woodchips mixed with poultry litter/Woodchips fed after poultry litter mix (same batch used for both)

The following procedure was consistent between experiments:

- The gasifier was started, buckets of woodchips weighed, recorded, and added to maintain proper level in the gasifier until temperatures reached steady state
- When the gasifier operation reached steady state (about one half hour after starting), the poultry litter/limestone/woodchip mixture was started feeding (automatically, by the feed system)
    - The time was recorded when the first bit of the mixture dropped into the gasifier

    - The time was recorded when the last bit of the mixture dropped into the gasifier
- After the last of the mixture was fed, the 200 lbs of woodchips were started feeding using the automatic feed system
    - The woodchips and poultry litter chunks that (together with associated limestone percentage) that were sorted by the sorting screen were separated and weighed to be subtracted from the input amount
- After the last of the 200 lbs of woodchips were fed, the flame front was allowed to advance to the top, charring all the raw chips and consuming any remaining moisture. As soon as this occurred, the gasifier was turned off, sealed and allowed to cool overnight.
    - Woodchips that were sorted by the sorting screen were weighed and recorded to be subtracted from the 200 lb total

The following data collection methods were consistent between experiments:

- Syngas was side stream sampled, dried, analyzed, and recorded continuously from the first steady-state before litter/limestone/woodchip addition until end of run for: O_2, CO, CO_2, CH_4, and H_2
- Moisture of syngas was probe monitored and recorded continuously
- Gasifier performance data was recorded by the onboard computer continuously
- At least 24 hours after every experiment (to allow cool-down), ash was collected from the various collection points (Section 3.1.1), weighed, and sampled.
    - The char from the 200 lbs of woodchips was collected from the top of the gasifier, down to level 5, and labeled ‘Woodchip Char’

  - The rest of the gasifier char was collected (Figure 3.6), sample labeled ‘Rest of Gasifier’. The gray, amorphous poultry litter/limestone ash was separated by hand for the first three runs, sample labeled ‘PL Ash’
  - The char below the gasifier grate was collected (Figure 3.7) and combined with the char collected from just before the heat exchanger entrance (Figure 3.8), sample labeled ‘Below Grate’
  - The char was collected from inside and at the exit of the heat exchanger using a Shop-Vac (Figure 3.9), labeled ‘HEX’
  - The char was collected from the filter box using the onboard auger, labeled ‘Filter’

Two experiments were run for each limestone percentage (3.71, 5.71, and 7.71 % limestone). In one experiment for each set point, representative ash and char samples were taken from each of the above locations for comparison of variation in ash composition through the gasifier. In the other three experiments, ‘Rest of Gasifier’ and ‘PL Ash’ were combined and analyzed as one sample labeled ‘Gasifier’. Also, ‘Filter’, ‘HEX’ and ‘Below Grate’ were combined and analyzed as one sample labeled ‘After Grate’. For all experiments, a sample from the ‘Woodchip Char’ was analyzed for Loss on Ignition (LOI), as dictated in Section 3.1.2.

3.2.3 Data Analysis

The data collected for each experiment was analyzed using various methods in order to understand and interpret the results. Syngas volume percentage was used to calculate syngas HHV and biomass and ash analyses were used to perform mass balances. In performing these analyses, several assumptions were made:

- Only species present in syngas are O_2, CO, CO_2, CH_4, H_2, N_2, and H_2O
- All gases behave as ideal
- All biomass and limestone is homogeneous in composition, on a dry basis
- CO_2 in limestone is fully consumed during gasification
- Limestone and poultry litter, after being mixed, travel together in the same wet weight ratio as they were combined for each experiment (This assumption is used to factor in sorted litter and residual litter in the storage bins)
- The ash content of the 'Woodchip Char' has the same composition as the ash content of the raw woodchips

When calculating composite syngas HHV, the HHV per unit mass (kJ/kg) of each of the combustible components (CO, CH_4, and H_2) were referenced from Turns, 2000 and Glassman, 2008 (29) (30). To get the volumetric heating value of each gas, the HHV's of each gas were converted to a molar basis and then multiplied by the molar density of an ideal gas at 0˚C, 1 atm (the standard to which the gasifier flow is corrected to).

$$ideal\ gas\ molar\ density_{0\,^{\circ}C,1\,atm} = \frac{n}{V} = \frac{P}{R_U \cdot T} = 44.615\left[\frac{mole}{m^3}\right] \tag{3.1}$$

P = 101,325 Pa

$R_U = 8.3145\,\frac{J}{mole \cdot K}$

T = 273.15 K

$$Species\ HHV\ \left[\frac{KJ}{m^3}\right] = \frac{\left(Species\ HHV\ \left[\frac{KJ}{kg}\right]\right)\cdot\left(Species\ MW\ \left[\frac{kg}{kmole}\right]\right)\cdot\left(44.615\left[\frac{mole}{m^3}\right]\right)}{1000\ \left[\frac{mole}{kmole}\right]} \tag{3.2}$$

The composite HHV at 0˚C, 1 atm is then just the molar fraction (or volume fraction as dictated by the gas analyzers) of each gas multiplied by its corresponding volumetric HHV and summed up.

$$\begin{aligned} Syngas\ HHV\ \left[\frac{KJ}{m^3}\right] &= (Mole\ fraction\ CO)\cdot\left(CO\ HHV\ \left[\frac{KJ}{m^3}\right]\right) \\ &+ (Mole\ fraction\ CH_4)\cdot\left(CH_4\ HHV\ \left[\frac{KJ}{m^3}\right]\right) \\ &+ (Mole\ fraction\ H_2)\cdot\left(H_2\ HHV\ \left[\frac{KJ}{m^3}\right]\right) \end{aligned} \tag{3.3}$$

To find the element mass percentage (% E) from the corresponding oxide mass percentage (% $\mathrm{E}_x\mathrm{O}_y$), the oxide mass percent was multiplied by the ratio of element's weight in one molecule of the oxide to the molecular weight of the oxide.

$$\%\,E = \left(\%\,\mathrm{E}_x\mathrm{O}_y\right)\cdot\frac{x\cdot A_E}{(x\cdot A_E)+(y\cdot A_O)} \tag{3.4}$$

A_E=Atomic Weight of Element

A_O=Atomic Weight of Oxygen (15.999)

In the Exploration of Poultry Litter Gasification Section (Section 4.1), experiments were performed examining methods to achieve consistent gasification of poultry litter. Replications of experiments were performed only if results from initial experiments were deemed promising. With this in mind, early experiments only were performed once or twice, but later experiments saw more iterations as results were approaching the performance and consistency desired. In the Quantification of Contaminant Retention Study (Section 4.2) 6 total experiments were performed, two at each limestone set point. This allowed averages to be calculated and trends observed both overall and at each variable each set point.

Chapter 4

Results and Discussion

4.1 Exploration of Poultry Litter Gasification

The proximate, ultimate, and ash analyses of the poultry litter pellets used in the experiments are shown in Tables 4.1-4.3. This composition is typical for poultry litter. The silica percentage in the ash is relatively high, but this varies from farm to farm depending on the amount of dirt that gets mixed with the litter in the pens. Na_2O is slightly lower than the average expected quantity as well, usually in 5-9% range. Additionally, ash fusion analyses showed initial deformation occurring at 1120˚C in a reducing atmosphere and 1149˚C in an oxidizing environment.

Table 4.1: Poultry litter pellet proximate analysis

Parameter	% as received	% dry basis
Moisture	11.32	-
Ash	25.12	28.33
Volatile matter	52.54	59.25
Fixed carbon, by dif.	11.02	12.42
HHV [MJ/kg]	12.40	13.98

Table 4.2: Poultry litter pellet ultimate analysis

Parameter	% dry basis
Hydrogen	3.44
Carbon	36.72
Nitrogen	1.44
Oxygen, by diff.	28.45
Sulfur	0.77
Chlorine	0.847
Ash	28.33

Table 4.3: Poultry litter pellet ash analysis

Oxide	% ignited basis
SiO_2	45.30
Al_2O_3	2.48
Fe_2O_3	1.08
CaO	11.93
MgO	4.75
Na_2O	4.37
K_2O	13.00
TiO_2	0.28
MnO_2	0.34
P_2O_5	10.56
SrO	0.03
BaO	0.05
SO_3	5.82

4.1.1 Initial Tests and Woodchip Dilution

An initial feasibility test was performed employing the poultry litter pellets in the standard gasifier setup. The gasifier was started using woodchips and after steady-state operation was reached, the pellets were fed for several hours. However, upon inspection after the run, the entire gasifier was clogged with solid poultry litter clinkers that had to be removed with an air chisel (Figure 4.1).

Figure 4.1: Poultry litter clinker from initial trial, ~18 cm wide

This result was in agreement with most of the literature and showed the need for additional measures to be taken when attempting to gasify poultry litter consistently. Accordingly, the next runs were performed using a mixture of poultry litter pellets diluted with woodchips (the typical feedstock used in this gasifier), and with an eye to reducing the temperature of the gasifier through limited superficial velocity and reduced secondary air flow.

The first of these runs was a test to explore exactly what level of control over the gasifier temperature existed. The fusion of the pellets was most likely due to their low ash fusion temperature, a contribution of the alkali metals, chlorine, and silica present in poultry litter. Lowering the temperatures in the gasifier, especially the peak temperatures, was thought to alleviate at least some of the clinkering. Several trials were conducted running only woodchips and attempting to stabilize reduced temperatures.

The initial attempt consisted of simply reducing the set point temperatures in each stage of air injection for the gasifier. Although the peak temperature was reduced with this technique, the operation was not stable and the flame front rose to the top of the downdraft gasifier. This occurred because as air injection is reduced at each level (to reduce the temperature in that level), additional air was added at the uncontrolled gasifier inlet (top) to provide the total flow rate of air required for the syngas production rate specified (65m^3/hr).

In subsequent trials, to reduce the gasifier superficial velocity, the lower set point temperatures were used in conjunction with lower syngas flow rates until the syngas flow rate was reduced to 40m^3/hr (the minimum allowed by the gasifier). The net reduction in average reaction temperature was less than 50˚C using this technique.

The next runs were conducted to determine if the clinkering tendency of poultry litter could be mitigated by diluting the poultry litter pellets with wood chips. Trials with 20 percent and 40 percent poultry litter (by weight) in wood chips were conducted. Initially the trial with 20 percent poultry litter appeared to be successful and produced no external operating anomalies such as increased pressure drop across the gasifier. Consequently, without purging the existing material, a trial using 40 percent poultry litter was conducted. During each of these trials a suitable quality syngas was produced for the duration. However, as the 40% trial progressed, the operating temperature profile and the gasifier pressure drop became unstable and the trial was aborted. The gasifier was then cleaned and the ash was found to contain significant quantities of clinkered poultry litter pellets (Figure 4.2).

Figure 4.2: Poultry litter pellet clinkers from 40% pellet run

Subsequent trials and analyses showed that clinkering was actually occurring with the 20 percent trial but the low concentration of poultry litter pellets and the long residence time in the gasifier caused the problem to not be evident during the roughly 4 hour initial trial.

Additional tests were performed attempting to limit the gasifier temperature while feeding poultry litter by adjusting set-points, depressing overall gas flow rate, using wet woodchips to depress the flame front, and combinations of each. None of these options yielded either stable operation or a reduction of the pellet clinkering.

However, a pattern was observed in the clinker formation and location throughout the runs. Clinkers tend to be on the order of 6-8 cm in diameter, or roughly the size of a baseball. The pellet agglomerations tended to be found hung-up between levels 3-4 or 4-5 (Figure 4.3). This trend appeared to be independent of trial length or dilution percentage.

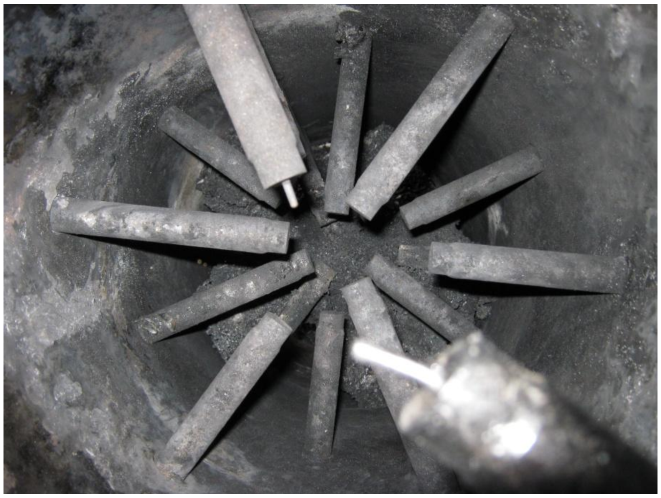

Figure 4.3: View from top of gasifier of poultry litter pellet clinkers hung up between levels 3 and 4 after loose biomass char had been removed. Level 5 is obscured by clinkers

4.1.2 Flue Gas Recirculation

According to the ash fusion analysis conducted by Wyoming Analytical Laboratories, initial deformation was found to be occurring at1120˚C in a reducing environment and 1149˚C in an oxidizing environment. Both of these temperatures, however, are greater than any observed in the gasifier under normal operating conditions. A plot of the average temperature profile inside the gasifier over a typical 4 hour run can be seen in Figure 4.4. Levels 1-5 correspond to thermocouples located at the 5 levels of secondary air injection.

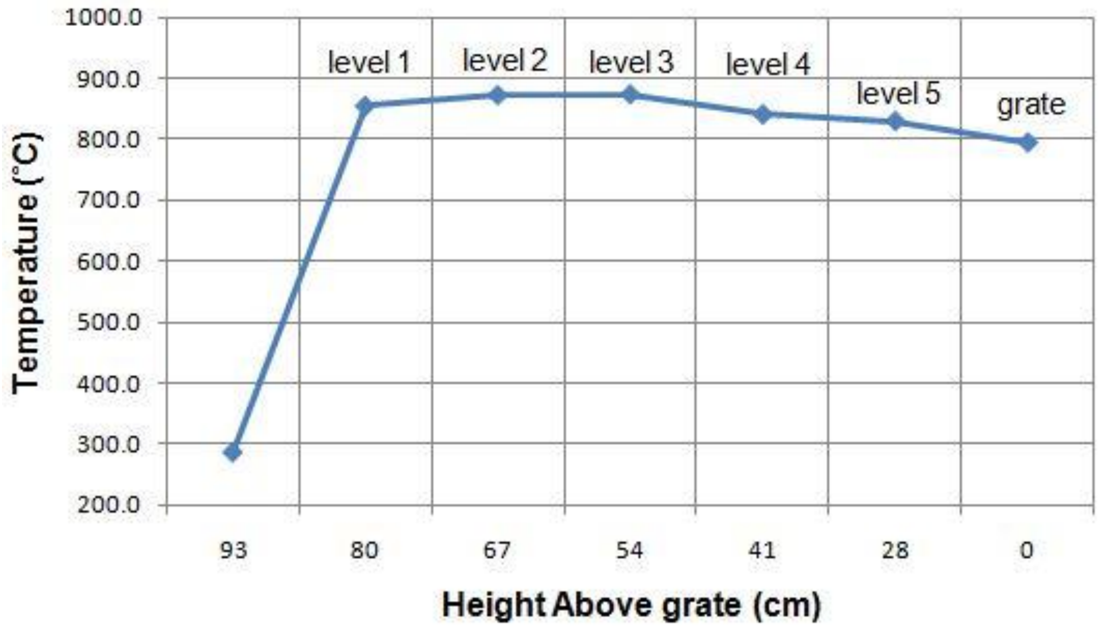

Figure 4.4: Average gasifier temperature profile during a typical run with pine chips

While this represents the average over time, it should be noted that peak temperatures observed during standard operation seldom eclipse 950˚C and never exceed 1100˚C unless the flame front escapes the gasifier top and is recorded by the top-most thermocouple.

Given these observations, it was perplexing as to why pellet adhesion was occurring with such severity at these low temperatures despite the efforts put forth to abate them. However, when examining the clinkers formed during some of the experiments, it was discovered that several had distinct impressions corresponding to the shape of the secondary air injection nozzles (Figure 4.5).

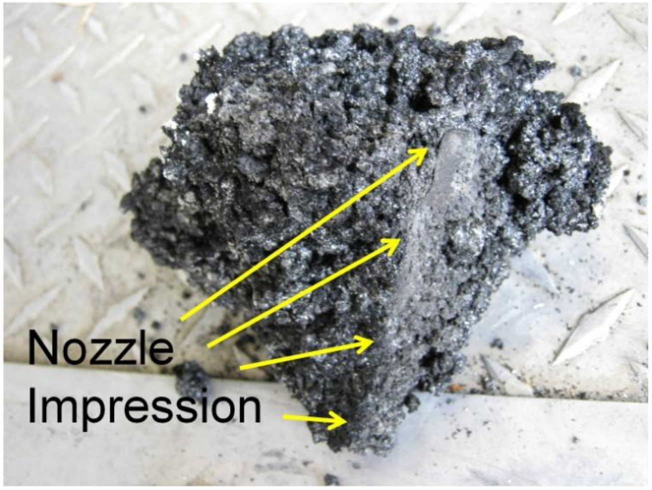

Figure 4.5: Impression of nozzle in poultry pellet clinker

This gave rise to the theory that local ‘hot spots’ exceeding the ash fusion temperature were to blame for the clinker formation. In the reducing environment of the gasifier, the highest temperatures would be where oxygen is most available and actual combustion could occur locally. Limiting this oxygen supply through the use of a diluent, the most practical option being flue gas, was a prospective solution. In addition to diluting the throughput of oxygen to the gasifier char, the primary species present in flue gas (CO_2 and H_2O) could potentially participate in two of the dominant endothermic reactions to actually lower the temperature locally (11) (13):

$C + CO_2 \rightarrow 2CO + 14.42$ MJ/ kg of carbon gasified

$C + H_2O \rightarrow CO + H_2 + 10.92$ MJ /kg of carbon gasified

To easily produce, control, and cool a flue gas stream, a propane water heater was used, as detailed in the Experimental Setup section. The lowest average gasifier operating temperature profile obtained is shown in Figure 4.6, for comparison to the standard profile from Figure 4.4.

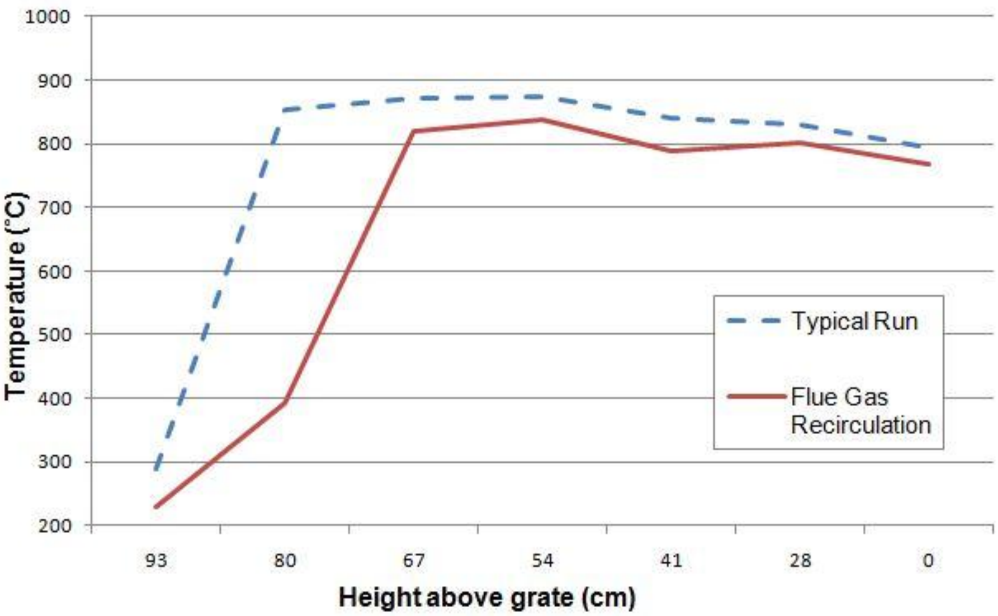

Figure 4.6: Average gasifier temperature profile during flue gas recirculation poultry litter

The overall average temperature of the gasifier achieved using this method was 662˚C, 102˚ cooler than the 764˚C average of the typical run. This was obtained by reducing the syngas production rate to 55Nm³/hr (from the standard 65) to limit the superficial velocity through the gasifier and by diluting the secondary air by an average of 42.5%. That is, the average O_2 reading of the secondary air was 12%, 42.5% less than the 20.9% concentration of the measured ambient air. This test was conducted using a 40% mixture of poultry litter pellets to pine chips by weight for a duration of 3 hours and 20 minutes.

A negative effect manifested in the use of flue gas injection was a reduction in syngas quality. During a standard run with the gasifier using pine chips, the average dry syngas composition (by volume) that can be expected and corresponding higher heating value is approximately:

O_2 [%]	CO [%]	CO_2 [%]	CH_4 [%]	H_2 [%]	HHV [MJ/m³]
0.5	20	12	1.5	18	5.4

*Syngas over duration of a typical run can be seen in Appendix D, Figure D.1

A composition along these lines was observed when gasifying the 40% poultry litter pellet mixture under normal operation in a previous experiment that resulted in clinker formation. However, use of the flue gas recirculation technique resulted in an inferior average syngas composition and consequently an approximately 25% reduction in higher heating value:

O_2 [%]	CO [%]	CO_2 [%]	CH_4 [%]	H_2 [%]	HHV [MJ/m^3]
1.3	13.1	14.3	1.1	15.2	4.0

*Syngas performance over duration of run can be seen in Appendix D, Figure D.2

Despite the successful overall reduction in temperature, examination after the experiment showed that clinkering of the poultry litter pellets was neither eliminated nor significantly reduced. Clinkers were still recovered that had impressions of the nozzles, similar to Figure 4.5.

From the experiments run and observations made, it can be seen that the fusion experienced by the poultry litter pellets in the gasifier is temperature independent, at least within the controllable range.

4.1.3 Limestone Additive

The next option, as described in the literature, was the use of limestone additive to prevent fusion of gasified litter (5) (16) (27). A further benefit of the addition of limestone to the gasifier environment was the potential for the capture and retention in the ash of volatilized chlorine.

Powdered limestone was used for the experiments and the analysis is shown in Table 4.4.

Table 4.4: Powdered limestone analysis

Oxide	% dry basis
SiO_2	1.60
Al_2O_3	0.51
Fe_2O_3	0.59
$CaCO_3$	81.86
$MgCO_3$	15.01
Na_2O	0.01
K_2O	0.17
TiO_2	0.05
MnO_2	0.06
P_2O_5	0.05
SrO	0.07
BaO	0.01
SO_3	0.16

The analysis shows that the limestone used was of good quality, being high in calcium carbonate and low in silica and other constituents. As recommended in the literature, 5% by weight (limestone/litter) powdered limestone was used to evenly coat the poultry litter pellets in a cement mixer. This mixture was then diluted to 40% by weight with pine chips to prevent extreme blockage if the experiment was unsuccessful. Ninety kg of this mixture was fed for four hours with very little departure in gasifier performance or syngas composition from a standard woodchip feedstock run. Upon examination of the char, it was discovered that although clinkers had been formed, most were smaller in size than usual (4-5 cm diameter) and two larger ones (12-14 cm) had proceeded beyond the lowest level of nozzles, where few usually advance.

A second, identical experiment was run and after 90 kg of the mixture was gasified, pine chips were fed for an additional four hours in an attempt to flush the poultry litter mixture through the gasifier. A significant amount of poultry litter pellets did feed past the last air injection nozzles, but they were found in the form of a large agglomeration containing both woodchip and pellet remains. However, the furthest advancing, pellet-containing part of this agglomeration appeared to blend seamlessly into a layer of easily crumbled, dense, gray, amorphous ash approximately 4 cm above the grate. This suggested that the pellets, having been fully depleted of their carbon content, no longer possessed the extreme traits of fusion displayed when found higher in the gasifier. A sample of this ash was analyzed and was found to contain oxides associated with both the limestone and poultry litter ash as well as a chlorine concentration of 3.57% (Table 4.5).

Table 4.5: Dense, gray, easily crumbled, amorphous ash analysis

Oxide	% dry basis
SiO_2	24.50
Al_2O_3	1.30
Fe_2O_3	1.25
CaO	37.78
MgO	2.49
Na_2O	0.89
K_2O	15.18
TiO_2	0.16
MnO_2	1.34
P_2O_5	1.99
SrO	0.17
BaO	0.30
SO_3	4.09
Loss on ignition	8.55
Chlorine	3.57

The chlorine concentration found (3.57%) is more than four times that of the raw poultry litter pellets (0.847 %) and indicates the successful capture of a measurably significant portion. This was a promising result with regards to the end goal of limiting chlorine volatilization and entrainment in the product gas. The clinkering issue, however, demanded further attention if poultry litter was to be gasified consistently, leading to the set of experiments described next.

4.1.4 Raw Poultry Litter and Limestone Addition

A trial of raw, un-pelletized, woodchip-diluted poultry litter was seen as an alternative to the dense, seemingly non-porous litter pellets. This mixture would offer a more even distribution of the litter as well as allow easier carbon conversion. Results from previous runs using poultry litter pellets indicated that long residence times were necessary if total carbon conversion was to be achieved. This is due most likely to the low porosity of the highly compacted pellets limiting the gas diffusion and isolating reactions to the surface of the pellets. Additionally, trials could be run using the limestone additive mixed more evenly with the problem feedstock, as opposed to only coating the surface of pellets. Dilution of the raw litter with woodchips would be necessary for implementation in the downdraft gasifier and feed system due to the high percentage of fines.

Ninety kg of the 20% raw litter mixture fed for three hours for a total mass flow rate of 30 kg/hr. Over 90 kg of woodchips were fed for four hours following the poultry litter mixture to assure advancement of the mixture to the grate and allow for accurate assessment of performance following the trial.

The trial performed well and a syngas similar to pure woodchips was produced for the duration of the run. Only two small clinkers resulted from this experiment, and both were found past the last level of nozzles inside the gasifier, indicating clean passage through the area where pelletized litter had been hung up.

A second experiment of 40% litter was run to determine the upper limit of raw poultry litter substitution. This was found to be too much for the gasifier, producing a large agglomeration between levels four and five.

To test the effect of limestone addition, 5% lime (to raw litter weight) was evenly mixed with the raw litter before being diluted to 40% with woodchips. Since 40% un-amended litter appeared to exceed the upper limit, this concentration would be a good benchmark for comparison. The mixture was found to gasify much better than either the litter without lime or the pelletized litter mixed with lime. No clinker formation was found to occur, only the existence of an amorphous, grey, crumbly ash (Figure 4.7). This ash was easily broken up by hand and was likely to continue through the gasifier without much issue.

During the experiment a large pressure drop across the gasifier built up, but was alleviated by the continuing oscillation of the grate shaker. Even if this pressure drop proves to be persistent, operation was reliable and steady enough to conduct further tests in quantifying deleterious species capture rates.

An identical experiment was performed to test how consistent this method was and very similar results were found. The syngas composition and resulting HHV were slightly compromised by air leaks resulting from the elevated gasifier differential pressure (seen in Appendix D, Figure D.3), but gasifier performance was satisfactory for beginning the Quantification of Contaminant Retention Study.

Figure 4.7: Easily crumbled, grey amorphous ash from raw poultry litter with limestone

4.1.5 Summary of Results

A summary of the primary techniques explored in the study is presented in Table 6.

Table 4.6: Summary of primary experiments and results, avg. syngas HHV≈5.4 MJ/m³

Technique used	Gasifier char state	Syngas Quality	Notes
20% pellets, 80%woodchips	6-8cm clinkers, nozzle impressions	Average	
40% pellets, 60%woodchips	6-8cm clinkers, nozzle impressions	Average	
Flue gas recirculation, 40% pellets	6-8cm clinkers, nozzle impressions	Below average, 4.0 MJ/m³	~100˚C reduction in avg. temp.
Limestone addition, 40% pellets	4-5cm clinkers, agglomeration past nozzles	Average	
20% raw litter, 80% woodchips	Minimal clinker formation and only past the nozzles	Average	
40% raw litter, 60% woodchips	Large agglomeration	Average	
Limestone addition, 40% raw litter	No clinkers: amorphous, grey, crumbly ash	Below average, ~4.0 MJ/m³	Reduction in syngas quality due to increased gasifier pressure and resulting air leak

4.2 Quantification of Contaminant Retention Study

The goal in these experiments was to quantify the percentage of contaminants retained in the ash when gasifying poultry litter. The proximate, ultimate, and ash analyses of the charcoal, woodchips, and raw poultry litter used in these tests are presented in Tables 4.7-4.9. The limestone used was the same as that in Sections 4.1.3-4.1.4 and can be seen in Table 4.4. The raw poultry litter has a lower ash content and a higher HHV than the pelletized litter used previously, making it a better fuel candidate from the beginning. When compared to the average from the literature (Section 2.1), the ash is still low, but HHV is average. The sulfur and chlorine content are lower than average as well. The silica content is lower than the poultry litter pellets, potentially aiding in its resistance to clinkering (as discussed in Section 2.5).

Table 4.7: Proximate analysis of charcoal, woodchips, and poultry litter (% dry basis)

Parameter	Charcoal	Woodchips	Poultry Litter
Ash	5.64	0.28	19.63
Volatile matter	16.81	81.71	63.99
Fixed carbon, by dif.	77.55	18.01	16.38
HHV [MJ/kg]	30.17	19.40	15.48

Table 4.8: Ultimate analysis of charcoal, woodchips, and poultry litter (% dry basis)

Parameter	Charcoal	Woodchips	Poultry Litter
Hydrogen	1.88	5.03	3.87
Carbon	80.44	49.33	36.69
Nitrogen	0.52	0.53	0.77
Oxygen, by dif.	11.49	44.70	38.44
Sulfur	0.01	0.13	0.10
Chlorine	0.0221	0.0030	0.502
Ash	5.64	0.28	19.63

Table 4.9: Ash analysis of charcoal, woodchips, and poultry litter (% Ignited Basis)

Oxide	Charcoal	Woodchips	Poultry Litter
SiO_2	6.51	13.99	25.96
Al_2O_3	0.43	2.99	2.87
Fe_2O_3	0.97	6.55	1.47
CaO	78.06	35.50	28.29
MgO	2.15	11.95	4.65
Na_2O	0.90	1.78	3.33
K_2O	5.16	12.50	11.31
TiO_2	0.00	0.00	0.07
MnO_2	2.04	3.73	0.23
P_2O_5	1.07	5.81	15.83
SrO	0.29	0.16	0.03
BaO	0.43	0.47	0.00
SO_3	1.91	4.39	3.52
Chlorine	0.07	0.22	3.13
Total	99.98	99.99	100.00

The low Ash and Chlorine content of the charcoal and woodchips relative to the litter, paired with the low alkali and phosphorus content of the charcoal ensured that the poultry litter was by far the dominant source of Na, K, P, and Cl in the experiments. For all experiments, poultry litter accounted for 90.6±0.6% Na, 83.6±0.9% K, 95.5±0.2% P, and 93.6±0.4% Cl fed into the gasifier (Appendix A, Tables A.3-8).

Results between experiments were very similar from a gasifier performance, qualitative analysis, and syngas production standpoint. During all runs, gasifier differential pressure started climbing after the poultry litter mixture had been feeding for about one hour, due to the large amount of fines present in poultry litter. By one and a half hours it had reached 25” H_2O (6.2 kPa), the maximum in the measured range for the onboard manometer, where it remained for the duration of the test. Consequently, air was drawn into the system anywhere there were small leaks and syngas quality suffered. It was discovered after sampling syngas from different parts of the system that the primary source of the leak was somewhere in the filter box. The dry average syngas composition and HHV during the feeding of the litter/limestone/woodchip mixture for one of the experiments (8.95% limestone/dry litter) is as follows:

O_2 [%]	CO [%]	CO_2 [%]	CH_4 [%]	H_2 [%]	HHV [MJ/m^3]
5.6	14.9	8.5	0.8	12.1	3.8

*Syngas variation during this typical run can be seen in Appendix D, Figure D.4

This result was very typical for all experiments. Since it was found that all O_2 was entering through leaks in the filter box, and assuming that 3.76 moles of N_2 entered for every mole of O_2 in air, a corrected syngas composition and corresponding HHV could be calculated:

O_2 [%]	CO [%]	CO_2 [%]	CH_4 [%]	H_2 [%]	HHV [MJ/m^3]
0.0	20.4	11.6	1.1	16.6	5.1

This corrected composition and HHV is what would be achieved if leaks were eliminated from the system and is very comparable to the standard woodchip syngas composition as described in Section 3.1.1. However, the root of the problem is the high pressure across the gasifier which is an issue that needs to be addressed if gasifying poultry litter is to be further pursued.

Ash recovered from each section of the gasifier was visibly identical between experiments, the only minor difference being ‘PL Ash’ crumbling slightly less easily at the 3.71% limestone set point, perhaps indicating an approach towards the threshold of clinkering for a minimum amount of limestone. A sample of the ‘Woodchip Char’ collected from the top of the gasifier using a Shop-Vac can be seen in Figure 4.8. A dime is pictured as a size reference.

Figure 4.8: ‘Woodchip Char’ sample, collected from the top of the gasifier

When the gasifier was opened at the seam above the grate, the distinction between what appears to be the poultry litter and limestone ash and the charred wood and charcoal was evident. The poultry litter ash, as previously described in Section 4.1.4, is gray, crumbly and amorphous in nature, and can be seen as the light gray sections of ash in Figure 4.9.

Figure 4.9: Ash mound as seen when gasifier is opened at crack above grate. Poultry litter ash is the light gray section in the middle of the mound

After being separated from the charcoal and wood char by hand and crumbled, the poultry litter and limestone ash can be seen in Figure 4.10. This was separated, weighed, and sent for analysis as 'PL Ash' in the first experiment for each of the three limestone set points (3.71, 5.71, and 7.71 % Limestone/Wet Litter), but mixed with the rest of the gasifier char for the second. The charcoal and wood char not included in the 'PL Ash' sample was labeled 'Rest of Gasifier' and can be seen in Figure 4.11.

Figure 4.10: Crumbled poultry litter ash as sent for analysis in one experiment for each limestone set point (3.71, 5.71, and 7.71 % Lime/Wet PL), labeled 'PL Ash'

Figure 4.11: 'Rest of Gasifier' sample, comprised mostly of charcoal and wood char

The char that settled in the chamber below the gasifier grate and just before the heat exchanger, a section where syngas is between 600-750˚C, was labeled 'Below Grate' and can be seen in Figure 4.12.

Figure 4.12: Char collected from chamber below gasifier grate, labeled 'Below Grate'

The char that settled inside and just after the exit of the heat exchanger was labeled 'HEX' and can be seen in Figure 4.13. It is much finer than that below the grate. Syngas in this section is cooled from 600-630˚C down to 100-110˚C.

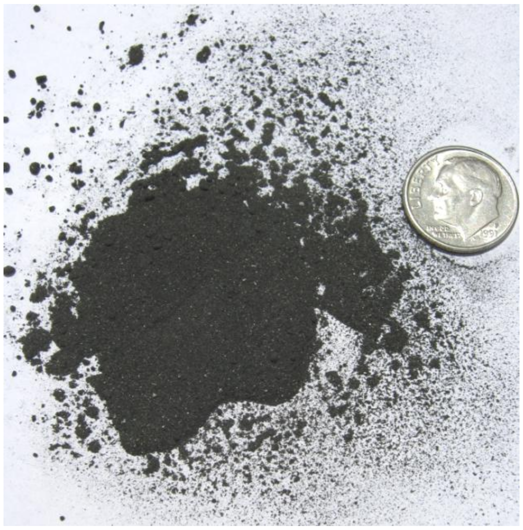

Figure 4.13: Char from inside and just after the heat exchanger, labeled ‘HEX’

The final place char is found is the filter box, samples labeled ‘Filter’. This char is very similar to the ‘HEX’ sample, only slightly darker and more powdery (Figure 4.14). Syngas in this section is filtered through bags and cools from 100-110˚C to 50-60˚C.

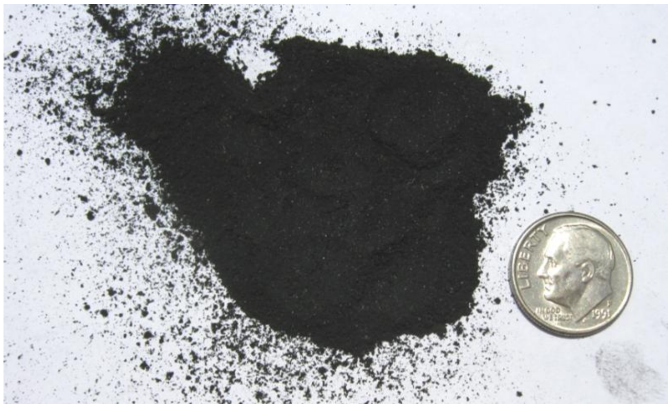

Figure 4.14: Char collected from filter box, labeled ‘Filter’

In the second experiment for each of the three limestone percentages (3.71, 5.71, and 7.71 %), the char comprising the ‘Below Grate’, ‘HEX’, and ‘Filter’ samples was combined, mixed, and then sampled as ‘Past Grate’. In these same three experiments, all char labeled ‘PL Ash’ and ‘Rest of Gasifier’ was combined, mixed, and sampled as ‘Gasifier’.

4.2.1 Contaminant Mass Balances

The procedure followed was that dictated in Section 3.2.2, however after the first four experiments it was discovered that a small amount of the biomass fines were falling below the conveyer in the onboard feed system and never making it into the gasifier. Therefore, during the final two experiments, the small portion of poultry litter mixture that fell through was collected and weighed as was the small portion of the 200 lbs (90.72 kg) of woodchips fed after the poultry litter mixture using the onboard conveyer. The two runs yielded similar results with 4.64 lbs of woodchips and 10.05 lbs of poultry litter mix being collected for one and 5.10 lbs of woodchips and 12.75 lbs of poultry litter mix collected for the other. The average of these two (4.86 lbs woodchips and 11.40 lbs of PL mix) was then assumed as the loss for each of the previous four experiments. To find the composition of the PL mix that was recovered, it was assumed that the same ratio of woodchips fell through from both the 200 lbs woodchip batch and from the woodchips in the poultry litter mixture (130 lbs). This amount (i.e., for the average: $\frac{4.86}{200} \cdot 130$) was then subtracted from the PL mix recovered and what remained was assumed to be poultry litter and lime present in the same ratio as they were mixed for each experiment (i.e. 3.71, 5.71, or 7.71% Limestone/Wet PL).

The analyses for each of the raw feedstocks (charcoal, woodchips, poultry litter, and limestone), coupled with the experimentally found moisture content, predetermined weight, and experimental losses were used to determine the total amount of each contaminant of interest (K, Na, P, Cl) and a tracer element (Ca) fed into the gasifier. In the same manner, using the mass of ash collected, lab analyses, and experimentally determined LOI's the amount of each contaminant and tracer mineral recovered in the ash was determined. Ratios of mass recovered in char to mass fed into the gasifier were then calculated for each element in every experiment, giving a retention percentage of the elements when gasified. Additionally, total ash content fed into the gasifier was calculated from the feedstock weight and ash analysis, as was total ash content recovered from the char. These values were then compared and used to calculate a percent difference of total ash content collected to total ash content expected. These mass balances and analyses can be seen in Appendix A.

Not factoring in the assumed and measured losses from the onboard conveyor, the retention percentage of each element for every experiment can be seen in Table 4.10, arranged in order of increasing Limestone/Dry poultry litter percentage. The average retention percentage at each Limestone/Wet Poultry Litter set point can be seen in Table 4.11.

Table 4.10: Retention percentage of notable elements, not accounting for conveyor losses

% Limestone/Wet PL	% Limestone/Dry PL	P	K	Cl	Na	Ca
3.71	4.24	83.2%	80.4%	63.3%	73.5%	74.5%
3.71	4.31	112.4%	91.9%	92.7%	101.4%	104.8%
5.71	6.49	91.7%	90.4%	89.3%	89.2%	89.6%
5.71	6.69	100.3%	80.8%	73.1%	96.1%	90.6%
7.71	8.92	71.9%	81.0%	76.4%	60.9%	65.5%
7.71	8.95	88.3%	86.4%	82.0%	84.8%	83.9%
	Average:	91.3%	85.2%	79.5%	84.3%	84.8%

Table 4.11: Average retention percentage of notable elements at the three limestone set points, not accounting for conveyor losses

% Limestone/Wet PL	P	K	Cl	Na	Ca
3.71	97.8%	86.1%	78.0%	87.4%	89.7%
5.71	96.0%	85.6%	81.2%	92.6%	90.1%
7.71	80.1%	83.7%	79.2%	72.8%	74.7%

To compare the effect of factoring in the conveyor losses, Table 4.12 shows the absolute percent difference between total ash content put into the gasifier and total ash content recovered in the char, with and without the conveyor losses factored in. It also shows the percentage of the total input ash content that the conveyer losses account for in each run.

Table 4.12: % of total input ash content accounted for by conveyer losses and absolute % difference between total input ash and output ash with and without conveyor losses factored in. *designates runs where conveyer losses were collected and weighed, losses for all others are the average of the two

% Limestone/Wet PL	% Limestone/Dry PL	% of input ash	Abs. % Diff. betweent total ash in and total ash out	
			With losses factored in	Without losses factored in
3.71	4.24	9.4%	12.6%	20.8%
3.71*	4.31*	8.1%	7.7%	1.0%
5.71	6.49	9.2%	0.2%	9.4%
5.71	6.69	9.5%	0.4%	9.1%
7.71*	8.92*	12.2%	25.4%	33.4%
7.71	8.95	9.2%	7.8%	16.3%
	Average:	9.6%	9.0%	15.0%

It can be seen that including the conveyer losses gains an average 6.0% improvement in ash percent difference for all runs. Also, the losses account for an average 9.6% of the input ash. Because of this, all results presented henceforth will have the conveyor losses factored in.

The retention percentage of notable elements, losses factored in, is presented in Table 4.13. Compared to Table 4.10, phosphorus is 6.3% closer and calcium is 7.4% closer on average to 100% retention. In the literature (Section 2.3) it was found that P and Ca did not volatilize at gasification or combustion temperatures and thus are expected to be accounted for fully in the gasifier char. Ca particularly is expected to be fully retained in the ash and was used in the literature as a foundation for normalizing data. The average retention percentage at each limestone set point can be seen in Table 4.14.

Table 4.13: Retention percentage of notable elements, conveyor losses factored in

% Limestone/Wet PL	% Limestone/Dry PL	P	K	Cl	Na	Ca
3.71	4.24	93.7%	89.4%	71.0%	82.2%	81.0%
3.71	4.31	124.4%	100.5%	102.5%	111.7%	112.4%
5.71	6.49	102.9%	100.1%	100.0%	99.5%	97.3%
5.71	6.69	112.5%	89.7%	81.9%	107.3%	98.8%
7.71	8.92	82.0%	91.2%	87.0%	69.0%	72.6%
7.71	8.95	98.9%	95.7%	91.7%	94.5%	91.3%
	Average:	102.4%	94.4%	89.0%	94.0%	92.2%

Table 4.14: Average retention percentage of notable elements, conveyor losses factored in

% Limestone/Wet PL	P	K	Cl	Na	Ca
3.71	109.0%	95.0%	86.8%	97.0%	96.7%
5.71	107.7%	94.9%	91.0%	103.4%	98.1%
7.71	90.5%	93.4%	89.3%	81.7%	81.9%

The data from Tables 4.13-14 is presented graphically in Figures 4.15-17, plotted as percent retention vs. limestone percent (on a wet litter basis). The data points for the two runs at each limestone set point are displayed as diamonds, and the average for those points is shown as an asterisk with a curve fit.

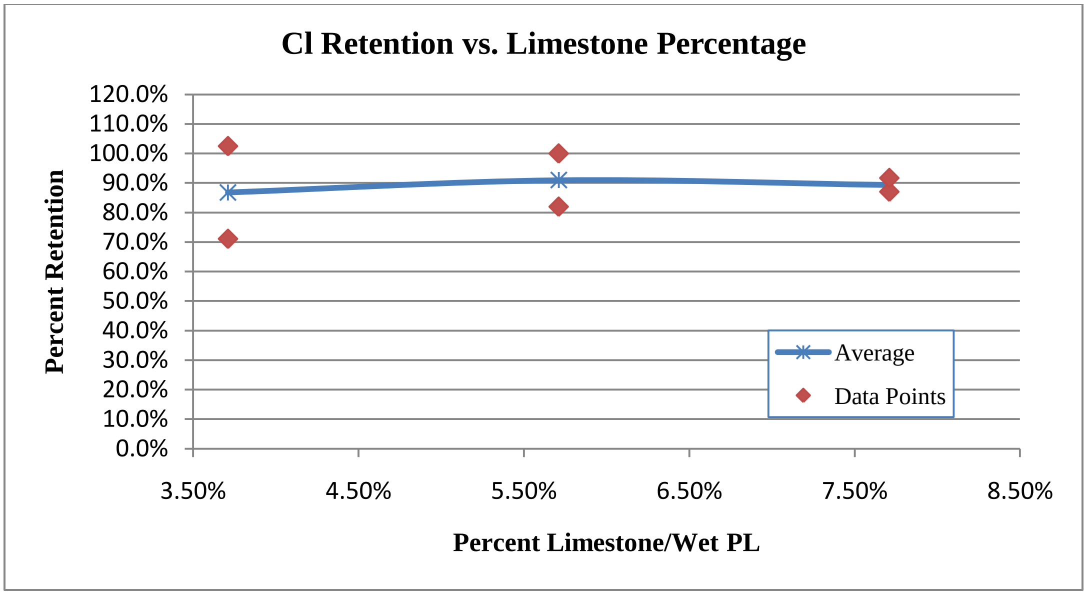

Figure 4.15: Chlorine Retention vs. Limestone Percentage

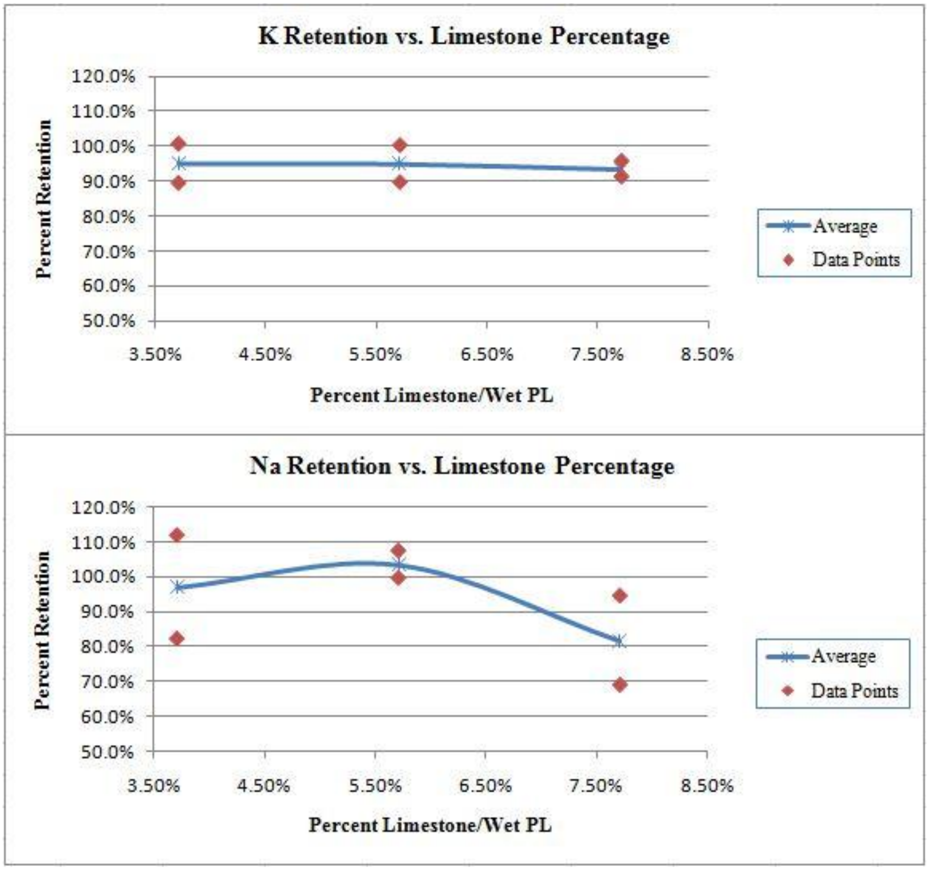

Figure 4.16: Alkali Retention vs. Limestone Percentage

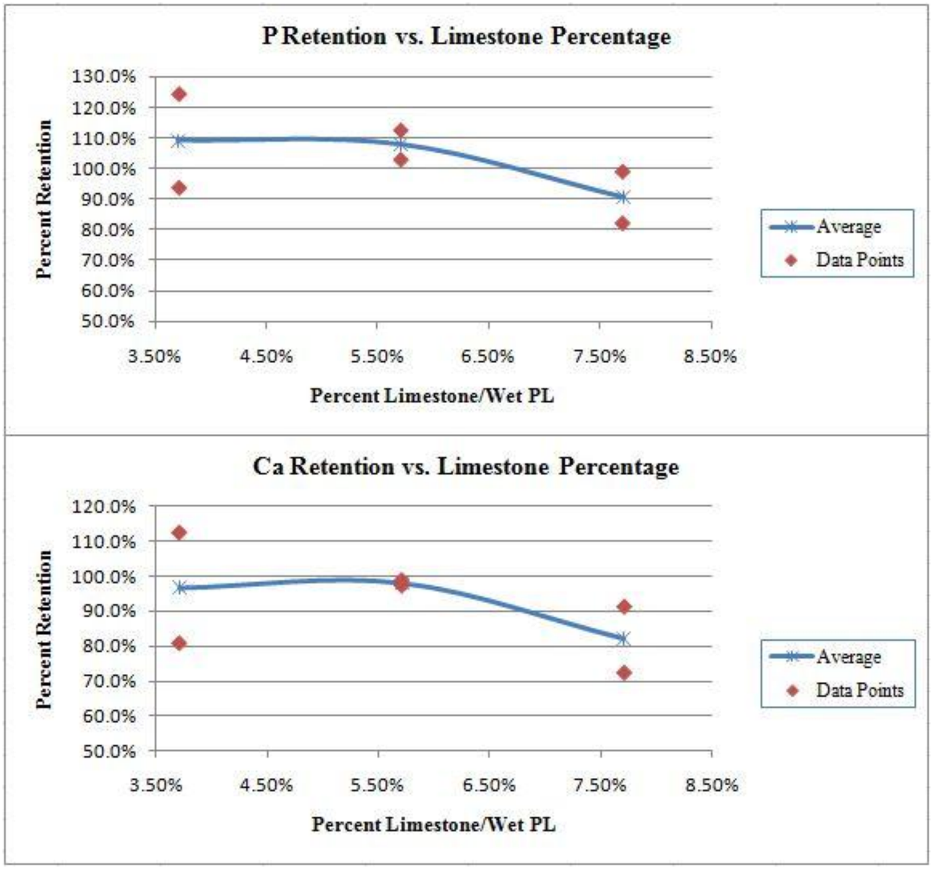

Figure 4.17: Phosphorus and Calcium Retention vs. Limestone Percentage

Chlorine is retained quite well, the average being 89.0%. The average at each set point doesn't vary much from the overall average, indicating little effect of limestone percentage on chlorine retention, at least within the range tested. The average potassium retention appears steady between limestone percentages, straying little from the overall average of 94.4%. The trend lines for Na, P, and Ca, however, all decline quite substantially with increasing limestone percentage. It may be possible for Ca that as more limestone is mixed with the raw poultry litter, there is also more that is lost as dust while mixing or that falls through the conveyor while feeding. However, phosphorus shows a similar decrease and the extremely low P content in limestone (0.05% dry basis, Table

4.4.) prevents that theory for accounting for the losses of both of these elements that were expected to be fully retained. Analyzing the numbers from Tables 4.13 and 4.12 it can be seen that the experiment contributing most to the low average of Na, P, and Ca at 7.71% limestone also has the largest percent difference between total ash in and out: 25.4% even after including the conveyor losses. Additionally, it can be observed from Table 4.13 that the calcium retention percentage for each experiment is very indicative of the percent retention of the other elements for that run. For example, in an experiment when Ca is lower than the average, all other parameters are lower than average as well. The same trend can be observed for the experiment with a Ca balance of greater than 100%. With these observations in mind, and borrowing the technique discussed from the literature, each experiment was normalized to the expected value of 100% Ca (22). Table 4.15 shows the retention percentage for all experiments when the results for each experiment were normalized to Ca. The average retention percentage at each % Limestone/Wet Litter set point can be seen in Table 4.16.

Table 4.15: Retention percentage of notable elements, normalized to Ca

% Limestone/Wet PL	% Limestone/Dry PL	P	K	Cl	Na	Ca
3.71	4.24	115.7%	110.4%	87.7%	101.5%	100.0%
3.71	4.31	110.7%	89.5%	91.2%	99.4%	100.0%
5.71	6.49	105.7%	102.9%	102.7%	102.3%	100.0%
5.71	6.69	113.8%	90.7%	82.9%	108.6%	100.0%
7.71	8.92	113.0%	125.7%	119.9%	95.2%	100.0%
7.71	8.95	108.3%	104.7%	100.4%	103.4%	100.0%
	Average:	111.2%	104.0%	97.5%	101.7%	100.0%

Table 4.16: Average retention percentage of notable elements, normalized to Ca

% Limestone/Wet PL	P	K	Cl	Na	Ca
3.71	113.2%	100.0%	89.5%	100.5%	100.0%
5.71	109.8%	96.8%	92.8%	105.4%	100.0%
7.71	110.7%	115.2%	110.1%	99.3%	100.0%

The data from Tables 4.15-16 is presented graphically in Figures 4.18-19, plotted as percent retention vs. limestone percent (on a wet litter basis). The data points for the two runs at each limestone set point are displayed as diamonds, and the average for those points is shown as an asterisk with a curve fit.

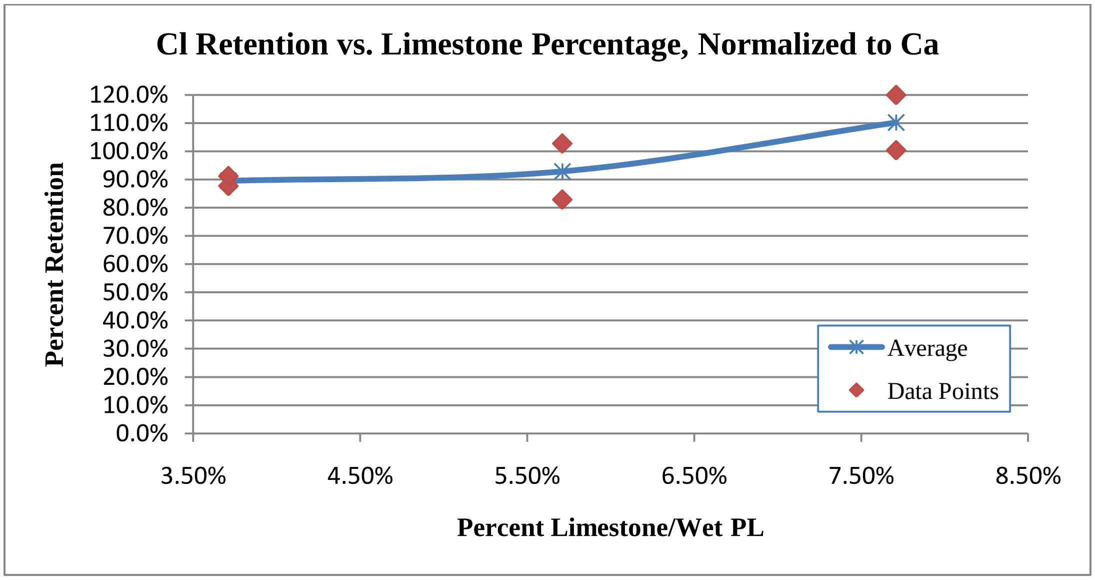

Figure 4.18: Chlorine Retention vs. Limestone Percentage, Normalized to Calcium

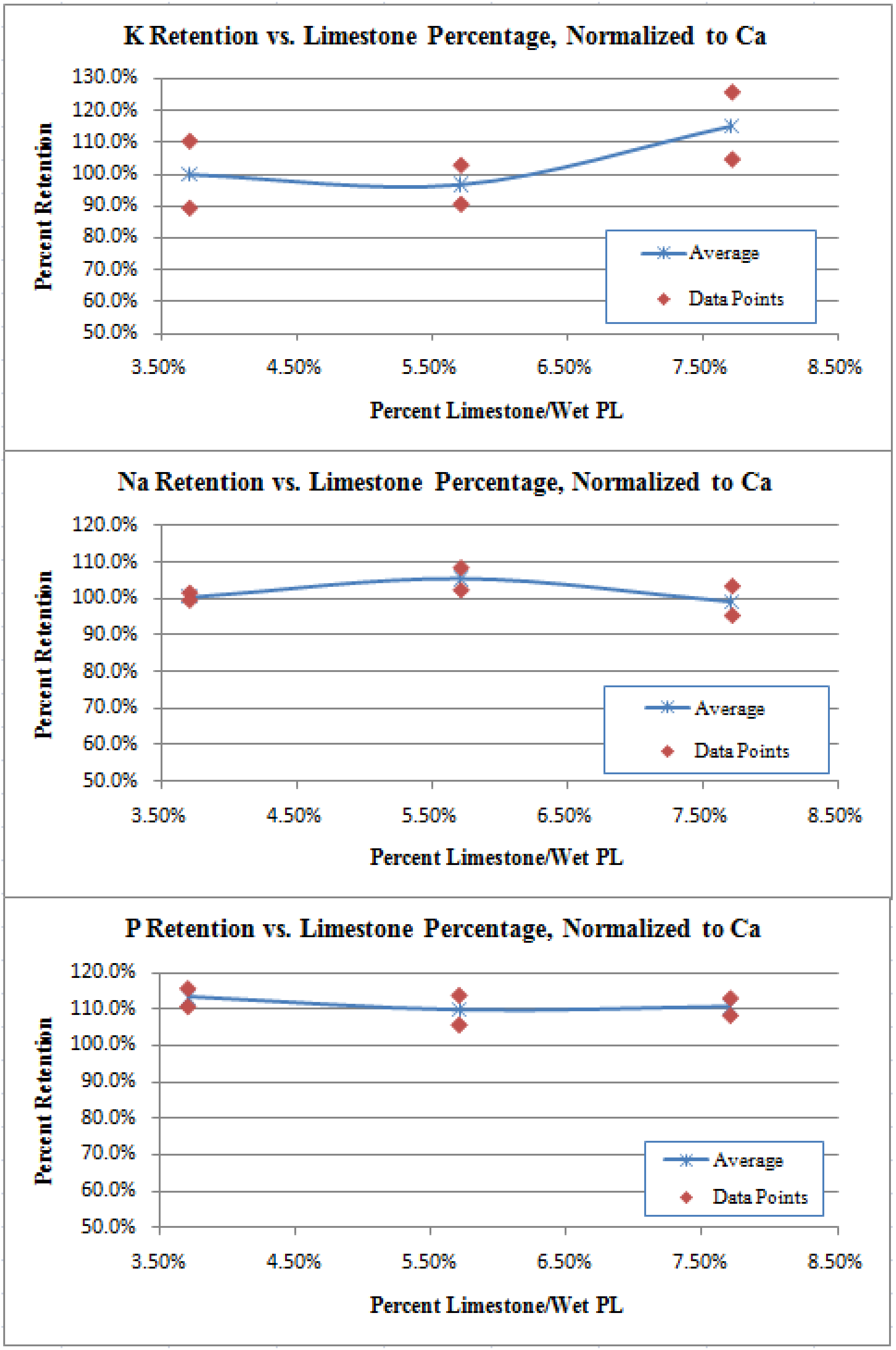

Figure 4.19: Potassium, Sodium, and Phosphorus Retention vs. Limestone Percentage

Normalizing to calcium tightened up most of the data points. The span between the two data points at each limestone percentage improved on average from 16.8% to 11.0% for every element excluding Ca. The phosphorus trend line is now flattened out and the average retention at the 7.71% limestone set point is in line with the averages at 3.71% and 5.71%, which both changed very little. However, now all data points for P as well as several for Na, K, and Cl are above 100%. The trend lines for both Cl and K appear to indicate an increase in retention with an increase in limestone addition, which was the hypothesized result (an increase in Cl capture by the limestone limiting K reaction and volatilization with Cl), however the peak for both is at least 110%.

Overall, it is difficult to say whether the trend lines actually represent a trend, due to limited number of data points and the substantial scatter of the points. However, on average, nearly all of the contaminates appear to be captured. The lowest average retention percentage over all runs, regardless of losses included or normalization, was Cl and at worst the average retention percentage was 78.0% (for 3.71% limestone, not including conveyor losses). Including the known conveyor losses, an average 89.0% Cl was captured over all runs and at least 94.4% on average was captured of P, K, and Na. When normalized to calcium, an average 97.5% Cl was captured and at least 100% on average was captured of P, K, and Na.

4.2.2 Contaminant Distribution

In one of the experiments at each of the three limestone percentages, the char collected from each section of the gasifier was weighed and analyzed separately, instead of combining and mixing it. Doing this allowed insight into the distribution of elements throughout the gasifier. Figure 3.5 shows the average temperature of the syngas as it proceeds from the grate through the heat exchanger and finally out of the filter box. This temperature profile is significant when compared with the contaminant profiles. Figures 4.20-22 show the mass percent of K_2O, Na_2O, P_2O_5, SO_3, and Cl in the ash of the char samples at the three limestone/wet poultry litter percentages.

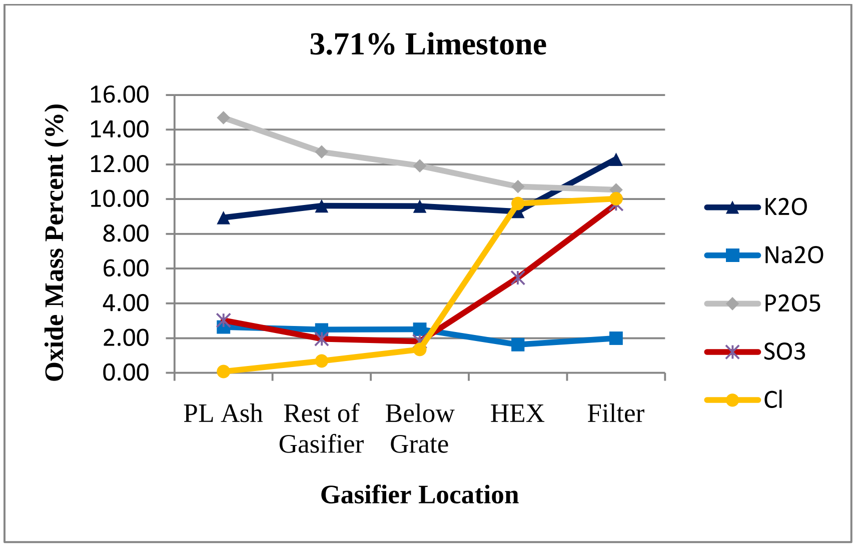

Figure 4.20: Mass percent of oxides in char ash throughout the gasifier, at 3.71% limestone/wet litter

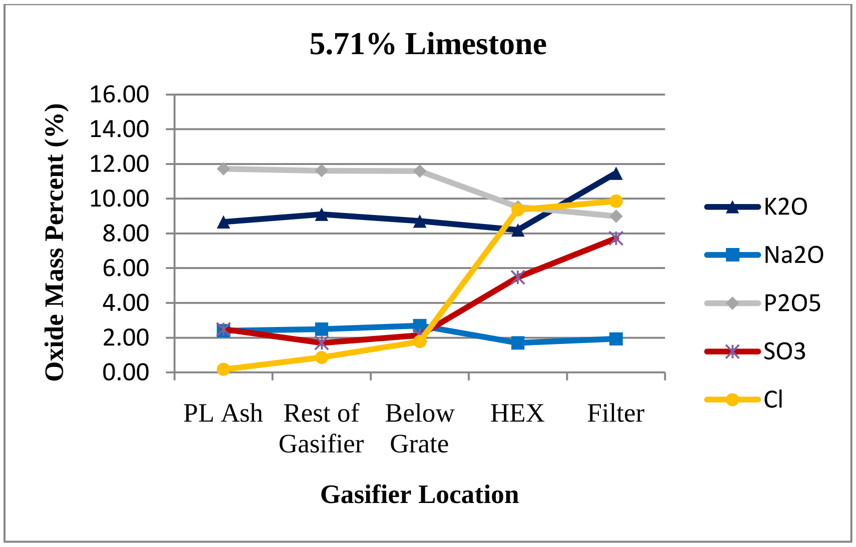

Figure 4.21: Mass percent of oxides in char ash throughout the gasifier, at 5.71% limestone/wet litter

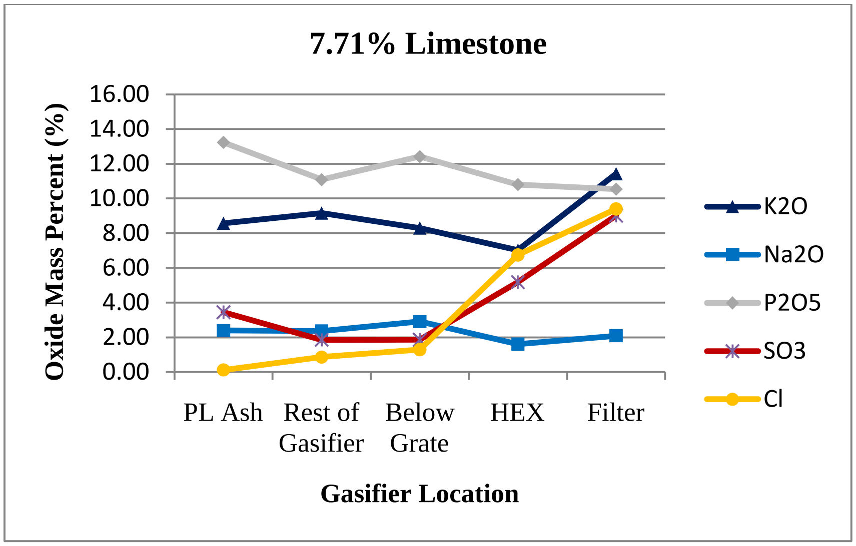

Figure 4.22: Mass percent of oxides in char ash throughout the gasifier, at 7.71% limestone/wet litter

While the limestone percentage doesn't appear to have an effect on the contaminant profile, it is obvious from the three figures that there is a trend in element concentrations. Na_2O and P_2O_5 decrease slightly and seem to mirror each other as you progress through the gasifier. K_2O concentration decreases slightly and then spikes at the Filter location. SO_3 and Cl both increase significantly at the heat exchanger (HEX) and Filter. While sulfur is not one of the main contaminants of interest, the concentration trend was noteworthy and validated presentation. The trend observed for both Cl and S, and to a lesser extent K, is an increase in concentration in the cooler parts of the gasifier. The syngas in the heat exchanger cools from ~610˚C down to ~110˚C and in the Filter down to ~60˚C. At these temperatures some of the volatilized elements appear to be re-condensing and getting sequestered in the char. A second, even more telling graph can be seen in Figures 4.23-25, which shows the percentage of total mass collected of each major element at four locations in the gasifier system: Inside the Gasifier, Below the Grate, in the Heat Exchanger, and in the Filter Box.

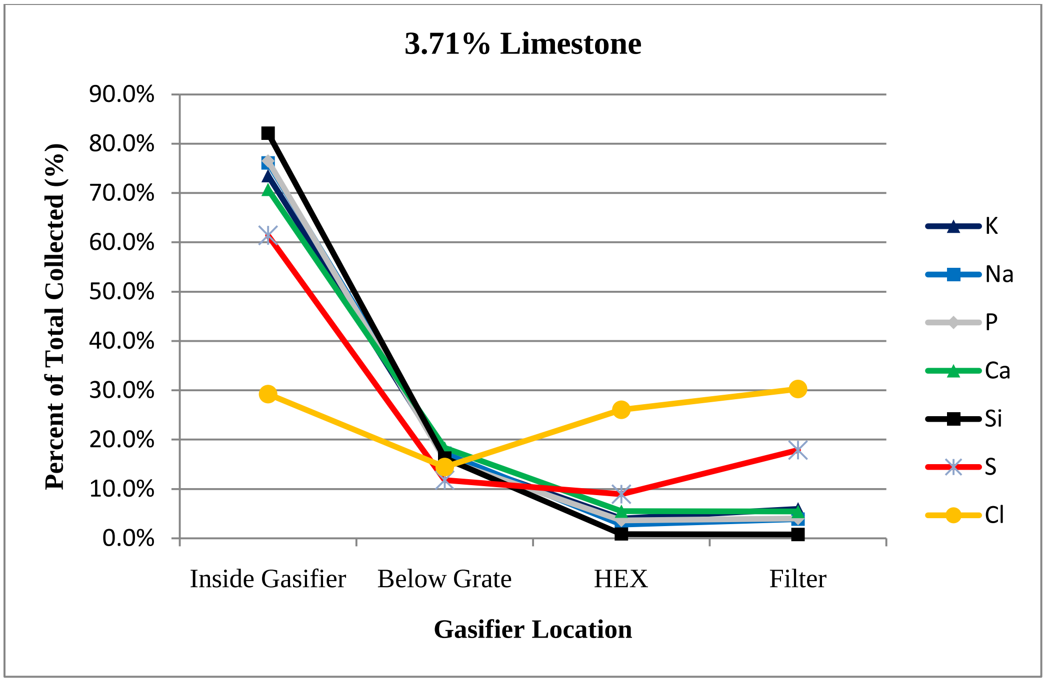

Figure 4.23: Percentage of total mass collected of each element at different locations in the gasifier, at 3.71% limestone/wet litter

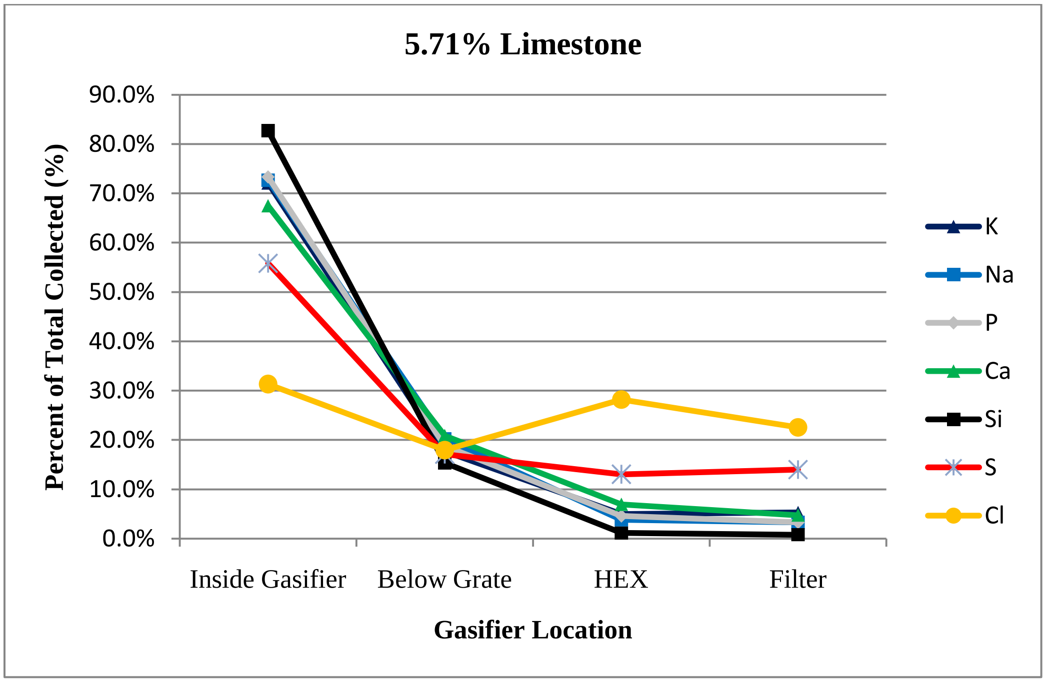

Figure 4.24: Percentage of total mass collected of each element at different locations in the gasifier, at 5.71% limestone/wet litter

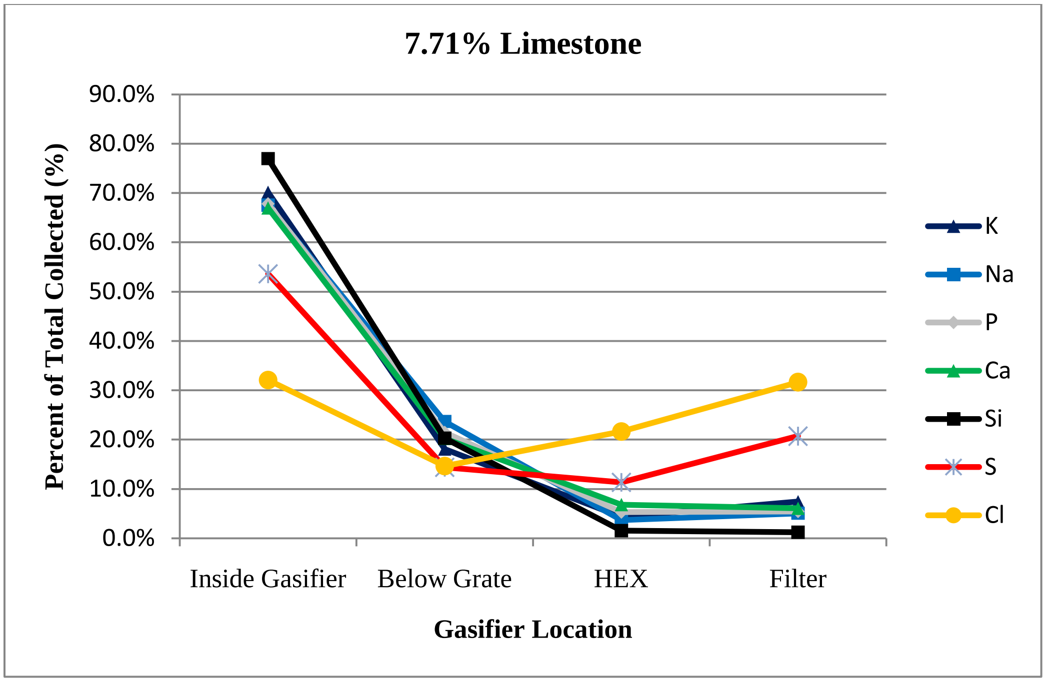

Figure 4.25: Percentage of total mass collected of each element at different locations in the gasifier, at 7.71% limestone/wet litter

Once again, limestone percentage doesn't appear to have an effect on the distribution, however the distribution is very consistent for each element between the three experiments. Almost all the elements follow a similar pattern: about 70% or more is recovered Inside the Gasifier, between 18% and 23% is recovered Below the Grate, and between 1% and 8% is recovered in the Heat Exchanger and Filter Box. The outliers are chlorine and sulfur, who both appear to volatilize and migrate more readily than the other elements, leaving the gasifier but re-condensing and getting captured in the cooler Heat exchanger and Filter Box sections of the gasifier system. On average, 69.1% of the chlorine was captured past the gasifier grate, and 52.6% was captured in the Heat Exchanger and Filter Box. The average retention of 30.9% of the Cl inside the gasifier agrees well with results of Bjorkman, et al. in Figure 2.1, showing the retention of ~37% when pyrolyzing switchgrass at 900 ˚C. From Figures 4.20-25, the conclusion can be drawn that cooling and filtering the syngas is necessary for the maximum capture and retention of chlorine and sulfur in the char. While potassium follows the same trend as the other elements in Figures 4.23-25, the consistent increase in concentration at the Filter Box location in Figures 4.20-22 suggest that cooling the syngas to between 60-100˚C aids in the retention of this element as well, which according to the literature is most likely in the form of KCl. The ratios of Cl to K in the Filter location and HEX location allow this as a possibility, but can neither explicitly confirm nor deny it.

4.2.3 Conclusions, Recommendations, and Sources of Error

Through experimentation, it was shown that downdraft gasification is effective as a means of sequestering contaminants harmful to the cement manufacturing process while extracting the usable chemical energy from poultry litter in the form of syngas. Conservatively, 89% of the chlorine can be retained in the char, as well as 94% of the potassium and sodium, along with 100% of the phosphorus. It does, however, appear to be necessary to cool and filter the syngas in the range of 60-110˚C to obtain maximum removal of the contaminants, particularly Cl and K, from the syngas stream. Although sulfur is not a contaminant of high interest when compared to the coal and coke used in the cement kiln, results show that cooling and filtering the syngas limits its throughput as well. Variation of limestone percentage did not appear to have a large effect on the capture rates, at least within the range tested, although the low set point of 3.71% limestone to wet poultry litter (4.24-4.31% dry) seemed to approach the minimum limestone percentage necessary to avoid clinkering. As a result, a limestone percentage in the range of the middle set point (5.71% limestone to wet poultry litter, 6.5-6.7% dry) emerged as the preferred amount, limiting the use of an extra additive while providing a factor of safety against clinkering issues.

It is yet to be determined, however, the effectiveness of the techniques used in the experiments towards gasifying poultry litter of higher ash or chlorine contents. The raw litter used successfully in the experiments had an ash content of about 20% on a dry basis. As seen in the literature as well as the litter pellets used for earlier tests, ash content can be as high as 33% on a dry basis, with an average in the literature of 25.2%. With this in mind, the recommended ratio of 6.5-6.7% limestone to dry litter found in the experiments would be about 33-34% limestone to poultry litter ash. Additional considerations to explore are: methods of eliminating the high pressure drop across the gasifier due the poultry litter fines; further experimentation with poultry litter pellets, perhaps with limestone pre-mixed in; use of different gasifier types; and measurement of the concentration of contaminants in the syngas itself to round out the mass balance and verify retention in the char.

There were many potential sources of error encountered in the experiments. Due to the large scale of experiments and small size of the biomass and char samples analyzed, much of the accuracy depended on the mixing and sampling involved. While mixing or sampling fine char such as that collected from the heat exchanger or filter box (seen in Figures 4.13-14) probably resulted in an accurate representative sample, char such as that marked ‘Rest of Gasifier’ was very non-homogeneous (as seen in Figure 4.11) and a given sample could vary highly in its accuracy of representation. While the ash analyses didn’t vary greatly between experiments, the LOI varied by as much as 20% in one case between similar samples. An example of a problem encountered when mixing is the presence of white, 1.5” (3.8 cm) deposits found inside the gasifier, circled in Figure 4.26).

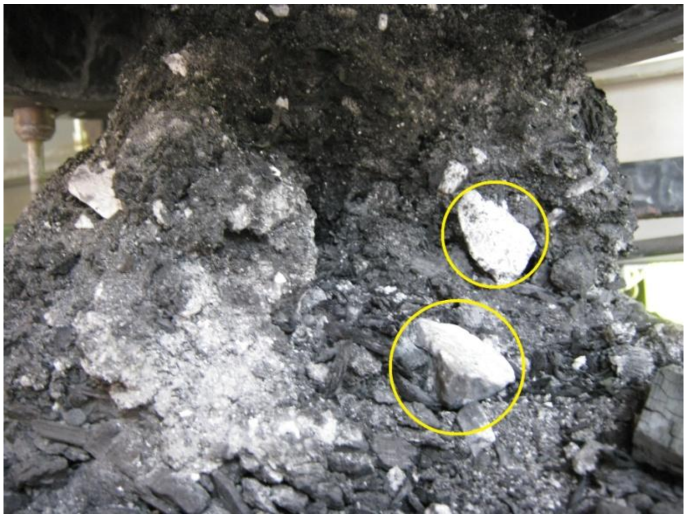

Figure 4.26: Ash mound found when gasifier is opened at seam above the grate, white deposits circled

Three to four of these deposits were found in every experiment and an attempt was made to crush them before mixing and retrieving a sample. One deposit was collected and sent for analysis, showing it had only a 2.22% LOI and was comprised of 57.91% CaO and 40.34% MgO on an ash basis. If these deposits weren’t crumbled and fully mixed in on every run, Ca recovery in the char would be lower than it should be. Another source of error was losses in the form of dust and fines. As reported, fines from the feedstock fell below the conveyer in the onboard feed system, yet they were only collected and quantified for two of the experiments. Dust was observed to be created and carried away with the wind during the mixing of limestone, poultry litter, and woodchips before each experiment as well as during the experiments when being fed into the gasifier. The feedstock with the finest particles was the limestone, and if this accounted for most of the dust loss there would also be a preferential loss of Ca before entry into the gasifier. This may account for the lower than expected Ca retention in some of the runs, as well as the retention rates greater than 100% when normalized to Ca. Overall, these factors most likely account for the scatter observed in the data points when calculating mass balances.

Chapter 5

Conclusions

Downdraft gasification has been explored as a means to extract chemical energy from poultry litter while limiting the throughput of potentially deleterious components with regards to use in firing a cement kiln. Experiments with temperature depression via flue gas recirculation, feedstock dilution using woodchips, and experiments employing limestone as an additive to prevent fusion and aid in chlorine retention in the ash have been carried out. Flue gas recirculation allowed the reduction of the gasifier secondary air oxygen concentration by 40-45%, yielding an approximately 100˚C depression in average temperature. Results have shown that the clinkering is temperature independent, at least within the controllable temperature range. Limestone also had only a slight effect on the fusion when used to coat the pellets. However, limestone addition did display some promise in regards to chlorine capture, as ash analyses showed chlorine concentrations of more than four times greater in the limestone infused ash as compared to raw poultry litter. Experiments were conducted to explore the effectiveness of mixing limestone with raw poultry litter, the object being to coat more surface area and have a more even mixture. These resulted in the most consistent experiments with no ash clinkering.

Once consistent gasification of raw poultry litter was achieved through a combination of woodchip dilution (60% woodchips:40% poultry litter) and addition of limestone at 5% of the wet poultry litter mass (~6.5% Limestone/Dry Poultry Litter), experiments were performed to determine the capture rates of the contaminants pertinent to cement kilns. Limestone percentage was varied to explore its effect on chlorine retention at set points of 3.71, 5.71, and 7.71% Limestone to Wet Poultry Litter, the middle quantity slightly inflated from the previously used 5% to account for lower moisture of the litter used in these experiments. It was found that limestone percentage, at least within the tested range, had little effect on neither the retention of contaminants nor distribution of contaminants through the gasifier system. On average, 89% of the chlorine was retained in the gasifier char, as was 94% of both the potassium and sodium, and 100% of the phosphorus. When data was normalized to 100% calcium retention (expected from the literature), an average 100% of the Na, K, and P were shown to be retained, as well as 97.5% of the Cl. The contaminant profile, developed from analyses of char samples from different sections of the gasifier system, showed that 69.1% of the chlorine retained was captured past the gasifier grate and 52.6% was captured in the significantly cooler Filter Box and Heat Exchanger sections of the gasifier system. Additionally, peaks in concentration of sulfur and potassium were observed in these same sections. From these results, it appears necessary to cool and filter the syngas in the range of 60-110˚C to obtain maximum removal of Cl, as well as K and S, from the syngas stream.

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Appendices

Appendix A

Contaminant Mass Balance Spreadsheets

Table A.1: Ash contents of the input feedstocks

Ash Content (% wt), dry basis			
Charcoal	Poultry Litter	Woodchips	Lime
5.64	19.63	0.28	56.31

Table A.2: Analyses of feedstocks used in mass balances and oxide to element % mass conversion factor. Limestone total ≠100% b/c CaO and MgO are calculated from carbonate percentages (seen in Table 4.4)

Oxide to Element Conversion	**Input Ash analyses [% mass, ash basis]**				**Limestone [% mass, dry basis]**
	Oxide	Poultry Litter	Woodchips	Charcoal	
0.467	SiO2	25.96	13.99	6.51	1.60
0.529	Al2O3	2.87	2.99	0.43	0.51
0.699	Fe2O3	1.47	6.55	0.97	0.59
0.715	CaO	28.29	35.50	78.06	43.41
0.603	MgO	4.65	11.95	2.15	7.18
0.742	Na2O	3.33	1.78	0.90	0.01
0.830	K2O	11.31	12.50	5.16	0.17
0.599	TiO2	0.07	0.00	0.00	0.05
0.436	P2O5	15.83	5.81	1.07	0.05
	BaO	0.00	0.47	0.43	0.01
	MnO2	0.23	3.73	2.04	0.06
0.401	SO3	3.52	4.39	1.91	0.16
	SrO	0.03	0.16	0.29	0.07
	Cl	3.13	0.22	0.07	0.00
	TOTAL	100.71	100.04	100.00	53.87
	Cl (Dry Basis)	0.502	0.003	0.022	0.000

Table A.3: Spreadsheet for 4.24% limestone/dry litter from 5/24/2010
** Denotes average value used for conveyor fall-through losses

Moisture Content (wet basis)				
	Charcoal	Warm up chips	Poultry Litter	Mix/After PL Chips
tin	13.5	13.7	13.7	13.5
wet	120.8	145.1	134.8	131.2
dry	114.7	128.7	119.9	115.2
moisture %	5.68	12.48	12.30	13.59

	Input [lbs], 2.6 lbs Limestone				
		wet	wet - (Sorted + Fall through)	dry	Theoretical Ash
	Charcoal	43.10	43.10	40.65	2.29
	Warm up Chips	30.30	30.30	26.52	0.07
PL MIX	**PL**	70	60.99	53.49	10.50
	Chips	130	123.64	106.83	0.30
	lime	2.60	2.27	2.27	1.28
	After PL Chips	200	188.09	162.52	0.46
	total	476.00	448.39	392.28	**14.90**
	Lime/Litter percentage	3.71%	3.71%	4.24%	

Elements IN [lbs]					
P	K	Cl	Na	Ca	
0.011	0.098	**0.009**	0.0153	1.2791	Charcoal
0.002	0.008	**0.001**	0.0010	0.0188	Warm up Chips
0.725	0.986	**0.269**	0.2594	2.1232	**PL**
0.008	0.031	**0.003**	0.0039	0.0759	**Chips**
0.000	0.003	**0.000**	0.0002	0.7029	**lime**
0.012	0.047	**0.005**	0.0060	0.1154	After PL Chips
0.758	1.173	**0.286**	0.286	4.315	***total***
0.032	0.187	**0.018**	0.026	2.192	***total (non PL)***
95.75%	84.02%	**93.76%**	90.76%	49.20%	*ratio from PL/total*

	Sorted/Fall-through	**[lbs]**		**Sorted**	**Fall-through**
	Sorted PL+Lime	1.10	Mix Chips	3.20	3.16
	Sorted Mix Chips	3.20	PL	1.06	7.95
**	*Fall-through Chips/PL/Lime*	11.40	Lime	0.04	0.30
	Sorted 200 lbs	7.05	***total***	4.30	11.40
**	*Fall-through 200 lbs*	4.86	After PL Chips	7.05	4.86

	Output [lbs]			
		Recovered	Dry	Actual Ash
Gasifier	**Woodchips char**	5.90	5.90	0.15
	PL Ash	1.10	1.10	1.08
	Rest of Gasifier	18.50	18.46	8.46
	Below Grate	4.65	4.64	2.18
	HEX	0.95	0.94	0.54
	Filter	1.40	1.37	0.61
	total	32.50	32.40	**13.03**
			Ash Percent diff:	12.55%

Elements OUT [lbs]							
P	K	Cl	Na	Ca	Si	S	
0.0037	0.0153	**0.0003**	0.0019	0.0374	0.0096	0.0026	**Woodchips char**
0.0694	0.0803	**0.0009**	0.0211	0.3007	0.1087	0.0131	**PL ash**
0.4696	0.6753	**0.0582**	0.1558	2.1335	1.0418	0.0664	**Rest of Gasifier**
0.1131	0.1734	**0.0294**	0.0405	0.6402	0.2296	0.0158	Below Grate
0.0255	0.0420	**0.0530**	0.0065	0.1922	0.0121	0.0119	HEX
0.0282	0.0627	**0.0616**	0.0091	0.1900	0.0109	0.0239	Filter
0.7096	1.0490	**0.2034**	0.2349	3.4940	1.4128	0.1337	***total***
93.7%	89.4%	**71.0%**	82.2%	81.0%	**Ratio OUT/IN**		
				19.03%	% Difference		
115.7%	110.4%	**87.7%**	101.5%	100%	Norm. to Ca		

Output Ash Analyses																	
		Oxide to Element Multiplier	0.467	0.529	0.699	0.715	0.603	0.742	0.830	0.599	0.436			0.401		
	Moist (% As Rec)	LOI (% Dry Basis)	SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	CaO (%)	MgO (%)	Na_2O (9	K_2O (%)	TiO_2 (%	P_2O_5 (%)	BaO (%)	MnO_2 (%)	SO_3 (%)	SrO (%)	Cl (%)
PL 5/24	0.00	1.6	21.49	2.61	1.35	38.88	5.58	2.63	8.94	0.12	14.68	0.05	0.51	3.02	0.06	0.08
Rest of Gasifier 5/24	0.20	54.17	26.34	3.26	1.44	35.28	5.59	2.48	9.61	0.08	12.72	0.06	0.58	1.96	0.06	0.69
Below Grate 5/24	0.32	53.05	22.57	2.56	1.42	41.16	4.54	2.51	9.60	0.07	11.91	0.09	0.62	1.81	0.08	1.35
HEX 5/24	1.39	41.88	4.75	1.62	1.35	49.39	6.78	1.62	9.29	0.00	10.72	0.20	1.12	5.47	0.13	9.74
Filter 5/24	2.47	55.01	3.80	1.29	1.76	43.28	5.97	1.99	12.30	0.00	10.53	0.20	1.25	9.72	0.14	10.02
Woodchip Char		97.50														

Table A.4: Spreadsheet for 6.49% limestone/dry litter from 5/17/2010
** Denotes average value used for conveyor fall-through losses

Moisture Content (wet basis)				
	Charcoal	Warm up chips	Poultry Litter	Mix/After PL Chips
tin	13.7	13.7	13.5	13.5
wet	107.0	127.5	140.4	135.6
dry	100.6	111.2	125.3	118.7
moisture %	6.86	14.32	11.90	13.84

	Input [lbs], 4 lbs Limestone				
		wet	wet - (Sorted + Fall through)	dry	Theoretical Ash
	Charcoal	47.55	47.55	44.29	2.50
	Warm up Chips	46.85	46.85	40.14	0.11
PL MIX	**PL**	70	61.26	53.97	10.59
	Chips	130	123.84	106.70	0.30
	lime	4.00	3.50	3.50	1.97
	After PL Chips	200	187.59	161.63	0.45
	total	498.40	470.59	410.22	**15.93**
	Lime/Litter percentage	5.71%	5.71%	6.49%	

Elements IN [lbs]					
P	K	Cl	Na	Ca	
0.012	0.107	**0.010**	0.0167	1.3936	Charcoal
0.003	0.012	**0.001**	0.0015	0.0285	Warm up Chips
0.732	0.995	**0.271**	0.2617	2.1422	**PL**
0.008	0.031	**0.003**	0.0039	0.0758	**Chips**
0.001	0.005	**0.000**	0.0003	1.0860	**lime**
0.011	0.047	**0.005**	0.0060	0.1148	After PL Chips
0.766	1.196	**0.290**	0.290	4.841	***total***
0.034	0.202	**0.019**	0.028	2.699	***total (non PL)***
95.52%	83.15%	**93.43%**	90.23%	44.25%	*ratio from PL/total*

	Sorted/Fall-through	[lbs]		Sorted	Fall-through
	Sorted PL+Lime	1.00	Mix Chips	3.00	3.16
	Sorted Mix Chips	3.00	PL	0.95	7.80
**	*Fall-through Chips/PL/Lime*	11.40	Lime	0.05	0.45
	Sorted 200 lbs	7.55	***total***	4.00	11.40
**	*Fall-through 200 lbs*	4.86	After PL Chips	7.55	4.86

	Output [lbs]			
		Recovered	Dry	Actual Ash
Gasifier	**Woodchips char**	3.45	3.45	0.09
	PL Ash	1.00	1.00	1.00
	Rest of Gasifier	19.50	19.45	10.35
	Below Grate	6.10	6.10	2.93
	HEX	1.40	1.38	0.87
	Filter	1.60	1.54	0.66
	total	33.05	32.92	**15.90**
			Ash Percent diff:	0.15%

Elements OUT [lbs]							
P	K	Cl	Na	Ca	Si	S	
0.0022	0.0090	**0.0002**	0.0011	0.0221	0.0057	0.0015	**Woodchips char**
0.0511	0.0719	**0.0017**	0.0178	0.2494	0.1340	0.0099	**PL ash**
0.5247	0.7827	**0.0889**	0.1908	2.9060	1.1173	0.0703	**Rest of Gasifier**
0.1480	0.2117	**0.0520**	0.0584	0.9829	0.2335	0.0251	Below Grate
0.0363	0.0594	**0.0817**	0.0110	0.3265	0.0171	0.0191	HEX
0.0260	0.0632	**0.0654**	0.0095	0.2236	0.0121	0.0205	Filter
0.7882	1.1978	**0.2899**	0.2887	4.7106	1.5198	0.1465	***total***
102.9%	100.1%	**100.0%**	99.5%	97.3%	**Ratio OUT/IN**		
				2.69%	% Difference		
105.7%	102.9%	**102.7%**	102.3%	100%	Norm. to Ca		

Output Ash Analyses																
	Oxide to Element Multiplier		0.467	0.529	0.699	0.715	0.603	0.742	0.830	0.599	0.436			0.401		
	Moist (% As Rec)	LOI (% Dry Basis)	SiO2 (%)	Al2O3 (%)	Fe2O3 (%)	CaO (%)	MgO (%)	Na2O (%)	K2O (%)	TiO2 (%)	P2O5 (%)	BaO (%)	MnO2 (%)	SO3 (%)	SrO (%)	Cl (%)
PL Ash 5/17	0.00	0.06	28.69	3.87	1.48	34.92	4.96	2.40	8.67	0.10	11.71	0.07	0.45	2.48	0.06	0.17
Rest of Gasifier 5/17	0.25	46.77	23.09	3.39	1.74	39.27	6.02	2.48	9.11	0.07	11.61	0.09	0.70	1.70	0.07	0.86
Below Gasifier 5/17	0.07	51.98	17.07	2.14	1.57	46.98	4.80	2.69	8.71	0.05	11.58	0.13	0.66	2.14	0.10	1.78
HEX 5/17	1.24	36.92	4.20	1.46	1.61	52.38	6.63	1.70	8.20	0.00	9.52	0.23	1.20	5.47	0.15	9.37
Filter 5/17	3.93	56.83	3.91	1.19	2.86	47.15	5.23	1.93	11.47	0.00	8.99	0.29	1.43	7.72	0.17	9.86
Woodchip Char		97.48														

Table A.5: Spreadsheet for 8.95% limestone/dry litter from 5/19/2010
** Denotes average value used for conveyor fall-through losses

Moisture Content (wet basis)				
	Charcoal	Warm up chips	Poultry Litter	ix/After PL Chips
tin	13.5	13.7	13.7	13.5
wet	130.1	151.0	98.9	126.7
dry	123.2	130.6	87.1	111.1
moisture %	5.92	14.86	13.85	13.78

	Input [lbs], 5.4 lbs Limestone				
		wet	wet - (Sorted + Fall-through)	dry	Theoretical Ash
	Charcoal	44.00	44.00	41.40	2.33
	Warm up Chips	41.75	41.75	35.55	0.10
PL MIX	**PL**	70	60.96	52.51	10.31
	Chips	130	123.54	106.52	0.30
	lime	5.40	4.70	4.70	2.65
	After PL Chips	200	189.59	163.46	0.46
	total	491.15	464.54	404.14	**16.15**
	Lime/Litter percentage	7.71%	7.71%	8.95%	

Elements IN [lbs]					
P	K	Cl	Na	Ca	
0.011	0.100	**0.009**	0.0156	1.3026	Charcoal
0.003	0.010	**0.001**	0.0013	0.0252	Warm up Chips
0.712	0.968	**0.264**	0.2546	2.0845	**PL**
0.008	0.031	**0.003**	0.0039	0.0757	**Chips**
0.001	0.007	**0.000**	0.0003	1.4589	**lime**
0.012	0.047	**0.005**	0.0060	0.1161	After PL Chips
0.746	1.163	**0.282**	0.282	5.063	***total***
0.034	0.195	**0.018**	0.027	2.978	***total (non PL)***
95.50%	83.20%	**93.50%**	90.34%	41.17%	*ratio from PL/total*

	Sorted/Fall-through	**[lbs]**		**Sorted**	**Fall-through**
	Sorted PL+Lime	1.50	Mix Chips	3.30	3.16
	Sorted Mix Chips	3.30	PL	1.39	7.65
**	*Fall-through Chips/PL/Lime*	11.40	Lime	0.11	0.59
	Sorted 200 lbs	5.55	***total***	4.80	11.40
**	*Fall-through 200 lbs*	4.86	After PL Chips	5.55	4.86

	Output [lbs]			
		Recovered	**Dry**	**Actual Ash**
Gasifier	**Woodchips char**	9.20	9.20	0.11
	PL Ash	0.65	0.65	0.63
	Rest of Gasifier	18.00	17.90	9.53
	Below Grate	5.90	5.87	2.93
	HEX	1.30	1.29	0.83
	Filter	1.75	1.70	0.87
	total	36.80	36.60	**14.90**
			Ash Percent diff:	7.75%

Elements OUT [lbs]							
P	K	Cl	Na	Ca	Si	S	
0.0027	0.0111	**0.0002**	0.0014	0.0271	0.0070	0.0019	**Woodchips char**
0.0364	0.0448	**0.0007**	0.0112	0.1905	0.0543	0.0087	**PL ash**
0.4611	0.7247	**0.0819**	0.1673	2.8780	0.9146	0.0707	**Rest of Gasifier**
0.1584	0.2014	**0.0378**	0.0630	0.9346	0.2574	0.0218	Below Grate
0.0391	0.0482	**0.0559**	0.0098	0.3145	0.0193	0.0172	HEX
0.0400	0.0825	**0.0818**	0.0135	0.2798	0.0154	0.0314	Filter
0.7377	1.1128	**0.2584**	0.2662	4.6244	1.2679	0.1517	***total***
98.9%	95.7%	**91.7%**	94.5%	91.3%	**Ratio OUT/IN**		
				8.66%	% Difference		
108.3%	104.7%	**100.4%**	103.4%	100%	Norm. to Ca		

Output Ash Analyses																
		Oxide to Element Multiplier	0.467	0.529	0.699	0.715	0.603	0.742	0.830	0.599	0.436			0.401		
	Moist (% As Rec)	LOI (% Dry Basis)	SiO2 (%)	Al2O3 (%)	Fe2O3 (%)	CaO (%)	MgO (%)	Na2O (%	K2O (%)	TiO2 (%	P2O5 (%)	BaO (%)	MnO2 (%)	SO3 (%)	SrO (%)	Cl (%)
PL 5/19	0.00	3.08	18.43	2.77	1.46	42.31	6.53	2.39	8.57	0.06	13.23	0.06	0.55	3.45	0.06	0.12
Rest of Gasifier 5/19	0.57	46.73	20.52	2.84	1.28	42.24	7.16	2.37	9.16	0.06	11.08	0.08	0.65	1.85	0.07	0.86
Below Gasifier 5/19	0.51	50.16	18.82	2.39	1.28	44.70	5.46	2.90	8.29	0.03	12.41	0.11	0.65	1.86	0.08	1.29
HEX 5/19	0.98	35.63	4.99	1.66	1.27	53.10	7.96	1.60	7.01	0.00	10.80	0.14	0.96	5.17	0.12	6.75
Filter 5/19	2.87	48.80	3.78	1.27	2.05	44.99	5.90	2.09	11.43	0.00	10.54	0.23	1.30	9.01	0.14	9.40
Woodchip Char		98.84														

Table A.6: Spreadsheet for 4.31% limestone/dry litter from 6/3/2010

Moisture Content (wet basis)				
	Charcoal	Warm up chips	Poultry Litter	Mix/After PL Chips
tin	13.5	13.7	13.5	13.7
wet	182.8	145.3	163.2	165.9
dry	174.1	133.1	142.4	144.3
moisture %	5.14	9.27	13.89	14.19

	Input [lbs], 2.6 lbs Limestone				
		wet	wet - (Sorted + Fall through)	dry	Theoretical Ash
	Charcoal	45.55	45.55	43.21	2.44
	Warm up Chips	61.90	61.90	56.16	0.16
PL MIX	**PL**	70	60.62	52.20	10.25
	Mix Chips	130	123.73	106.17	0.30
	Lime	2.60	2.25	2.25	1.27
	After PL Chips	200	186.00	159.60	0.45
	total	510.05	480.05	419.59	**14.85**
	Lime/Litter percentage	3.71%	3.71%	4.31%	

Elements IN [lbs]					
P	K	Cl	Na	Ca	
0.011	0.104	**0.010**	0.0163	1.3596	Charcoal
0.004	0.016	**0.002**	0.0021	0.0399	Warm up Chips
0.708	0.962	**0.262**	0.2531	2.0719	**PL**
0.008	0.031	**0.003**	0.0039	0.0754	**Chips**
0.000	0.003	**0.000**	0.0002	0.6986	**lime**
0.011	0.046	**0.005**	0.0059	0.1134	After PL Chips
0.743	1.163	**0.281**	0.281	4.359	***total***
0.035	0.201	**0.019**	0.028	2.287	***total (non PL)***
95.33%	82.70%	**93.17%**	89.94%	47.53%	*ratio from PL/total*

Sorted/Fall-through	**[lbs]**		**Sorted**	**Fall-through**
Sorted PL+Lime	2.70	Mix Chips	3.25	3.02
Sorted Mix Chips	3.25	PL	2.60	6.78
Fall-through Chips/PL/Lime	10.05	Lime	0.10	0.25
Sorted 200 lbs	9.35	***total***	5.95	10.05
Fall-through 200 lbs	4.65	After PL Chips	9.35	4.65

	Output [lbs]			
		Recovered	**Dry**	**Actual Ash**
Gasifi	**Woodchips char**	7.35	7.35	0.74
	Gasifier	18.55	17.88	11.81
	After Grate	6.80	6.68	3.45
	total	32.70		**16.00**
			Ash Percent diff:	-7.74%

Elements OUT [lbs]					
P	K	Cl	Na	Ca	
0.0186	0.0763	**0.0016**	0.0097	0.1865	**Woodchips char**
0.7243	0.9185	**0.0706**	0.2454	3.5036	**Gasifier**
0.1809	0.1745	**0.2160**	0.0594	1.2071	After Grate
0.9238	1.1693	0.2882	0.3144	4.8972	***total***
124.41%	100.52%	**102.47%**	111.72%	112.35%	**Ratio OUT/IN**
				-12.35%	% Difference
110.7%	89.5%	91.2%	99.4%	100%	Norm. to Ca

Output Ash Analyses																
	Oxide to Element Multiplier		0.467	0.529	0.699	0.715	0.603	0.742	0.830	0.599	0.436			0.401		
	Moist (% As Rec)	LOI (% Dry Basis)	SiO2 (%)	Al2O3 (%)	Fe2O3 (%)	CaO (%)	MgO (%)	Na2O (%)	K2O (%)	TiO2 (%)	P2O5 (%)	BaO (%)	MnO2 (%)	SO3 (%)	SrO (%)	Cl (%)
Gasifier 6/3	3.59	33.94	19.40	2.44	1.21	41.49	5.79	2.80	9.36	0.04	14.05	0.03	0.44	2.39	0.11	0.60
After Grate 6/3	1.74	48.33	12.71	1.68	1.28	48.92	5.27	2.32	6.09	0.02	12.00	0.06	0.55	4.09	0.16	6.26

Table A.7: Spreadsheet for 6.69% limestone/dry litter from 5/26/2010
** Denotes average value used for conveyor fall-through losses

Moisture Content (wet basis)	Charcoal	Warm up chips	Poultry Litter	lix/After PL Chips
tin	13.7	13.7	13.5	13.5
wet	115.1	121.3	146.5	157.0
dry	110.1	116.5	127.1	136.9
moisture %	4.93	4.46	14.59	14.01

	Input [lbs], 4 lbs Limestone					Elements IN [lbs]					
		wet	wet - (Sorted + Fall through)	dry	Theoretical Ash	P	K	Cl	Na	Ca	
	Charcoal	36.25	36.25	34.46	1.94	0.009	0.083	**0.008**	0.0130	1.0844	Charcoal
	Warm up Chips	39.00	39.00	37.26	0.10	0.003	0.011	**0.001**	0.0014	0.0265	Warm up Chips
PL MIX	**PL**	70	61.35	52.40	10.29	0.711	0.966	**0.263**	0.2541	2.0801	**PL**
	Mix Chips	130	124.64	107.18	0.30	0.008	0.031	**0.003**	0.0040	0.0761	**Chips**
	lime	4.00	3.51	3.51	1.97	0.001	0.005	**0.000**	0.0003	1.0877	**lime**
	After PL Chips	200	186.99	160.80	0.45	0.011	0.047	**0.005**	0.0059	0.1142	After PL Chips
	total	479.25	451.74	395.61	**15.06**	0.742	1.143	**0.280**	0.279	4.469	***total***
	Lime/Litter percentage	5.71%	5.71%	6.69%		0.031	0.177	**0.017**	0.025	2.389	***total (non PL)***
						95.76%	84.52%	**94.01%**	91.20%	46.54%	*ratio from PL/total*

	Sorted/Fall-through	**[lbs]**		**Sorted**	**Fall-through**
	Sorted PL+Lime	0.90	Mixed Chips	2.20	3.16
	Sorted mix Chips	2.20	PL	0.85	7.80
**	*all-through Chips/PL/Lime*	11.40	Lime	0.05	0.45
	Sorted 200 lbs	8.15	***total***	3.10	11.40
**	*Fall-through 200 lbs*	4.86	After PL Chips	8.15	4.86

	Output [lbs]				Elements OUT [lbs]					
		Recovered	Dry	Actual Ash	P	K	Cl	Na	Ca	
Gasifi	**Woodchips char**	6.75	6.75	0.36	0.0092	0.0376	**0.0008**	0.0048	0.0920	**Woodchips char**
	Gasifier	19.25	19.21	12.09	0.6713	0.8964	**0.0676**	0.2515	3.4076	**Gasifier**
	After Grate	5.55	5.48	2.67	0.1546	0.0906	**0.1609**	0.0427	0.9180	After Grate
	total	31.55		**15.12**	0.8352	1.0246	0.2293	0.2990	4.4175	***total***
					112.53%	89.66%	**81.94%**	107.31%	98.85%	**Ratio OUT/IN**
			Ash Percent diff:	-0.41%					1.15%	% Difference
					113.8%	90.7%	82.9%	108.6%	100%	Norm. to Ca

Output Ash Analyses																	
	Oxide to Element Multiplier		0.467	0.529	0.699	0.715	0.603	0.742	0.830	0.599	0.436			0.401		
	Moist (% As Rec)	LOI (% Dry Basi	SiO2 (%)	Al2O3 (%)	Fe2O3 (%)	CaO (%)	MgO (%	Na2O (%)	K2O (%)	TiO2 (%)	P2O5 (%)	BaO (%)	MnO2 (%)	SO3 (%)	SrO (%)	Cl (%)
Gasifier 5/26	0.22	37.08	21.74	3.13	1.58	39.45	6.36	2.81	8.93	0.09	12.73	0.09	0.63	1.98	0.06	0.56
After Grate 5/26	1.26	51.21	12.05	1.97	1.61	48.04	6.07	2.15	4.08	0.06	13.25	0.14	0.88	4.96	0.10	6.02
Woodchip Char		94.63														

Table A.8: Spreadsheet for 8.92% limestone/dry litter from 6/1/2010

Moisture Content (wet basis)				
	Charcoal	Warm up chips	Poultry Litter	lix/After PL Chips
tin	13.5	13.7	13.7	13.5
wet	132.5	144.2	116.4	144.2
dry	125.1	131.3	102.5	129.6
moisture %	6.22	9.89	13.53	11.17

	Input [lbs], 5.4 lbs Limestone				
		wet	wet - (Sorted + Fall through)	dry	Theoretical Ash
	Charcoal	37.10	37.10	34.79	1.96
	Warm up Chips	35.10	35.10	31.63	0.09
PL MIX	**PL**	70	59.85	51.75	10.16
	Mix Chips	130	123.29	109.51	0.31
	Lime	5.40	4.62	4.62	2.60
	After PL Chips	200	186.50	165.67	0.46
	total	477.60	446.45	397.97	**15.58**
	Lime/Litter percentage	7.71%	7.71%	8.92%	

Elements IN [lbs]					
P	K	**Cl**	Na	Ca	
0.009	0.084	**0.008**	0.0131	1.0948	Charcoal
0.002	0.009	**0.001**	0.0012	0.0225	Warm up Chips
0.702	0.954	**0.260**	0.2509	2.0541	**PL**
0.008	0.032	**0.003**	0.0040	0.0778	**Chips**
0.001	0.007	**0.000**	0.0003	1.4324	**lime**
0.012	0.048	**0.005**	0.0061	0.1177	After PL Chips
0.734	1.133	**0.277**	0.276	4.799	***total***
0.032	0.180	**0.017**	0.025	2.745	***total (non PL)***
95.65%	84.14%	**93.89%**	91.01%	42.80%	*ratio from PL/total*

Sorted/Fall-through	**[lbs]**		**Sorted**	**Fall-through**
Sorted PL+Lime	1.50	Mix Chips	3.40	3.32
Sorted Mix Chips	3.40	PL	1.39	8.76
Fall-through Chips/PL/Lime	12.75	Lime	0.11	0.68
Sorted 200 lbs	8.40	***total***	4.90	12.75
Fall-through 200 lbs	5.10	After PL Chips	8.40	5.10

	Output [lbs]			
		Recovered	**Dry**	**Actual Ash**
Gasifi	**Woodchips char**	7.45	7.45	0.46
	Gasifier	18.15	18.09	8.22
	After Grate	6.25	6.19	2.95
	total	31.85		**11.63**
			Percent diff:	25.36%

Elements OUT [lbs]					
P	K	**Cl**	Na	Ca	
0.0116	0.0475	**0.0010**	0.0060	0.1162	**Woodchips char**
0.4398	0.7383	**0.0755**	0.1349	2.4171	**Gasifier**
0.1504	0.2482	**0.1642**	0.0494	0.9486	After Grate
0.6017	1.0341	0.2407	0.1903	3.4820	***total***
82.01%	91.23%	**87.01%**	69.04%	72.55%	**Ratio OUT/IN**
				27.45%	% Difference
113.0%	125.7%	119.9%	95.2%	100%	Norm. to Ca

Output Ash Analyses																
	Oxide to Element Multiplier		0.467	0.529	0.699	0.715	0.603	0.742	0.830	0.599	0.436			0.401		
	Moist (% As Rec)	LOI (% Dry Basis)	SiO2 (%)	Al2O3 (%)	Fe2O3 (%)	CaO (%)	MgO (%)	Na2O (%	K2O (%)	TiO2 (%)	P2O5 (%)	BaO (%)	MnO2 (%)	SO3 (%)	SrO (%)	Cl (%)
Gasifier 6/1	0.35	54.56	17.64	3.43	1.57	41.15	6.75	2.21	10.82	0.08	12.26	0.11	0.69	2.52	0.08	0.92
After Grate 6/1	0.93	52.32	12.56	2.11	1.58	44.96	5.82	2.25	10.13	0.02	11.67	0.11	0.78	3.61	0.10	5.56
Woodchip Char		93.85														

Appendix B

Sample Calculations

To calculate the input mass of K from poultry litter in the 6.49% limestone experiment in Table A.4:

$$m_{K_{litter,IN}} = \left(m_{litter,wet} - m_{litter,sorted} - m_{litter,fall\ thru}\right) \cdot \left(1 - \frac{Moisture\ \%_{litter}}{100}\right) \cdot \left(\frac{\%\ Ash_{litter}}{100}\right) \cdot \left(\frac{K_2O\ \%_{litter}}{100}\right) \cdot \left(\frac{\%\ K}{K_2O\%_{litter}}\right) \quad (B.1)$$

$$= (70.00\ lbs - 0.95\ lbs - 7.80\ lbs) \cdot \left(1 - \frac{11.90\%}{100}\right) \cdot \left(\frac{19.63\%}{100}\right) \cdot \left(\frac{11.31\%}{100}\right) \cdot (0.830)$$

$$m_{K_{litter,IN}} = 0.995\ lbs$$

Similarly, the amount of K from each biomass input can be determined. The mass of K from each source can then simply be summed to get total K put in the gasifier.

To calculate the mass of K recovered from the char Below the Grate:

$$m_{K_{Below\ Grate,OUT}} = \left(m_{Below\ Grate,wet}\right) \cdot \left(1 - \frac{Moisture\ \%_{Below\ Grate}}{100}\right) \cdot \left(1 - \frac{\%\ LOI_{Below\ Grate}}{100}\right) \cdot \left(\frac{K_2O\ \%_{Below\ Grate}}{100}\right) \cdot \left(\frac{\%\ K}{K_2O\%_{Below\ Grate}}\right) \quad (B.2)$$

$$= (6.10\ lbs) \cdot \left(1 - \frac{0.07\%}{100}\right) \cdot \left(1 - \frac{51.98\%}{100}\right) \cdot \left(\frac{8.71\%}{100}\right) \cdot (0.830)$$

$$m_{K_{Below\ Grate,OUT}} = 0.2117\ lbs$$

Similarly, the amount of K from each location can be determined. The mass of K from each location can then simply be summed to get total K recovered.

To find the amount of poultry litter in the mixture of fines collected from below the conveyor in Table A.4:

$$m_{litter,fall-thru}$$

$$= \left[m_{fall-thru,mix} - \left(\frac{m_{chips,fall-thru}}{200.00\ lbs\ chips}\right) \cdot (130.00\ lbs\ mixed\ chips)\right] \cdot \left(\frac{m_{litter,wet}}{m_{litter,wet} + m_{limestone}}\right) \qquad (B.3)$$

$$= \left[11.40\ lbs - \left(\frac{4.86\ lbs}{200.00\ lbs\ chips}\right) \cdot (130.00\ lbs\ mixed\ chips)\right] \cdot \left(\frac{70.00\ lbs}{70.00\ lbs + 4.00\ lbs}\right)$$

$$m_{litter,fall-thru} = 7.80\ lbs$$

Appendix C

Uncertainty Analysis

Uncertainty associated with measured quantities is presented in this appendix, however the largest sources of uncertainty in the experiments are unquantifiable and derive from mixing and sampling of char and biomass as well as unknown losses. The uncertainty of various measuring devices is shown in Table C.1.

Table C.1: Uncertainty of instruments used

Device	**Units**	**Uncertainty**
Thermocouples	˚C	±2.2˚C
CAI Nova Analyzer	% Volume	CO: ±0.6% CO_2: ±0.6% CH_4: ±0.3% O_2: ±0.5%
HiTech K1550 Analyzer	% Volume	H_2: ±2%
Ohaus CD-11 Digital Scale	lbs	±0.05 lbs

The uncertainty estimates from the ash, moisture, and elemental analyses are shown in Table C.2.

Table C.2: Uncertainty of biomass and char analyses, units are % mass. Oxide and Cl are on an Ash basis

Parameter	Uncertainty
Moisture, as received	±0.1%
Ash, dry basis	±0.1%
Na2O	y = 0.0024x + 0.0205
MgO	y = 0.0035x + 0.0291
Al2O3	y = 0.0026x + 0.0849
SiO2	y = 0.0028x + 0.1343
P2O5	y = 0.0158x + 0.0056
SO3	y = 0.0145x + 0.0821
K2O	y = 0.0101x + 0.0104
CaO	y = 0.0056x + 0.0759
TiO2	y = 0.0155x + 0.0364
MnO2	y = 0.01x + 0.0046
Fe2O3	y = 0.0104x + 0.0234
SrO	y = 0.0556x + 0.0015
BaO	y = 0.0087x + 0.004
Cl	y = 0.028x + 0.02

Because uncertainty propagation through to the calculated retention percentage is dependent on the particular elemental oxide and its concentration, a general equation will be formulated and example result calculated. The general form of the propagated uncertainty equation, as denoted by Beckwith, 1990 for a function $f(x_1, x_2 \ldots x_n)$ is (31):

$$U_f = \pm\sqrt{\left(U_{x_1}\frac{\partial f}{\partial x_1}\right)^2 + \left(U_{x_2}\frac{\partial f}{\partial x_2}\right)^2 + \cdots + \left(U_{x_n}\frac{\partial f}{\partial x_n}\right)^2} \tag{C.1}$$

For the actual weight of feedstock *i* put into the gasifier (m_i), the measure weight ($m_{wet,i}$) minus the weight of the sorted feedstock ($m_{sorted,i}$) and conveyor loss weight ($m_{loss,i}$) is:

$$m_i = m_{wet,i} - m_{sorted,i} - m_{loss,i} \tag{C.2}$$

$$U_{m_i} = \pm\sqrt{\left(U_{m_{wet,i}}\frac{\partial m_i}{\partial m_{wet,i}}\right)^2 + \left(U_{m_{sorted,i}}\frac{\partial m_i}{\partial m_{sorted,i}}\right)^2 + \left(U_{m_{loss,i}}\frac{\partial m_i}{\partial m_{loss,i}}\right)^2} \tag{C.3}$$

$$= \pm\sqrt{\left(U_{m_{wet,i}}(1)\right)^2 + \left(U_{m_{sorted,i}}(-1)\right)^2 + \left(U_{m_{loss,i}}(-1)\right)^2} \tag{C.4}$$

Using the uncertainty of the electronic scale (±0.05 lbs) for each measured weight:

$$U_{m_i} = \pm 0.0866 \tag{C.5}$$

The total mass calculated for each element *E*, from each feedstock *i* put into the gasifier is then:

$$m_{E_{i,IN}} = m_i \cdot \left(\frac{Dry\ \%_i}{100}\right) \cdot \left(\frac{\%\ Ash_i}{100}\right) \cdot \left(\frac{E_xO_y\%_i}{100}\right) \cdot \left(\frac{\%\ E}{E_xO_y\%_i}\right) \tag{C.6}$$

**Note: $Dry\ \%_i = (100 - \%\ Moisture_i)$

**Note: Oxide to Element Conversion factor $\left(\frac{\%\ E}{E_xO_y\%_i}\right)$ is from eq. (3.4), and is a constant

Uncertainty of $m_{E_{i,IN}}$ is:

$$U_{m_{E_{i,IN}}} = \pm\sqrt{\left(U_{m_i}\frac{\partial m_{E_{i,IN}}}{\partial m_i}\right)^2 + \left(U_{Dry\ \%_i}\frac{\partial m_{E_{i,IN}}}{\partial Dry\ \%_i}\right)^2 + \left(U_{\%\ Ash_i}\frac{\partial m_{E_{i,IN}}}{\partial \%\ Ash_i}\right)^2 + \left(U_{E_xO_y\%_i}\frac{\partial m_{E_{i,IN}}}{\partial E_xO_y\%_i}\right)^2} \tag{C.7}$$

$$= \pm\sqrt{\left(U_{m_i}\frac{m_{E_{i,IN}}}{m_i}\right)^2 + \left(U_{Dry\,\%_i}\frac{m_{E_{i,IN}}}{Dry\,\%_i}\right)^2 + \left(U_{\%\,Ash_i}\frac{m_{E_{i,IN}}}{\%\,Ash_i}\right)^2 + \left(U_{E_xO_y\%_i}\frac{m_{E_{i,IN}}}{E_xO_y\%_i}\right)^2} \quad \text{(C.8)}$$

$$= \pm m_{E_{i,IN}}\sqrt{\left(\frac{U_{m_i}}{m_i}\right)^2 + \left(\frac{U_{Dry\,\%_i}}{Dry\,\%_i}\right)^2 + \left(\frac{U_{\%\,Ash_i}}{\%\,Ash_i}\right)^2 + \left(\frac{U_{E_xO_y\%_i}}{E_xO_y\%_i}\right)^2} \quad \text{(C.9)}$$

It becomes apparent at this point, the dependence of uncertainty on the specific element and feedstock of interest. The equations for $U_{E_xO_y\%_i}$were given in Table C.2. The uncertainty of Moisture % and % Ash can be found in the same table, and $U_{m_i}$was found in eq. (C.5).

$$U_{m_{E_{i,IN}}} = \pm m_{E_{i,IN}}\sqrt{\left(\frac{(0.0866\ lbs)}{m_i}\right)^2 + \left(\frac{(0.1\%)}{Dry\,\%_i}\right)^2 + \left(\frac{(0.1\%)}{\%\,Ash_i}\right)^2 + \left(\frac{(m(E_xO_y\%_i)+b\,\%)}{E_xO_y\%_i}\right)^2} \quad \text{(C.10)}$$

From here, values will be used from the K in poultry litter data of the 6.43% limestone experiment in Table A.4. This will represent a general value of uncertainty.

From Table A.4: m_{litter}=61.26 lbs, $Dry\ \%_{litter}$= (100-11.90) = 88.1%,

$m_{K_{litter,IN}}$=0.995 lbs

From Table A.1: $\%\ Ash_{litter}$= 19.63%

From Table A.2: $K_2O\%_{litter}$ = 11.31%

From Table C.2: $U_{K_2O\%_{litter}}$ = 0.0101($K_2O\%_{litter}$) + 0.0104 = ±0.125

$$U_{m_{K_{litter,IN}}} = \pm 0.01221 \quad \text{(C.11)}$$

Repeating equation (C.10) for the rest of the sources of K:

$$U_{m_{K_{Charcoal,IN}}} = \pm 0.00231$$

$$U_{m_{K_{warm\ up\ chips,IN}}} = \pm 0.00417$$

$$U_{m_{K_{mix\ chips,IN}}} = \pm 0.01108$$

$$U_{m_{K_{limestone,IN}}} = \pm 0.000373$$

$$U_{m_{K_{after\ litter\ chips,IN}}} = \pm 0.01678$$

Using a similar approach as (C.2)-(C.4), the uncertainty for total K input (found to be 1.196 lbs) is:

$$U_{m_{K_{Total,IN}}} = \pm 0.02400 \tag{C.12}$$

Similarly, the uncertainty for the total K recovered in the char is:

$$U_{m_{K_{Total,OUT}}} = \pm 0.01078 \tag{C.13}$$

Therefore, uncertainty of the ratio $\frac{m_{K_{Total,OUT}}}{m_{K_{Total,IN}}}$, presented as “retention percent K” is:

$$U_{retention\,\%\,K} = \pm(retention\ \%\ K)\sqrt{\left(\frac{U_{OUT}}{m_{K_{Total,OUT}}}\right)^2 + \left(\frac{U_{IN}}{m_{K_{Total,IN}}}\right)^2} \tag{C.14}$$

$$\boxed{U_{retention\,\%\,K} = \pm 2.201\%}$$

Uncertainties for other retention percentages can be found similarly.

Appendix D

Additional Figures

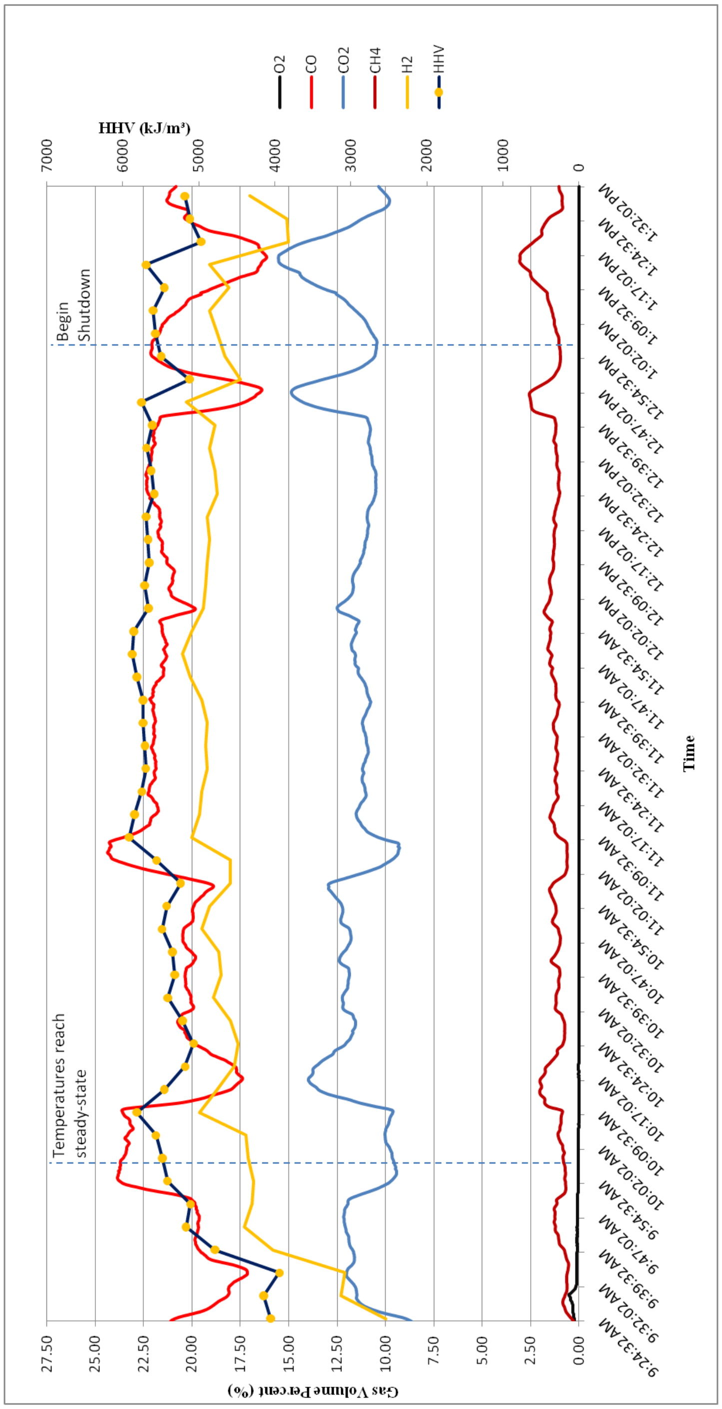

Figure D.1: Dry syngas composition vs. Time for a standard woodchip run, fluctuations in composition are typical, with an average HHV ~5400 kJ/m³

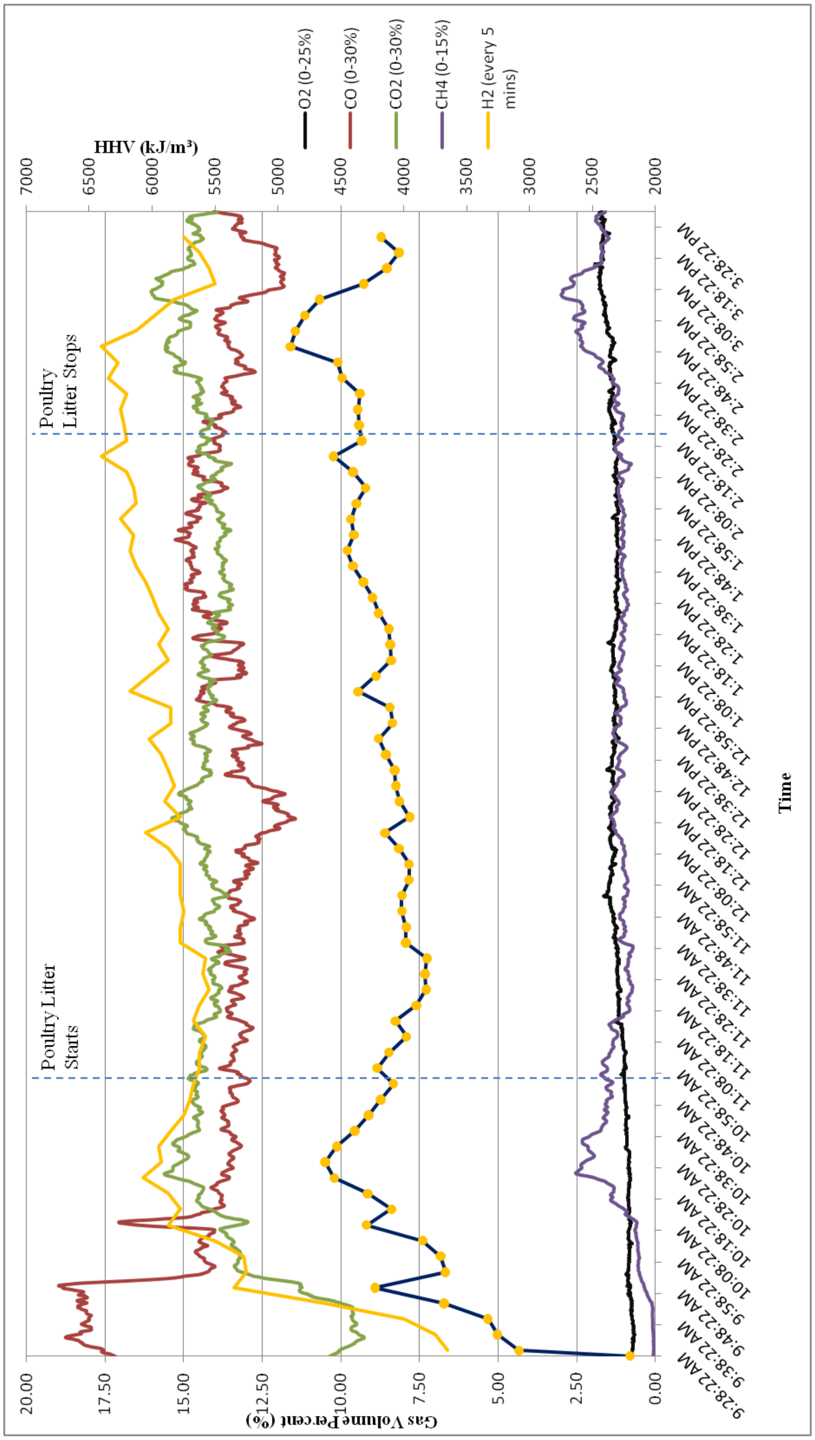

Figure D.2: Dry syngas composition vs. time during flue gas recirculation experiment (Section 4.1.2)

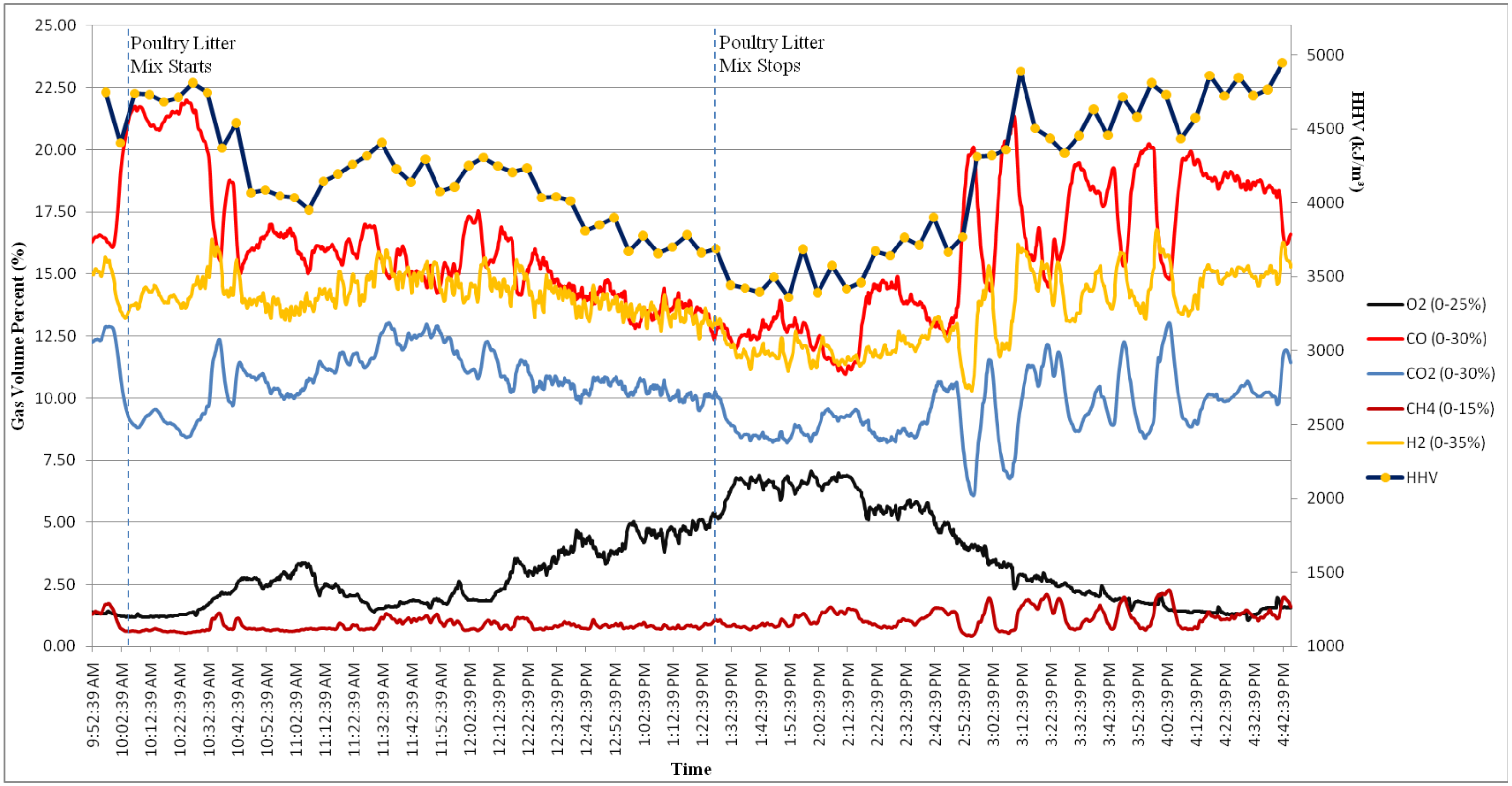

Figure D.3: Dry syngas composition vs. time during raw litter, 5% limestone, and 60:40 (woodchip:litter) experiment (Section 4.1.4)

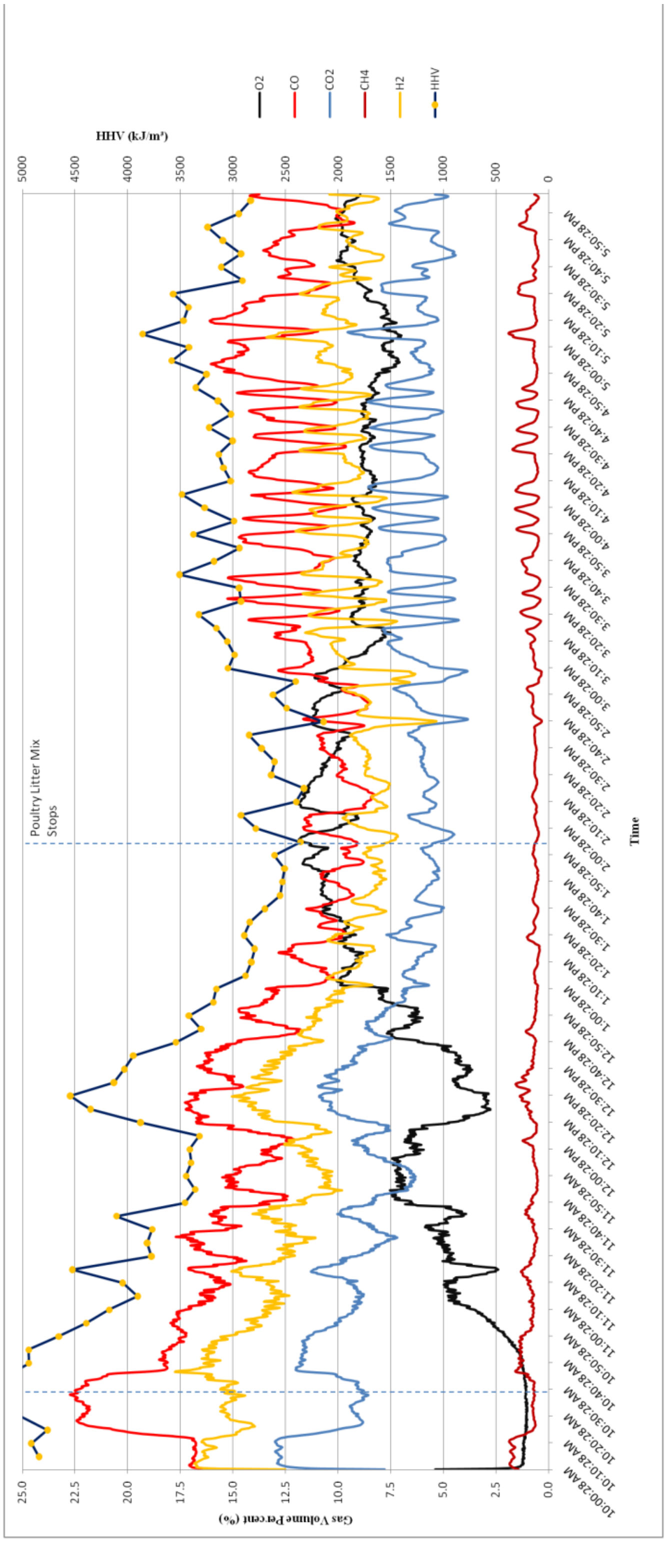

Figure D.4: Dry syngas composition vs. time during 8.95% Limestone/Dry Litter experiment. Very typical of all experiments in contaminant retention study (Section 4.2)