VALUE ADDED PRODUCTS FROM POULTRY LITTER USING FRACTIONATION, PYROLYSIS, AND PELLETIZING

by

KAUSHLENDRA SINGH

(Under the Direction of L. Mark Risse and K. C. Das)

ABSTRACT

In raw form, poultry litter has certain draw backs for both energy production (high ash content and moisture content, a corrosive nature, and low energy content) and fertilizer (ow bulk density, and low nutrient content). We envisioned combining fractionation, pyrolsis, and pelletizing processes for value added utilization of poultry litter. The dissertation is divided into five major studies.

The first "fractionation and decomposition kinetics" study explains the decomposition behavior of poultry litter under pyrolysis conditions. The second "screening and pyrolysis" confirms that the pyrolysis of the coarse fraction (screen#20) produced 44.47% char which retained only 43.53% of total feedstock energy. Overall, the pyrolysis products captured 57.23% of total feedstock energy and 53.86% of total feedstock carbon. The light phase of the condensate (4.94 ± 2.70% of the dry biomass) had a calorific value of 34.83 ± 0.91 MJ/kg and could be further refined as low grade fuel. The third "screening and pyrolysis parameter" study concludes that the highest calorific value of the char coal (17.39 ± 1.37MJ/kg) was made from coarse fraction at 300°C and heating rate of 30°C/min, which captured 68.71 ± 9.37% of the feedstock energy. Most of the nitrogen was retained by char followed by the medium phase of the condensate

The third study concludes that the highest calorific value of the char coal (17.39 ± 1.37MJ/kg) was made from coarse fraction at 300°C, which captured 68.71 ± 9.37% of the feedstock energy. Most of the nitrogen was retained by char followed by medium phase of the condensate. The fourth "compression behavior" study concludes that the fine fraction of the poultry litter was densified from a bulk density of 466.65 ± 14.25 kg/m3 up to 1537.37 kg/m3 at 4000 N compressive load or 124.965 ± 0.844 MPa pressure. Neither the aqueous nor bio-oil phase possessed binding properties but did possess lubrication properties.

The fifth "Co-firing poultry litter char with coal" shows that the calorific value significantly increased and ash content decreased with increase in amount of standard coal in the mixtures. A mixture of 60% char and 40% standard coal harvested 78% of the coal energy, reduced ash content by 62%, and ammonia content by 41% compared to poultry litter char itself. The results of this dissertation will benefit the poultry industry by reducing storage and transportation cost and generating income from poultry litter through value added products.

INDEX WORDS: poultry litter, pyrolysis, fractionation, screening, pelleting, char, bioenergy

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by

KAUSHLENDRA SINGH

B.Tech., G. B. Pant University of Agriculture and Technology, India, 1997

M.Tech., Indian Institute of Technology, India, 1999

A Dissertation Submitted to the Graduate Faculty of The University of Georgia in Partial Fulfillment of the Requirements for the Degree

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KAUSHLENDRA SINGH

Major Professors:	L. Mark Risse K. C. Das
Committee:	Sidney Thompson John Worley Thomas Adams William Kisaalita

Electronic Version Approved:

Maureen Grasso
Dean of the Graduate School
The University of Georgia
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DEDICATION

To my inspiration, Ipsita, and motivation, Litha.

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CHAPTER 1

INTRODUCTION

Poultry litter or broiler litter is a waste product resulting from periodic cleanout of poultry production facilities. Generally, a poultry house is typically cleaned to the ground level after 4-8 flocks having growth cycles of 47-49 days. Poultry litter is a combination of manure, bedding materials, feathers, and spilled feed. One management practice of partial cleanout is known as "decaking". The "broiler cake" is litter that has become caked because of spilled water or high humidity. Cake is removed after the harvest of each flock using a "decaking machine" that removes the cake and leaves the uncaked litter in the house. The poultry industry produces more than 50 billion tons of waste every year. Region 4 of EPA leads the nation in the production of poultry and poultry litter. Georgia ranks first in the United States in production of poultry and poultry products, supplying approximately 12% of U. S. production (Risse and Cheadle, 1996). The abundance of poultry litter production in region 4 and in Georgia has led growers to consider different utilization methods of poultry litter. Poultry litter is primarily applied to land because it is an excellent source of organic fertilizer. An alternative is to use poultry litter as an economical source of energy. This energy can be used either for space heating or power generation through combustion, gasification, co-firing or pyrolysis.

While poultry litter is an excellent source of organic nutrients for crop production, many farms produce more nutrients than the region or farm can effectively use resulting in regional and farm level nutrient imbalances. These nutrient imbalances can cause runoff resulting in eutrofication in some water bodies. According to the Georgia Watershed Agricultural Non-point

Source Pollution Assessment, approximately 39% of total Phosphorus produced from animal waste could potentially be exported to the State's waterways (Risse and Cheadle, 1996). The report also stated that some 1,419 miles of streams and 10,700 acres of lakes in Georgia are not meeting their designated uses, primarily due to rural non-point source pollution. EPA and State environmental agencies have tried to address this problem through nutrient management planning efforts.

Recently, nutrient management regulations for land application of poultry litter have motivated scientists to study the potential for alternative uses of poultry litter. Some alternative uses include a source of energy or a feed stock for making fertilizer pellets (Mukhtar et al., 2002; Keener et al., 2002; McMullen et al., 2004; and Lopez et al., 2005). In the United States, it is estimated that using poultry litter as fuel could save 283 million gallons of LP Gas equivalent fossil fuel energy source (Reardon et al., 2001).

According to Reardon et al. (2001), if poultry litter were used for fuel, almost every poultry farm would have surplus energy after meeting its own demand. A hypothetical poultry farm with production capacity 100-110k birds per year will produce 125 dry tons of litter per year. If 100 tons of that litter is used in a 75% efficient gasifier it would produce the equivalent of 9300 gallons of LP Gas. The value of the resulting 25 tons of ash (for fertilizer) would be $1250. This hypothetical poultry farm only uses 6000 gallons of LP Gas in a year (equivalent of 82 dry tons of litter). Direct combustion, gasification, co-firing with coal and pyrolysis are the known options available for extracting energy from poultry litter. Heating the biomass with unlimited oxygen is called combustion. Gasification is a process of heating the biomass in limited oxygen and in pyrolysis oxygen is absent during the heating process. Every method has its own advantages and limitations. During direct combustion, gasification and co-firing, NOx and NH3 emissions may cause environmental concerns. Also, high ash and moisture content require supporting fuel, and high volatiles cause corrosion of boilers. All of these methods require storage of poultry litter. Long-term storage causes microbial decomposition of litter resulting in reduced heating value (Jirjis, 2004). In general, broiler litter is a lower quality fuel than coal due to its high mineral and ash content (Mukhtar et al., 2002). Despite the drawbacks of combusting raw poultry litter as fuel, FIBROWATT LLC has built three electricity generation plants in the United Kingdom (Ward, 2003) and is building five such power plants (Minnesota, Arkansas, Maryland, Mississippi, North Carolina) in the United States (HRE, 2007).

A combined solution for utilization of raw poultry litter can be accomplished through screening of the poultry litter. According Nedgwa (1990) and Coloma (2005), a simple screening of poultry litter can concentrate the nitrogen in the fine fraction which increases its value as fertilizer. They concluded that a screens # 18 and screen # 20 with mesh opening of 1.0 mm and 0.85 mm respectively were the most suitable screen sizes for getting a nutrient dense screened fraction. Coloma (2005) suggested that the best option to utilize the coarse fraction would be combustion or gasification for energy production with some improved technology.

One proven technology for improving the quality of fuel from poultry litter is catalytic steam gasification (Jones, 1998; Sheth and Turner 2002; and Sheth and Bagchi, 2005). Detailed studies describing the thermodynamics or kinetics of catalytic gasification and control of ammonia emissions during gasification were done by these scientists. Although, charcoal derived from pyrolysis of poultry litter was the primary fuel source in these studies, no attempt was made to study the thermodynamics and to optimize the process parameters involved in the pyrolysis of poultry litter. Recently however, Kim and Agblevor (2007) investigated the pyrolysis kinetics of chicken litter at three heating rates 5, 10, and 20 ºC/min and reported that most of the material decomposed between 270 ºC and 590 ºC, which was slightly lower than that of wood chips. Interestingly, Kim and Agblevor (2007) did not support their explanation for the kinetic behavior of chicken litter either with experiments or with established facts.

The thermodynamics and kinetics of pyrolysis of any biomass depend upon its composition and pyrolytic conditions (Raveendran et al., 1995, 1996 and Antal and Gronli, 2003). Depending upon the pre-treatment of the biomass and pyrolytic conditions including pyrolysis temperature, pyrolysis pressure, vapor phase residence time and heating rate, different proportions of energy products: gases, char, and bio-oil are formed as a result of pyrolysis (Antal and GrØnli, 2003). The proportional composition of cellulose, hemi cellulose, lignin and minerals in a biomass also plays a significant role in the proportion of pyrolysis products. The composition of poultry litter differs from most biomass due to high mineral content and significant fat and protein content (Coloma 2005); however no known research has studied the thermodynamics, kinetics, and effect of pyrolytic conditions on the pyrolysis of screened poultry litter.

The long term goal of this research project is to study fractionation and pyrolysis of poultry litter to produce energy and a value added fertilizer. It is expected that fractionation would reduce the mineral content and increase the volatile yield during pyrolysis of the coarse fraction. Pyrolysis would result in three energy products: gases, bio-oil, and char. This same screening process produces a fine fraction that is nutrient dense and thus more valuable as feedstock for fertilizer pellets. To pelletize the nutrient dense fraction in an energy efficient way, there was a need to characterize the compaction behavior of this fraction. The fertilizer pellets should be uniform in nutrient content and durable for handling and transport. Bio-oil might be used as an additive to produce durable and nutrient dense pellets. The objectives for this study were to:

1. explain the differences in calorific values of poultry litter fractions obtained from screen #20 using proximate, ultimate, mineral, and compositional analysis data.
2. analyze thermal-chemical decomposition behavior and heat consumption during the thermo-chemical decomposition process under pyrolytic conditions for raw poultry litter and its coarse and fine fractions obtained using screen #20.
3. study the effect of screen size and pyrolysis on fuel properties of poultry litter and characterize the bio-oil to determine its nutrient and energy content.
4. explain the effect of fractionation, pyrolysis temperature and heating rate on production, nutrient content, and gross heating values of char and bio-oil.
5. explain the compaction behavior of the fine fraction of poultry litter (particle size < 0.85mm) and evaluate the binding efficiency of pyrolysis condensate (aqueous and oily phases) obtained from the pyrolysis of coarse fraction (particle size > 0.85 mm).
6. quantify the calorific value and ash content for the poultry litter char when co-firing with coal at 0, 20, 40, 60, 80, and 100 % and study the loss of nitrogen, sulfur, and mercury during combustion of the selected mixture.

This research complements the technology of catalytic gasification of poultry litter; enables the increased production of volume dense energy products “char and bio-oil”, and produces technical knowledge for producing fertilizer pellets. This research also opens the gateway for safe and eco-friendly utilization of poultry litter.

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CHAPTER 2

REVIEW OF LITERATURE

Poultry litter is mostly land applied as a fertilizer but sometimes, it is treated physically, thermally or biologically to add value to it and reduce adverse environmental impacts. This review focuses on physical and thermal treatment of poultry litter. The review chapter is divided into two main sections. The first section provides a comprehensive summary of the literature on physical and thermal treatment of poultry litter. The comprehensive summary presented in the first section recommends fractionation of the poultry litter to separate a nutrient dense fine fraction which can be pelletized to make fertilizer pellets. The remaining coarse fraction is recommended to produce energy products using pyrolysis. The second section explains the fundamental process governing the pyrolysis, physical and chemical changes in the biomass during the pyrolysis process, characterization of pyrolysis products, and its use. The second section also covers the fundamental mechanisms and processes governing the densification process of pelletizing.

2.1 Poultry Litter and Poultry Cake

Poultry litter is a waste resulting from periodical cleanout of poultry houses to promote bird health and limit build-up of wet manure. Generally, a poultry house is cleaned to ground level (total cleanout) after 4-8 flocks (growth cycles of 47-60 days). Poultry litter is a combination of manure, bedding materials (wood shavings, rice or pine needles or peanut hulls), feathers, dead birds and spilled feed.

Between each flock, a partial cleanout known as “decaking” is often performed. The “broiler cake” is fresh manure combined with some bedding materials and spilled feed that has become caked due to spilled water or high humidity. During “decaking” the cake is removed after a harvest of each flock using a decaking machine. This machine fractionatesthe cake and some portion of the bedding material’s finer fraction is returned to floor while coarser fraction (cake) is removed from the house.

Sistani et al. (2003) studied the amount of broiler litter and broiler cake production and characterized the nutrient composition of the litter and cake. In this study no significant difference was noticed in pH, total carbon (TC), total nitrogen, total phosphorous, water extractable phosphorous, NH_4-N, and NO_3-N of broiler cake and broiler litter. However broiler cake contained significantly more Ca, Mg, K, Cu, Fe, Mn, and Zn than broiler litter. Sistani et al. (2003) suggested the need for further investigations to generalize the conclusions of his study.

2.2 Physical and thermal treatment of poultry litter

There are physical, thermal, and biological treatment options available for animal waste. Physical treatment includes compaction, mechanical separation and gravity settling. Thermal treatment involves combustion, gasification, and pyrolysis. Biological treatment is based on decomposition using bacteria such as anaerobic digestion and composting.

2.2.1 Physical treatment of poultry litter using screening

Ndegwa (1990) and Coloma (2005) studied the fractionation of poultry litter by screening. Ndegwa (1990) considered the following factors for the study: 1) number of flocks (1, 2, and 3 flocks) raised on the litter; 2) type of house (open and dark house) from which the litter was sampled; 3) percent N, P, and K as a function of number of flocks raised on the litter; 4) percent of N. P. and K as a function of house type; 5) percent of N, P, and K within each fraction of litter; and 6) efficiency of each type of separation system (drum separator and vibratory screen separator). Samples were collected from open and dark houses located in North Georgia. Ndegwa et al. (1990) fractionated the poultry litter by using 6 mesh screen (3.3 mm opening) and 20 mesh screen (0.85 mm opening) with optimal operating pitch of 12°. Samples obtained from one-flock-grown poultry litter were also separated using a rotary drum separator, set at approximately 11°. The moisture content of the poultry litter ranged between 18 and 25% (w. b.).

Ndegwa et al. (1991) reported that the three fractions obtained were distinct in physical appearance. According to the report, as the number of flocks raised increased from one to three, the fine fraction increased from 24 to 41%, medium fraction decreased from 47 to 40% and coarse fraction decreased from 26 to 16%. The fine fraction which was comprised of those materials through a 20 mesh screen (0.85 mm opening) in size was believed to consist primarily of manure, small amounts of spilled feeds and very fine saw dust. The middle fraction that retained between 6 mesh screen (3.3 mm opening) and 20 mesh screen (0.83 mm opening) was mostly wood chips, saw dust and some other material. The coarse fraction, having particle size greater than 6 mesh screen (3.3 mm opening), consisted mostly of larger wood shavings, wood chips, feathers and conglomerate clods. It was noticed that the fine fraction increased approximately 70% when the number of flocks raised on litter increased from one to three. The fine fraction was significantly larger for poultry litter obtained from dark houses than for poultry litter obtained from open houses. There was no significant difference in the amount of fine fraction obtained from the two separation methods.

The fine fraction had the highest nitrogen content whereas, phosphorous and potassium were uniformly distributed in all three fractions. A significant variation ($\alpha=0.05$) was observed in N and K content when the number of flocks raised on the litter varied from one to three, however, type of house had no significant effect on N-P-K content.

In a second major study of physical treatment of poultry litter using screening, Coloma (2005) studied: 1) the fractionation of mass, nutrients, carbon, and energy as a result of screening; 2) the differences in AN:P_2O_5 ratio and C:N ratio between treated litter (screened and retained) and untreated litter (control); 3) the effect of screening on litter bulk density; 4) the nutrient composition of litter ash; and 5) the advantages of creating a blend of broiler litter with inorganic nitrogen to meet the N:P_2O_5 needs of the crop.

Litter was collected from a commercial farm and stored in three bins. Three experiments were conducted. To study the effect of screening on fractionation of solids, plant nutrients, carbon, and bulk density, 0.8 kg broiler litter samples were screened using four standard sieves screen # 5, screen # 10, screen # 18, and screen # 20 with mean size opening of 4.0, 2.0, 1.0, and 0.85 mm, respectively. Two fractions were obtained for each sieve: a screened fraction, which contained the litter particles that passed through the screen, and a retained fraction, which contained the coarser litter particles that remained on the screen. Major and minor plant nutrients, minerals, pH, density, total solids, volatile solids, ash content, and carbon content were determined for the untreated, screened, and retained fraction. The results of the experiment indicated that the fraction of the litter that passed through a screen was significantly affected by screen size.

A significant variation in plant nutrients in untreated litter from sample to sample motivated Coloma (2005), to compare the concentration factors (normalized concentrations in screened or retained fractions) instead of comparing the nutrient contents of screened and retained fractions.

A significant increase in concentration was noticed for all the defined constituents (TN, Or-N, Ca, Cu, and ash) when the screen size was decreased from 4.0 mm to 1.0 mm; however, further decrease in screen size to 0.85 mm resulted in a decrease in concentration in the screened fraction for most constituents as compared to a 1.0 mm screen. The experimental research concluded that screening with a screen size smaller than 1.0 mm openings would not have an advantage for the purpose of increasing plant nutrient concentration in the screened fraction.

In the results of experiment 1, Coloma (2005) also reported that the bulk density of the screened fraction was not significantly different from the untreated litter; however, a significantly lower bulk density was reported for retained (coarse) fraction than untreated litter. This means that the transportation cost of the screened litter per unit weight should be no more than that for untreated litter. A 6% increase in the C:N ratio for the coarse fraction, regardless of screen size, was reported. The screening also did not significantly affect the AN: P_2O_5 ratio of the screened or retained fraction.

In a second experiment Coloma (2005), studied the effect of screening on litter energy content using the screening process similar to experiment 1. The biomass energy content on a dry matter basis (kcal/kg_{DM}) was determined for untreated and screened fractions; however, the energy content of the retained fraction was determined by difference. To determine the biomass energy, a sample was analyzed for crude protein (CP), fat (F), non-digestible fiber, and non-fiber carbohydrates (C) on a dry matter basis. Total energy content (TE) on a dry matter basis was calculated using the following empirical equation:

$$TE = \left(5.65\frac{kcal}{g}CP\right) + \left(9.45\frac{kcal}{g}F\right) + \left(4.18\frac{kcal}{g}TC\right) \ldots..(2.1)$$

Where 5.65 kcal/g, 9.45 kcal/g, and 5.65 kcal/g are the average values of energy content of carbohydrates, fat, and protein respectively.

There were no significant differences among screened samples. The fractionation of biomass energy was the result of fractionation of litter mass (Coloma, 2005).

The third experiment was done to determine the composition of poultry litter ash. Litter ash was analyzed for the following quantities: total ammoniacal nitrogen (TAN = NH_4^+-N + NH_3-N), total phosphorous (expressed as P_2O_5), total potassium (expressed as K_2O), calcium (Ca), magnesium (Mg), sulphur, zinc (Zn), copper (Cu), manganese (Mn), sodium (Na), pH, and moisture. Statistical comparisons were performed between nutrient concentrations in the ash and in the untreated litter. No significant concentration of TN was found in ash; however, concentrations of P_2O_5, K_2O, Ca, Mg, Cu, and Na doubled in the fine fraction of poultry litter ash as compared to untreated litter. Sulfur, Zn, and Mn concentrations were reported 65% to 80% higher in ash relative to untreated litter.

The studies on physical treatment of poultry litter using fractionation done by Ndegwa (1990) and Coloma (2005) led to the conclusion that a screen size of # 18 or # 20 with mesh openings of 1.0 mm and 0.85 mm, respectively were the most suitable screen sizes for getting a nutrient dense screened fraction. The retained (coarse) fraction from this screen had a C: N ratio equal to 10.65, which is far less than that required for composting (20 to 40). Coloma (2005) concluded that the best option to utilize the coarse fraction would be as a combustion product for heat generation.

2.2.2 Physical treatment of poultry litter using densification

McMullen et al. (2005) studied the effect of storage moisture content on bulk density, particle density, durability, and compressive strength of poultry litter pellets. Hardwood shavings broiler litter was ground through a 5/8-in screen followed by addition of 3% vegetable oil. During the pelletizing process using a pellet mill manufactured by California pellet mill, the die temperature was kept at 75˚C. The pellets were cooled to 22˚C and 40% relative humidity. The moisture content of the pellets was controlled by varying the relative humidity of the environmental chamber. The particle density, bulk density, durability, rupture force, moisture sorption, thermal conductivity, thermal diffusivity, and specific heat of the pellets were determined. McMullen et al. (2005) reported that bulk density decreased and particle density increased with increase in moisture content. The force required to rupture the pellets varied from 316 N at 6.0% moisture to 68 N at 22% w.b. Durability of pellets also decreased with moisture content. The moisture absorption in the pellets increased with increases in temperature and relative humidity. The thermal properties of the pellets were unaffected by the moisture content.

The measurement of the flow properties of litter: internal angle of friction, cohesion, unconfined yield stress, and major consolidating stress was studied by Fasina (2006). The referenced paper reported the procedure for measuring flow properties using an automated shear tester (ShearScan TS12, Sci-Tec, Inc., Worthington, Ohio) for peanut hulls, switch grass, and poultry litter (with wood shavings as bedding material). The authors ground all the samples to three screen sizes: 0.8 mm (1/32”), 1.6 mm (1/16”), and 3.2 mm (1/8”). The testing procedure for flow properties was similar to one described by Mohsenin (1970). According to Fasina (2006) the flow behavior was independent of the particle size. The poultry litter was least compressible compared to other feedstocks, however, the poultry litter was considered an easy flowing material compared to switch grass and peanut hulls due to its high flow behavior index.

2.2.3 Fuel properties and thermal treatment of poultry litter

Growing interest in the utilization of poultry litter as fuel motivated some studies on the economic and technical feasibility of using poultry litter as an inexpensive source of energy (NRBP, 1999; Reardon et al., 2001; and Lichtenberg et al, 2002). These studies mentioned that every poultry farm could have surplus energy after meeting its own energy demand if poultry litter was correlated to energy. In the United States, the combustion of poultry litter could save 283 million gallons of LPG equivalent fossil fuel energy. Co-firing, direct combustion, gasification, and pyrolysis are the potential options available for heat treatment of the poultry litter (Mukhtar, 2002; Keener, 2002; McMullen, 2004; Lopez, 2005; Sheth and Bagchi, 2005; and Lima and Marshall, 2005).

Mukhtar et al. (2002) performed the ultimate and proximate analyses on excreted broiler manure (EM), cleanout litter (CL), dried and ground litter (DL), coal and a 90:10 blend of coal and CL (C90:DL10) to determine broiler litter (BL) fuel quality and characteristics. Results showed that C90:DL10 exhibited fuel quality similar to coal. Mukhtar et al. (2002) pointed out that the broiler litter had a higher percentage of its combustibles in the form of volatile matter than coal. Although increased volatile matter potentially enhanced the combustion, high levels of ash in the fuel decreased the flame temperature and heating value. The high volatile emissions fouled and corroded the boiler tubes. The broiler litter contained a significantly higher amount of CaO, K_2O, MgO, P_2O_5, and Na_2O than coal. Mukhtar (2002) concluded that broiler litter is a low quality fuel compared to coal due to its higher nitrogen, sulfur, moisture, ash, and lower heating value.

2.2.4 Combustion of poultry litter

Lopez et al. (2005) documented the thermal performance and poultry litter consumption rate in a two staged combustion furnace. The study was done for varying air inlet rates with different litter-wood mixtures (0-40% wood by weight). Lopez et al. (2005) showed that the heating value for the fuel blend ranged from 9,300-16,300 kJ/kg. The litter consumption rate was 27-110 kg/h with primary air flow rate of 150-450 m^3/h. The ash production ranged from 0.15-0.32 kg/ kg of litter combusted. Keener et al. (2002) performed combustion analyses of poultry manure from egg layers and pullets. The heating value of poultry litter was reported at 9,300 kJ/kg and ash content ranged from 32 to 47% of the dry matter. Keener et al. (2002) concluded that 20% inclusion of poultry manure with coal didn’t change the emission pattern but approximately 50% more ash was produced. The direct combustion of poultry litter had problems such as boiler corrosion and ammonia emission, which motivated research into the gasification of poultry litter.

2.2.4 Gasification of poultry litter

Sheth and Turner (2002) mentioned that broiler litter could be an attractive candidate for catalytic steam gasification for the following reasons: 1. Char produced from the broiler litter is more reactive than the char produced from coal; 2. The presence of a significant amount of mineral, specifically potassium in the litter, which may serve as an inherent catalyst; 3. low sulfur content limits the production of hydrogen sulphide. Jones (1998) reported the following major chemical reactions involved during steam gasification:

Pyrolysis:

$$Biomass \rightarrow Char + Volatiles \text{ .....(2.1)}$$

Water gas reaction:

$$C + H_2O(g) \rightarrow CO + H_2; \Delta H_{r,298K} = 131.3 kJ/mol \text{ .....(2.2)}$$

$$C + 2H_2O(g) \rightarrow CO_2 + 2H_2; \Delta H_{r,298K} = 90.1 kJ/mol \text{ .....(2.3)}$$

Boudart reaction:

$$C + CO_2 \rightarrow 2CO; \Delta H_{r,298K} = 172.5 kJ/mol \text{ .....(2.4)}$$

Hydro-gasification reaction:

$$C + 2H_2 \rightarrow CH_4; \Delta H_{r,298K} = -74.8 kJ/mol \text{ .....(2.5)}$$

Shift reaction:

$$CO + H_2O(g) \rightarrow CO_2 + H_2; \Delta H_{r,298K} = -41.2 kJ/mol \text{ .....(2.6)}$$

Methanation reaction:

$$CO + 3H_2 \rightarrow CH_4 + H_2O(g); \Delta H_{r,298K} = -206.1 kJ/mol \text{ .....(2.7)}$$

If poultry litter could be represented as $C_u H_v N_w O_x S_y$, then the overall gasification reaction, in the presence of excess steam and catalyst can be written as following:

$$C_uH_vN_wO_xS_y + Ash + mH_2O \xrightarrow{K-catalyst} CO + CO_2 + CH_4 + H_2 + H_2S + NH_3 + H_2O + Ash \text{ .....(2.8)}$$

Jones (1998) suggested that the production of CO and H_2 rich synthesis gas may be achieved when the gasification operation is carried out at low pressures (approximately 100 psi or 0.88 MPa), moderate temperatures (approximately 1400 ºF to 1500 ºF, or 760 ºC to 815 ºC), and at low H/O ratio (approximately 1 to 2). Seth and Turner (2002) determined the optimum conditions for steam gasification of poultry litter using a bench-scale, high-pressure, high-temperature, fixed-bed gasification unit in differential bed down draft mode. In this experiment temperature, pressure, steam flow rate, and catalyst type and its loading rate using the screening test matrix were evaluated. About 2.5 g of the pyrolyzed catalyzed broiler litter was gasified for 255 minutes during these experiments under the desired conditions of temperature, pressure, and steam/water flow rate. Tar formation during pyrolysis the step and subsequent clogging of gas discharge lines was controlled by performing pyrolysis of catalyzed litter in a separate muffle furnace

Sheth and Turner (2002) concluded that high gasification temperatures provided high conversion and >95% conversion of carbon was achieved in about 1 hour at approximately 1350ºF to 1400ºF. The conversion rate was affected by catalyst loading; however loading beyond 10 to 15 wt % did not enhance the gasification performance significantly. A fuel gas fraction produced was recorded significantly higher at 0.88 to 2.64 MPa pressure than at 0.44 MPa pressure. There was significant interaction between pressure and amount of catalyst.

Sheth and Bagchi (2005) investigated the fate of nitrogen and phosphorous during gasification and pyrolysis of poultry litter, with or without using a catalyst. They also studied the gasification of pyrolysed char. Steam gasification of poultry litter was done to avoid the possibility of NO_x emission; however, ammonia was released from the poultry litter because heat treatment caused the break down of uric acid. No phosphine emissions were recorded. The kinetics of ammonia formation during steam gasification of poultry litter were described as the following (Sheth and Bagchi, 2005):

The release of nitrogen from the litter solid phase to the gaseous phase as nitrogen gas,

$$2(N-X)_{solid} \rightarrow N_2(g) + X_2(s) \text{.....(2.9)}$$

The ammonia synthesis takes place in the gaseous phase,

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g) \text{.....(2.10)}$$

The ammonia dissolves and reacts with the dilute hydrochloric acid,

$$NH_{3(g)} + H_2O_{(l)} + HCl_{(aq)} \rightarrow NH_4Cl_{(aq)} + H_2O_{(l)} \ldots..(2.11)$$

The pyrolysis of poultry litter was conducted for production of pyrolysed char by placing a 10 g sample of poultry litter into a cylindrical stainless steel container (reactor) placed in a muffle furnace (Sheth and Bagchi, 2005). The reactor was continuously purged with argon (~200 cm^3/min flow rate) during the pyrolysis (300 to 700 ºC for three hours) to remove the gaseous products, which were passed through the dilute hydrochloric acid solution for recovery of gaseous nitrogen. The gasification of pyrolysed char was carried out in a fixed bed reactor. The char obtained from pyrolysis was crushed and screened with screen# 30 and screen# 100. The medium fraction with particles between screen # 30 and screen# 100 were placed into the fixed bed reactor for the gasification experiment. The ammonia released was recovered by a method similar to the previous experiment. The results of the study showed that percent nitrogen released as ammonia during pyrolysis decreased, from approximately 25% to 6%, when pyrolysis temperature increased from 300 to 700 ºC. The ammonia liberation increased sharply to 70% when gasification was followed by pyrolysis because of the increased gas phase hydrogen concentration. Sheth and Bagchi (2005) reported that depending upon the conditions, 20 to 70% of the nitrogen present in the litter can be released as ammonia during steam gasification/ pyrolysis. Ammonia release decreased with increase in temperature and with the inclusion of a catalyst.

2.2.5 Pyrolysis of poultry litter

Pyrolysis is formally defined as decomposition induced in organic materials by heat in the absence of oxygen. Pyrolysis is a thermal process that transforms materials into gaseous components, organic condensate when condensed, and a solid residue (coke) containing fixed carbon and ash (EPA, 1992). Agblevor and Kim, (2005), in their study, reported that pyrolysis could be a good option to utilize poultry litter in generating bio-oil, char, and valuable products. Lima and Marshall (2005) used poultry litter for granular activated carbon production and optimized conditions for its production. They pyrolyzed the pelletized manure samples at 700 ºC for one hour followed by activation in an inert atmosphere under steam at different water flow rates, for a period ranging from 15 to 75 min. The bio-oil yields, resulting from pyrolysis of poultry litter, were relatively low (20 to 30%) compared to wood derived bio-oils (Agblevor and Kin, 2005). They also mentioned that its viscosities were very high compared to wood and herbaceous bio-oils. The high char yield was attributed to the high ash content.

Kim and Agblevor (2007) investigated the pyrolysis kinetics of poultry litter at three heating rates 5, 10, and 20 ºC/min and reported that most of the material decomposed between 270 ºC and 590 ºC, which was slightly lower than the range for wood chips. According to them the major difference between pyrolysis behavior of wood and chicken litter was that the wood chips followed two stage decomposition compared to three stage decomposition of chicken litter. Kim and Agblevor (2007) ambiguously contradicted previously proven research. It’s a known fact that the first stage in wood decomposition is attributed to the decomposition of cellulose, hemi cellulose, and lignin and the second stage is attributed to de-volatilization of charcoal, however, Kim and Agblevor (2007) reported that the first stage in litter was attributed to decomposition cellulose and hemi cellulose, second stage to lignin, and third stage to de-volatilization of charcoal. Interestingly, Kim and Agblevor (2007) did not support their explanation for kinetic behavior of poultry litter either with composition analysis or with established facts.

The review of the literature on physical and thermal treatment of poultry litter indicated that the fractionation of poultry litter followed by the pyrolysis of the coarse fraction to develop energy products and pelletizing the fine fraction to develop compact nutrient dense fertilizer could add value to the poultry litter. In order to better understand the pelleting and pyrolysis processes.

2.3 Biomass pyrolysis and its mechanism

Biomass pyrolysis is defined as thermal decomposition of biomass or an organic matrix in the absence of atmospheric oxygen. The pyrolysis process produce a solid residue, liquid condensate, and gas products. Pyrolysis is called carbonization or slow pyrolysis when the resulting principal product is solid char. However; if the preferred product is liquid condensate, the process is called fast pyrolysis. Mohan et al. (2006) summarized the general changes that take place during general pyrolysis, especially during slow pyrolysis:

1. initially heat transfers into the biomass or organic matrix from a heat source through conduction and convection and increases the biomass temperature. The detailed mechanism of heat transfer is not known but may be studied according to Kaviany (1991).
2. After biomass reaches a particular temperature, a primary pyrolysis reaction starts and its particular component depending upon temperature (Cellulose, hemicellulose, lignin, and extractives) decomposes, releasing volatiles and forming charcoal.
3. The hot volatiles flow toward un-pyrolysed biomass and transfer heat to the relatively cooler surfaces.
4. This heat released from hot volatiles cause condensation on colder surfaces of the biomass followed by secondary reactions to produce tar.

5. These auto catalytic secondary and primary reactions occur simultaneously in the biomass.
6. Depending upon residence time/ temperature/pressure profiles of the reactions zones, reforming, water gas shift reactions, radicals' recombination, and dehydration may also occur.

Bridgewater (2004) described the essential features of fast prolysis for producing liquids. During fast pyrolysis, very high heating (heat fluxes of 50 W/cm^2, Mohan et al., 2006) and heat transfer rates (10^3 to 10^4 kJ/s Zhang et al., 2007) are maintained at the reaction surface of very finely ground biomass feed. The reaction temperatures are maintained at 500˚C and vapor phase temperature is maintained at 400 to 450˚C. Vapors are allowed to stay in the reaction zone for no more than 2 seconds. Vapors are rapidly cooled to give bio-oil.

Fundamental principles and mechanisms governing pyrolysis

Pyrolysis is a complex phenomenon of heat, mass, and momentum transfer. Let us consider a packed bed of wood balls of diameter 1mm packed inside a cylinder made of stainless steel, the cylinder is oriented with its axis perpendicular to the ground. Let us assume that the void space between the wood balls act like macro pores and pores within the wood balls are micro pores. Also assume that nitrogen is purged from the bottom uniformly across the cross-section of the cylinder. The cylinder is placed inside a furnace at 600˚C for pyrolysis. The volatiles leave the packed bed from the top cross-section via a pipe. Heat is transferred inside the packed bed in the radial direction toward the center. The major mechanisms are: (1) heat transfer; (2) chemical reaction; (3) mass transfer due to volatiles and gasses; and (4) Mass transfer due to particulate matter through momentum transfer.

Heat transfer: The heat transfer inside the packed bed takes place through the following (Moghtaderi, 2006):

1. heat transfer due to conduction (micro pores) and convection (macro pores) from the heat source,
2. heat loss/gain due to chemical reaction (exothermic or endothermic),
3. convective thermal transport due to outward mass flow of volatiles,
4. internal convective heat transfer between volatiles and solid biomass,
5. accumulation of volatiles on the biomass and pressure buildup inside the wood particle (latent heat of volatiles),
6. heat loss due to mass flow of particulate matter from the packed bed (specific heat of particulate matter which is leaving the packed bed due to momentum transferred into it), and
7. desorption of fuel moisture due to external heat.

It is almost impossible to represent these processes in the mathematical form as many of the processes are not well understood. While conceptualizing a mathematical model, assumptions and approximations are made to simplify the situation.

Chemical reaction: There are multiple models available in the literature to represent the chemical kinetics of the pyrolysis process. These models are categorized into (1) simple thermal models and (2) comprehensive models (Moghtaderi, 2006). The simple thermal models are based on energy and mass balance and include simple algebraic models, analytical models, and integral models. The comprehensive models combine kinetic scheme, mass and energy balance to calculate the rate of pyrolysis. These are further classified into analytical and numerical type models. The most complex model is also called two stage semi global pyrolysis models, and for wood it may be given as in figure 2.1 (Moghtaderi, 2006):

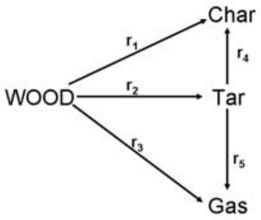

Figure 2.1. Two-stage semi-global reaction scheme for wood pyrolysis. The 'r' represents the reaction rates for the given reaction. Source: Moghtaderi (2006).

This model considers both primary and secondary reactions. The model assumes that the wood first decomposes into char, heavy molecular tar vapors and gases. These tar vapors further decompose into low molecular weight compounds and gases. The kinetic data for the above model was presented by Moghtaderi (2006).

Mass transfer due to volatiles and gases: The water vapors, volatiles, tar vapors, and gas products are produced during the pyrolysis of wood in its micro and macro pores. These products when produced during the thermo-chemical reaction at the macro pore are driven away from parent location by sweep gas nitrogen through forced convection. Some of such volatiles condense on the other wood particles or char which are not at the thermodynamic equilibrium with the volatiles. Some of the vapors undergo secondary reaction decomposing further into low molecular weight volatile compounds, charcoal and gases.

When these volatiles and gas products are formed inside the micro pore region, they first escape to the macro pore region through diffusion and natural convection, then are carried away by the sweep gas through forced convection. Moghtaderi (2006) mentioned that depending upon the thermo-chemical properties of wood, either of the mass transfer processes, diffusion or convection, or both may occur. They took an example of 2 cm thick Autralian Radiata pine wood slab undergoing pyrolysis at two temperatures 500 and 900 K. They used thermo-chemical properties of wood and volatiles and estimated the characteristic time for diffusion mass transfer and mass transfer due to convective flow inside the micro pores. Under these conditions, they found that mass transfer due to diffusion is negligible compared to mass transfer due to convection and hence Autralian Radiate pine might be considered as non porous material with no micro pores. Moghtaderi (2006) also mentioned some research where the assumption of non porous material did not hold. It may happen in wood with similar density but different longitudinal permeability. In such a situation, the mathematical model must account for diffusion and pressure build-up within the porous structure taking into consideration non-isobaric mass transport.

Mass transfer due to particulate matter through momentum transfer: Lab experiments showed that much of particulate matter is also captured in exhaust gas filters and condensed bio-oil. This particulate matter comes from one of two locations: (1) small particles of biomass blown away by sweep gas; (2) small char particles produced from either secondary cracking of volatiles or primary char particles blown away by sweep gas. This phenomenon is often not covered in any of the mathematical models available in the literature. The pneumatic transport of the particulate matter could be a potential area of study to decide the sweep gas flow rate.

2.3.1 Physical and chemical transformations in the biomass during pyrolysis

When the temperature of wood biomass reaches 230 to 250˚C, its color becomes reddish brown or chocolate. This stage is called wood retification (Antal and Gronli, 2003). Wood becomes brown or black when torrefied at 280˚C. At higher temperatures, the wood biomass turns into conventional charcoal. The physical structure of the wood biomass is chemically composed of carbon, hydrogen, oxygen, and nitrogen with traces of sulfur and ash (Yaman, 2003). All these components are present in biomass in form of high molar mass compounds carbohydrate polymers and oligonomers (65 to 75% of the biomass); lignin (18 to 35%); and low molar mass organic extractives/ inorganic material (4 to 10%) (Mohan et al., 2006). Each component shows specific thermal degradation behavior during pyrolysis as discussed below.

Cellulose constitutes 40-50% of the weight of wood biomass (Mohan et al., 2006). They described cellulose as a linear polymer of glucose (5000-10000 glucose units) having molecular weight more than 10^6. Cellulose degrades at 240-350˚C producing anhydrocellulose and levoglucosan. The later is produced when a glucosan radical forms, and it does not get a chance to bridge with oxygen present in cellulose polymer. The in-depth chemistry of this reaction is presented by Mohan et al. (2006).

Hemicellulose accounts for 25-35% of the weight of wood biomass (Mohan et al, 2006). It is a complex polysaccharide (Yaman, 2003) and has lower molecular weight than cellulose. An average polymer of hemicellulose contains only 150 monomers of repeating saccharides. Unlike cellulose, which has only glucose in its chain structure, hemicellulose contains heteropolysaccharide and thermally degrades in the temperature range of 130-194˚C (Mohan et al, 2006). The differences in thermal decomposition chemistry of hemicellulose and cellulose are not well-known.

Lignins are characterized as highly branched, substituted, mononuclear aromatic polymers forming a lignocellulosic complex in the biomass (Yaman, 2003), and this amorphous structure of lignin accounts for 16 to 33% of the mass of wood biomass (Mohan et al, 2006). The thermal decomposition of lignin occurs at 280 to 500˚C yielding phenol via cleavage of ether and carbon-carbon linkages. According to Mohan et al. (2006) lignin produces more residual char than cellulose or hemicellulose. The liquid component of lignin pyrolysis is composed of menthol, acetic acid, acetone, and water; and the gaseous component is mainly methane, ethane, and carbon-mono-oxide.

Inorganic minerals do not degrade during pyrolysis and remain in solid residue. Extractives decompose at higher rate and lower temperature than lignin but in a similar way (Raveendran et. al, 1996).

The physical and chemical changes in the biomass during pyrolysis and in turn, the physiochemical properties of pyrolysis products depend upon feedstock properties and pyrolysis conditions (heating rate, peak temperature, sweep gas flow rate, pressure, and presence of catalyst.

2.3.2 Physical properties of charcoal

Charcoal is generally characterized based on its use. Charcoal is not only used as a source of energy but it is also widely used as a metallurgic redundant, electrode material, soil amendment, and an absorbent. A good quality charcoal is defined in Antal and Gronli (2003) as: “Charcoal of good quality retains the grains of the wood; it is jet black in color with shining luster in a fresh cross-section. It is sonorous with a metallic ring, and does not crush nor does it soil the fingers.” The charcoal produced at different temperatures carries different properties.

Antal and Gronli (2003) presented a picture showing the effect of temperature on the properties (carbon content, water sorption, specific gravity, hydrogen content, and electrical resistivity etc) of charcoal (fig. 2.2). A better way to define carbonization efficiency is the fixed carbon content of the charcoal. Antal and Gronli (2003) mentioned that increasing the peak temperature during pyrolysis not only increased fixed carbon content but also decreased oxygen content in the residue. Similar effect was noticed when heating rate was decreased from 10°C/min to 2°C/min. The fixed carbon content has a direct relationship with the heating value of the charcoal. While most of the research papers preferred experimentally measured calorific values, all the papers have reported higher heating values. In the absence of any measured value, the equation developed by Channiwala and Parikh (2002) can predict higher heating value (MJ/kg) with an absolute error of up to 1.45% and bias error of 0.00%.

$$HHV = 0.3491.C + 1.1783.H + 0.1005.S - 0.1034.O - 0.015.N - 0.0211.A \quad .....(21)$$

Where C, H, N, S, O, and A represents carbon, hydrogen, nitrogen, sulfur, oxygen, and ash content expressed as a percentage (dry basis). The input values may be determined from ultimate and proximate analysis. Equation (21) is valid for a wide range of C (0 to 92.25%), H (0 to 25.15%), O (0 to 50.00%), N (0 to 5.6%), S (0 to 94.08%), and Ash (0 to 71.4%).

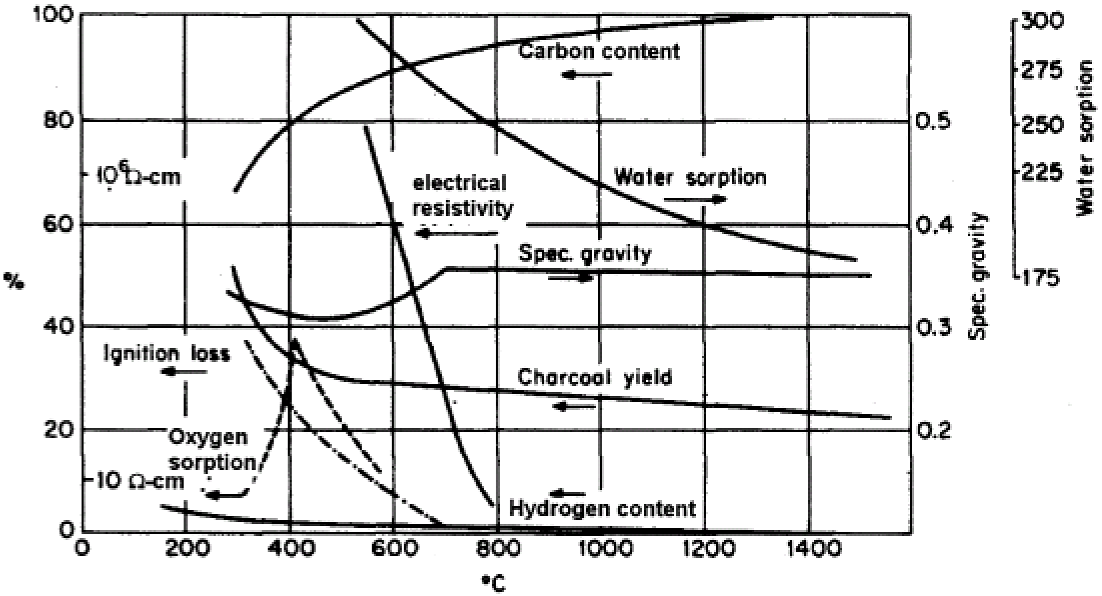

Figure 2.2. Effect of pyrolysis temperature on the properties of charcoal. Source: Antal and Gronli (2003)

While reviewing the mechanical properties of the charcoal, Antal and Gronli (2003) reported that compressive strength of charcoal decreased with increase in peak temperature and heating rate and that fragility of the charcoal was high for softwood. The modulus of elasticity, which is a key to mechanical properties, decreased to a minimum level near 330˚C and after that it regained its initial value (Antal and Gronli, 2003).

The surface area, pore structure, and adsorption properties of the charcoal are also affected by peak temperature, however heating rate had little influence on char micro-porosity (Antal and Gronli, 2003). Deashing of the biomass increases the surface area of the charcoal. According to Antal and Gronli (2003), the surface area and pore properties may be greatly influenced by sweep gas flow rate. At low temperature, the surfaces of the charcoal are inhibited by chemical functionalities, which are gradually lost with increases in temperature rendering a highly reactive carbon structure.

The electrical receptivity of the charcoal is also directly affected by peak temperature (fig.2.2). The literature reported that microcrystalline structures are formed in wood charcoal carbonized at 900˚C. The bulk density of the charcoal is linearly proportional to the feedstock's bulk density with a factor of 0.82 (Antal and Gronli, 2003).

The reactivity of the charcoal in the air may be summarized in three terms: (1) pyrophoricity; (2) chemisorption; and (3) ignition. Tightly packed charcoal fines with high volatile contents and water sprayed charcoals are prone to self ignition (Antal and Gronli, 2003). According to the review, oxygen chemisorption is the root of this problem. Since most of the chemical bonds of the carbon are left dangling or unbalanced, the charcoal has a tendency to absorb oxygen and moisture (Antal and Gronli, 2003). They reported that charcoal prepared at 400 to 550˚C showed maximum oxygen absorption. However, the charcoals prepared at higher temperature had low chemisorbed oxygen. The ignition behavior is strongly influenced by the presence of chemisorbed oxygen and make up of the mineral matter content of the charcoal.

2.3.3 Physical and chemical properties of bio-oil

The bio-oil produced is characterized by the amount of suspended char, alkali metal content, pH, viscosity, water content, heterogeneity, pour point, heating value, flash point, water insoluble content, stability, ash content, and carbon, hydrogen, nitrogen, and sulfur contents. The determination methods of various physical properties are discussed in Oasmaa et al. (1997). Zang et al. (2007) summarized the properties of pyrolysis oil. Physically, the pyrolysis liquid is a free flowing dark brown liquid with distinctive smoky smell (Bridgewater, 2004). High nitrogen present in the liquid may give it a dark green tinge color. They considered bio-oil as multi-component mixtures of different size molecules. Some of the physical characteristics of the pyrolysis liquids are discussed in the following paragraphs:

Water content of the bio-oil depends upon initial feedstock moisture content. The pyrolysis reaction also produces water as a product. Typically, pyrolysis liquids contain 15 to 35% water (Bridgewater, 2004). Water content is a good characteristic of bio-oil because water reduces the viscosity and improves the flow behavior. On the negative side, water content reduces the heating value of the bio-oil.

Typically, the bio-oil contains: C: 57%, H: 6.0%, O: 37%, N: trace, and ash. The amount of ash is dependent on the parent feedstock. Oxygen is distributed in more than 300 compounds which are present in pyrolysis liquids (Zhang et. al, 2007). High oxygen content results in approximately 50% energy density of that for conventional fuels. The severe pyrolysis conditions of high temperature, fast heating rate, and residence time directly reduces the oxygen content.

Depending upon the feedstock, the process conditions, and efficiency of collection of low boiling point components, the viscosity of pyrolysis liquids may range from 35 to 1000 cp at

40˚C (Bridgewater, 2004). They also reported that at high storage temperatures, the chemical species present in bio-oil reacts and produce larger molecules resulting in increased viscosity.

The substantial amounts of organic acids present in bio-oil give a pH value of 2-3. This low pH makes bio-oil highly corrosive, especially at high temperatures (Zhang et al., 2007). They also reported that the heating value of the bio-oil depends upon the biomass feedstock, production process, reaction condition and collecting efficiency. According to the review, the bio-oils produced from wood or agricultural residues have a heating value of about 20 MJ/kg and a yield up to 70-80%. Bridgewater (2004) described bio-oil as non flammable but combustible liquid due to its high non-volatile content.

The density of wood derived bio-oil was reported to be 1.2 kg/L which was higher compared to light fuel oil (Bridgewater, 2004). They reported that the pyrolysis liquids cannot be completely vaporized again. It boils below 100˚C. At high temperatures, smaller molecules of the reactive species form large polymers.

Ash present in bio-oil may cause serious corrosion problems (Zhang et al., 2007). The presence of sodium, potassium and vanadium are the prime cause of corrosion while calcium is a cause of deposition.

Mohan et al. (2006) classified the chemical compounds found in bio-oil into five categories: (1) hydroxyaldehydes, (2) hydroxyketones, (3) sugars and dehydrosugars, (4) carboxylic acids, and (5) phenolic compounds. According to the review, the phenolic compounds are mainly derived from lignin decomposition. They reported the highest concentration (besides water) of hydroxyacetaldehydes (10% by weight) followed by acetic acid and formic acid. The composition of the bio-oil is strongly influenced by pyrolysis conditions and the presence of catalyst (fig. 2.3).

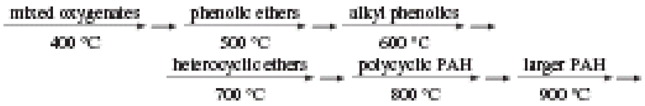

Figure 2.3. Effect of pyrolysis temperature on bio-oil chemistry. Mohan et al. (2006)

At high temperatures, alkyl groups cleave from aromatic compounds and condense into PAH (polycyclic aromatic hydrocarbons). Mohan et al. (2006) mentioned that complete characterization of bio-oil is a Herculean task. To perform major analysis of bio-oil, liquids must be analyzed by GC-MS (volatile compounds), HPLC and HPLC/electrospray MS (non-volatile compounds), FTIR spectroscopy (functional groups), GPC (molecular weight distribution), and NMR (types of hydrogens or carbons in specified structural groups, bonds, area integrations).

Although bio-oil is a hot topic among the scientific community, no literature is available on the effect of pyrolysis conditions (heating rate, peak temperature, pressure, and sweep gas flow rate) on the physical and chemical properties of bio-oil. The available literature mostly focuses on the effect of these process parameters on the yield of bio-oil and charcoal.

2.3.4 Applications of bio-oil

Although research has shown very promising applications for bio-oil, its usage in the real world is at the infancy stage, which may change with the development of new technology. The following sections discuss the possible applications of bio-oil.

Heat production: Although the heating value of the bio-oil is lower than diesel due to the presence of excessive oxygen and water, flame combustion tests yield promising results (Mohan et al., 2006). The heating value may be improved by reducing the water content. Other issues that need attention are initial ignition delay, viscosity, pH, and emission levels. Bridgewater (2004) mentioned the possibility for the solution to handling problems (storage, pumping, filtration, and atomization) and improved burner design for enhanced performance to consume bio-oil at large scale in furnaces and boilers.

Electricity production: Bridgewater (2004) suggested that bio-oil could be a good substitute for diesel engines because it offers a potentially high efficiency power generation (up to 45%), if slight modifications can be made in the diesel engine i.e. fuel pump, linings, and injection system to accommodate its high acidity and viscosity (Mohan et al., 2006). Emulsification of the bio-oil with standard diesel could be an option. According to Bridgewater (2004), the use of bio-oil should be limited to low speed engines with relatively high compression ratios; however, blends of bio-oil with cetane improving agents like methanol may be used in high speed diesel engines. They also reported that NO_x and SO_2 emissions were lower than those from regular diesel; however, particulate matter was higher.

Synthesis gas production: Mohan et al. (2006) summarized that 83% (by weight) or 450L syn gas per kilogram of bio-oil was converted to gas during gasification of bio-oil, generating a mixture of gases (H_2, CH_4, CO, CO_2, C_2 to C_n compounds). The product gases contained almost equal amount of synthesis gas, methane, and ethane. They reported the synthesis gas production of 450 L/kg of bio-oil having high heating value of 1300 to 1700 BTU/SCF.

Transport fuel: Mohan et al. (2006) reported that acid-catalyzed dehydration of bio-oil produced liquid alkanes with a number of carbon atoms ranging from C_7 to C_{15}. According to them, the synthesized material captured 90% of the energy of the carbohydrate and H_2 feeds and could be a potential component for making green transport fuel. With existing upgrading methods, Bridgewater (2004) did not see bio-oil as a promising alternative for fuel (either aromatics for gasoline blending or naptha); however, he envisioned bio-oil as a source for hydrogen production (6 kg per 100 kg of biomass when biomass is first converted to bio-oil having bio-oil yield of 70%). According to the review, the aromatics production for gasoline blending was 20% by weight of bio-oil or 45% by energy content of the bio-oil. In contrast to this, the naptha yield was 25% by weight or 55% by energy content of the bio-oil.

Chemical production: The only known application for bio-oil derived chemicals are liquid smoke (browning agent for meat industry), and phenolic resin also called natural resin (curing agent for wood-based composites production) (Mohan et al., 2006). Bridgewater (2004) categorized chemical extraction or chemical synthesis from bio-oil into two categories. In the first category, whole bio-oil may act like a particular chemical when other active compounds are neutralized. BioLime, a slow release nitrogen fertilizer, and wood preservative are some examples of whole bio-oil.

The second category of products is extracted from bio-oil by separating water soluble and insoluble fractions. In addition to liquid smoke, the water soluble fraction can also produce calcium salts of carboxylic acids, which may be used as road deicer. As mentioned before, the phenolic resins may be used as adhesives in plywood and producing particleboard (Bridgewater, 2004).

Bridgewater (2004) mentioned that specific chemicals like Glycolaldehyde and Levoglucosan (10% by weight of bio-oil at 96% purity) can be extracted from the bio-oil. The first is used by the meat industry and the later has wide applications in the pharmaceutical industry. Despite the potential in bio-oil in chemical production, its production cost with existing technologies posses a limitation for its commercial application.

2.4 Densification

The densification process increases the density of the feedstock and is often achieved through either a pellet or briquette formation process. The physical properties of biomass and process variables play a significant role in the pellet formation process. Knowing the compaction behavior of the biomass enables the processor to design energy efficient compaction equipment. The behavior of biomass particles under pressure in terms of density change and cohesion of particles to support binding after the pressure is released are two important aspects of compaction behavior (Tabil, 1996). Compaction of biomass may be considered as a three stage process which may occur simultaneously: particle rearrangement at low pressure, elastic and plastic deformation at high pressure, and local melting of material if the melting points of the ingredients are reached (Tabil, 1996). The possible mechanism during the three stages can be grouped into five major groups (Mani, 2005; and Tabil, 1996):

1. The attraction forces (van der Waal's, electrostatic, and magnetic) increase between two biomass particles when they are placed at intra molecular distances.
2. The capillary pressure and interfacial forces promote the binding of particles when liquid is present.
3. Adhesion and cohesion forces are produced when the areas of contact of thin adsorption layers increase during the compaction process.
4. Solid bridges develop at high temperatures and pressures due to diffusion of molecules from one particle to another.
5. Particles interlock or fold about each other when biomass contains a significant amount of fibers, platelets, and bulky material providing bonding strength.

2.4.1 Factors affecting pellet quality

Tabil (1996) presented a comprehensive review on the subject and mentioned that fat, fiber, starch, moisture content, moisture affinity, bulk density, and spectrum of particle size affect pellet quality. Poultry litter is primarily composed of neutral detergent fiber followed by protein, acid detergent fiber, fat and lignin. It also contains significant amounts of minerals.

The high amount of protein present in the poultry litter gives good pellet production rates and good quality of pellets because proteins plasticize under heat which when supplied either externally or generated internally due to friction. While fibers are natural binders providing strength to the pellet, fibers are difficult to compress resulting in low pellet production rates. The pellet quality is directly affected by mean particle size. Medium to finely grind material provides more surface area for binding and is easier to pass through a die than coarse material; however, considerable variability in the grain particle size within one feedstock may mask the effect of particle size (Tabil, 1996).

In addition to feedstock properties, machine and process variables like steam conditioning, roll and die size, die speed, cooling and drying, storage conditions, and the inclusion of a binder affect pellet quality. Conditioning feedstock with constant quality steam at a constant pressure to supply heat and moisture promotes gelatinization, releases and activates natural binders, releases natural lubricants, activates artificial binders, improves moisture content, and improves feeding conversion resulting in low energy consumption during pellet formation (Tabil, 1996). The pellets are generally cooled and dried after formation. The cooling and drying conditions may seriously affect the pellet quality, pellet beak-down, spoilage caused by molds, and cracking. It is recommended that long cooling and drying times should be considered to reduce the temperature by 3 to 5˚C from manufacturing temperature and moisture content between 10.5 to 12.5% to reduce fines in manufactured pellets (Tabil, 1996).

When exposed to high humidity and temperature during storage, the pellets absorb moisture and expand in size. With 4% addition of moisture, the water molecules increase the bonding strength between the particles. Any further addition of moisture causes poor pellet quality because free water has negligible binding strength (Tabil, 1996).

The inclusion of binders provides strength to the pellets. Binders may be classified into three main groups (Tabil, 1996):

1. Matrix type binders like paraffin, clay, dry starch, and dry sugars, are required in substantial quantities because particles are embedded in a continuous matrix with low film strength.
2. Film type binders like starch, bentonite, gums, alginates, and lignosulfates, are dissolved with water at the particle surface and re-crystallize across the particle boundary when water is evaporated.
3. Chemical binders like calcium hydraoxide with carbon dioxide and sodium silicate with calcium chloride, depend upon the chemical reaction between the binder and material being agglomerated.

In addition to the process variables, machine variables like die speed and roll and die size also affect the pellet quality. Information on the machine variables may be obtained from Tabil (1996).

2.4.1 Compaction models to express compaction behavior

Compression test are done to characterize the compaction behavior of the feedstock under pressure. The compression test provides a force-deformation or force-time curve for a given sample (fig. 2.4).

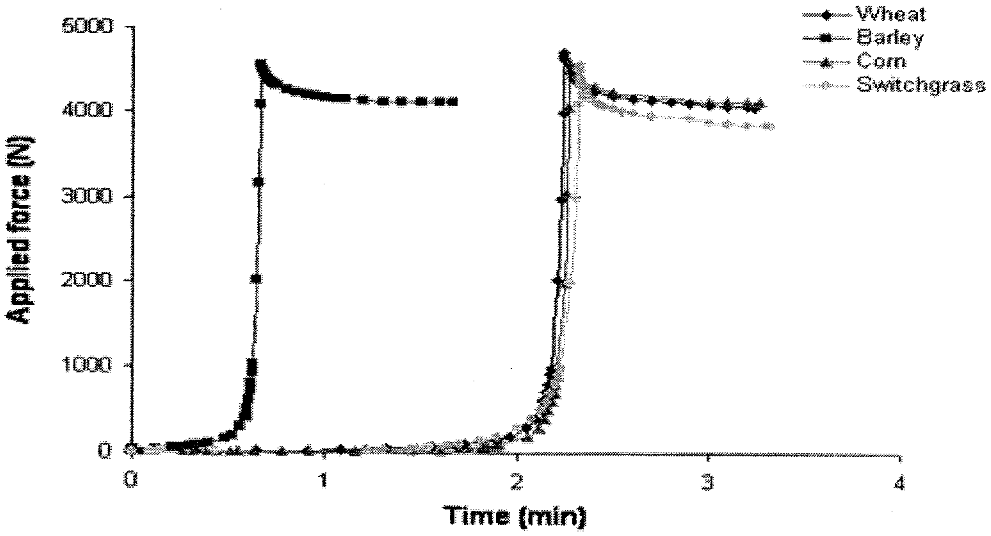

Figure 2.4. The compaction behavior results in typical compression curve for the biomass subject to test. Source: Mani (2005).

The test data is used to calculate the specific energy required to compress the material and to mathematically express the compression behavior. The mathematical expression of the compression behavior can be done by fitting the test data with compaction models (table 2.1) which are well reviewed by Tabil (1996) and Mani (2005).

Table 2.1 Compression models reviewed by Tabil (1996) and Mani (2005).

Sl.No.	Model name	Model	Symbols and Comments
1.	Heckel (1961)	$\ln\left[\frac{1}{1-\rho_r}\right] = m_0 P - b_0$ $\rho_r = \frac{\rho}{\rho_1 X_1 + \rho_2 X_2}$	Compression behavior of compressed powder which is a mixture of two components.
2.	Shivanand and Sprockel (1992)	$b_0 = \ln\left[\frac{1}{1-\rho_r}\right]$	High value of ρ_f indicates that there will be high volume reduction due to particle rearrangement. m_0 is reciprocal of the mean yield pressure required to induce plastic deformation. The onset plastic deformation takes place at low pressure when a value of m_0 is high.
3.	Jones (1960)	$\ln(\rho) = m_1 \ln(P) + b_1$	Compression model for metal powders.
4.	Walker (1923)	$V_R = m_2 \ln(P) + b_2$ $V_R = \frac{V}{V_S}$	Characterizes the compaction of non-metallic powders.
5.	Cooper and Eaton (1962)	$\left[\frac{V_0 - V}{V_0 - V_s}\right] = a_1 e^{-\frac{k_1}{P}} + a_2 e^{-\frac{k_2}{P}}$	Assumed that compaction proceeds through particle rearrangement and deformation.
6.	Kawakita and Ludde (1971)	$\frac{P}{C} = \frac{1}{ab} + \frac{P}{a}$ $C = \frac{V_0 - V}{V_0}$ $C_\infty = \frac{V_0 - V_\infty}{V_0} = a$	Holds for soft and fluffy powders.

Where, ρ_1, and ρ_2 are particle densities of the components in the mixture (kg/m^3); ρ_f is the packing fraction or relative density of the material after particle rearrangement; ρ is the bulk density of the compacted powder mixture (kg/m^3); m_0 and b_0 are the Heckel model constants; P is the applied pressure (MPa); X_1 and X_2 are the mass fraction of components of the mixture; m_1 and b_1 are Jones constants; V is the volume of the compact at pressure P (m^3); V_S is the void free solid volume (m^3); m_2 and b_2 are the Walker's model constant; a and b are the kawakita constants; and C is the degree of volume reduction; V_0 is the volume of compact at zero pressure (m^3); a_1, a_2, k_1, and k_2 are the experimentally determined Cooper Eaton model constants.

2.4.2 Diametral compression test

Diametral compression tests are mostly used to test the strength of tablets in the medical industry. According to Tabil (1996) there are five ways in which tablets/pellets fracture when compressed along the diameter:

1. Failure due to compression at local loading points;
2. Failure due to shear at local loading points;
3. Failure due to point loading along the maximum shear loci;
4. Failure due to transfer of load to each half-disc after breakage along the vertical diameter also called “triple-cleft”.
5. Ideal failure due to tension giving straight crack.

The ideal failure conditions can be obtained by carefully controlled loading of the samples. It is recommended that three sheets of blotting paper, each 0.3 mm thick, should be used for padding the steel platens of the test instrument to get tensile failure. The horizontal stress (σ_t) remains constant along the vertical diameter for constant compressive load; however, vertical stress (σ_c) and maximum shear stress (τ) varies along the vertical diameter (fig. 2.5). The horizontal stress may be given by the following expression:

$$\sigma_t = \frac{2F}{\Pi . d . l} \quad \text{.....(2.11)}$$

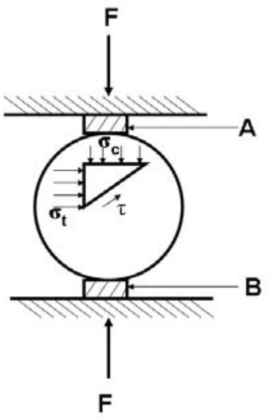

Figure 2.5. Schematic representation of the stress distribution across the loaded cylinder held between deformable plates A and B. The applied force (F) causes compressive stress (σ_c), tensile stress (σ_t), and shear stress (τ) inside the cylinder. Source: Tabil (1996).

2.5 Summary

This chapter started with the definition of poultry waste followed by discussion on physical and thermal treatment of poultry litter. Among the physical treatments, screening and densification were discussed; whereas combustion, gasification, and pyrolysis were discussed under thermal treatment options. The discussion forms a basis for this study focused on using fractionation of poultry litter to produce a nutrient dense fine fraction which can be pelletized. The remaining coarse fraction can be pyrolyzed to obtain char and bio-oil. The vision may be represented graphically (figure 2.6).

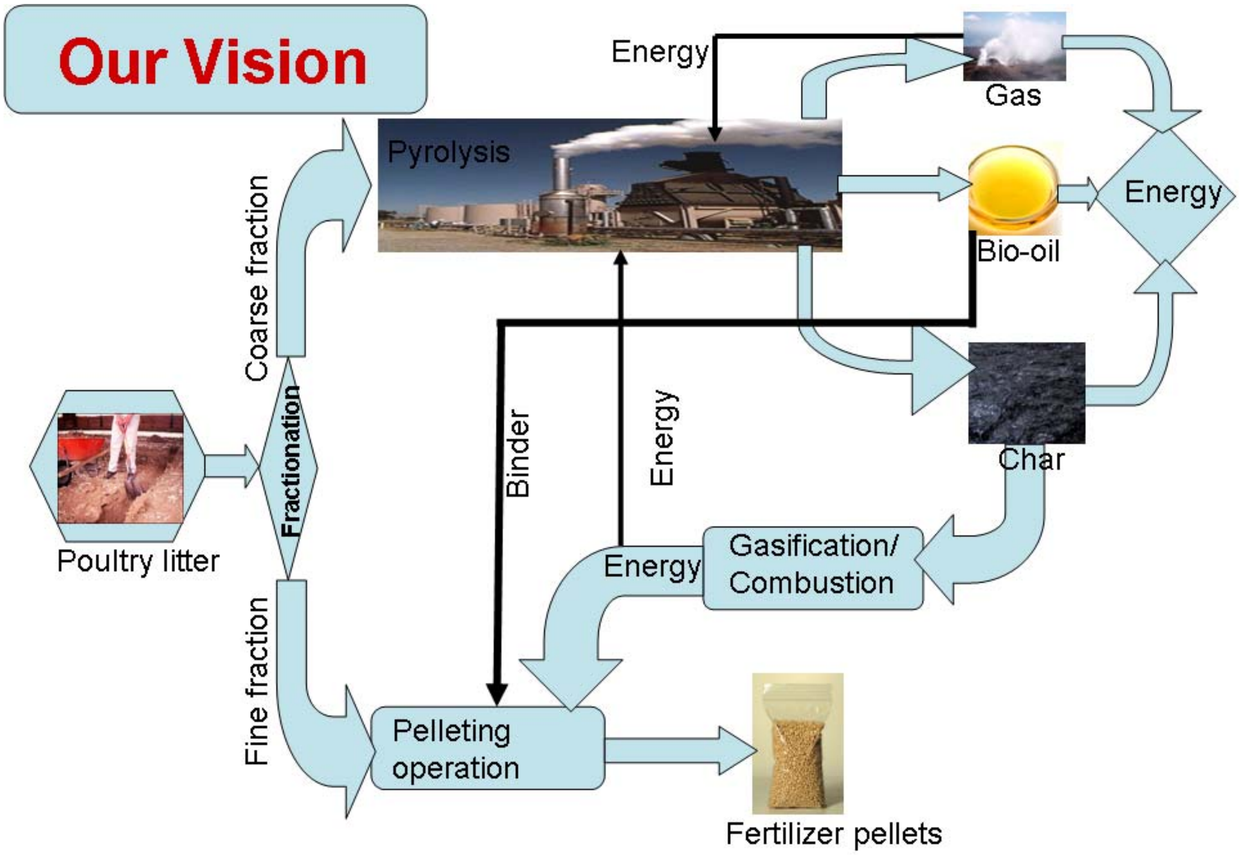

Figure 2.6. The vision for producing value added products from poultry litter using fractionation and pyrolysis.

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CHAPTER 3

EFFECT OF FRACTIONATION ON FUEL PROPERTIES OF POULTRY LITTER

Singh, K, M. Risse, J. Worley, K. C. Das, S. Thompson. 2008. Journal of Applied Engineering in Agriculture 24(3): 383-388.

Abstract

In raw form, poultry litter has certain draw backs for both energy production and fertilizer. These include high ash content and moisture content, a corrosive nature, low heat content, and low nutrient content. Fractionation divides poultry litter into a fine, nutrient rich fraction and a coarse, energy rich fraction. In this research, poultry litter was divided into coarse and fine fractions using a # 20 screen. The following analyses were performed on the raw poultry litter and its coarse and fine fractions: higher heating value, proximate, ultimate, compositional, mineral, thermogravimetric (TGA), and differential scanning calorimeter (DSC) analysis. Preliminary results show that the coarse fraction from screen # 20 is potentially a much better feedstock for energy production than whole litter. The results of this study may be directly applied to the poultry industry to promote value added utilization of litter and to improve the efficiency of energy producing industries using poultry litter as feedstock.

Keywords: Agricultural waste, Bioenergy, Poultry litter, Poultry manure, Fractionation.

Introduction

Poultry litter or broiler litter is a waste product resulting from periodical cleanout of poultry production facilities. Generally, a poultry house is cleaned to ground level after 4 to 8 flocks having growth cycles of 47 to 49 days. Poultry litter is a combination of manure, bedding materials, feathers, and spilled feed. One management practice of partial cleanout is known as "decaking." The "broiler cake" is litter that has become caked because of spilled water or high humidity. Cake is removed after the harvest of each flock using a "decaking machine" that removes the cake and leaves the uncaked litter in the house. The poultry industry produces more than 50 billion tons of waste every year. Region 4 of the EPA leads the nation in the production of poultry and poultry litter. Georgia ranks first in the United States in production of poultry and poultry products, supplying approximately 12% of U.S. production (Risse and Cheadle, 1996). The abundance of poultry litter production in region 4 and in Georgia has led growers to consider different utilization methods of poultry litter. Poultry litter is primarily applied to land because it is an excellent source of organic fertilizer. An alternative use is to use poultry litter as an economical source of energy. This energy is used either for space heating or power generation through combustion, gasification, co-firing, or pyrolysis.

While poultry litter is an excellent source of organic nutrients for crop production, many farms produce more nutrients than the region or farm can use resulting in regional and farm level nutrient imbalances. These nutrient imbalances can cause eutrofication in some water bodies. According to the Georgia Watershed Agricultural Non-point Source Pollution Assessment, approximately 39% of total Phosphorus produced from animal waste could potentially be exported to the State's waterways (Risse and Cheadle, 1996). The report also stated that some

1419 miles of streams and 10,700 acres of lakes in Georgia are not meeting their designated uses, primarily due to rural non-point source pollution. EPA and State environmental agencies have tried to address this problem through nutrient management planning efforts. Recently, stringent regulations for land application of poultry litter have motivated scientists to study the potential use of poultry litter as an economical source of energy. In some alternative use studies, poultry litter has been evaluated as a source of energy or a feed stock for making fertilizer pellets (Keener et al., 2002; Mukhtar et al., 2002; McMullen et al., 2004; Lopez et al., 2005). In the United States, it is estimated that using poultry litter as fuel could save 283 million gallons of LPG-equivalent fossil fuel energy source (Reardon et al., 2001).

According to Reardon et al. (2001), if poultry litter were used for fuel, almost every poultry farm would have surplus energy after meeting its own demand. Generally a poultry farm with production capacity 100 to 110 k birds per year will produce 125 dry tons litter per year. If 100 tons of that litter is used in a 75% efficient gasifier it would produce the equivalent of 9300 gallons of LPG, or $10,000 in equivalent value. The value of the resulting 25 tons of ash (for fertilizer) would be $1250. This hypothetical poultry farm only uses 6000 gal of LPG in a year or 82 dry tons of litter. Direct combustion, gasification, co-firing with coal, and pyrolysis are the known options available for extracting energy from poultry litter. Heating the biomass with unlimited oxygen is called combustion. Gasification is a process of heating the biomass in limited oxygen and in pyrolysis oxygen is absent during the heating process. Every method has its own advantages and limitations. During direct combustion, gasification and co-firing, NOx and NH_3 emissions may cause environmental concerns. Also, high ash and moisture content require supporting fuel, and high volatiles cause corrosion of boilers. Both of these methods require storage of poultry litter. Long-term storage causes microbial decomposition of litter resulting in reduced heating value (Jirjis, 2004). In general, broiler litter is a lower quality fuel than coal due to its high mineral and ash content (Mukhtar et al., 2002). Despite the drawbacks of combusting raw poultry litter as fuel, the Fibrowatt LLC (Langhorne, PA, USA) has built three electricity generation plants in the United Kingdom (Ward, 2003) and is building five such power plants (Benson, Minnesota, Arkansas, Maryland, Mississippi, North Carolina) in the United States (HRE, 2007).

A combined solution to utilization of raw poultry litter lies in the process which involves screening the poultry litter. Ndegwa et al. (1990) fractionated poultry litter by using #6 and #20 mesh screens and divided the poultry litter into three fractions: coarse, medium, and fine. The fine fraction (fraction that passed through screen #20 or mesh size 0.85 mm) had the highest nitrogen content whereas, phosphorous and potassium were uniformly distributed in all three fractions. Coloma (2005) studied the effect of screening on fractionation of mass, density, and nutrients. The results of that study agreed with Ndegwa et al. (1990). The best option to utilize the remaining coarse fraction would be energy production with some improved technology like pyrolysis because pyrolysis would remove corrosive volatiles from the feedstock.

The long-term goal of this research project is to study the pyrolysis of the coarse fraction of screened poultry litter. Fractionation would reduce the mineral content and increase the volatile yield during pyrolysis. Pyrolysis would result in three energy products: gases, bio-oil, and char. This same screening process produces a fine fraction that is nutrient dense and thus more valuable as feedstock for fertilizer pellets. It is very important to study the effect of fractionation of poultry litter on the fuel properties and thermal degradation kinetics.

This article presents the results of the first step of a research project conducted to understand the effect of fractionation of poultry litter using screen #20, on fuel properties including heating value, proximate and ultimate analysis, mineral and ligno-cellulose composition, and thermal decomposition behavior under pyrolytic conditions. The specific objectives of this research are:

- To study the effect of fractionation of poultry litter using screen #20 on higher heating value, ash content, and volatile matter content of the poultry litter;
- To analyze thermal-chemical decomposition behavior and heat consumption during the thermo-chemical decomposition process under pyrolytic conditions for raw poultry litter and its coarse and fine fractions obtained using screen #20.

The potential impact to the poultry industry is the value added utilization of its waste and management of nutrients. The research will provide extensive knowledge about the usefulness of fractionation and pyrolysis for producing energy and pelleted fertilizers. The research will not only help in developing energy efficient fertilizer pelleting technology but also open new avenues for developing poultry litter as a source of energy for the commercial market. The use of the bio-oil produced as a binder or for developing other value added products from poultry litter is another unique potential output of this research project. The research could potentially help the industry generate income from poultry litter, reduce storage and reduce transportation costs, and aid in on-farm nutrient management by reducing phosphorous pollution from poultry litter.

Materials and Methods

Litter samples were collected from a standard broiler farm in Georgia according to EPA method (EPA-821-B-04-006, 2004). All the poultry litter samples were refrigerated at 2°C to 4°C prior to use to avoid microbial decay. Samples were screened using Screen #20 (0.85 mm) (USA Standard Testing Sieve, Fisher Scientific Co., Pittsburgh, PA) on an electrical sieve shaker (Model CL 5028, Soil Testing Inc, Evanston, Ill.) and sample sizes were reduced using ASTM D

6913 standard methods. Prior to actual screening, the standard shaking period was determined for the poultry litter according to the same standard. After screening, all the samples were dried at 45°C for 24 h in an oven (Isotempoven, Fisher Scientific Co.). All the samples were ground to 4 mm (FRITSCH, Pulverisette, Industries Trane, Idar, Oberstein) followed by further reduction in particle size to less than 1 mm (Thomas Scientific, Swedesboro, NJ).

Heating value was measured according to ASTM D5865 standard (2003b) using a Bomb Calorimeter (Model 1351, Parr Instrument Co. (Parr), Moline, Ill.). Proximate analysis (Ash, volatiles, fixed carbon, and moisture content) was done according to ASTM D3174 (2003a) using a Thermo Gravimetric Analyzer (Model TGA701, LECO Corp., St. Joseph, Mich.). Samples of the raw poultry litter, its coarse and fine fractions, and raw pine chips were sent to the Soil, Plant, and Water Laboratory (Athens, Ga.) for ultimate, compositional and mineral analysis.

The Soil, Plant, and Water Laboratory performed the compositional analysis using a wet chemistry method. According to this method, the content of fat and other extractives was determined by petroleum ether extraction in a Soxtec HT6 system. The fat free and oven dried material were further digested with neutral detergent solution (30.0 g of sodium lauryl sulfate, 18.61 g of ethylenediamine – tetraaceitc disodium salt, 6.81 g of sodium phosphate dibasic, 10.0 mL of triethylene glycol in 1 L of distilled water) and alpha-amylase to remove the soluble constituents such as starch, sugars, pectin, amino acids, proteins, etc. The remaining solid formed by hemicellulose, cellulose, and lignin, commonly known as neutral detergent fiber (ANKOM200), was further extracted using acid detergent solution (20-g cetyl trimethylammonium bromide (CTAB) in 1 L of 1 N H_2SO_4). The fraction removed was accounted as hemicellulose. The remaining solid (Acid Detergent Fiber) was further extracted with strong sulfuric acid (24 N or 72 mass % of H_2SO_4) to remove the cellulose. The remaining solid residue was considered to be the lignin. The content of proteins was determined by the combustion method. The percent crude protein was determined by multiplying the nitrogen content by a factor that depends on the type of biomass studied. The ash samples were analyzed for metals using inductively coupled plasma spectrometry (ICP, Perkin-Elmer Elan 6000 ICP-MS equipment, Waltham, Massachusetts) at the UGA Agricultural and Environmental Services Laboratory.

The statistical significance of the differences in higher heating value, ash content, and volatile content were determined according to randomized complete block design (RCBD) with two replications considered as block and three measurements on each replication using statistical analysis software (SAS 9.1, SAS Institute Inc., Cary, N.C.). The same RCBD experimental design was used to determine the statistical significance of the differences in compositional, mineral and ultimate analysis with two replications considered as block and single measurement on each replication.

The Thermo Gravimetric Analysis (TGA) and Differential Scanning Calorimeter (DSC) analysis was performed by heating the three fractions of poultry litter and a sample of raw pine chips (in 70-µL Alumina crucible for TGA, and 100µL Aluminum crucible for DSC) from 25°C to 600°C in three segments: (1) isothermal heating for a minute at 25°C, (2) heating at the rate of 10°C/min from 25°C to 600°C, and (3) isothermal heating for a minute at 600°C (Model TGA/SDTA 851 and DSC873, Mettler Toledo, Star Systems, Columbus, Ohio). An inert atmosphere and the removal of gases and condensate products were achieved using 50 $cm^3.min^{-1}$ of nitrogen. The output from TGA and DSC analysis were analyzed and differences in thermal decomposition behavior were explained by the data obtained from compositional, mineral, and ultimate analysis in the light of previous research works.

Results and Discussion

Characterization of Poultry litter and its fractions

One key to evaluating the screening process is determining a standard shaking period. We determined that for an 8-in. diameter and screen #20, the standard shaking period is 2 min when a 500- to 700-g sample is placed on the top sieve. There were some clear visible differences among raw poultry litter, fine fraction, and coarse fraction. The fine fraction has a powder-like appearance whereas the coarse fraction is primarily wood pieces and feathers. The heating value measurements showed that the coarse fraction had 7% higher heating value than the fine fraction (fig. 3.1a). The proximate analysis concluded that the coarse fraction had 11% less ash than the fine fraction (fig. 3.1c). In addition to less ash, the coarse fraction had 3% higher volatiles than the fine fraction (fig. 3.1b). The results of ultimate and compositional analysis explain these differences.

The compositional analysis showed that poultry litter is comprised of mostly protein and ash content, followed by cellulose and hemicellulose (table 1). In contrast to poultry litter, pine chips were mainly comprised of cellulose and lignin followed by hemicellulose with almost no ash and protein, as expected for a lignocellulosic biomass. Among the raw litter and its two fractions, the fine fraction holds a significantly higher amount of protein (p-value = 0.0045 at 95% confidence level) than the coarse fraction (fig. 3.2). Generally, heating value increases with increase in fixed carbon (Demirbaş, 2001) and the coarse fraction did have relatively higher fixed carbon and significantly lower nitrogen content (p-value = 0.009) at 95% confidence level than the fine fraction (table 3.2).

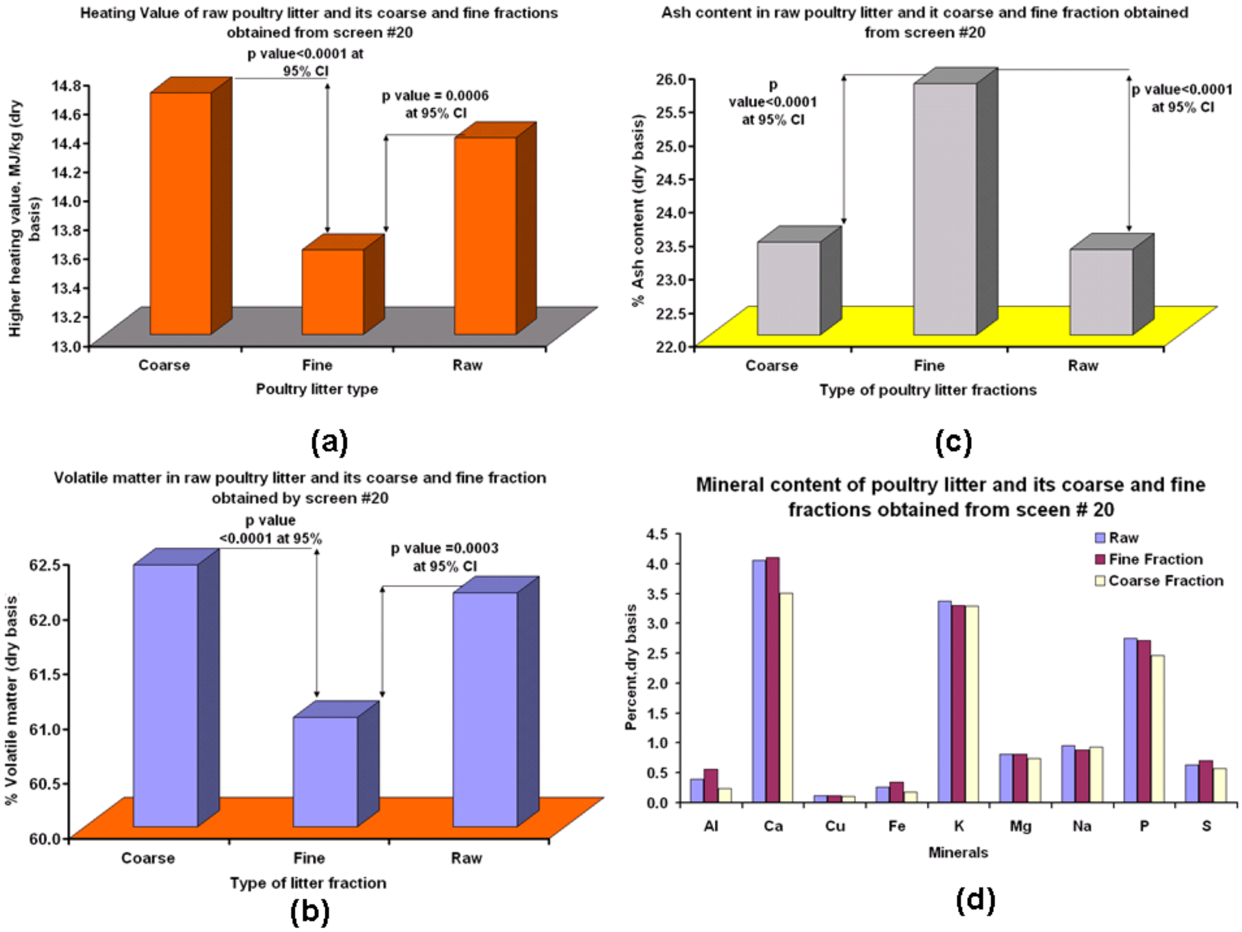

Figure 3.1. (a) Heating value, (b) ash content, (c) volatile matter content, (d) mineral content of poultry litter and its coarse and fine fractions obtained from screen # 20. Each value shown in (a), (b), and (c) is a mean of 6 measurements (2 replications with 3 measurements on each sample). The p-values were obtained for the statistical t-test values.

Table 3.1. Compositional analysis of poultry litter, its coarse and fine fractions obtained using screen # 20 (percent dry basis) and pine chips. (% dry basis)

Feedstock	Extractives (fats)	Protein	Cellulose	Hemicellulose	Lignin	Ash	Total
Raw Litter	9.1 ± 5.3	31.2 ± 0.4	14.3 ± 0.2	18.5 ± 1.4	1.8 ± 2.0	23.3 ± 1.4	98.2
Coarse Fraction	6.1± 3.0	28.2 ± 0.6	12.6 ± 4.5	18.5 ± 3.7	2.0 ± 1.0	23.4 ± 0.3	90.8
Fine Fraction	10.1 ± 0.2	35.4 ± 0.1	15.4 ± 0.3	13.5 ± 0.2	1.1 ± 0.5	25.8 ± 0.6	101.3
Pine chips	0.53	1.2	54.5	9.9	26.8	0.5 ± 0.2	96.6

Table 3.2. Ultimate and proximate analyses of studied biomass (percent dry basis)

Fraction	C	N	S	Volatile	Fixed C	Ash
Raw Litter	35.5 ± 0.41	4.5 ± 0.07	0.9 ± 0.08	62.1 ± 1.0	13.5 ± 0.52	23.3 ± 1.47
Coarse Fraction	34.5 ± 0.57	4.2 ± 0.14	0.9 ± 0.01	62.4 ± 0.27	14.1 ± 0.23	23.4 ± 0.31
Fine Fraction	34.0 ± 0.32	5.7 ± 0.32	1.0 ± 0.05	61.0 ± 0.60	13.4 ± 0.20	25.8 ± 0.56
Pine chips	51.0	0.1	0.02	79.4 ± 0.61	18.3 ± 0.55	0.5 ± 0.20

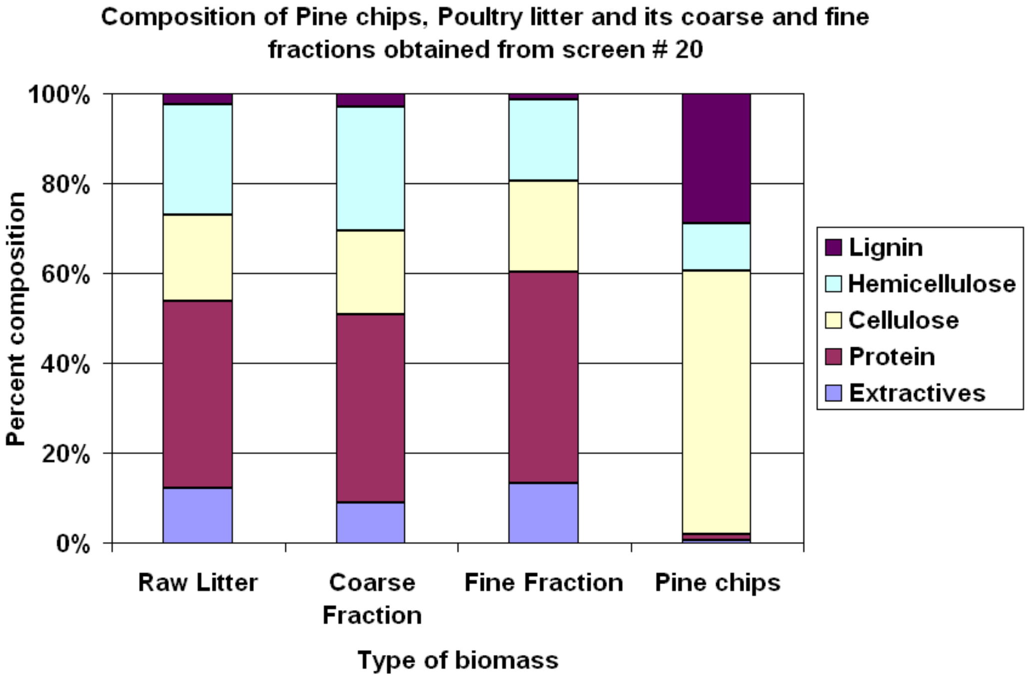

Figure 3.2. Distribution of protein, cellulose, hemicellulose, lignin, and extractives in the pine chips, raw litter, and its coarse and fine fractions.

All the poultry litter fractions contain a considerable amount of inorganic materials including aluminum (Al), calcium (Ca), potassium (K), magnesium (Mg), sodium (Na), phosphorous (P), and sulfur (S) compared to pine chips (table 3.3). Potassium and sodium salts are known to act as catalysts in the thermal degradation of cellulose lowering the decomposition temperature, reducing the yield of levoglucosan and increasing both the overall reaction rate and the yield of char (Szabo et al., 1996; Zaror et al., 1985). Calcium is known to catalyze hemicellulose pyrolysis. It is also evident that the fine fraction of the poultry litter holds a significantly higher amount of cationic minerals, especially aluminum (Al) (p-value 0.035), iron (Fe) (p-value 0.048), and sulfur (S) (p-value 0.034) than the coarse fraction at 95% confidence level (fig. 3.1d). Interestingly, this effect was not noticed for potassium (K) and sodium (Na).

Table 3.3. Poultry litter and its fraction contains following minerals (% dry basis)*. Mineral content of pine wood was reported by Mishra et al. (1993).

Metal	Al	Ca	Cu	Fe	K	Mg	Mn	Na	P	S	Zn
Raw	0.39 ±0.1	4.06 ±0.1	0.12 ±0.0	0.27 ±0.1	3.37 ±0.0	0.81 ±0.0	0.06 ±0.0	0.96 ±0.0	2.75 ±0.0	0.63 ±0.0	0.06 ±0.0
Coarse Fraction	0.23 ±0.0	3.50 ±0.3	0.11 ±0.0	0.18 ±0.0	3.29 ±0.1	0.75 ±0.1	0.06 ±0.0	0.94 ±0.0	2.47 ±0.3	0.58 ±0.0	0.06 ±0.0
Fine Fraction	0.56 ±0.0	4.10 ±0.5	0.11 ±0.0	0.35 ±0.0	3.30 ±0.2	0.81 ±0.0	0.06 ±0.0	0.88 ±0.1	2.72 ±0.2	0.71 ±0.0	0.06 ±0.0

* Cd, Cr, Mo, and Pb metals were <10 ppm

In summary, the characterization of poultry litter, its coarse and fine fractions obtained from screen #20 (0.85 mm), and pine chip bedding material concluded that the coarse fraction had higher heating value and volatile content than the fine fraction. The fine fraction had higher protein, nitrogen, and ash content. The fine fraction also contained a significantly higher amount of the minerals Aluminum (Al), Iron (Fe), and Sulfur (S). The compositional analysis proved that poultry litter differs from pine chips due primarily to its high protein, ash, and fat content.

Thermal analysis of Poultry litter fractions and pine chips

The differential thermo gravimetric (d.t.g) curve which is an output of the TGA analysis showed that the pyrolytic decomposition of the coarse fraction closely follows the path of raw poultry litter, however, the d.t.g of the fine fraction deviates at the first peak after 200°C (fig. 3.3a).

The d.t.g curves obtained were very similar to the one reported by Kim and Agblevor (2007) for poultry litter and wood chips. The decomposition of all studied materials started at around 200°C. The first peak for the decomposition of poultry litter fine fraction occurred at 270°C, however, the first peak for raw poultry litter and the coarse fraction appeared at 285°C. This peak can be associated with the sodium and potassium catalytic thermal degradation of cellulose and hemicellulose. The decomposition of hemicellulose is dominant in the temperature zone 250°C to 350°C (Raveendran et al., 1995), but it is possible that the high amount of cations like potassium (K) and sodium (Na) in raw poultry litter and its fractions caused the accelerated catalytic decomposition of hemicellulose resulting in the shift in first peak. The second d.t.g peak in all the poultry litter fractions corresponds to the same temperature 315°C at which a shoulder is observed in the pine chip samples. This shoulder is commonly associated with protein thermal degradation but can also be associated with the cellulose catalyzed thermal degradation. According to Peng et al. (2001) two microalgae showed the peak decomposition temperature at 330°C, one with protein (61.44%) and ash (4.34%) *Spirulina platensis* (SP) and another with relatively low protein (52.64%) and high ash (7.38%) *Chlorella protothecoides* (CP), during the TGA analysis conducted at the heating rate of 15°C/min.

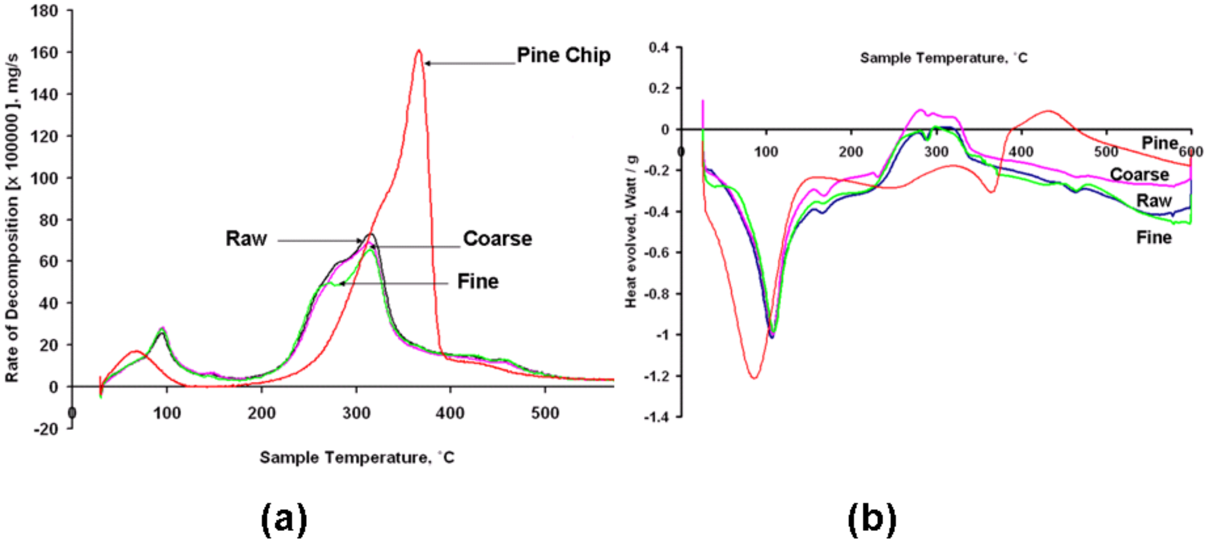

Figure 3.3. Thermo-Gravimetric Analysis (TGA) and Differential Scanning Calorimeter (DSC) analysis of raw poultry litter and its coarse and fine fractions obtained from screen # 20 showed distinct differences among the three. (a) d.t.g curve showing the reaction kinetics or decomposition rate of the biomass obtained from TGA data. (b) Heat evolved during the pyrolysis reaction obtained from DSC data.

Assuming that protein decomposition is unaffected by the ash content and considering the fact that decreasing the heating rate from 15°C/min to 10°C/min would decrease the protein peak decomposition temperature from 330°C (Peng et al., 2001), it is reasonable to attribute the second common peak (315°C) to the decomposition of protein. Generally, cellulose decomposes in a narrow range of temperature from 350°C to 500°C (Raveendran et al., 1996). So the possibility of contribution of the catalytic decomposition of cellulose cannot be completely overruled at the second peak. The fine fraction showed two distinct peaks because the high protein content created the second peak and the catalytic effect of high minerals on the lignocellulosic content formed the first peak. The peak observed at around 365°C in pine chips d.t.g curves is usually associated with the thermal degradation of cellulose. The flat tailing sections of the d.t.g curves are commonly attributed to lignin, which is known to decompose slowly over a very broad temperature range. As expected, the poultry litter solid residue (includes char and mineral) at the end of pyrolysis was considerably larger than for pine chips. This result was expected since pine chips are richer in cellulose and contain lower amounts of ash.

The heat evolved during the pyrolysis reactions is shown in the DSC curves (fig. 3.3b). Only the coarse fraction of poultry litter and pine chips reached exothermic reactions but at different temperature zones. The DSC curves of the coarse fraction and the pine chips can be seen above x-axis (fig. 3b) showing positive heat evolved during the pyrolysis process. The exothermic zone for the coarse fraction was 260°C to 330°C; however, for pine chips it was from 390°C to 465°C. The DSC curves of the fine fraction and raw poultry litter didn't show any exothermic nature due to the high amount of metals in their ash. The ash might be acting like a heat sink for the fine fraction and raw poultry litter. So, pyrolyzing the coarse fraction for value-added energy products at the peak temperature of 350°C to 400°C would consume less heating input for this type of poultry litter achieving approximately 86% of the total conversion. Increasing the peak temperature to 500°C would achieve 96% of the total fractional conversion. This result may not apply for poultry litter with bedding material other than pine chips.

Conclusions

In the light of this preliminary study, the following conclusions may be drawn:

- The coarse fraction is a better source of energy than raw poultry litter or fine fraction due to its high heating value and volatile content and low ash content.
- Pyrolysing the coarse fraction of poultry litter for achieving high fixed carbon and in turn high heating value is a good option because not only does the high sodium (Na) and potassium (K) content cause a catalytic affect on its prolysis reaction, but also the exothermic nature of the pyrolysis reaction would consume less heat.
- The pyrolysis of the coarse fraction should be carried out at the peak temperature of 350°C to 400°C to make it feasible because after 330°C, the pyrolysis reaction again becomes endothermic in nature.
- High protein and mineral content of the fine fraction makes it a suitable fertilizer source.

The results will be used to modify the experimental design for the ongoing project. These results may directly be adopted by research institutions working in the same area and industries like Fibrowatt LLC to modify their energy production process. All the preliminary results supported the hypothesis of the ongoing project goals titled "Adding value to the poultry litter using fractionation, pyrolysis, and pelleting." While considering practical application of the results, one must consider the fact that actual fuel cost, efficiency, capitol cost, and environment regulatory policies plays significant role the sustainability analysis of energy production by any pathway.

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CHAPTER 4

SCREENING AND PYROLYSIS OF POULTRY LITTER

Singh, K, M. Risse, J. Worley, K. C. Das, S. Thompson. To be submitted to Transactions of ASABE.

Abstract

Although production of activated carbon, catalytic gasification of poultry litter char, combustion, and physical treatment of poultry litter using screening have been thoroughly studied, eco-friendly and value added utilization still challenges the poultry industry. This paper presents results that suggest that screening and pyrolysis treatments can be combined for value added utilization of poultry litter. Poultry litter was sampled from three commercial farms and given nine treatments: one control, four coarse fractions, and four fine fractions obtained using each of the fours screens # 5, 10, 18, and 20. All the treated samples were pyrolyzed in a batch reactor to produce char and condensate at 500°C under a nitrogen flow rate of 2 lpm. The condensate was separated into three fractions based on density. Bomb calorimeter, proximate, and ultimate analysis were performed on un-pyrolysed but screen-treated samples, char, and three phases of condensate. The results show that the pyrolysis of the coarse fraction (screen#20) produced 44.5% char which retained only 43.5% of total feedstock energy. Overall, the pyrolysis products captured 57.2% of total feedstock energy and 53.8% of total feedstock carbon. The light phase of the condensate (4.94 ± 2.7% of the dry biomass) had a calorific value of 34.83 ± 0.91 MJ/kg and could be further refined as low grade fuel.

Keywords: poultry litter, pyrolysis, screening, bioenergy, biofuels.

Introduction

Utilization of poultry litter for energy production can improve water quality by reducing nutrient imbalance in areas where poultry litter production exceeds the needs for nutrients on local croplands and pastures. Nedgwa (1990) and Coloma (2005) recommended a simple screening of poultry litter, using screen # 18 and screen # 20 with mesh opening of 1.0 mm and 0.85 mm respectively, to concentrate the nitrogen in a fine fraction which increases its value as fertilizer. Coloma (2005) suggested energy production from the remaining coarse fraction by combustion or gasification.

In combustion studies, Lopez et al. (2005) documented the thermal performance and poultry litter consumption rate in a two staged combustion furnace. Keener et al. (2002) concluded that including 20% poultry manure with coal didn’t change the emission pattern but approximately 50% additional ash was produced. The direct combustion of poultry litter exhibited problems like boiler corrosion and ammonia emission, which motivated studies in the gasification of poultry litter.

Catalytic steam gasification of poultry litter, its kinetics, thermodynamics, and control of ammonia emissions during gasification have been widely studied (Jones, 1998; Sheth and Turner 2002; and Sheth and Bagchi, 2005). Although, charcoal derived from pyrolysis of poultry litter was the primary fuel source in these studies, no attempt was made to study the pyrolysis of poultry litter. However, very recently, Kim and Agblevor (2007) and Singh et al (2007) presented pyrolysis kinetics for poultry litter. Lima and Marshall (2005) used poultry litter to produce granular activated carbon and optimized conditions for its production.

This paper presents the results of a study which combined screening and pyrolysis for value added utilization of poultry litter. Fractionation should reduce the mineral content and increase the condensate yield during pyrolysis. Pyrolysis would result in three energy products: gases, bio-oil, and char. The specific objectives of this study were:

- To study the effect of screen size and pyrolysis on fuel properties of poultry litter.
- To characterize the bio-oil to determine its nutrient and energy content.
- To study the efficiency of the pyrolysis process.

The study results will help the poultry industry by adding value to poultry litter and by reducing excess phosphorous.

Materials and Methods

Poultry Litter Sampling Method

Containers of (approximately 100 kg) poultry litter were obtained from three commercial poultry farms. The litter came from total cleanout of poultry houses that had grown at least three flocks of birds since the last cleanout and contained pine shavings as bedding material. The first lot of poultry litter was sampled according to the procedure described in Appendix E of EPA-821-B-04-006 (2004). The second lot was taken from a storage pile that had been delivered to a site for application. The third lot of poultry litter was taken from a pile in the middle of a poultry house that was ready to be loaded onto a truck. The three different lots of poultry litter represented the target population and variability among the poultry litter loads coming from various poultry farms.

The sampled litter was stored in a refrigerated room below 4ºC to avoid microbial decomposition. Sub-samples of 6.0 to8.0 kg sampled from the containers of poultry litter were used for assigning treatments randomly.

Experimental design and procedure

Sub-samples obtained from each of the farms were fractionated using four standard sieves, one sieve at a time: screen # 5 with 4.0 mm openings, screen # 10 with 2.0 mm opening, screen # 18 with 1.0 mm opening, and screen # 20 with 0.85 mm opening. Two fractions, retained (coarse fraction) and screened (fine fraction), were obtained for each sieve. The coarse fraction contained the particles which did not pass through the screen; while, the fine fraction had particles which passed through the screen openings. The separation of mass due to the screening process was not recorded because it was well established by Ndegwa (1990) and Coloma (2005). A total of nine treated samples, whole poultry litter (control) and eight fractions were obtained for one block (one commercial farm). It is appropriate to mention that one sub-sample was used to get one fraction (either coarse or fine). In other words, coarse and fine fractions coming from a particular screen were independent of each other. The screen treated sub-samples were initially dried at 45°C for at least two days in an oven (Isotempoven, Fisher Scientific) to control the effect of moisture during pyrolysis. Each of the dried fractions was pyrolyzed in a batch reactor at 500ºC and the weight of oil and char produced was measured. The condensate was separated into three phases (heavy, medium, and light phase) using a separatory funnel by gravity-density separation (fig. 4.1).

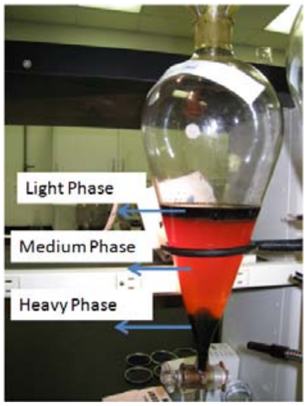

Figure 4.1. Separation of condensate into three phases was done using a separatory funnel.

The screen treated dried sub-samples were ground to 4mm (FRITSCH, Pulverisette, Industries Trane, Idar, Oberstein) followed by further reduction in particle size to less than 1 mm (Thomas Scientific) for analytical procedures. Charcoal samples were ground for four minutes in a mixer mill (8000 M MIXER/MILL, Spex Sample Prep). Calorific value of the ground char and treated sub-samples without pyrolysis were measured according to ASTM D5865 using a Bomb Calorimeter (Model 1351, Parr Instrument Company (Parr), Moline, IL). Proximate analysis was performed according to ASTM D 5142-04 using a Thermogravimetric Analyzer (Model TGA701, LECO, St. Joseph, MI). The calorific value and proximate analysis data was analyzed according to a randomized complete block design with three poultry farms considered as blocks using statistical analysis software (SAS 9.1, SAS Institute Inc., Cary, N.C.). Despite high standard deviations in some instances (due to variability among poultry farms), the treatment response means were significantly different. The benefit of using a randomized complete block design was that it portioned degrees of freedom and variance corresponding to it during analysis of variance. The differences in calorific values of screen treated poultry litter and its char were explained by proximate analysis data (Singh et al., 2007).

After the analysis of char, the optimum sieve for producing the highest calorific value and lowest ash content char was selected and the three phases of condensate corresponding to coarse fraction char for that screen were characterized. The moisture contents of the three phases of condensate were measured using Karl Fisher Titrator (Model Mettler Toledo DL 31, Star Systems, Columbus, OH) and calorific values of the heavy and the light fractions of condensate were measured using a bomb calorimeter. The calorific value of the medium phase was estimated using an empirical equation (Channiwala and Parikh, 2002) because it was below detection limit for the bomb calorimeter instrument. The ultimate analysis was performed on the coarse fraction, char, and three phases of condensate derived using the optimum screen using a CHNS analyzer (Model LECO CHNS-932, LECO Corporation, St. Joseph, MI). The data obtained from this analysis was used to characterize the bio-oil fractions and to calculate the efficiency of the pyrolysis process.

Batch pyrolysis Experiments

Approximately, 2.0 to 3.0 kg of biomass was pyrolysed in each test into a cubical pyrolysis reactor under the nitrogen atmosphere achieved through 2 l/min of nitrogen flow (fig. 4.2). The reactor was heated until the biomass temperature reached 500 ˚C using a 30400 thermolyne furnace.

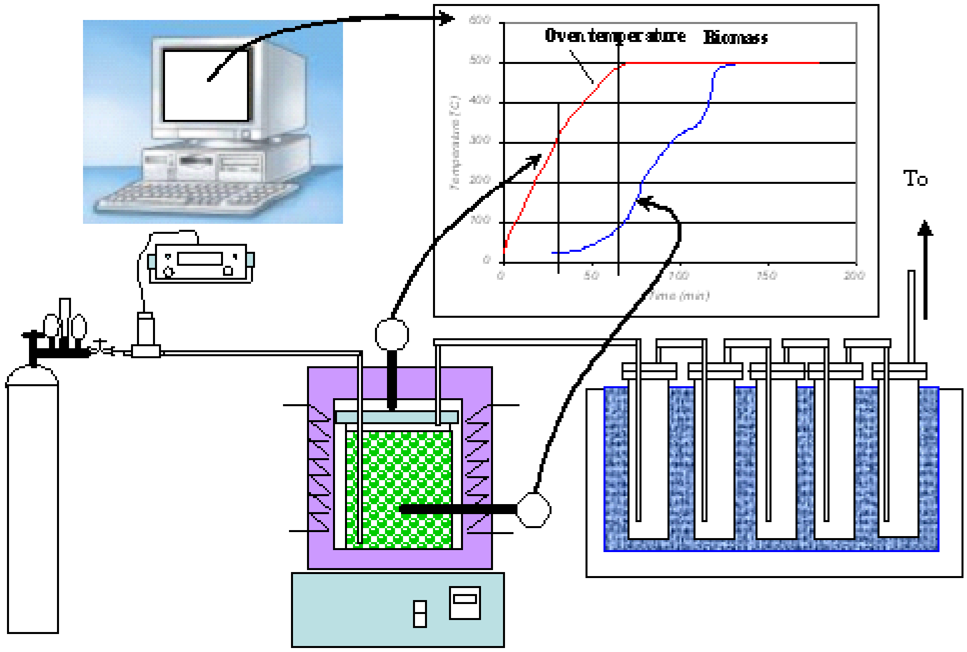

Figure 4.2. Batch Pyrolysis installations used for objective 1 and biomass temperature profile recorded on a computer (1) Computer connected to thermocouples, (2) Carrier gas cylinder, (3) Mass flow controller (4) Oven, (5) Pyrolysis reactor, (6) Chiller, (7) Condensing traps (Source: Garcia-Perez et al., 2007).

The furnace was set for 575˚C. The pyrolysis vapors were rapidly removed from the hot biomass and quenched in four ice cooled traps connected in series and maintained at 0°C. After each test, the reactor was allowed to cool under a nitrogen atmosphere. After the biomass cooled to room temperature for four-five hours under a nitrogen atmosphere, the reactor was opened and char was collected.

Data Quality Control

The data quality was maintained through routine controls including: calibration, and determination of blanks. One calibration standard and one blank were used in a batch of samples coming from one commercial farm. During calorific value measurements Parr certified benzoic acid (Benzoic acid no. 3415, Parr Instr. Co, IL) was used as a calibration standard; however, Leco certified standard coal (Proximate Plus Coal Reference Material, Part no. 502-442, lot no. 23075C, LECO Corporation, St. Joseph MI) was used for proximate analysis. The data quality control standard used for ultimate analysis was Sulfamethazine (Leco 502-209, LECO Corporation, St. Joseph MI). The data quality indicators were precision, accuracy, bias, and data completeness.

Precision

Precision is a measure of the repeatability of results or of the agreement among individual measurements of the same parameter under the same prescribed conditions. For each series of replicate analyses, the precision was calculated as:

$$\Pr ecision(\%) = 100 * \left[\frac{s}{x} \right] \ldots\ldots (4.1)$$

where: s = standard deviation between the replicate analyses; and x = mean of the instrument responses replicate analyses.

Accuracy

Accuracy is the closeness of a measurement to a reference value, and reflects the systematic distortion of a measurement process. For each instrument tested, multiple challenge data points were collected. The accuracy of the instrument was determined by:

$$Accuracy(\%) = 100 * \left[\frac{S - x}{S} \right] \ldots\ldots(4.2)$$

where: S = standard value of the authentic traceable standard; and x = mean of the instrument responses to the replicate analysis.

Bias

Bias is a systematic or persistent distortion of a measurement process that causes errors in one direction. Bias in determination of the calorific value was eliminated since samples were treated identically to the benzoic acid used in the determination of the calorimeter heat capacity (ASTM D5865). Since ash content determination using ASTM D3174 was an empirical test method, the degree of absolute bias cannot be determined.

Data Completeness

Data completeness is a measure of the amount of valid data obtained from a measurement system, expressed as a percentage of the number of valid measurements that should have been collected.

Results and Discussion

Moisture Loss during Initial Drying

The poultry litter coming from three different poultry farms had significant variation in moisture content as shown by the initial drying results. The percent moisture loss during initial drying was 11.46 ± 2.54 for the first lot, 9.22 ± 2.64 for the second lot, and 18.31± 6.60 for the third lot of poultry litter. It is appropriate to mention here that the third lot of poultry litter was too wet to screen so it was air dried with fans for a week before the screening treatments were performed. The mean moisture loss from the third lot had a high standard deviation because sub-samples were drawn over a period of fifteen days while poultry litter was exposed to the atmosphere.

Calorific value of Screened Poultry Litter

The calorific values obtained for raw poultry litter 14.73 ± 1.45 MJ/kg were comparable to the calorific values reported in literature 14.45 MJ/kg by Dávolas et al. (2002); 14.26 MJ/kg by

Mukhtar et al. (2002); 14.98 MJ/kg by Priyadarsan et al. (2004); and 14.40 MJ/kg by Singh et al. (2007). The screening process using screen #18 and screen # 20 divided poultry litter into an energy-dense coarse and an energy-scarce fine fraction (table 4.1). Analysis of variance showed that 90.5% of variability in the calorific value of screened poultry litter can be explained by blocking and treatment effects. The coarse fraction (15.19 ± 1.34 MJ/kg) obtained from screen # 20 had the highest calorific value which was significantly higher than the fine fraction (12.96 ± 2.95 MJ/kg) obtained from the same screen (p-value = 0.0021). Similar influence was found when fractionation was done using screen # 18 (p-value = 0.0360). The blocking was effective in the experiment design. Had it been a completely randomized design, each treatment would have been replicated 4.08 times to achieve the same precision for analysis of variance. These results contradicted Coloma (2005) who showed no significant difference in calorific values between coarse and fine fractions obtained from the same screens. Coloma (2005) used an empirical equation to estimate the calorific value of poultry litter samples using total carbohydrate, crude protein and fat content data but did not account for the ash content. The differences in calorific values can be explained by proximate analysis because the screening process did not divide cellulose, hemicelluloses, fat, and lignin content; however, it concentrated protein into the fine fraction obtained from screen #20 (Singh et al., 2007).

This statement was re-emphasized by a regression analysis which showed that blocking effect, moisture, volatile matter, ash, fixed carbon content explained 95.39% variability in calorific value of screened poultry litter out of which volatile matter content was the most influential variable (p-value < 0.0001) besides blocking affect.

Table 4.1. Calorific value (moisture free basis) of screen treated poultry litter feedstock and char derived from its pyrolysis performed at 500°C.

Sl. No.	Details	Screen Treated Poultry Litter Char, MJ/kg	Screen Treated Poultry Litter Feedstock, MJ/kg
1	Raw	13.86 ± 3.02	14.73 ± 1.45
2	Screen # 5 Coarse	14.12 ± 2.16	14.95 ± 1.32
3	Screen # 5 Fine	14.42 ± 3.08	14.37 ± 1.74
4	Screen # 10 Coarse	14.51 ± 1.78	15.16 ± 1.38
5	Screen # 10 Fine	14.52 ± 3.43	14.18 ± 2.07
6	Screen # 18 Coarse	15.04 ± 2.03*	15.05 ± 1.48*
7	Screen # 18 Fine	13.81 ± 3.43	13.66 ± 1.91**
8	Screen # 20 Coarse	14.91 ± 1.83*	15.19 ± 1.34*
9	Screen # 20 Fine	13.17 ± 3.03**	12.96 ± 2.95**

Numbers followed by the * are not significantly different at 95% confidence level.

Analysis of variance proved that treatments contributed 90.4% variability in volatile matter, ash, and fixed carbon content of poultry litter fractions. Both screens, # 20 and #18, not only concentrated volatile matter in the coarse fractions but also yielded ash-rich fine fractions (table 4.2). However; the coarse fractions obtained from the two screens had similar volatile matter and ash content. The effect of fractionation was not observed for fixed carbon content. This analysis supported the conclusion that the high calorific value of the coarse fractions obtained from screen #18 and #20 were due to its significantly higher volatile matter and lower ash content than its corresponding fine fraction. The efficiency of blocking was 5.2 which means using randomized complete block design saved 5.2 replications per treatment.

Table 4.2. Proximate analysis (percent of moisture free feedstock) of poultry litter fractions obtained from screening treatment.

Sl. No.	Treatment	Moisture[a]	Volatile Matter	Ash	Fixed Carbon
1	Raw	15.22 ± 6.51	65.15 ± 4.28	24.55 ± 3.88	10.30 ± 0.68
2	Screen # 5 Coarse	11.31 ± 0.53	65.41 ± 4.05	23.75 ± 4.54	10.85 ± 0.69
3	Screen # 5 Fine	14.77 ± 1.11	63.37 ± 6.08	26.31 ± 7.99	10.32 ± 1.93
4	Screen # 10 Coarse	13.21 ± 1.28	65.56 ± 4.72	23.45 ± 4.84	10.99 ± 0.23
5	Screen # 10 Fine	12.35 ± 4.43	63.63 ± 6.13	25.85 ± 8.38	10.53 ± 2.26
6	Screen # 18 Coarse	13.34 ± 2.60	66.38 ± 3.58*	22.48 ± 4.05*	11.13 ± 0.50
7	Screen # 18 Fine	12.04 ± 4.49	62.24 ± 7.16**	27.98 ± 8.70**	9.77 ± 1.67
8	Screen # 20 Coarse	13.07 ± 5.30	65.97 ± 4.23*	23.08 ± 4.60*	10.95 ± 0.51
9	Screen # 20 Fine	11.04 ± 4.28	61.87 ± 7.67**	28.66 ± 9.65**	9.47 ± 1.98

[a] The moisture content shown is after initial 48 hours drying at 45°C. Numbers followed by the * and with no letters are not significantly different at 95% confidence level.

Similar to Nedgwa (1990) and Coloma (2005), this analysis proved that screening of poultry litter using either screen #18 or #20 not only made the coarse fractions energy rich but it also concentrated the nutrients in the fine fractions.

Pyrolysis Products Yield

Since the initial feedstock used for pyrolysis varied in moisture content (table 4.2), char and condensate yield were calculated on a moisture free feedstock basis according to the following expressions:

$$Y_{Char(m.f.)} = \frac{Y_{Char}}{1 - \frac{mc_{feedstock}}{100}} \ldots\ldots (4.3)$$

$$Y_{Condensate(m.f.)} = \frac{Y_{Condensate} - mc_{feedstock} + mc_{char} * Y_{Char}}{1 - \frac{mc_{feedstock}}{100}} \ldots\ldots (4.4)$$

Where: Y_{Char} = char yield with moisture; $Y_{Condensate}$ = condensate yield with moisture; $Y_{Char\ (m.f.)}$ = char yield without moisture; $Y_{Condensate\ (m.f.)}$ = condensate yield without moisture; $mc_{feedstock}$ = moisture content of feedstock; and mc_{Char} = moisture content of char.

The pyrolysis product yield could not be verified in the absence of published data for batch pyrolysis of poultry litter. According to Schnitzer et al. (2007), fast pyrolysis gave 27% char, 15% bio-oil fraction 1 (light bio-oil), 35% fraction 2 (heavy bio-oil), and 10% gas yield. Screening treatment explained 90.5% variability in char yield (table 4.3). Screen # 20 coarse fraction gave significantly lower char yield (44.47 ± 4.18) than its corresponding fine fraction (49.01 ± 6.75) (p-value: 0.0131). A similar influence for screen # 18 was noticed (p-value = 0.0422). The higher char yield from the fine fractions than coarse fractions may be attributed to their significantly high ash content (p-value = 0.0458). There was no difference in ash content between the two coarse fractions obtained from screen #18 and screen #20.

Statistically, screening treatments had no significant effect on either condensate or gas yield (table 4.3); however, 73.9% of total variability in condensate yield was explained by heating rate, moisture content, volatile matter content and screening treatment. The moisture significantly influenced condensate yield as received (p-value 0.0071) but did not matter for moisture free condensate yield data. In contrast, only 34.9% of total variability was explained by these variables for gas yield. The efficiency of blocking was 5.78 in char yield analysis.

Table 4.3. Char, condensate, and gas yield (percent of moisture free feedstock) resulting from pyrolysis of poultry litter after screening treatment.

Sl. No.	Treatment	Char	Condensate	Gases
1	Raw	46.22 ± 6.13	30.33 ± 6.08	23.45 ± 2.68
2	Screen # 5 Coarse	45.41 ± 6.94	29.62 ±3.45	24.97 ± 10.04
3	Screen # 5 Fine	44.70 ± 6.49	30.71 ± 8.09	24.59 ± 5.21
4	Screen # 10 Coarse	43.89 ± 5.57	32.09 ± 6.06	24.02 ± 1.16
5	Screen # 10 Fine	46.38 ± 4.76	30.12 ± 2.14	23.51 ± 2.70
6	Screen # 18 Coarse	43.15 ± 3.41*	31.88 ± 3.16	24.98 ± 0.66
7	Screen # 18 Fine	46.74 ± 6.44**	30.35 ± 4.22	22.91 ± 4.26
8	Screen # 20 Coarse	44.47 ± 4.18*	30.68 ± 4.85	24.85 ± 1.52
9	Screen # 20 Fine	49.01 ± 6.75**	30.15 ± 7.65	20.85 ± 3.25

Numbers followed by the * and with no letters are not significantly different at 95% confidence level.

Condensate Phase Yield

Again screening treatments had no significant influence on the heavy, medium, or the light phase of condensate (table 4.4). The blocking effect, heating rate, moisture content, volatile matter content and screening treatment explained 49.5% of the variability in the yield of the heavy phase.

These variables explained 89.13% of the variability in the medium phase yield out of which only moisture had a significant effect on the yield of this phase (p-value 0.0048). However; the same set of variables explained 87.6% of the variability in the yield of the light phase. The moisture had a significant effect (p-value 0.0126) on the yield of this phase too. Other possible factors affecting the phase yield would be initial sample weight, variability in gas flow, condenser efficiency and particle size which may affect heat and mass transfer.

Table 4.4. Phase yield as percentage of total condensate (as recorded) resulting from pyrolysis of poultry litter after screening treatment.

Sl. No.	Treatment	Heavy Phase	Medium Phase	Light Phase
1	Raw	5.45 ± 2.35	83.58 ± 2.04	10.97 ± 1.69
2	Screen # 5 Coarse	2.43 ± 3.07	80.08 ± 3.86	17.50 ± 4.75
3	Screen # 5 Fine	3.12 ± 0.60	85.61 ± 2.76	11.27 ± 2.42
4	Screen # 10 Coarse	2.95 ± 1.62	84.11 ± 3.18	12.94 ± 4.14
5	Screen # 10 Fine	3.66 ± 1.76	83.68 ± 5.42	12.66 ± 3.69
6	Screen # 18 Coarse	2.76 ± 0.43	82.77 ± 5.44	14.47 ± 5.81
7	Screen # 18 Fine	4.16 ± 0.84	82.87 ± 4.65	12.96 ± 5.06
8	Screen # 20 Coarse	3.64 ± 3.37	80.78 ± 4.39	15.58 ± 7.48
9	Screen # 20 Fine	4.65 ± 2.31	81.06 ± 4.00	14.29 ± 5.38

Calorific value of Screened Poultry Litter Char

The variability in calorific values of various charcoals may be explained by the effect of treatments up to 90.5% (table 4.1). Chars resulting from coarse fractions of screen #20 and #18 had the highest calorific values but not significantly different from its un-pyrolyzed feedstock. It was interesting to note that screen # 20 coarse fraction char had significantly higher calorific value than its fine fraction char (p-value = 0.0329) but similar to the calorific value of screen # 18 coarse fraction char. The differences in calorific value of chars made from pyrolysis of screened poultry litter may be explained by proximate analysis results. Regression analysis showed that blocking effect, moisture, volatile matter, ash, fixed carbon content explained 99.05% of the variability in calorific value of char of screened poultry litter out of which ash content was the most influential variable (p-value < 0.0001) besides blocking effect (table 4.5). There was no difference in volatile matter content among the nine treatments; however, the fine fraction char from screen # 20 had the highest ash content. Generally, high fixed carbon content gives high calorific value and screen # 20 and #18 coarse fraction chars had the highest fixed carbon contents which justified its energy richness. This analysis concluded that one should use screen #20 to separate the nutrient rich fine fraction if the remaining coarse fraction is intended to be used for pyrolysis.

Table 4.5. Proximate analysis (percent of moisture free basis) of poultry litter char made after screening treatment of poultry litter.

Sl. No.	Treatment	Moisture	Volatile	Ash	Fixed Carbon
1	Raw	1.17 ± 0.97	15.19 ± 0.89	52.45 ± 7.51	32.36 ± 6.63
2	Screen # 5 Coarse	1.03 ± 0.83	15.40 ± 0.93	52.11 ± 6.39	32.50 ± 5.49
3	Screen # 5 Fine	0.99 ± 0.85	14.50 ± 2.32	52.36 ± 10.86	33.14 ± 8.54
4	Screen # 10 Coarse	1.08 ± 0.89	15.04 ± 1.51	51.02 ± 6.64	33.95 ± 5.20
5	Screen # 10 Fine	0.43 ± 0.62	15.85 ± 3.58	51.20 ± 12.07	32.96 ± 8.49
6	Screen # 18 Coarse	0.98 ± 0.80	14.84 ± 1.22	50.05 ± 5.80*	35.11 ± 5.23*
7	Screen # 18 Fine	1.60 ± 0.38	15.00 ± 2.39	54.06 ± 11.39*	30.94 ± 9.04*
8	Screen # 20 Coarse	1.11 ± 0.95	14.91 ± 1.70	50.23 ± 5.65**	34.85 ± 5.26**
9	Screen # 20 Fine	1.40 ± 0.22	15.51 ± 2.43	55.54 ± 10.25***	28.95 ± 9.15***

Numbers followed by the * and with no letters are not significantly different at 95% confidence level.

Properties of Bio-oil (Condensate)

The three fractions of the condensate were distinct in appearance (fig. 4.1). The heavy fraction was black in appearance and looked semi-solid but was ductile at room temperature. The medium fraction was an orange-red water-like liquid. The light fraction was a dark grey easy flowing liquid. The heavy and the light fractions were energy rich; however, the medium phase was mostly water (p-value < 0.0001). The energy content of the medium phase was estimated using the following equation by (Channiwala and Parikh, 2002) because it was too low to determine it with bomb calorimeter.

$$HHV = 0.3491C + 1.1783H + 0.1005S - 0.1034O - 0.0151N - 0.0211A \ldots.. \quad (4.5)$$

The equation holds for the following ranges of C, H, N, S, and O. 0.00% ≤ C ≤ 92.25%, 0.43% ≤ H ≤ 25.15%, 0.00% ≤ O ≤ 50.00%, 0.00% ≤ N ≤ 5.6%, 0% ≤ S ≤ 94.08%, 0% ≤ A ≤ 71.4%, and 4.745 MJ/kg ≤ HHV 55.35 MJ/kg %. Though the nitrogen content of the medium phase was significantly lower than the other two phases (p-value< 0.0001), the total nitrogen content would be higher in medium phase than other two phases (discussed in later section) because medium phase consisted of 80.78 ± 4.39% of the total condensate yield compared to 3.64 ± 3.37% heavy and 15.58 ± 7.48% light phase yield (table 4.4). The medium phase liquid did contain significantly more oxygen than the other two phases (p-value<0.0001), which may be justified by its high moisture content.

Table 4.6. Properties of the three phases of the condensate obtained from pyrolysis of the coarse fraction (screen # 20, 0.85 mm) of poultry litter.

Type	Carbon	Hydrogen	Nitrogen	Sulfur	Oxygen	Calorific value, MJ/kg	Moisture Content
Heavy Phase	$67.36 \pm 5.18^{*}$	$8.79 \pm 0.17^{*}$	$7.33 \pm 0.25^{*}$	0.29 ± 0.04	16.22 ± 5.32	$27.85 \pm 1.65^{*}$	$4.58 \pm 1.58^{*}$
Medium Phase	$6.90 \pm 1.84^{**}$	$10.98 \pm 0.4^{**}$	$4.30 \pm 1.00^{**}$	0.08 ± 0.02	77.75 ± 2.80	7.23 ± 1.04[a]*	$43.80 \pm 1.39^{**}$
Light Phase	$73.01 \pm 3.74^{***}$	$8.93 \pm 0.54^{*}$	$6.39 \pm 0.78^{*}$	0.63 ± 0.15	11.03 ± 4.38	$34.83 \pm 1.02^{*}$	$3.17 \pm 0.87^{*}$

[a] This calorific value was estimated using an empirical equation developed by Channiwala and Parikh (2002). Numbers followed by the * are not significantly different at 95% confidence level.

The light phase contained significantly higher carbon than the medium phase (p-value <0.0001) and the heavy phase (p-value = 0.0251) (table 4.6). The differences in carbon content were consistent with the differences in calorific values of the three phases. It would be appropriate to mention that most of the sulfur was retained in the light phase followed by heavy and medium phases (p-value <0.0001). Based on this analysis, it may be concluded that the lightest phase and the heaviest phase are promising for energy production; however, the medium phase may best be used for fertilizer or other applications.

Efficiency of Pyrolysis

The efficiency of the pyrolysis process may be calculated by energy conversion efficiency of char or condensate, fixed carbon yield, and char carbon yield (Antal, 2003). The energy conversion efficiency (η_{Energy}) and fixed carbon yield (FC_{Yield}) may be estimated using the following expressions:

$$\eta_{Energy} = Y_{Char\ /\ Condensate} \frac{HHV_{Char\ /\ Condensate}}{HHV_{Feedstock}} \text{ ..... (4.6)}$$

Where: η_{Energy} = energy conversion efficiency; $Y_{Char/Condensate\ Yield}$ = char or condensate yield (%); $HHV_{Char/Condensate}$ = calorific value of char or condensate (MJ/kg); and$HHV_{Feedstock}$ = calorific value of the feedstock biomass.

$$FC_{Yield} = Y_{Charyield} \frac{FC}{100 - Ash} \text{ ..... (4.7)}$$

Where: FC_{Yield} = fixed carbon yield; Ash = percent ash content of the feedstock; and FC = fixed carbon content of the char.

Energy Conversion Efficiency

The char energy conversion efficiency and fixed carbon yield for various treatments are listed in table 4.7. Screening treatments explained 73.02% percent variability in energy conversion efficiencies. The highest energy conversion efficiency was recorded for the fine fraction from screen #20 at 43.52%. It was significantly higher than its corresponding coarse fraction (43.53 ± 3.25%). This means that screen #20 coarse fraction char retained 43.53% of total energy from its parent feedstock. Heavy and light phases of the condensate held 2.84 ± 0.79% and 10.89 ± 4.95% of the feedstock energy. Therefore, it can be concluded that pyrolysis products retained 57.26% of the total energy in the feedstock (coarse fraction of poultry litter from screen #20).

Fixed Carbon Yield

All the chars had same fixed carbon yield which was expected since fixed carbon is produced from decomposition of lignocellulosic biomass and screening did not significantly separate cellulose, lignin, and hemicelluloses (Singh, 2007). The fixed carbon yields shown in Table 6 are lower than those reported for chestnut (21.4%) and Oak (29.5%) (Antal, 2003).

Table 4.7. Char energy conversion efficiency and fixed carbon yield resulting from pyrolysis of poultry litter after screening treatment.

Sl. No.	Treatment	Char Energy Conversion Efficiency	Fixed Carbon Yield
1	Raw	42.76 ± 2.84	19.47 ± 0.86
2	Screen # 5 Coarse	42.47 ± 4.07	19.07 ± 1.07
3	Screen # 5 Fine	44.15 ± 2.74	19.61 ± 0.38
4	Screen # 10 Coarse	41.84 ± 4.15	19.25 ± 0.88
5	Screen # 10 Fine	46.81 ± 0.39	20.19 ± 0.98
6	Screen # 18 Coarse	42.92 ± 1.93	19.38 ± 0.53
7	Screen # 18 Fine	46.37 ± 2.22	19.54 ± 1.29
8	Screen # 20 Coarse	43.53 ± 3.25*	19.98 ± 0.95
9	Screen # 20 Fine	49.85 ± 7.17**	19.27 ± 0.53

Numbers followed by the * and with no letters are not significantly different 95% confidence level.

Carbon yield

To check char carbon yield (Y_C) equation 8 (Antal, 2003) was used along with data presented in table 8.

$$Y_C = Y_{Char} \frac{\%CharC}{\% feedC} \text{ ….. (4.8)}$$

Where % char C is the % carbon content of the dry char, and % feed C is the % carbon content of the dry feed. A similar equation may be extended to estimate condensate carbon yield ($Y_{CondensateC}$).

Table 4.8. Ultimate analysis of coarse fraction (screen # 20, 0.85 mm) of poultry litter and its char.

Type	Carbon	Hydrogen	Nitrogen	Sulfur	Oxygen
Coarse fraction	33.48 ± 2.71	5.64 ± 0.44	3.91 ± 0.46	0.45 ± 0.06	56.52 ± 3.08
Char	40.81 ± 2.96	2.02 ± 0.18	4.63 ± 0.30	0.89 ± 0.11	51.64 ± 3.16

The results of the ultimate analysis were comparable to Singh et al. (2007). Char coal captured 47.71 ± 5.35% of the feedstock carbon. Similarly, phase 1, phase 2, and phase 3 captured 2.71±0.61%, 4.38±1.19%, and 9.07±4.37% of the feedstock carbon. Based on this analysis, it may be concluded that the pyrolysis process captured 53.86% of the feedstock carbon in its products.

Change in Char Relative to Feedstock

To visualize the situation from another angle, table 4.9 lists the ratios of proximate analysis results of char to its feedstock screen treated poultry litter. There were no significant difference among the relative volatile matter, ash or fixed carbon (table 9) but the pyrolysis process removed 72 to 75% of the volatile matter from feedstock and the resulting chars had two times more ash but three times more fixed carbon content than its parent feedstock poultry litter.

Table 4.9. Ratio of volatile matter, ash and fixed carbon content of poultry litter char coal to its feedstock.

Sl. No.	Treatment	Char VM /feedstock VM	Char ash/feedstock ash	Char FC /Feedstock FC
1	Raw	0.23 ± 0.00	2.14 ± 0.04	3.16 ± 0.78
2	Screen # 5 Coarse	0.24 ± 0.00	2.22 ± 0.18	2.99 ± 0.40
3	Screen # 5 Fine	0.23 ± 0.01	2.04 ±0.24	3.19 ± 0.23
4	Screen # 10 Coarse	0.23 ± 0.01	2.20 ± 0.19	3.09 ± 0.43
5	Screen # 10 Fine	0.25 ± 0.03	2.03 ±0.25	3.11 ± 0.16
6	Screen # 18 Coarse	0.22 ± 0.02	2.25 ±0.17	3.15 ± 0.34
7	Screen # 18 Fine	0.24 ± 0.01	1.98 ±0.23	3.14 ± 0.48
8	Screen # 20 Coarse	0.23 ± 0.03	2.21 ±0.23	3.18 ± 0.39
9	Screen # 20 Fine	0.25 ± 0.04	2.02 ±0.39	3.02 ± 0.32

Distribution of Nitrogen among Pyrolysis Products

Figure 4.3 gives a visual presentation of the distribution of carbon, hydrogen, nitrogen, and sulfur among pyrolysis products: char, condensate (heavy, medium, and light phases) and gases presented as percentage of parent feedstock carbon, hydrogen, nitrogen, and sulfur (coarse fraction, screen # 20, 0.85 mm). Most of the carbon either remained in the char (47.19 ± 5.31%) or was lost in gases (30.50 ± 4.44%). The majority of sulfur was retained in the char (77.69 ± 11.08%). Char held the maximum nitrogen (46.63 ± 9.75%), followed by the medium phase of the condensate (33.16± 4.79%).

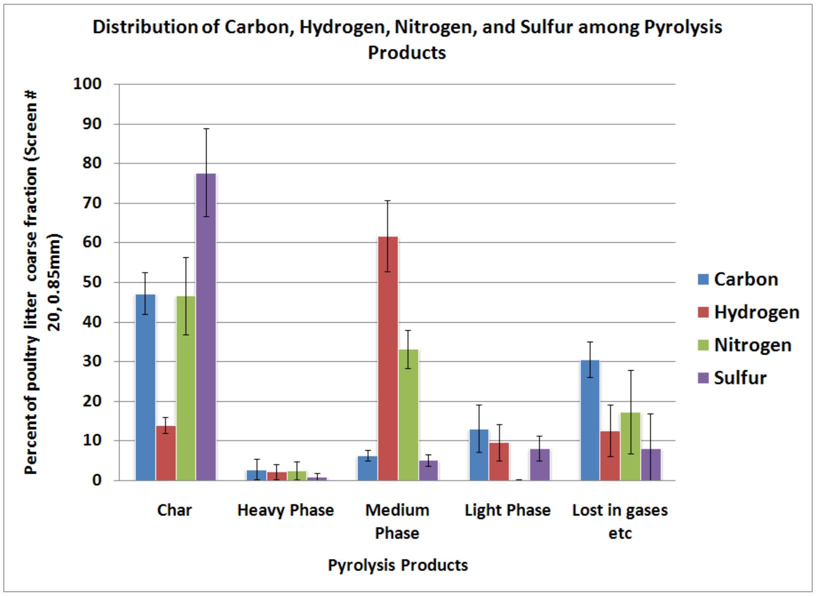

Figure 4.3. Distribution of carbon, hydrogen, nitrogen, and sulfur among pyrolysis products (char, condensate heavy, medium, and light phases, and gases) was presented as percentage of parent feedstock carbon, hydrogen, nitrogen, and sulfur (coarse fraction, screen # 20, 0.85 mm).

Data Quality Control

All the data presented in this paper fell within acceptable limits of the data quality indicators for precision, accuracy, bias, and data completeness for all the analytical procedures (table 4.10).

Table 10. Data quality indicators for various measurements.

Data Quality Indicators	Precision (%)	Accuracy (%)	Bias	Data Completeness (%)
Acceptable Limit	<15	± 20	Randomize	75
Volatile Matter Content	0.64	-1.84	Randomized	100
Ash Content	2.69	1.73	Randomized	100
Fixed Carbon Content	0.24	1.37	Randomized	100
Calorific Value	0.26	0.23	Randomized	100
Carbon	0.57	0.00	Randomized	100
Hydrogen	2.15	0.00	Randomized	100
Nitrogen	6.57	0.00	Randomized	100
Sulfur	0.74	0.00	Randomized	100

Conclusions

The study led to the following conclusions:

- Although both screens #18 and #20 concentrated the energy into a coarse fraction, screen #20 was more effective, and thus should be used to separate an energy rich coarse fraction.
- The pyrolysis of the coarse fraction from screen #20 produced 44.47% char which retained 43.53% of total feedstock energy.
- The fixed carbon yield was 19.0 to 20.0 % and was independent of screening.
- The pyrolysis process captured 57.23% of total feedstock energy and 53.86% of the total feedstock carbon.
- Pyrolysis of poultry litter removed approximately 75% of the volatiles from poultry litter but increased ash content and fixed carbon content by two and three fold respectively.
- The light phase condensate (4.94 ± 2.70% of the dry biomass) had calorific value 34.83 ± 0.91 MJ/kg and could be further refined as low grade fuel.

Screening and pyrolysis could be a good option for value added utilization of poultry litter for energy production. The process produced energy, nutrient dense heavy and light condensates and char which could be transported to remote locations to remove nutrients from areas with nutrient imbalances. The medium phase of the condensate can be mixed with nutrient rich fine fraction to produce fertilizer.

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CHAPTER 5

EFFECT OF FRACTIONATION AND PYROLYSIS ON FUEL PROPERTIES OF POULTRY LITTER

Singh, K, M. Risse, J. Worley, K. C. Das, S. Thompson. To be submitted to Journal of Air and Waste Management.

Abstract

Raw poultry litter has certain draw backs for energy production such as high ash and moisture content, a corrosive nature and low heating values. A combined solution to utilization of raw poultry litter may involve fractionation and pyrolysis. Fractionation divides poultry litter into a fine nutrient rich fraction and a coarse carbon dense fraction. Pyrolysis of the coarse fraction would remove the corrosive volatiles as bio-oil leaving clean char.

This paper presents the effect of fractionation and pyrolysis process parameters on the calorific value of char and on the characterization of bio-oil. Poultry litter samples collected from three commercial poultry farms were divided into ten treatments which included two controls (raw poultry litter and its coarse fraction having particle size greater than 0.85 mm) and other eight treatments which were combination of three factors: Type (raw poultry litter or its coarse fraction), heating rate (30 ºC/min or 10 ºC/min), and pyrolysis temperature (300 ºC or 500 ºC). After the screening process, the poultry litter samples were dried and pyrolyzed in a batch reactor under nitrogen atmosphere and char and condensate yields were recorded. The condensate was separated into three fractions based on its density: heavy, medium, and light phase. Calorific value, proximate and nutrient analysis were performed for char, condensate and feedstock. Results showed that the highest calorific value of the char coal (17.39 ± 1.37MJ/kg) was made from coarse fraction at 300°C and heating rate of 30°C/min, which captured 68.71 ± 9.37% of the feedstock energy. Most of the nitrogen was retained by char followed by medium phase of the condensate; however, heavy and light fractions of the condensate were rich in energy.

Keywords: poultry litter, pyrolysis, fractionation, screening, char, bioenergy

Introduction

In regions where land application has resulted in accumulation of phosphorus in the soil and potential water quality impairment, alternative utilization strategies or methods of moving poultry litter to areas that need additional plant nutrients should be implemented. Besides direct land application, many alternative uses for poultry litter have been proposed including use as an energy source or as a feed stock for making fertilizer pellets[1, 2, 3, and 4]. As an energy source, raw poultry litter has certain draw backs such as high ash and moisture content, a corrosive nature, and low heat content. Therefore, the litter must be processed into a form which can be used efficiently in energy production units.

Physical treatment using screening is one option. It has been shown that fractionation using screen #20 (0.85 mm) divided the poultry litter into a nutrient dense fine fraction[5, 6] and a coarse fraction. The screening process increased the carbon to nitrogen ratio (C: N) by 6% in coarse fraction (10.45±0.64 recorded for raw poultry litter)[6]. The C:N ratio was still not enough for composting which requires C: N in the range of 20 to 40. The coarse fraction had significantly higher calorific value and volatile matter content but lower ash content than raw poultry litter and fine fraction[7].

Pyrolysis is another option to remove corrosive components like VOCs in the form of exhaust gases or bio-oil leaving clean char behind. Pyrolysis is a thermal process that transforms material into gaseous components, organic condensate when condensed, and a solid residue (coke) containing fixed carbon and ash[8]. An attempt to produce activated carbon through pyrolysis of pelletized poultry litter samples at 700ºC followed by its activation was also noticed[9].

This study combined both options. Fractionation was used to reduce the ash content and the pyrolysis process was used to produce clean char which could be a good source of energy or a valuable soil amendment. The preliminary results show that the oil produced from pyrolysis of poultry litter may cross-link at high temperatures producing a water insoluble compound with potentially strong binding properties for making pellets from fine fraction.

Pyrolysis kinetics studied through thermogravimetric analysis showed that a catalytic affect on the prolysis reaction reduced its peak decomposition temperature from 365ºC (pine chips) to 315ºC for the coarse fraction from poultry litter with pine shaving bedding material[7]. This affect was caused by high sodium (Na) and potassium (K) content. The differential scanning calorimeter analysis exhibited that only the coarse fraction showed the exothermic nature of the pyrolysis reaction not the raw poultry litter or fine fraction[7]. The pyrolysis of the coarse fraction should be carried out at the peak temperature of 350 to 400˚C to make it feasible because after 330 ˚C, the pyrolysis reaction again becomes endothermic in nature[7].

This paper presents the effect of fractionation, pyrolysis temperature and heating rate on production, nutrient content, and gross heating values of char and bio-oil. The proposed vision will also result in reduced impacts of nutrients and pathogens on water quality from poultry farms (improved nutrient balance and reduction in excess land application) as well as on non-poultry farms that utilize the fertilizer pellets (slower release nutrient source that is less prone to runoff and leaching). Pyrolysis of the course fraction will result in the production of energy for the pelleting process and yield a char that could serve as a coal replacement. This would replace non-renewable energy sources with a more sustainable supply.

Materials and Methods

Poultry Litter Sampling

Container loads of poultry litter were purchased from three commercial poultry houses (approximately 200 kg from each). The purchased poultry litter came from total cleanout of the poultry houses that had grown at least three flocks of birds since the last cleanout and contained pine shavings for bedding material. The first lot of poultry litter was sampled according to the procedure described in Appendix E of EPA-821-B-04-006 (2004). The second lot was taken from a storage pile that had been delivered to a site for application. The third lot of poultry litter was taken from a pile in the middle of poultry house that was ready to be loaded onto a truck. The three different lots of poultry litter represented target population and variability among the poultry litter loads coming from various poultry farms. The sampled litter was stored in a refrigerated room below 4ºC to avoid microbial decomposition. Sub-samples of 8.0 to10.0 kg sampled from the containers of poultry litter were used for assigning treatments randomly.

Experiment Design

A randomized complete block design (RCBD) with each commercial farm considered as block and ten treatments per block was used to study the effect of fractionation and pyrolysis process variables. The first two treatments were controls: raw poultry litter and its coarse fraction without pyrolysis; however, the remaining eight treatments were a combination of 3 factors each at 2 levels. The factor and its levels were: Type (raw poultry litter and its coarse fraction), heating rate (30 ºC/min and 10 ºC/min), and pyrolysis temperature (300 ºC and 500 ºC). For char and bio-oil yield data single responses for every replication were used; however, statistical significance for calorific value, volatile matter, ash, and fixed carbon content, and nutrient content were done with three measurements per replication using statistical analysis software (SAS 9.1, SAS Institute Inc., Cary, N.C.). The benefit of using a randomized complete block design was that it portioned degrees of freedom and variance corresponding to the variability due to diversity in poultry litter not due to treatments during analysis of variance.

Contrast of control versus other treatment, the main effect of each factor level and the significance of their interaction were studied. The process was optimized for highest gross heating value and minimum ash content of char. Completion of this testing supplied information on selecting the optimum heating rates and temperatures for pyrolysis for producing maximum bio-oil and char with the highest heating value and lowest ash content. The differences in calorific values of screen treated poultry litter and its char were explained by proximate analysis data (Singh et al., 2007).

After the analysis of char, the pyrolysis process for producing the highest calorific value and lowest ash content char was selected. The three phases of condensate corresponding to selected process were characterized. The data obtained from this analysis was used to characterize the bio-oil fractions and to calculate the efficiency of the pyrolysis process.

Processing

Each batch of poultry litter was divided into ten sub-samples. Fractionation was conducted using screen # 20 (0.85 mm) (USA Standard Testing Sieve, Fisher Scientific Company, USA) on an electrical sieve shaker (Model CL 5028, Soil Testing Inc, Evanston, IL, USA) and sample sizes were reduced using ASTM D 6913 standard methods. After screening, all the samples were dried at 45˚C for 48 hours in an oven (Isotempoven, Fisher 97 Scientific).

Batch Pyrolysis Experiments

Approximately, 3.0 to 4.0 kg of the biomass was pyrolyzed in a 12” diameter and 24” long cylindrical basket (316 AL stainless steel) sitting inside a 14” diameter and 32” long cylindrical reactor (316 AL stainless steel) (fig. 5.1). The reactor was heated using a custom designed open top cylindrical furnace supplied by Mellen and company. The heating of the furnace was controlled via a programmable microcontroller. In order to achieve 300˚C at the thermocouple located inside the biomass, the furnace was programmed to ramp the furnace temperature from room temperature to 425˚C at the desired heating rate followed by soaking at 425˚C for five hours. Whenever, the biomass temperature reached 300˚C, the furnace temperature was lowered to 375˚C.

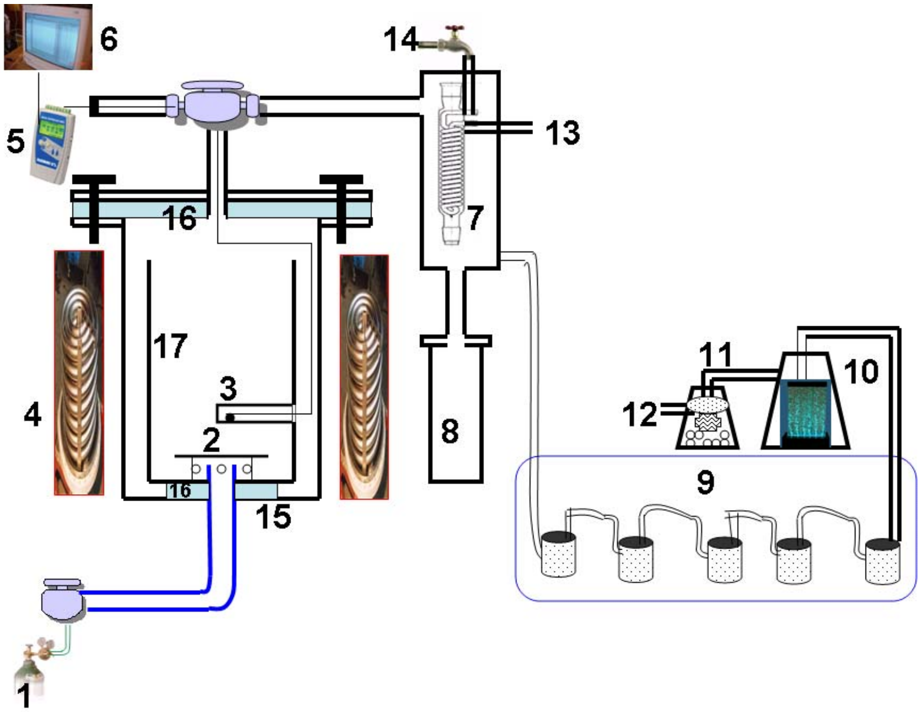

Figure 5.1: Batch pyrolysis reactor was used for objective 2. The various components in pyrolysis setup are: 1. Nitrogen gas (NI 300, National Welders, GA)), 2. Gas diffuser, 3. Thermocouple to measure biomass temperature (XCIB-K-1-3-10 Omega, Stamford, CT), 4. Furnace (CV Furnace model MA100058, Mellen Company, Concord, NH), 5. Data logger (OM-DAQPRO-5300, Omega, Stamford, CT), 6. Computer, 7. Condenser coil (0.25” 316 AL stainless steel), 8. Condensate collector (4” diameter, 12” long 316 AL stainless steel cylinder), 9. Ice bath condenser made of five cylinders identical to #8, 10. Water bubbler, 11. Filter made of dry rite, quartz wool, and glass wool (Leco Corporation, St. Joseph, MI), 12. Exhaust, 13. Water discharge to drain, 14. Water inlet to condenser, 15. Reactor, 16. Gasket (3000 ˚F Ceramic paper 300-080-2, Cotronics Corp.Broooklyn, N. Y.), 17. Biomass holding basket.

This step enabled us to hold the biomass at the 300˚C temperature for one hour. After one hour holding time, the furnace was allowed to cool. Similarly, to achieve 500˚C at the biomass, the furnace was programmed to ramp its temperature from room temperature to 575˚C at the desired heating rate followed by a soaking period at 575˚C for five hours. Whenever, the biomass reached 500˚C, the program was terminated and the furnace was allowed to cool. During the heating and cooling process, the reactor was purged with four liters per minute of nitrogen to keep the inert atmosphere and remove the volatiles from the hot zone. The volatiles were first passed through a water cooled condenser and the condensate was collected at the bottom of the condenser. The remaining volatiles were quenched into five ice-cooled stainless-steel cylinders. After the ice-cooled condensers, the uncondensed volatiles were passes through a water bubbler followed by an aerosol trap filter made of dry rite, quartz wool, and glass wool. After, the trap filters, the gases were released to the atmosphere.

The reactor was opened and char was collected after the biomass showed its temperature equal to room temperature for four-five hours under nitrogen atmosphere. The weight of oil and char produced was measured. The condensate was collected and separated into three phases obtained through gravity-density separation (fig. 5.2).

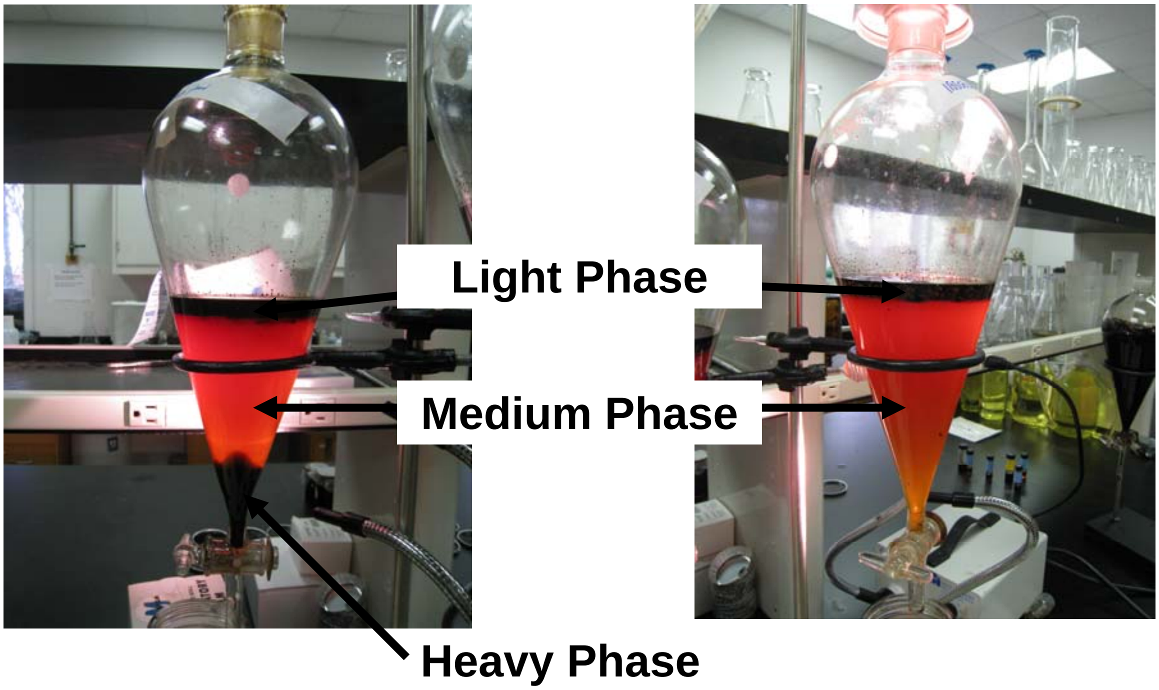

Figure 5.2: Pyrolysis condensate phase separation.

Analytical Procedure

After treatments were assigned, all the biomass samples were ground to 4mm (FRITSCH, Pulverisette, Industries Trane, Idar, Oberstein) followed by further reduction in particle size to less than 1 mm (Thomas Scientific). Char samples were ground for 4 minutes (8000 M (MIXER/MILL) Spex Sample Prep). Heating value was measured on ground samples according to ASTM D5865[11] standard using a Bomb Calorimeter (Model 1351, Parr 100 Instrument Company (Parr), Moline, IL). Proximate analysis (Ash, volatiles, fixed carbon and moisture content) was done according to ASTM D3174[12] using a Thermo Gravimetric Analyzer (Model TGA701, LECO Corporation, St. Joseph, MI). Samples of the raw poultry litter, its coarse and fine fractions, and raw pine chips were sent to the Soil, Plant, and Water Laboratory, 2400 College Station Road, Athens, GA for nutrient analysis.

The moisture contents of the three phases of condensate were measured using Karl Fisher Titrator (Model Mettler Toledo DL 31, Star Systems, Columbus, OH) and calorific values of the heavy and the light fractions of condensate were measured using a bomb calorimeter. The calorific values of the condensate phases which were not determined by bomb calorimeter phase were estimated using an empirical equation[18]. The ultimate analysis was performed on the coarse fraction, chars, and three phases of condensate corresponding to optimum screen using a CHNS analyzer (Modle LECO CHNS-932, LECO Corporation, St. Joseph, MI).

Data Quality Control

Detailed quality control and quality assurance procedures were specified in a quality assurance project plan. Routine controls and procedures for individual instruments were carried out according to the individual standard operating procedure. At minimum, these routine controls included: Calibration, and Determination of blanks. Three calibration standards and three blanks were used in a batch of samples coming from one commercial farm. During calorific value measurements Parr certified benzoic acid (Benzoic acid no. 3415, Parr Instr. Co, IL) was used as a calibration standard; however, Leco certified standard coal (Proximate Plus Coal Reference Material, Part no. 502-442, lot no. 23075C, LECO Corporation, St. Joseph MI) was used for proximate analysis. The data quality control standard used for ultimate analysis was Sulfamethazine (Leco 502-209, LECO Corporation, St. Joseph MI). The data quality indicators were precision, bias, accuracy, and data representativeness and completeness.

Precision

Precision is a measure of the repeatability of results or of the agreement among individual measurements of the same parameter under the same prescribed conditions. Precision of the analytical instruments was performed by repeated analysis of independent traceable standards. For each series of replicate analyses, the precision was calculated as:

Equation 4.1.

$$\Pr ecision(\%) = 100 * \left[\frac{s}{x} \right]$$

where:

s = standard deviation between the replicate analyses

x = mean of the instrument responses replicate analyses.

Accuracy

Accuracy includes a combination of random error (precision) and systematic error (bias) components of both sampling and analytical operations. Accuracy is the closeness of a measurement to a reference value, and reflects the systematic distortion of a measurement process. To the extent possible, accuracy was determined from replicate analyses of authentic, traceable standards. For each instrument tested, multiple challenge data points were collected. The accuracy of the instrument was determined by:

Equation 4.2.

$$Accuracy(\%) = 100 * \left[\frac{S - x}{S} \right]$$

where:

S = standard value of the authentic traceable standard

x = mean of the instrument responses to the replicate analysis.

Bias

Bias is a systematic or persistent distortion of a measurement process that causes errors in one direction. Bias in determination of the calorific value was eliminated provided samples are treated identically to the benzoic acid used in the determination of the calorimeter heat capacity (ASTM D5865). Since ash content determination using ASTM D3174 was an empirical test method, the degree of absolute bias cannot be determined.

Data Completeness

Data completeness is a measure of the amount of valid data obtained from a measurement system, expressed as a percentage of the number of valid measurements that should have been collected.

Results and Discussion

Moisture Content of Initial Feedstock

Poultry litter sampled from the three commercial farms varied significantly, especially the third batch. When this batch was sampled, all the poultry litter was piled in a row along the middle of the poultry house. Immediately after sampling, the third batch was too wet to screen. It was allowed to air dry for a week before the screening began. After screening each sample was allowed to dry for 48 hours. Table 5.1 shows the average weight loss during the initial drying performed after the screening treatment. The standard deviation for the initial drying in block 3 was very high (7.24) because the sub-samples were drawn over the period of 1/14/2008 to 1/29/2008 for the screening process. The sub-samples drawn initially were moister than those drawn later.

Table 5.1. Percent moisture loss during initial drying after screening.

Poultry Litter Sample	Initial sample weight, kg	Sample weight after 48 hours drying	% Weight loss
Block 1	4.73 ± 0.63	4.36 ± 0.55	7.74 ± 1.42
Block 2	5.32 ± 0.46	4.86 ± 0.44	8.64 ± 0.93
Block 3	4.36 ± 1.18	3.55 ± 1.06	15.79 ± 7.24

Pyrolysis Product Yield

Average char and condensate yield for raw poultry litter at 500ºC was 47.73 ± 1.09% (char) and 29.32 ± 2.65% (condensate) respectively; however, for coarse fraction it was 46.70 ± 1.47% (char) and 30.45 ± 2.26% (condensate). The reported values for char and bio-oil production from poultry litter through fast pyrolysis were 27% and 50%[13]. Moisture plays a significant role in deciding the product yield. The pyrolysis product yield was converted to a moisture free basis using proximate analysis before performing statistical analysis (table 5.2). Moisture free char and condensate yield was calculated according to the following expressions:

Equation 4.3.

$$Y_{Char(m.f.)} = \frac{Y_{Char}}{1 - \frac{mc_{feedstock}}{100}}$$

Equation 4.4.

$$Y_{Condensate(m.f.)} = \frac{Y_{Condensate} - mc_{feedstock} + mc_{char} * Y_{Char}}{1 - \frac{mc_{feedstock}}{100}}$$

Where:

Y_{Char} = char yield with moisture

$Y_{Condensate}$ = condensate yield with moisture

$Y_{Char\ (m.f.)}$ = char yield without moisture

$Y_{Condensate\ (m.f.)}$ = condensate yield without moisture

$mc_{feedstock}$ = moisture content of feedstock

mc_{Char} = moisture content of char

Under valid model assumptions, analysis of variance showed that only temperature significantly affects the char and bio-oil yield (p-value < 0.0001). It would be appropriate to mention that the desired heating rates were not achieved in the biomass. Heating rates of 2.92 ±

1.24ºC/min instead of 10 ºC/min and 2.46 ± 1.14 ºC/min instead of 30ºC/min were achieved because at such a big scale batch system thermal conductivity of poultry litter and variable moisture content in the feedstock dominated heat transfer rates. The blocking was effective in the experiment design and data analysis. The completely randomize design would have required 1.35 times the number of current replications for each treatment to achieve the same precision of F-test.

Table 5.2. Pyrolysis product yield (percent) presented on moisture free basis.

Type	Temperature 300ºC[a]		Temperature 500ºC[b]	
	Char	Condensate	Char	Condensate
Raw	68.11 ± 8.52	18.95 ± 4.96	47.73 ± 1.09	29.32 ± 2.65
Coarse Fraction	63.17 ± 8.14	22.60 ± 5.96	46.70 ± 1.47	30.45 ± 2.26

* Product yield was significantly different at two temperatures (p-value <0.0001)

Condensate phase yield

None of the treatment factors significantly affected yield of any fraction of the condensate (table 5.3). Unexpectedly, very high yields of light phase chocolate colored liquids were recorded when the poultry litter from the second batch was pyrolyzed at 300°C. Blocking effect, moisture, heating rate, pyrolysis temperature, feedstock volatile matter, ash, and fixed carbon content explained 77.5% of the total variability in yield of the heavy phase.

Table 5.3. Condensate was divided into heavy, medium and light fractions and the following data show fraction yield (percent of original condensate).

Sl. #	Treatment	Heavy	Medium	Light
1	Raw, 10˚C/min, 300˚C	3.89 ± 1.49	70.47 ± 17.93	25.64 ± 17.81
2	Coarse, 10˚C/min, 300˚C	3.83 ± 3.53	81.34 ± 5.54	14.84 ± 2.96
3	Raw, 30˚C/min, 300˚C	3.89 ± 3.29	76.97 ± 19.00	20.68 ± 16.26
4	Coarse, 30˚C/min, 300˚C	6.47 ± 2.96	68.65 ± 15.35	24.88 ± 14.16
5	Raw, 10˚C/min, 500˚C	5.71 ± 4.78	83.59 ± 1.60	11.72 ± 4.69
6	Coarse, 10˚C/min, 500˚C	6.58 ± 3.33	80.57 ± 3.18	13.46 ± 7.64
7	Raw, 30˚C/min, 500˚C	2.74 ± 3.62	84.30 ± 2.02	15.04 ± 2.53
8	Coarse, 30˚C/min, 500˚C	2.56 ± 3.65	84.62 ± 2.25	14.92 ± 1.59

The same set of variables explained 77.9% variability in the medium phase yield; however, 79.5% of the variability in the light phase yield was explained by a similar set of variables. The light phase yield was influenced by actual heating rate (p-value 0.039), replication (p-value =

0.0045), volatile matter (p-value= 0.07), ash content (p-value= 0.068), fixed carbon content (p-value= 0.068) and pyrolysis temperature (p-value= 0.02). Other possible sources of variability could be efficiency of condensers to condense low boiling point liquids, environmental factors, and variation in heat transfer due to the wide range in particle size distribution.

Pyrolysis Product Properties

Fuel Properties of char

The calorific values for raw poultry litter and its coarse fraction shown in table 5.4 were comparable to the published values[7, 14]. The heating value of wood char (28.70 MJ/kg) [15] was higher than that of poultry litter char shown in table 5.4. Treatments explained 99.59% variability in calorific values of raw poultry litter, its coarse fraction, and chars derived from them. Pair wise t-test showed that raw poultry litter had significantly lower calorific value than coarse fraction and chars. Among three treatment factors (temperature, screening, and heating rate), only screening significantly affected the calorific values of the various biomass (p-value= 0.0407).

Tukey's studentized range pair-wise comparison showed that the highest calorific value of the char (17.39 ± 1.27 MJ/kg) was made from coarse fraction pyrolyzed at 300°C and heating rate of 30°C/min (table 5.4), but statistically, it was similar to char made from Coarse fraction at the same temperature and heating rate of 10˚C/min. These two chars were statistically similar to the char made from coarse fraction heated up to 500°C at the heating rate of 30°C/min.

These differences in calorific values may be explained by differences in moisture, volatile matter, ash, and fixed carbon content of the feedstock[7]. Generally, heating value increases with increase in fixed carbon[16]; however, ash content also explained differences in calorific values of poultry litter[7]. That's why these differences were explained by proximate analysis results. These variables explained 97.2% of the total variability in calorific values. It was hard to conclude which one of them played a significant role because the third order term; i.e. the product of volatile, ash, and fixed carbon was significant (p-value= 0.0108).

Table 5.4. Calorific values of the control biomass and char along with the energy efficiency values for processes.

Treatment detail	Calorific Value MJ/kg
Raw, No Pyrolysis	13.80 ± 0.69^{a}
Coarse, No Pyrolysis	16.63 ± 2.24^{b}
Raw, 10˚C/min, 300˚C	15.83 ± 2.35^{b}
Coarse, 10˚C/min, 300˚C	17.03 ± 1.40^{c}
Raw, 30˚C/min, 300˚C	16.26 ± 1.69^{b}
Coarse, 30˚C/min, 300˚C	17.39 ± 1.27^{c}
Raw, 10˚C/min, 500˚C	16.36 ± 1.69^{b}
Coarse, 10˚C/min, 500˚C	16.57 ± 1.42^{b}
Raw, 30˚C/min, 500˚C	16.52 ± 2.18^{b}
Coarse, 30˚C/min, 500˚C	16.73 ± 1.61^{c}

Note: Numbers followed by same letter are not significantly different at 95% confidence level.

While analyzing the effect of fractionation, heating rate, pyrolysis temperature, it became clear that only peak temperature affected volatile matter, fixed carbon, and ash content (p-value < 0.0001). According to Least square difference, Tukey's studentized range, and Benferroni (Dun) pair-wise comparison test, the highest volatile matter was in the coarse fraction (67.50± 2.37%) and raw poultry litter (65.30 ± 4.42%) followed by char produced at 300°C (48.17 ± 8.14%) and the smallest volatile matter was recorded in char produced at 500°C (25.55 ± 5.22%) (table 5.5).

Table 5.5. Proximate analysis results (dry basis) for char.

Treatment detail	Volatile matter	Ash	Fixed carbon
Raw, No Pyrolysis	65.30 ± 4.42^{a}	23.93 ± 5.29^{a}	10.77 ± 1.21^{a}
Coarse, No Pyrolysis	67.50± 2.37^{a}	21.91 ± 2.15^{b}	10.59 ± 0.79^{a}
Raw, 10˚C/min, 300˚C	52.73 ± 7.06^{b}	30.63 ± 7.22^{a}	16.64 ± 4.00^{b}
Coarse, 10˚C/min, 300˚C	45.00 ± 11.34^{b}	33.61 ± 7.46^{a}	21.39 ± 5.46^{b}
Raw, 30˚C/min, 300˚C	45.73 ± 11.66^{b}	34.60 ± 9.13^{a}	19.68 ± 4.11^{b}
Coarse, 30˚C/min, 300˚C	48.17 ± 8.14^{b}	31.33 ± 7.78^{a}	20.49 ± 2.75^{b}
Raw, 10˚C/min, 500˚C	27.27 ± 5.82^{c}	43.65 ± 5.59^{c}	29.08 ± 5.74^{c}
Coarse, 10˚C/min, 500˚C	26.64 ± 6.09^{c}	43.25 ± 4.79^{c}	30.11 ± 5.14^{c}
Raw, 30˚C/min, 500˚C	28.00 ± 4.21^{c}	42.81 ± 7.77^{c}	29.19 ± 3.67^{c}
Coarse, 30˚C/min, 500˚C	25.55 ± 5.22^{c}	43.12 ± 6.01^{c}	31.33 ± 3.93^{c}

Note: Numbers followed by same letter are not significantly different at 95% confidence level.

The same pair-wise comparisons showed that the coarse fraction had the lowest ash content (21.91 ± 2.15%); however, raw poultry litter and all the chars prepared at 300°C had similar ash content (31.33 ± 7.78%). The highest ash content was recorded for chars prepared at 500°C (43.12 ± 6.01%) (table 5.5). The pair-wise tests showed that chars prepared at 500°C have higher fixed carbon content than chars prepared at 300°C followed by two controls. This analysis concluded that the differences in the calorific values of the treated biomass can only be explained by a combination of volatile matter, ash, and fixed carbon content, not by any one of these variables. Char prepared from coarse fraction at 300°C may be selected as a feedstock for energy production because it would contain lower ash content than char prepared from the same fraction at 500°C but the same energy content. In spite of having high ash content, the char made from coarse fraction at 500°C had same calorific value due to its high fixed carbon content; however, low ash and high volatile matter gave same heat content to char made from coarse fraction at 300°C.

Fuel properties of condensate

The condensate fractions (heavy, medium, and light) retrieved from the following two pyrolysis processes were selected for analysis because the char produced from the respective processes were similar in terms of calorific value: (1) coarse fraction (screen # 20, 0.85 mm) at 300°C and 30°C/min; and (2) coarse fraction (screen # 20, 0.85 mm) at 500°C and 30°C/min. The physical appearances of the heavy and medium fractions obtained from the two processes were the same; however, the light fractions were distinct in appearance. The heavy fraction was a dark black, semi solid, tar like substance. The medium fraction was orange-brown water-like liquid. The light fraction obtained from the first process was a dark brown, caramel easy-flowing liquid; however, the second process yielded a dark grey easy flowing liquid. The calorific value of the medium fractions and light fraction obtained at 300°C were below detection limit for the bomb calorimeter. The empirical equation[18] also showed that the calorific values of these fractions were 5.99 MJ/kg, 5.35MJ/kg, and 17.83±12.68MJ/kg respectively (table 5.6).

Table 5. 6. Properties of the three phases of the condensate obtained from pyrolysis of the: (1) coarse fraction (screen # 20, 0.85 mm) at 300°C and 30°C/min; (2) coarse fraction (screen # 20, 0.85 mm) at 500°C and 30°C/min of poultry litter.

Type	Carbon	Hydrogen	Nitrogen	Sulfur	Oxygen	Calorific value, MJ/kg	Moisture Content
coarse fraction (screen # 20, 0.85 mm) at 300°C and 30°C/min							
Heavy Phase	64.63 ± 3.55^{a}	8.362 ± 0.29^{a}	6.06 ± 0.69^{a}	0.95 ± 0.12^{a}	19.73 ± 4.50^{a}	28.03 ± 1.95^{a}	6.15 ± 2.96^{a}
Medium Phase	5.63 ± 2.06^{b}	10.62 ± 0.54^{a}	2.00 ± 0.60^{b}	0.08 ± 0.02^{bc}	81.66 ± 2.12^{b}	5.99 ± 0.37*^{b}	44.76 ± 5.99^{b}
Light Phase	26.98 ± 8.82^{b}	14.77 ± 8.40^{a}	3.40 ± 1.86^{b}	0.18 ± 0.10^{b}	61.90 ± 18.27^{b}	17.83 ± 12.68*^{a}	39.90 ± 4.53^{b}
coarse fraction (screen # 20, 0.85 mm) at 500°C and 30°C/min							
Heavy Phase	56.64 ± 19.13^{a}	8.18 ± 0.98^{a}	6.11 ± 0.35^{a}	0.47 ± 0.29^{bc}	28.60 ± 18.79^{a}	31.46 ± 2.99^{a}	4.00 ± 3.22^{a}
Medium Phase	5.42 ± 2.10^{b}	10.12 ± 0.38^{a}	3.04 ± 0.83^{b}	0.07 ± 0.01^{b}	81.35 ± 2.55^{b}	5.35 ± 0.54*^{b}	41.98 ± 9.09^{b}
Light Phase	66.97 ± 16.40^{a}	9.45 ± 0.21^{a}	7.08 ± 2.15^{a}	0.69 ± 0.38^{a}	15.82 ± 19.14^{a}	25.80 ± 3.21^{a}	12.69 ± 7.74^{a}

Note: [*] This calorific value was estimated using an empirical equation[18]. Numbers followed by same letter are not significantly different at 95% confidence level.

The heavy tar phases obtained from the two processes and light phase obtained at 500°C had similar heat content which was significantly higher than the medium fractions and light fraction obtained at 300°C.

These differences were well explained by the carbon and oxygen content of the individual fractions. For example, the carbon content in the light phase produced at 300°C was significantly lower than the light phase produced at 500°C (p-value= 0.0022) (table 5.6). High carbon content and low oxygen content gives a high calorific value product[18]. The nitrogen content of the products with high carbon content was also higher than medium phases and the light phase obtained at 300°C (p-value= 0.0091). But the total nitrogen content in the medium phase would be high due to its high yield. The high sulfur was also associated with the carbon rich phases.

Efficiency of the pyrolysis process

Energy conversion efficiency, fixed carbon yield and carbon yield are other ways to look at the pyrolysis process.

Energy conversion efficiency

Energy efficiency shows the percentage of biomass energy retained in the char.

Equation 4.5.

$$\eta_{Energy} = Y_{Char/CondensateYield} \frac{HHV_{Char/Condensate}}{HHV_{Feedstock}}$$

Where:

η_{Energy} = energy conversion efficiency

$Y_{CharYield/CondensateYield}$ = char yield or condensate yield(%)

$HHV_{Char/Condensate}$ = calorific value of char or condensate (MJ/kg)

$HHV_{Feedstock}$ = calorific value of the feedstock biomass

Char coal energy conversion efficiency was affected by the screening process and temperature. Statistically, coarse fractions had lower energy conversion efficiency than raw poultry litter (p-value= 0.0153) (table 5.7).

Table 5.7. Char coal energy efficiency and fixed carbon yield for pyrolysis processes.

Treatment detail	Char coal energy efficiency (%)	Fixed carbon yield
Raw, 10˚C/min, 300˚C	83.10 ± 17.93^{a}	17.12 ± 3.52^{a}
Coarse, 10˚C/min, 300˚C	62.71 ± 3.16^{b}	19.49 ± 3.92^{a}
Raw, 30˚C/min, 300˚C	77.09 ± 19.47^{a}	19.28 ± 3.25^{a}
Coarse, 30˚C/min, 300˚C	68.71 ± 9.37^{b}	19.41 ± 2.28^{a}
Raw, 10˚C/min, 500˚C	56.15 ± 7.34^{c}	24.33 ± 4.21^{b}
Coarse, 10˚C/min, 500˚C	46.83 ± 2.54^{d}	24.79 ± 4.19^{b}
Raw, 30˚C/min, 500˚C	57.85 ± 8.37^{c}	24.64 ± 0.83^{b}
Coarse, 30˚C/min, 500˚C	47.29 ± 2.30^{d}	25.77 ± 2.37^{b}

Note: Numbers followed by same letter are not significantly different at 95% confidence level.

Similarly, increasing pyrolysis temperature reduced energy conversion efficiency (p-value=0.0003). Coarse fraction char prepared at 300°C and 30°C/min retained 68.71± 9.37% of the total feedstock energy.

Fixed carbon yield

Fixed carbon yield for a pyrolysis process is defined as:

Equation 4.6.

$$FC_{Yield} = Y_{Charyield} \frac{FC}{100 - Ash}$$

Where:

FC_{Yield} = fixed carbon yield

Ash = percent ash content of the feedstock

FC = fixed carbon content of the char

Among treatment factors, only temperature significantly increased fixed carbon yield from 18.82 ± 3.30% to 24.89 ± 3.13% when raised from 300°C to 500°C regardless of poultry litter type. The measured values of the fixed-carbon yields ranged from 21.4% (chestnut) to 29.5% (oak) [17]. The calculated theoretical carbon yields based on the reported chemical compositions of the feedstock is approximately 36.7 wt%[17].

Carbon yield

To check char carbon yield (Y_C) [17] equation 7 was used along with data presented in table 5.8.

Equation 4.7.

$$Y_C = Y_{Char} \frac{\%CharC}{\% feedC}$$

Where:

% char C= percent carbon content of the dry char

% feed C = percent carbon content of the dry feed

The char prepared at 300°C captured 64.26 ± 6.35% of the total feedstock carbon; however, 51.65 ± 5.84% carbon yield was recorded when pyrolysis temperature was 500°C. The results of ultimate analysis of the two chars and its parent feedstock (coarse fraction) are presented in table 8.

Table 5.8. Ultimate analysis of coarse fraction (screen # 20, 0.85 mm) of poultry litter and its char made at 300 and 500°C.

Type	Carbon, %	Hydrogen, %	Nitrogen, %	Sulfur, %	Oxygen, %
Coarse fraction	32.28 ± 1.61^{b}	5.56 ± 0.42^{ac}	3.62 ± 0.50^{a}	0.46 ± 0.14^{a}	36.02 ± 0.81^{a}
Char, 300°C	39.34 ± 3.48^{a}	4.28 ± 1.02^{a}	5.02 ± 0.40^{b}	0.66 ± 0.07^{a}	19.34 ± 8.55^{b}
Char, 500°C	44.78 ± 6.08^{a}	3.44 ± 0.11^{ac}	5.90 ± 0.54^{c}	0.59 ± 0.09^{a}	3.92 ± 6.98^{c}

Both chars differed from the coarse fraction for their carbon content (p-value < 0.0248). Similarly, the char produced at 500°C contained higher nitrogen content (5.90 ± 0.54%) than the control (p-value= 0.0005) (3.62 ± 0.50%) and nitrogen content of char produced at 300°C (p-value= 0.0167) (5.02 ± 0.40%), which was significantly higher than control (p-value= 0.0030). The increased pyrolsis temperature decreased the oxygen content of the residual biomass.

Relative changes in Volatile Matter, Ash, and Fixed carbon

While analyzing the reduction in volatile matter, fixed carbon, and ash contents of char relative to their parent feedstock, it was noticed that both temperature (p-value < 0.0001) and fractionation (p-value = 0.0039) effectively reduced volatile matter content (Table 5.9). The RCBD design for the data analysis was extremely effective because CRD design would have taken 17.6 replications for each treatment to achieve the same efficiency for this F-test.

Similarly, char produced from the coarse fraction contains a significantly higher amount of ash (71.6% more than its parent coarse fraction) than char produced from raw poultry litter (59.7% more than its parent raw poultry litter) (p-value = 0.0058) (table 5.9). Heating poultry litter at 300°C increased ash content in char by 41.2%; however, char produced at 500°C was 90.2% (p-value < 0.0001) richer in ash.

Fractionation and pyrolysis are good options to increase fixed carbon content in char (p-value < 0.0001). Pyrolysis at 500°C increased fixed carbon by 2.79 times that of the original feed stock against 1.82 times increased at 300°C. On an average char produced from the coarse fraction increased fixed carbon by 2.42 times that of the original feedstock; however, raw poultry litter increased it only by 2.18 times.

Table 5.9. Ratio of volatile matter, ash, and fixed carbon content of char to feedstock was used to estimate the relative change with respect to feedstock.

Treatment detail	Change in volatile matter	Change in ash	Change in fixed carbon
Raw, 10˚C/min, 300˚C	0.81 ± 0.06^{a}	1.28 ± 0.04^{a}	1.53 ± 0.23^{a}
Coarse, 10˚C/min, 300˚C	0.66 ± 0.14^{b}	1.52 ± 0.22^{ab}	2.00 ± 0.36^{b}
Raw, 30˚C/min, 300˚C	0.70 ± 0.15^{ab}	1.44 ± 0.23^{a}	1.82 ± 0.26^{ab}
Coarse, 30˚C/min, 300˚C	0.71 ± 0.10^{ab}	1.41 ± 0.23^{a}	1.93 ± 0.13^{ab}
Raw, 10˚C/min, 500˚C	0.42 ± 0.09^{c}	1.86 ± 0.20^{bc}	2.68 ± 0.26^{c}
Coarse, 10˚C/min, 500˚C	0.39 ± 0.09^{c}	1.97 ± 0.09^{c}	2.84 ± 0.40^{c}
Raw, 30˚C/min, 500˚C	0.43 ± 0.04^{c}	1.81 ± 0.19^{bc}	2.71 ± 0.07^{c}
Coarse, 30˚C/min, 500˚C	0.38 ± 0.06^{c}	1.96 ± 0.09^{c}	2.95 ± 0.24^{c}

Note: Numbers followed by same letter are not significantly different at 95% confidence level.

Distribution of Nitrogen among pyrolysis products

The pyrolysis process not only decomposed poultry litter but it also distributed its carbon, nitrogen, and sulfur among its products: char, three fractions of condensate, and gas. As peak temperature of pyrolysis was increased from 300°C to 500°C, less carbon was captured in char (p-value< 0.0001); however, the light phase of the condensate captured excess carbon and increased its calorific value (fig. 5.3). There were no differences in percent carbon captured by heavy or medium phases of condensates produced at two different temperatures.

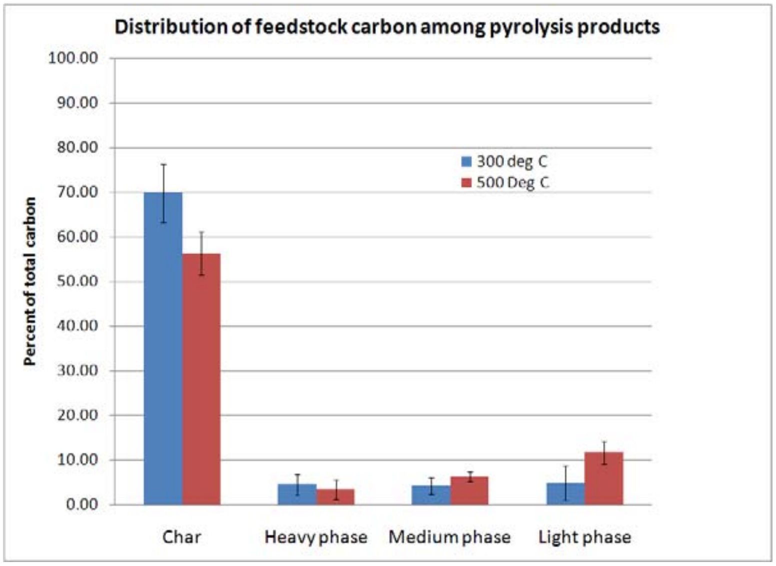

Figure 5.3: Distribution of feedstock carbon among pyrolysis products.

The nitrogen captured by char decreased with increase in temperature from 300 °C to 500 °C. The nitrogen which was lost from the solid residue was significantly stored in the medium phase of condensate (fig. 5.4).

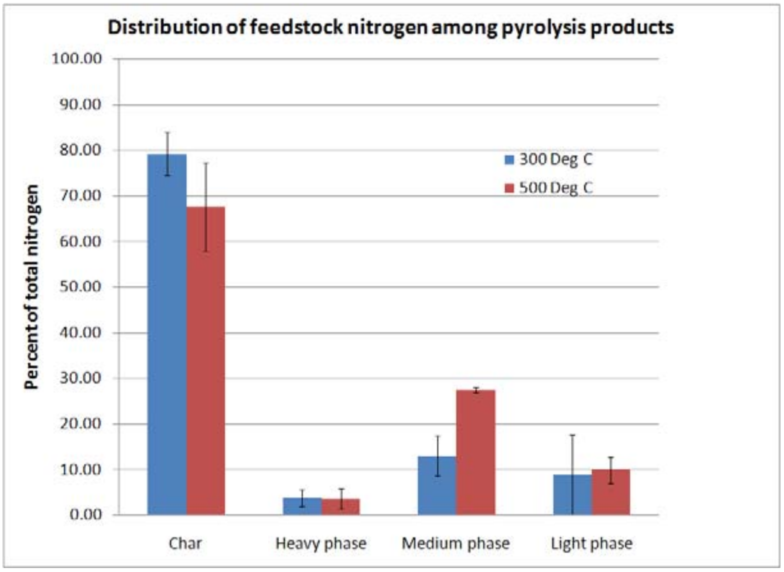

Figure 5.4: Distribution of feedstock nitrogen among pyrolysis products.

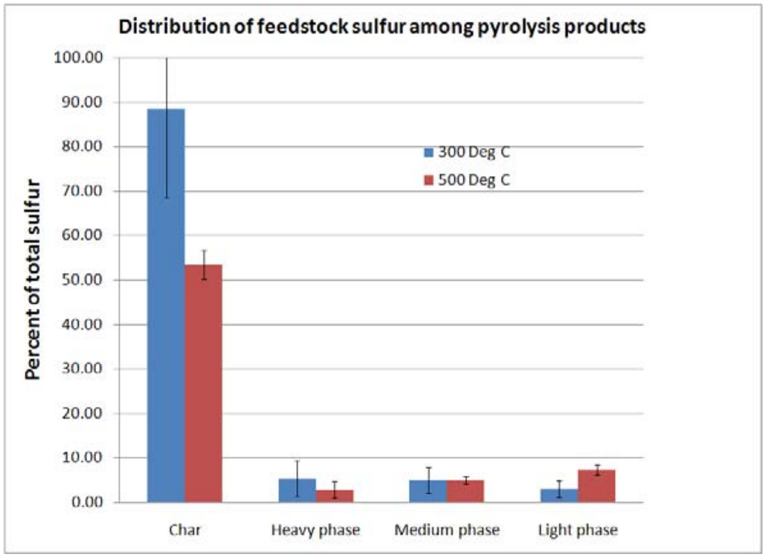

Figure 5.5: Distribution of feedstock sulfur among pyrolysis products.

The increased pyrolysis temperature also reduced sulfur in the char (fig. 5.5). The sulfur which was lost by biomass ended up either in the light phase of condensate or gas products. The char produced at 300°C had 41.83± 10.87 ppm arsenic content but no mercury. Almost all the Al, Ca, Fe, K, Mg, Na, and P remained in the char. The pyrolysis process reduced NH4-N in char by 99.14± 0.47% and NO3-N by 95.79± 5.45% at 500°C; however at lower temperature the reduction was almost 90% for NH4-N and NO3-N.

Data Quality Control

All the data collected during the research was acceptable because the data quality indicators precision, accuracy, bias, and data completeness for all the analytical procedures were within acceptable limits (table 5.10).

Table 5.10. Data quality indicators for various measurements.

Data Quality Indicators	Precision (%)	Accuracy (%)	Bias	Data Completeness (%)
Acceptable Limit	<15	± 20	Randomize	75
Volatile Matter Content	1.09	-1.75	Randomized	100
Ash Content	1.47	1.18	Randomized	100
Fixed Carbon Content	0.86	1.56	Randomized	100
Calorific Value	0.23	0.53	Randomized	100
Carbon	0.57	0.00	Randomized	100
Hydrogen	2.15	0.00	Randomized	100
Nitrogen	6.57	0.00	Randomized	100
Sulfur	0.74	0.00	Randomized	100

SUMMARY

The following conclusions may be drawn from the study:

- The highest calorific value of the char (17.39 ± 1.27 MJ/kg) was made from the coarse fraction pyrolyzed at 300°C at the heating rate of 30°C/min which captured 68.71± 9.37% of the total feedstock energy.
- The pyrolysis process doubles the ash content in char but increased fixed carbon by 2.42 times that of the original feedstock.
- Poultry litter must be heated above 500°C if the preferred product is light phase of the condensate to produce low grade liquid fuel but it would only capture 4.90 ± 3.91% of the feedstock carbon.

- The medium fraction (68.65 ± 15.35% and 84.62 ± 2.25% yield at 300 and 500°C) captured 13.02 and 27.54% of the total feedstock nitrogen at two temperatures and may be used as fertilizer.

Screening and pyrolysis may be used to produce char, liquid fertilizer and liquid fuel from poultry litter but the pyrolysis temperature must be selected based on the preferred product. This research recommends screening and pyrolysis of the coarse fraction at 300°C temperature to produce high calorific value and low ash char. One must consider fast pyrolysis to produce liquid fuel, but efficiency of fast pyrolysis must be considered.

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CHAPTER 6

COMPACTION BEHAVIOR OF SCREENED POULTRY LITTER AND BINDING EFFICENCY OF BIO-OIL

Singh, K, M. Risse, S. Mani, J. Worley, K. C. Das, S. Thompson. To be submitted to Transaction of ASABE.

Abstract

Excessive poultry litter has caused nutrient imbalance in some watersheds resulting in water quality impairment. Fractionation is an option suggested to concentrate the nutrient into a fine fraction (particle size < 0.85 mm) reducing total mass to be transported out of the problem area. Pelletizing this fine fraction has been considered to reduce volume or increase density from 466.65 kg/m^3. This paper explained the compression behavior of the fine fraction of poultry litter. To study the compaction behavior, fine fraction of poultry litter was pelletized into a single pellet making unit at 100°C and a compressive load of 500, 1000, 2000, 4000, 6000, and 8000N. The compressive pressure versus density data obtained from this experiment was fitted with models developed by Heckel, Jones, Walker, Cooper Eaton, and Kawakita and Ludde to explain the compression behavior. Pyrolysis condensate (aqueous phase and bio-oil phase) from pyrolysis of coarse fraction (particle size > 0.85 mm) of poultry litter was studied for its binding properties. To test the binding properties of pyrolysis condensate, the aqueous and bio-oil phase were mixed with fine fraction in 5% and 10% amounts to make pellets from a single pelleter under the same set of loads. These pellets were tested for hardness. Results showed that the fine fraction of the poultry litter was densified from a bulk density 466.65 ± 14.25 kg/m^3 up to 1537.37 kg/m^3 at 4000 N compressive load or 124.965 ± 0.844 MPa pressure. Neither the aqueous nor bio-oil phase possessed binding properties but aqueous did improve lubricity.

Keywords: poultry litter, fractionation, pellet, compaction, modeling.

Introduction

Poultry litter is a combination of manure, bedding material (typically pine shavings for Georgia), spilled feed, feathers, and dead birds. It is an excellent source of organic nutrients due to its high nitrogen (4.11%), phosphorous (1.19%), and potassium (2.33%) content in addition to calcium, magnesium, iron, sodium, and aluminum (Ndegwa, 1990). Excess poultry litter in relatively small areas like north Georgia in the United States can impair water quality due to excessive application (Wood et al. 1999). While evaluating sustainable utilization of poultry litter Ward (2003) suggested that pelletizing poultry litter in order to reduce transport cost and composting were two of the most sustainable options. Other options considered included combustion, gasification, biogas generation, phytase addition to feed in order to reduce phosphorous in ration, feed supplement, fertilizer use, and alum as a soil amendment. High transportation cost is primary impediment to moving poultry litter out of a watershed. The nutrient transport cost may also be reduced by removing coarse particles to form a nutrient rich fine fraction (particle size < 0.85mm) using simple screening (Ndegwa, 1990 and Coloma, 2005) and just transporting them. The bulk density of the fine fraction is similar to raw poultry litter 422.0 kg/m^3 (Coloma, 2005). Pelletizing can increase bulk densities by 2 to 10-fold (Mani, 2005) when performed correctly.

McMullen et al. (2005) studied the effect of storage moisture content on bulk density, particle density, durability, and compressive strength of poultry litter pellets. Broiler litter containing hardwood shavings was ground through a 5/8-in screen followed by the addition of 3% vegetable oil. The litter was pelletized in a California pellet mill with the die temperature held at 75˚C. The pellets were then cooled at 22˚C and 40% relative humidity. McMullen et al. (2005) reported that bulk density decreased and particle density increased with increases in moisture content. The force required to rupture the pellets varied from 316 N at 6.0% moisture (w.b) to 68 N at 22%. Durability of pellets also decreased with increased moisture content. Moisture absorption in the pellets increased with increase in temperature and relative humidity. The thermal properties of the pellets were unaffected by the moisture content.

Fasina et al. (2006) reported that the minimum pressure and moisture content required to compact poultry litter were 5.1 MPa and 26% respectively; however, specific energy required to produce compacted litter was less than 4.68 kJ/kg. The bulk density of poultry litter pellets increased from 1350 kg/m^3 to 1450 kg/m^3 when pressure required to pelletize was increased from 8 to 22 MPa. All of the above research on pelletizing poultry litter focused on physical properties of pellets, minimum pressure requirement, and changes in bulk density during pelletizing. This knowledge of the compaction mechanism of poultry litter is crucial to design of energy efficient compaction equipment and to study the effect of the process variable on pellet density.

The densification process increases the density of the feedstock and usually results in either a pellet or briquette. The physical properties of the biomass and process variables play a significant role in the pellet formation process. Knowing the compaction behavior of the biomass enables the processor to design energy efficient compaction equipment. The behavior of biomass particles under pressure in terms of density change and the cohesion of particles to support binding after the pressure is released are two important aspects of compaction behavior (Tabil, 1996). The compaction of biomass may be considered as a three stage process which may occur simultaneously: particle rearrangement at low pressure, elastic and plastic deformation at high pressure, and local melting of material if the melting points of the ingredients are reached (Tabil, 1996).

The inclusion of binders provides strength to the pellets. The binders may be classified into three main groups (Tabil, 1996). Matrix type binders like paraffin, clay, dry starch, and dry sugars, are required in substantial quantities because particles are embedded in a continuous matrix with its low film strength. Film type binders like starch, bentonite, gums, alginates, and lignosulfates, dissolve with water at the particle surface and re-crystallize across the particle boundary when water is evaporated. Chemical binders like calcium hydroxide with carbon dioxide and sodium silicate with calcium chloride, depend upon the chemical reaction between the binder and the material being agglomerated. Bio-oil from pyrolysis contains phenolic compounds, which have been transformed into phenolic resins. Phinolic resins are widely used as adhesives in plywood and producing particleboards (Bridgewater, 2004).

The objective of this study was to explain the compaction behavior of fine fraction of poultry litter (particle size < 0.85mm) and to evaluate the binding efficiency of pyrolysis condensate (aqueous and oily phases) obtained from pyrolysis of coarse fraction (particle size > 0.85 mm).

Materials and Methods

Poultry litter was collected from three commercial farms and screened through screen #20 (0.85 mm) to get fine (particle size < 0.85 mm) and coarse fractions (particle size > 0.85 mm). The fine fraction was divided into five subsamples. The coarse fraction was pyrolyzed at 500°C under nitrogen flow rate of 2 liter per minute to get pyrolysis condensate. The pyrolysis condensate was separated into a water-rich aqueous phase and energy-rich bio-oil phase using a separatory funnel. The five sub-samples of fine fractions were treated with no condensate, 5% aqueous and bio-oil phases, and 10% aqueous and bio-oil phases of the condensate. Each of the five samples was used to make five pellets using a single pelleter unit mounted on MTS Insight

Instron tester for each preset load. Compression of the sample was conducted at preset loads of 500, 1000, 2000, 4000, 6000, 8000 N and at crosshead speed of 50 mm/min.

The pellets formed were removed from the single pelleter and the mass, length and diameter of the pellet were measured. The pellets were stored for two weeks in zip-lock bags before the hardness test was performed according to ASAE S368.4 (2000). Specimens of the subsamples were sent to the Feed and Environmental Testing Lab at UGA for testing of nutrient content, and composition (cellulose, hemicelluloses, lignin, and crude protein) determination using standard analysis methods. The true density of the grinds was measured by Beckman air compression pycnometer (Model: Multipycnometer, Quantachrome Instruments, FL USA). The bulk density of the fine fraction was measured according to ASAE S 269.4 (1991). The particle size analysis for the fine fraction was performed according to ASAE S 319.3 (1996) using (USA Standard Testing Sieve, Fisher Scientific Company, USA) on an electrical sieve shaker (Model CL 5028, Soil Testing Inc, Evanston, IL, USA). Completely randomized design was used to analyze density and hardness responses for the treatments to study the binding efficiency of the pyrolysis condensate (SAS 9.1, SAS Institute Inc., Cary, N.C.).

Single Pellet Making Process and Hardness Testing

The compaction behavior of the biomass was studied using a single pelleter (fig. 6.1) attached to an Instron testing machine (Model MTS-Insight 30, MTS Systems Corporation, Minnesota, USA). The single pelleter consisted of a plunger and cylinder assembly (6.4 mm internal diameter and 135.5 mm long). A heating element, insulated from the atmosphere, was wrapped around the cylinder. The temperature inside the cylinder was measured using two T-type thermocouples located on the die wall and near the heater. The pelleter was fitted on a stainless steel base. The 6.35 mm plunger of the pelleter was connected to the Instron machine to provide the desired loading (fig. 6.2).

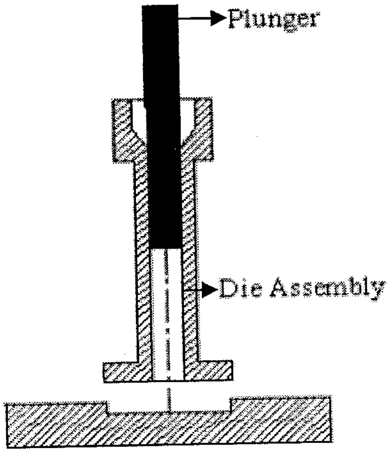

Figure 6.1. The single pelleter unit. Source: Mani (2005).

The compression behavior test was done for the fine fraction of poultry litter for the compression loads described in paragraph one of the Materials and Methods. The pelleter cylinder was heated to 100˚C prior to each test to achieve the commercial thermal environment. The compression test was performed by filling the pre-heated cylinder manually with the fine fraction. The material was compressed up to the desired preset load and held for 60 s before it was withdrawn. The force-deformation data during compression and the force-time data during relaxation were logged into computer. The compacted biomass was removed and stored for a hardness test. Prior to storage, the mass, length, and diameter of the compacted biomass were measured using calipers (Balance model PGW753i, aeADAM, Bradford, MA and Calipers model MITUTOYO Corp, Japan). The pressure-density data for each treatment was fitted with the compression models Heckel (1961), Sivanand and Sprockel (1992), Jones (1960), Walker (1923), and Kawakita and Ludde (1971) using Microsoft Excel software (Microsoft Office Corporation); however, Cooper and Eaton (1962) model was fitted using Proc NLIN of the Statistical Analysis Software (SAS 9.1, SAS Institute Inc., Cary, N.C.).

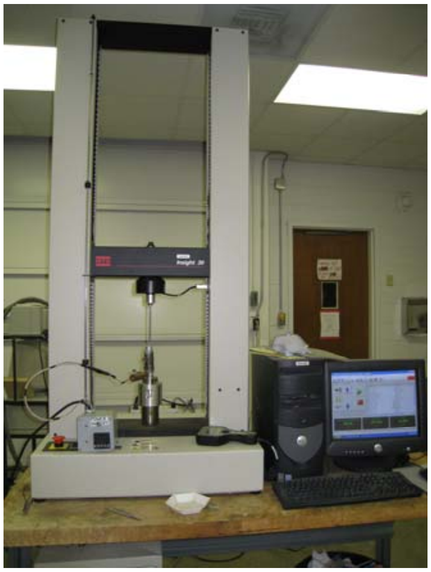

Figure 6.2. The single pelleter was connected to perform the compression behavior test.

Pellet hardness tests were performed on the same Instron machine according to ASAE S368.4 standards. The Instron machine was used at a cross head speed of 0.1 mm/min. The data was logged into a computer and the maximum load required to crush the pellet was recorded.

Results and Discussion

Poultry litter is primarily composed of neutral detergent fiber followed by protein (table 6.1). The crude protein in the fine fraction of poultry litter was higher than that in Alfalfa reported by Tabil (1996). It does contain a significant amount of minerals like calcium, magnesium, potassium, etc (table 6.3a and 6.3b). The high amount of protein present in the feedstock gives good pellet production rates and good quality of pellets because protein plasticizes under heat which is either supplied externally or generated internally due to friction (Tabil, 1996). Similarly, high calcium content also provides binding properties to poultry litter. The poultry litter fine fraction also has high fiber content. Although fibers are natural binders providing strength to the pellet, fibers are also difficult to compress resulting in low pellet production rates.

Table 6.1 . Composition (percent) of fine fraction of poultry litter (particle size < 0.85 mm) and alfalfa (Tabil, 1996).

Sl. No.	Component	Fine fraction of Poultry litter (as received)	Fine fraction of Poultry litter (dry basis)	Alfalfa (high quality) (as received)	Alfalfa (high quality) (dry basis)
1	Moisture content	12.99		6.80	
2	Crude protein	23.36	26.85	18.50	19.80
3	Acid detergent fiber (%)	22.99	26.42	0.40	0.40
4	Neutral detergent fiber (%)	32.42	37.26	37.20	40.00
5	Acid detergent lignin (%) ash free	3.46	3.98	51.60	52.70
6	Ash content (%)	34.13		9.70	10.40
7	Cellulose (%)	19.52	22.43	-	-
8	Hemi cellulose (%)	9.43	10.84	-	-
9	Calcium (%)	3.12	3.59	1.20	1.30
10	Phosphorous (%)	2.08	2.39	0.20	0.20
11	Nitrate (%)	0.17	0.20	Trace	Trace

The particle size of fine fraction of poultry litter was lower than that in Alfalfa (table 6.2). The pellet quality is directly affected by mean particle size. Medium to finely ground material provides more surface area for binding and is easier to pass through a die than coarse material; however, considerable variability in the grain particle size within one feedstock may mask the effect of particle size (Tabil, 1996). The mean particle size, bulk density and grind density of the fine fraction was 0.18 mm, 466.65 kg/m^3 and 1448.83 kg/m^3 respectively (table 6.2).

Table 6.2 . Physical characteristics of fine fraction of poultry litter (particle size < 0.85 mm) and alfalfa (Tabil, 1996).

Sl. No.	Physical characteristics	Fine fraction of Poultry litter (as received)	Alfalfa (high quality) (as received)
1	Particle size (mm)	0.18	0.35
2	Bulk density (kg/m^3)	466.65 ± 14.25	226
3	True grind density (kg/m^3)	1448.83 ± 4.05	1270

Table 6.3a and 6.3b show the nutrient composition of the fine fraction of poultry litter after inclusion of 5% or 10% of bio-oil and aqueous phase of the pyrolysis condensate. Inclusion of condensate increased ammonium nitrogen but not nitrate nitrogen which indicates that these liquids contain nitrogen in the ammonium phase only.

Table 6.3a. Nutrient composition (ppm) of fine fraction (particle size < 0.85 mm) of poultry litter (FPL), FPL with addition of 5 and 10% of bio-oil phase (BO) and aqueous phase (Aq) of pyrolysis condensate (as received).

Material	Al	B	Ca	Cr	Cu	Fe	K	Mg	Mn
FPL	8871	50.10	31240	12.55	259.5	5065	29540	7778	565.8
+5% BO	8074	50.28	35170	10.86	266.6	3670	29640	7495	592.6
+10% BO	7799	45.55	29590	11.87	241.3	3931	26200	6751	540.4
+5% Aq	7820	51.01	33070	11.20	270.2	3735	29830	7732	612.6
+10% Aq	8376	48.46	33590	10.52	267.6	4713	29120	7604	601.7

Table 6.3b. Nutrient composition (ppm) of fine fraction (particle size < 0.85 mm) of poultry litter (FPL), with addition of 5 and 10% of bio-oil phase (BO) and aqueous phase (Aq) of pyrolysis condensate (as received).

Material	NH_4-N	NO_3-N	Mo	Na	Ni	P	S	Si	Zn
FPL	4011	1760	10.71	8784	9.65	20840	8855	178.7	515.9
+5% BO	4240	1750	6.12	9002	9.65	20320	8966	245.5	530.6
+10% BO	4130	1630	3.83	7977	13.07	18450	8264	192.6	486.2
+5% Aq	4750	1690	4.59	9001	9.65	20770	8956	424.3	544.5
+10% Aq	5270	1620	4.59	8914	9.65	21370	8644	380.4	539.1

Compression Behavior

The Heckel model, which correlates change of relative density (ρ_f) of the pellet to the applied pressure, did not fit well with the pressure density data beyond 62 MPa pressure (fig. 6.3). After this pressure the change in relative density (ρ_f) of the compacted material exceeded unity.

$$\ln\left[\frac{1}{1-\rho_f}\right] = m_0 P - b_0 \quad .....(6.1)$$

$$\rho_f = \frac{\rho}{\rho_1 X_1 + \rho_2 X_2} \quad .....(6.2)$$

Where, ρ_1, and ρ_2 are particle densities of the components in the mixture (kg/m^3); ρ_f is the packing fraction or relative density of the material after particle rearrangement; ρ is the bulk density of the compacted powder mixture (kg/m^3); m_0 and b_0 are the Heckel model constants; P is the applied pressure (MPa); and, X_1 and X_2 are the mass fraction of components of the mixture. Sivananda and Sprockel (1992) correlated constant b_0 with (ρ_f) as following:

$$b_0 = \ln\left[\frac{1}{1-\rho_f}\right] \quad .....(6.3)$$

Constant m_0 is equal to the reciprocal of the mean yield pressure require to induce plastic deformation. The value of ρ_f was 0.63 and mean yield pressure required to induce plastic deformation was 26.32 MPa. That means that only 63% of the compaction of the fine fraction of poultry litter was achieved through particle rearrangement compared to 70% reported for alfalfa (Tabil, 1996). The alfalfa required 54.50 MPa pressure to induce plastic deformation; however, plastic deformation in fine fraction of poultry litter started at only 26.32 MPa of pressure.

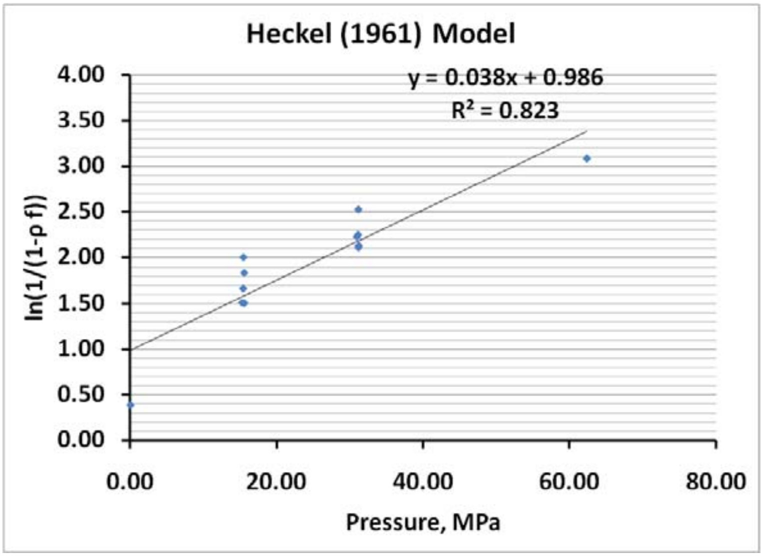

Figure 6.3 Heckel plot for fine fraction of poultry litter.

Jones (1960) represented the compression model for metal powders using equation (6.4):

$$\ln(\rho) = m_1 \ln(P) + b_1 \quad .....(6.4)$$

Where, m_1 and b_1 are Jones constants. Figure 6.4 showed that Jones model on fine poultry litter compression data (R^2= 0.88).

Walker (1923) used equation 6.5 to describe the relationship of the packed volume ration (V_R: ratio of volume of the compact at pressure P to the void free solid material volume) with the applied pressure. V_R is also considered as the resistance of the powder or grind.

$$V_R = m_2 \ln(P) + b_2 \quad \text{.....(6.5)}$$

$$V_R = \frac{V}{V_S} \quad \text{.....(6.6)}$$

Where, V is the volume of the compacted material at pressure P (m^3); V_S is the void free solid volume (m^3); and m_2 and b_2 are the Walker's model constants. Figure 6.5 shows the fit for compression data with the Walker's model (R^2= 0.87).

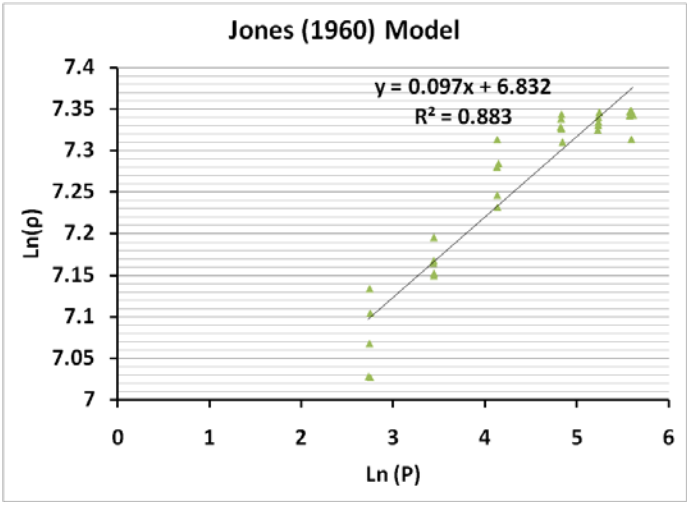

Figure 6.4 Fitting Jones (1960) model on compression data for fine poultry litter.

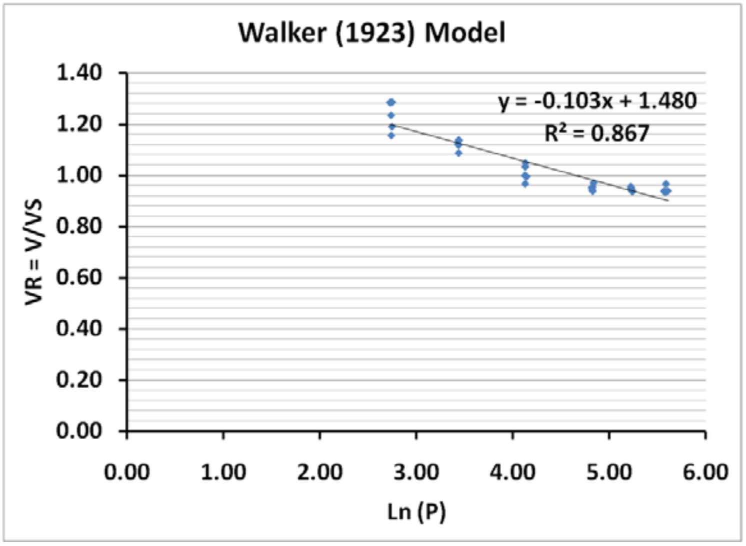

Figure 6.5 Fitting Walker (1923) model on compression data for fine poultry litter.

Kawakita and Ludde (1971) suggested the relationship between degree of volume reduction and pressure is given by equation 6.7.

$$\frac{P}{C} = \frac{1}{ab} + \frac{P}{a} \quad .....(6.7)$$

$$C = \frac{V_0 - V}{V_0} \quad .....(6.8)$$

Where, a and b are the constants; and C is the degree of volume reduction. The value of constant a equals to the value of C at infinitely large pressure. Figure 6.6 shows a Kawakita plot for the fine fraction of poultry litter (R^2= 0.99).

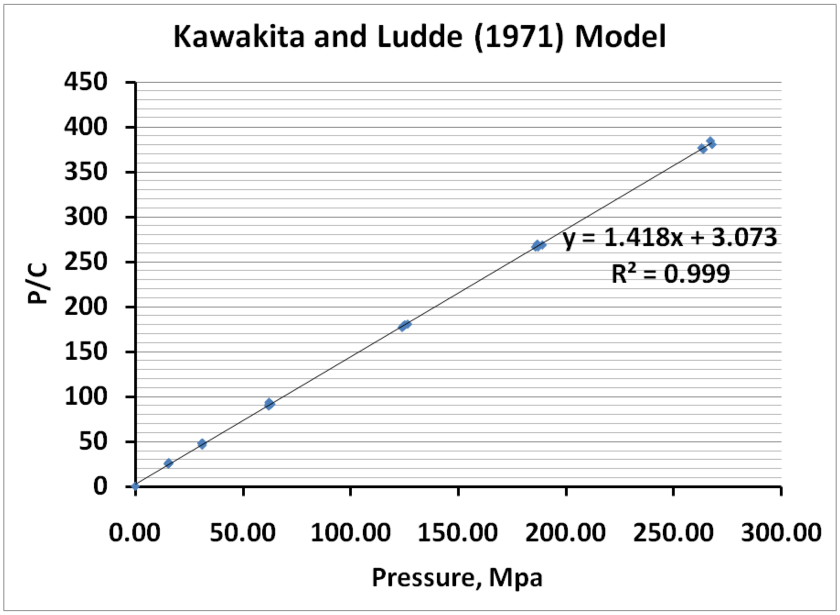

Figure 6.6. Kawakita plot for fine fraction of poultry litter.

The Kawalita and Ludde (1971) model fit the compression data very well with the compression data. The model constants a= 0.69 and 1/b= 2.15 MPa are related to the initial porosity of the bed and failure stress of the compacted material formed from individual particles (Mani, 2005).

The Cooper Eaton (1962) model assumed that compression proceeds through particle rearrangement and deformation.

$$\left[\frac{V_0 - V}{V_0 - V_s}\right] = a_1 e^{-\frac{k_1}{P}} + a_2 e^{-\frac{k_2}{P}} \quad \ldots..(6.9)$$

Where, V_0 is the volume of compacted material at zero pressure (m^3); a_1, a_2, k_1, and k_2 are the experimentally determined Cooper Eaton model constants. This model also fit the compression data well (p-value < 0.0001) with the compression data (fig. 6.7). The first term on the right hand side of equation 6.9 describes the filling of the voids which are of equal size as that of the particles through elastic deformation, slight fracturing, or plastic flow of particles. The second term describes the filling of voids smaller than the particles by plastic flow or fragmentation. The coefficient k_1 represents the pressure required to induce densification by particle rearrangement, whereas k_2 represents the pressure required to induce densification through deformation.

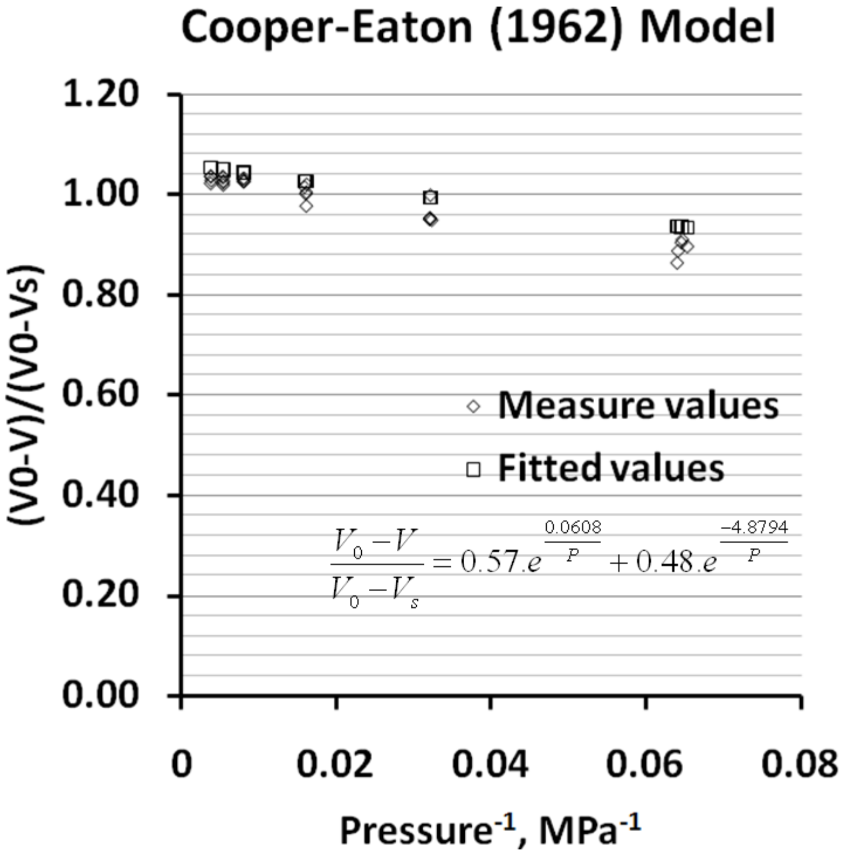

Figure 6.7. Cooper Eaton Model (p-value < 0.0001) for fine fraction of poultry litter.

The values of compression parameters obtained by fitting various models on compression data are listed in table 6.4. The relative density of the compressed particles after particle rearrangement (ρ_{f1}) for poultry litter was similar to high quality alfalfa grinds. The values of ρ_{f1}indicated that there was substantial reduction in volume due to particle rearrangement in fine poultry litter as well as alfalfa. The reciprocal of b in the Heckel model was the yield pressure required to induce plastic deformation (P_y). The values of P_y for poultry litter fine fraction (26.32 MPa) was lower than alfalfa (54.5 MPa) suggesting that poultry litter fine fraction samples were easier to deform or more compressible than high quality alfalfa grinds.

Table 6.4. Compression parameters of fine fraction of poultry litter and grinds of alfalfa (Tabil, 1996), and barley straw (12% moisture content and 0.8mm particle size) (Mani, 2005).

Model parameters*	Fine fraction of poultry litter	Alfalfa (high quality) (Tabil, 1996)	Barley Straw (Mani, 2005)
P_y (MPa)	26.32	54.5	-
ρ_{f1}	0.63	0.60	-
ρ_{f2}	0.57	0.60	
ρ_D	1.04	1.00	-
P_r (MPa)	0.06	5.40	3.1
P_D (MPa)	4.87	2.40	2.0
a	0.70	-	0.91
a*	0.68	-	0.91
1/b (MPa)	2.15	-	3.05
$(a_1 + a_2)$	1.04	1.00	0.98

* P_y = yield pressure required to induce plastic deformation, MPa (Heckel plot); ρ_{f1} = relative density of the grinds after particle rearrangement, fraction (Heckel plot), ρ_D = theoretical relative density of the sample at infinite pressure, fraction (Cooper-Eaton plot); P_r = pressure required to induce particle rearrangement, MPa (k_1 in Cooper-Eaton plot); ρ_{f2} = relative density after particle rearrangement, fraction ($a_1$in Cooper Eaton plot); P_D = pressure required to induce deformation, MPa (k_2 in Cooper Eaton plot); a = initial porosity of particle bed, fraction (Kawalita-Ludde plot), a* = theoretical initial porosity of biomass grind; 1/b = yield strength of compact formed, MPa (Kawalita-Ludde plot); and $(a_1 + a_2)$ = total compaction at infinite pressure, fraction (Cooper-Eaton plot).

The first intercept (a_1) in the Cooper-Eaton model yielded the relative density after particle rearrangement (ρ_{f2}); however, the second intercept (a_2) is the relative density after deformation. The poultry litter fine fraction had the values of a_1 (0.57) higher than a_2 (0.48). This suggested that the compaction process occurs partly by particle rearrangement and partly by deformation. The sum $(a_1 + a_2)$ should ideally be equal to one because it shows the theoretical relative density at infinite pressure but poultry litter fine fraction had $(a_1 + a_2)$ equal to 1.04. Similar behavior was noticed by Mani (2005) and Sivanand and Sprockel (1992) for some biomasses. This possibility may arise when entrapped air is present inside the particles and may not be accounted for true particle volume while measuring true grind density in a pycnometer.

The P_y value obtained from the Heckel model was higher than the P_D value estimated from the Cooper Eaton model because the P_D value included pressure required to induce elastic deformation; however, P_y value refers to pressure required to induce plastic deformation which usually occurrs at high pressure. The pressure required to induce particle rearrangement (P_r) was 0.06 MPa lower than P_D (4.87 MPa). In the fine fraction of poultry litter, particle rearrangement started at lower pressure than alfalfa (Tabil, 1996) and barley straw (Mani, 2005); however, the fine fraction required more pressure for particle deformation than both biomasses.

In the Kawakita and Ludde model, parameter a is related to the initial porosity a* of the biomass grinds. In this case, a was almost equal to a*. The value of 1/b for fine fraction of poultry litter was lower than barley straw which suggested that the pellets made fine fraction of poultry litter may have lower failure stress than compacted material made from barley straw grinds.

Comparison of pellet density and hardness

The pellet density was influenced by the interaction between binder (amount and type of binder) and applied pressure (p-value < 0.0001). At 500 N (approximately 15.0 MPa) compressive load, the inclusion of 5% or 10% aqueous phase or bio-oil resulted in higher density than pellets made from fine fraction itself. For 1000 N or approximately 31 MPa pressure, inclusion of 5% of either of the binders increased pellet density (table 6.5). At pressures beyond 31 MPa, the addition of binders resulted in either no difference (5% aqueous phase) or a decrease in pellet density.

The fine fraction produced maximum pellet density (1537.37 kg/m^3) at 4000 N compressive load or 124.965 ± 0.844 MPa; however, similar pellet density (1515.515 ± 20.624 kg/m^3) was produced by the mixture of fine fraction and 5% aqueous phase of the pyrolysis condensate at 2000N or 31.337 ± 0.192 MPa compressive load.

Table 6.5. Pressure of pellet formation, pellet density, change in pellet density during two week storage period, and pellet hardness for fine fraction of poultry litter FPL (particle size < 0.85 mm), FPL with addition of 5 and 10% of bio-oil phase (BO) and aqueous phase (Aq) of pyrolysis condensate.

Feedstock	Pressure, MPa	Pellet density, kg/m^3	Percent change in pellet density due to storage , kg/m^3	Pellet harness, N
Fine poultry litter	15.493 ± 0.113	1169.004 ± 34.403^{a}	9.679 ± 17.315	346.820 ± 48.292^{a}
	31.123 ± 0.086	1293.191 ± 43.259^{b}	0.922 ± 1.470	426.324 ± 39.699^{b}
	62.307 ± 0.371	1447.895 ± 36.753^{c}	0.517 ± 0.854	647.390 ± 58.915^{c}
	124.965 ± 0.844	1537.372 ± 14.589^{d}	-0.870 ± 0.774	656.152 ± 24.042^{c}
	186.973 ± 1.052	1532.434 ± 16.493^{d}	0.041 ± 1.141	709.048 ± 38.763^{d}
	266.764 ± 3.575	1552.571 ± 19.447^{d}	-0.905 ± 0.893	660.628 ± 26.740^{c}
Fine poultry litter with 5% Aqueous phase of pyrolysis condensate	15.762 ± 0.133	1283.439 ± 17.686^{a}	-1.567 ± 1.370	279.526 ± 17.228^{a}
	31.337 ± 0.192	1422.345 ± 28.011^{b}	-2.232 ± 0.316	445.674 ± 40.481^{b}
	62.497 ± 0.317	1515.515 ± 20.624^{c}	-1.147 ± 1.042	478.836 ± 14.711^{b}
	138.805 ± 5.678	1529.912 ± 18.015^{c}	-1.485 ± 0.864	518.636 ± 33.133^{c}
	197.877 ± 6.655	1530.393 ± 21.708^{c}	-0.558 ± 1.357	518.916 ± 60.539^{c}
	263.732 ± 7.517	1538.566 ± 7.158^{c}	-0.523 ± 0.412	498.372 ± 24.505^{b}
Fine poultry litter with 10% Aqueous phase of pyrolysis condensate	15.693 ± 0.073	1379.269 ± 38.220^{a}	-1.160 ± 1.156	263.780 ± 31.603^{a}
	31.530 ± 0.276	1472.588 ± 6..375^{b}	-1.834 ± 0.654	322.072 ± 24.825^{b}
	73.903 ± 2.236	1457.160 ± 9.826^{b}	1.072 ± 3.800	318.826 ± 38.335^{b}
	136.539 ± 3.559	1473.377 ± 14.005^{b}	-2.022 ± 0.830	342.282 ± 22.343^{b}
	201.224 ± 2.760	1481.752 ± 12.399^{b}	-0.881 ± 1.923	378.005 ± 47.101^{b}
	263.434 ± 6.511	1487.405 ± 28.850^{b}	-3.947 ± 6.255	374.668 ± 30.251^{b}
Fine poultry litter with 5% Bio-oil phase of pyrolysis condensate	15.703 ± 0.159	1328.249 ± 24.373^{a}	-1.207 ± 1.767	299.855 ± 5.313^{a}
	31.191 ± 0.71	1447.569 ± 32.099^{b}	-0.157 ± 1.717	438.798 ± 17.420^{b}
	56.144 ± 28.191	1501.256 ± 10.132^{c}	-1.668 ± 1.632	469.722 ± 23.263^{b}
	137.325 ± 7.236	1474.099 ± 14.941^{c}	2.053 ± 1.656	437.854 ± 21.643^{b}
	201.153 ± 5.863	1466.203 ± 24.086^{c}	0.336 ± 1.426	408.782 ± 49.533^{b}
	267.051 ± 4.016	1475.845 ± 13.575^{c}	-0.917 ± 1.129	383.570 ± 55.640^{a}
Fine poultry litter with 10% Bio-oil phase of pyrolysis condensate	15.724 ± 0.312	1348.796 ± 52.220^{a}	-1.506 ± 2.305	238.806 ± 19.325^{a}
	35.095 ± 1.299	1374.097 ± 55.646^{a}	1.113 ± 4.288	251.546 ± 20.685^{a}
	73.898 ± 3.238	1397.585 ± 12.217^{a}	-0.367 ± 1.087	259.666 ± 24.821^{a}
	138.291 ± 4.983	1387.130 ± 12.982^{a}	-0.880 ± 0.514	253.070 ± 17.429^{a}
	198.981 ± 2.991	1373.892 ± 12.128^{a}	-0.674 ± 0.513	223.588 ± 20.148^{a}
	252.693 ± 5.340	1381.605 ± 19.474^{a}	-0.580 ± 0.847	244.670 ± 16.011^{a}

Note: numbers followed by same letters are not significantly different at 95% confidence level. The letters compared numbers within feedstock.

Table 6.5 and figure 6.8 show the effect of compression pressure on pellet hardness. Neither aqueous phase nor bio-oil obtained from the pyrolysis condensate improved the hardness of the pellets. The addition of 5% aqueous phase or bio-oil at 1000 N compressive force did not improve pellet hardness. Fine fraction pellets achieved maximum hardness of 709.4 N when made at 6000 N compressive force or 186.973 ± 1.052 MPa pressure.

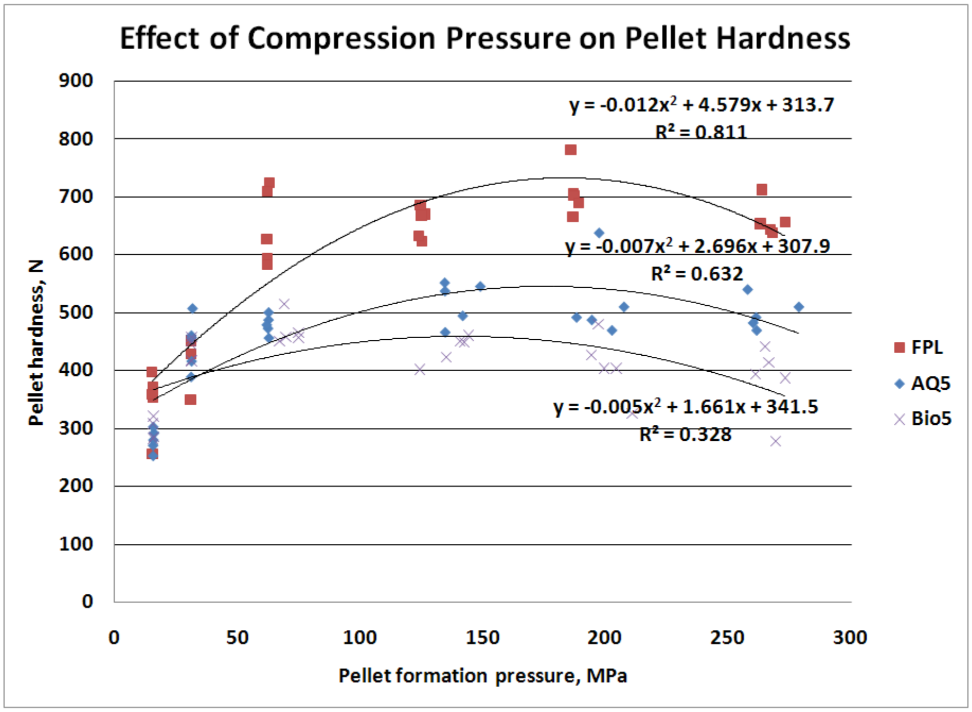

Figure 6.8. Effect of compression pressure on pellet hardness for fine fraction of poultry litter FPL (particle size < 0.85 mm), FPL with addition of 5 of bio-oil phase (BO) and aqueous phase (Aq) of pyrolysis condensate.

The pellets made with 5% aqueous phase of the pyrolysis condensate showed maximum hardness of 518.63 N (made at 138.805 ± 5.678 MPa compressive pressure); however, inclusion of 10% of the aqueous phase reduced the pellet hardness to 322.07 N (made at 31.530 ± 0.276 MPa compressive pressure). Pellets became fragile when bio-oil was added to the fine fraction. Five percent addition of bio-oil gave maximum strength of 438.79 N (made at 31.191 ± 0.71 MPa compressive pressure); however, inclusion of 10% bio-oil resulted 238.8 N hardness (made at 15.724 ± 0.312 MPa compressive pressure). The pellet hardness consistently decreases with the moisture content (Tabil, 1996). Aqueous phase of the condensate contains 45 to 50% moisture which decreased the strength of bonds holding the pellet particle together when added to the fine fraction of poultry litter. The pellets lost little strength when 5% of the aqueous phase of the pyrolysis condensate was added; however, it did provide lubrication during pellet formation and gave maximum pellet density at a compressive load lower than that achieved for fine fraction of poultry litter alone. Bio-oil is a high energy liquid and at high pressures its combustion at a local heat point within the pellet during its formation cannot be ruled out. Such localized combustion could contribute to low pellet density. It may be recommended from the analysis that 5% of the aqueous phase of the pyrolysis condensate may be added to the fine fraction before pelletizing. It would not only provide lubrication to achieve the highest pellet density at 31.337 ± 0.192 MPa pressure but also increase nitrogen content in the pellet. However, compressing the fine fraction of poultry litter at 500N (15 MPa approximately) is enough to increase density by three fold.

Conclusion

The following conclusions can be made based on the experiment and analysis conducted for the test conditions described in this research:

1. Among five compaction models, the Kawakita and Ludde and Cooper Eaton model gave the best fit to the compression data.
2. The compaction of the fine fraction of poultry litter started by particle rearrangement at 0.06 MPa followed by elastic deformation at 4.87 MPa and plastic deformation at 26.32 MPa achieving pellet density equal to 1.04 times that of true density.
3. Pelletizing the fine fraction of poultry litter increased bulk density from 466.65 ± 14.25 kg/m^3 to 1537.37 kg/m^3 (3.3/1 compression ratio) at 4000 N compressive load or 124.965 ± 0.844 MPa.

4. Although pyrolysis oil is used to make phienolic resin (a binding glue), neither aqueous phase or bio-oil phase affect pellet hardness; however, inclusion of 5% aqueous phase would provide lubrication to densify the fine fraction of poultry litter at 138.805 ± 5.678 MPa pressure instead of 186.973 ± 1.052 MPa giving maximum achievable density with lower energy input, but at the cost of reduced hardness.

The results may change significantly for test conditions other than used during the research. The bio-oil is considered as a chemical binder and the reactions required to activate binding properties of the bio-oil may take place at temperature higher than 100°C. Future work should focus on energy analysis of the compaction process involving compaction and extrusion energies. The analysis should also involve economic feasibility of the compaction process.

Acknowledgements

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CHAPTER 7

COFIRING FRACTIONATED POULTRY LITTER CHAR WITH STANDARD COAL

Singh, K, M. Risse, J. Worley, K. C. Das, S. Thompson. To be submitted to Transactions of ASABE

Abstract

Direct combustion, gasification, co-firing with coal, pyrolysis and biogas production have been considered to produce energy from poultry litter; however, NOx and NH_3 emissions cause environmental concerns and high volatiles cause corrosion of boilers when raw poultry litter is used. Screening litter and using the coarse fraction should reduce the emission and corrosion problems and concentrate the energy content. This paper quantifies calorific values and ash content of screened poultry litter char and standard coal mixtures. Char was prepared from a coarse fraction (particle size > 0.85 mm) at 300°C in a batch reactor. The poultry litter char was mixed with standard coal at the inclusion rates of 0, 20, 40, 60, 80, and 100%, and calorific value and ash content of the mixtures were measured. The results show that the calorific value significantly increased but ash content decreased with an increase in the amount of standard coal in the mixtures. A mixture of 40% standard coal and 60% screened poultry litter char was selected because it represented the best balance between increasing calorific value and decreasing ash content. By adding 40% coal to the coarse fraction poultry litter char and combusting the resulting mixture, heat output is increased by 78%, ash production reduced by 62%, and nitrogen loss (NOx and ammonia) reduced by 42%; however, SOx emission increased from 0.36% to 1.31%.

Keywords: poultry litter, fractionation, co-firing, combustion, emission.

Introduction

Poultry litter contains a high amount of nutrients like nitrogen (4.11%), phosphorous (1.19%), and potassium (2.33%) in addition to calcium, magnesium, iron, sodium, and aluminum (Ndegwa, 1990). But excessive land application of poultry litter in concentrated poultry production areas like north Georgia in the United States can impair water quality (Wood et al. 1999). Stringent regulations for land application of poultry litter motivated numerous studies of its potential use as an economical source of energy (Mukhtar et al., 2002; Keener et al., 2002; and Lopez et al., 2005).

Lopez et al. (2005) documented the thermal performance and poultry litter consumption rate in a two stage combustion furnace. The study was done for varying air inlet rates with different litter-wood mixtures (0-40% wood by weight). Lopez et al. (2005) showed that the heating value for the fuel blend ranged from 9,300-16,300 kJ/kg. The litter consumption rate was 27-110 kg/h with primary air flow rate of 150-450 m^3/h. The ash production ranged from 0.15-0.32 kg/ kg of litter combusted. Keener et al. (2002) performed combustion analyses of poultry manure from egg layers and pullets. The heating value of poultry litter was reported as 9,300 kJ/kg and ash content ranged from 32 to 47% of the dry matter. Keener et al. (2002) concluded that the 20% inclusion of poultry manure with coal didn't change the emission pattern, however, approximately 50% additional ash was produced. The direct combustion of poultry litter caused problems like boiler corrosion and ammonia emission, which motivated the study of gasification of poultry litter (Sheth and Turner, 2002).

Sheth and Turner (2002) proposed that broiler litter could be an attractive candidate for catalytic steam gasification for the following reasons: 1. char produced from the broiler litter is more reactive than coal; 2. the presence of a significant amount of minerals, specifically potassium in the litter, serve as an inherent catalyst; 3. low sulfur content limits the production of hydrogen sulfide.

Jones (1998) suggested that the production of CO and H_2 rich synthesis gas may be achieved when the gasification operation is carried out at low pressures (approximately 100 psi or 0.88 MPa), moderate temperatures (approximately 1400 ºF to 1500 ºF, or 760 ºC to 815 ºC), and at a low H/O ratio (approximately 1 to 2). Seth and Turner (2002) determined the optimum conditions for steam gasification of poultry litter using a bench-scale, high-pressure, high-temperature, fixed-bed gasification unit in differential bed down draft mode. In this experiment temperature, pressure, steam flow rate, and catalyst type and its loading rate using the screening test matrix were evaluated. Sheth and Turner (2002) concluded that high gasification temperatures provided more than a 95% conversion rate of carbon over a one hour period for temperatures at approximately 1350ºF to 1400ºF. The conversion rate was affected by catalyst loading; however loading beyond 10 to 15 % wb did not enhance the gasification performance significantly.

Sheth and Bagchi (2005) investigated the fate of nitrogen and phosphorous during gasification and pyrolysis of poultry litter, with or without using a catalyst. They also studied the gasification of char. Steam gasification of poultry litter was done to avoid the possibility of NO_x emission; however, ammonia was released from the poultry litter because heat treatment caused the break-down of uric acid. No phosphine emissions were recorded. The results of this study showed that the percent nitrogen released as ammonia during pyrolysis decreased, from 25% to 6%, when the pyrolysis temperature increased from 300 to 700 ºC. The ammonia liberation increased sharply to 70% when gasification was followed by pyrolysis because of the increased gas phase hydrogen concentration. Sheth and Bagchi (2005) reported that depending upon the conditions, 20 to 70% of the nitrogen present in the litter can be released as ammonia during steam gasification/ pyrolysis, which decreased with an increases in temperature and with the inclusion of a catalyst.

It is very clear, that during direct combustion, gasification and co-firing, NOx and NH_3 emissions may cause environmental concerns and high volatiles causing corrosion of boilers. The FIBROWATT LLC has built three electricity generation plants in the United Kingdom (Ward, 2003) and is building five such power plants (Minnesota, Arkansas, Maryland, Mississippi, North Carolina) in the United States (HRE, 2007), even though combustion of raw poultry litter has several disadvantages.

Nedgwa (1990) and Coloma (2005) suggest a relatively simple solution to improved utilization of raw poultry litter. They found that using screen # 18 or screen # 20 with mesh opening of 1.0 mm and 0.85 mm respectively to concentrate the nitrogen in the fine fraction produced a value added product. The coarse fraction may be used for combustion or gasification for energy production. The overall objective of this research was to investigate pyrolysis of the coarse fraction of screened poultry litter to get three energy products: gases, bio-oil, and char. The objective of this study was to quantify the calorific value and ash content of the poultry litter char when co-firing with coal at 0, 20, 40, 60, 80, and 100 % inclusion rates. The study also described the loss of nitrogen, sulfur, and mercury during combustion of this selected mixture.

Materials and Methods

Poultry litter was collected from three commercial farms and screened through #20 mesh (0.85 mm) to produce a coarse fraction (particle size > 0.85 mm). The coarse fraction was pyrolyzed at 300°C and 30°C/min under a nitrogen flow rate of 4 L/min according to the process described in chapter 5 to produce char. The char coming from pyrolysis of litter from each commercial farm was divided into six sub-samples or experimental units and mixed with 0, 20, 40, 60, 80, and 100% standard coal (NIST SRM 2684b Bituminous coal). The higher heating value (HHV or energy content) was measured according to ASTM D5865 using a bomb calorimeter (Model 1351, Parr Instrument Company (Parr), Moline, IL). The ash content was measured according to ASTM D3174 using a Thermogravimetric Analyzer (Model TGA701, LECO, St. Joseph, MI). Data obtained for calorific value and ash content was arranged in a randomized complete block design for analysis of variance and pair-wise comparison using statistical software from SAS (SAS 9.1, SAS Institute Inc., Cary, N.C.). A mixture of poultry litter char and standard coal was selected for high calorific value and low ash content.

To test the nitrogen, sulfur, and mercury emissions during the combustion of the selected mixture, CHNS analysis and mercury content measurements were performed on the mixture and its ash. The ash was obtained by performing combustion of the mixture in a Thermogravimetric Analyzer (Model TGA701, LECO, St. Joseph, MI). The CHNS analysis was performed using a CHNS analyzer (Model LECO CHNS-932, LECO Corporation, St. Joseph, MI). The mercury content was measured by the Agricultural and Environmental Sciences lab at the University of Georgia. Loss of nitrogen, sulfur, and mercury as a result of combustion were determined using the data from this analysis. These nitrogen, sulfur, and mercury losses for the selected mixture were compared with the results from poultry litter char and standard coal combustion.

Results and Discussion

The char made from the coarse fraction of poultry litter at 300°C possessed a calorific value of 17.43 ± 1.54 MJ/kg and its combustion yielded 31.33 ± 7.78% ash (Table 7.1). With every

20% addition of standard coal, the calorific value of the resulting coarse fraction of poultry litter char and coal mixture increased significantly while, the ash content of the resulting mixture decreased significantly.

Table 7.1. Calorific values and ash content of the poultry litter char and standard coal mixtures.

Mixture	Calorific value	Ash content
PL Char 100%	17.43 ± 1.54^a	31.33 ± 7.78^a
PL Char 80%, Standard Coal 20%	18.93 ± 0.89^b	24.59 ± 7.11^b
PL Char 60%, Standard Coal 40%	21.36 ± 0.22^c	19.46 ± 1.90^c
PL Char 40%, Standard Coal 60%	23.20 ± 0.67^d	18.42 ± 3.86^d
PL Char 20%, Standard Coal 80%	25.31 ± 0.08^e	14.17 ± 1.64^e
Standard Coal 100%	27.43 ± 0.17^f	10.85 ± 0.36^f

Note: Numbers followed by same letter are not significantly different.

In fact, calorific value increased linearly with addition of standard coal in poultry litter char (fig. 7.1), and the ash content decreased linearly for the same mixture. It is interesting to note that the addition of 20% standard coal in poultry litter char increased calorific value by 8.61% and reduced ash content 21.51%. Similarly, when the standard coal amount in the mixture was increased to 40%, the calorific value increased by 22.55%, and the ash content dropped 37.89%. The ash content of the mixture was 19.46%, which was double the ash content resulting from combustion of standard coal (10.85%).

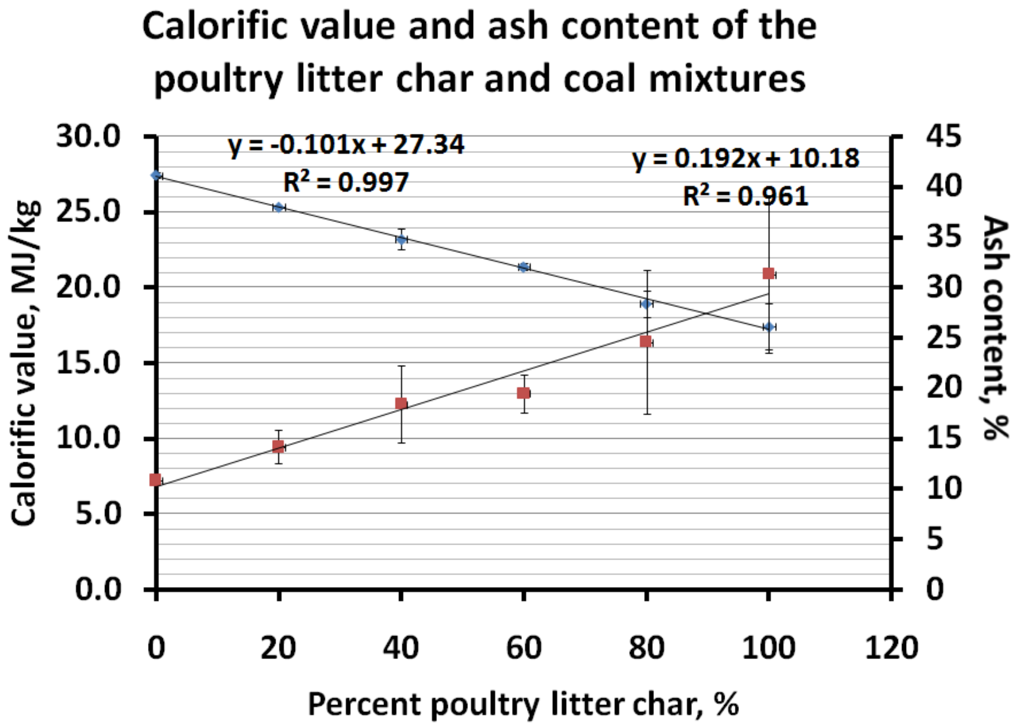

Figure 7.1. Calorific value decreased and ash content increased with increased proportion of poultry litter char in the mixtures with standard coal.

Processors like Fibrowatt LLC. may choose the mixture using figure 7.1 depending upon their need; however, the mixture with 60% poultry litter char and 40% standard coal seemed reasonable to select based on this analysis. By adding 40% coal in coarse fraction poultry litter char, the resulting mixture gave heat output equivalent to 78% of the coal energy, reduced ash content by 62% and reduced nitrogen loss (NOx and ammonia) by 42%. Certainly, the mixture will produce high flame temperature and better steam and in turn, more electricity than raw poultry litter. The high flame temperatures will result in improved combustion efficiency.

Table 7.2 shows the loss of nitrogen, sulfur and mercury due combustion of poultry litter char; the mixture of poultry litter char and standard coal; and standard coal. It is interesting to note that increasing the amount of poultry litter char to the mixture significantly lowered sulfur (SOx) and mercury emission but increased nitrogen emissions (ammonia and NOx).

Table 7.2 . Loss of nitrogen, sulfur, and mercury into atmosphere due to combustion of 100 g of feedstock.

Description of Feedstock	Nitrogen, g	Sulfur, g	Mercury, μg
Poultry litter char (PL)	5.43 ± 0.45[a]	0.36 ± 0.08[a]	< 1.0[a]
Mixture of 60% PL and 40% Standard coal (SRM2684B)	2.24 ± 0.89[b]	1.31 ± 0.15[b]	4.41 ± 0.28[b]
Standard coal (SRM2684B)	1.10 ± 0.85[b]	2.73 ± 0.10[c]	9.77 ± 0.04[c]

Note: The numbers followed by same letter are not significantly different at 95% confidence level.

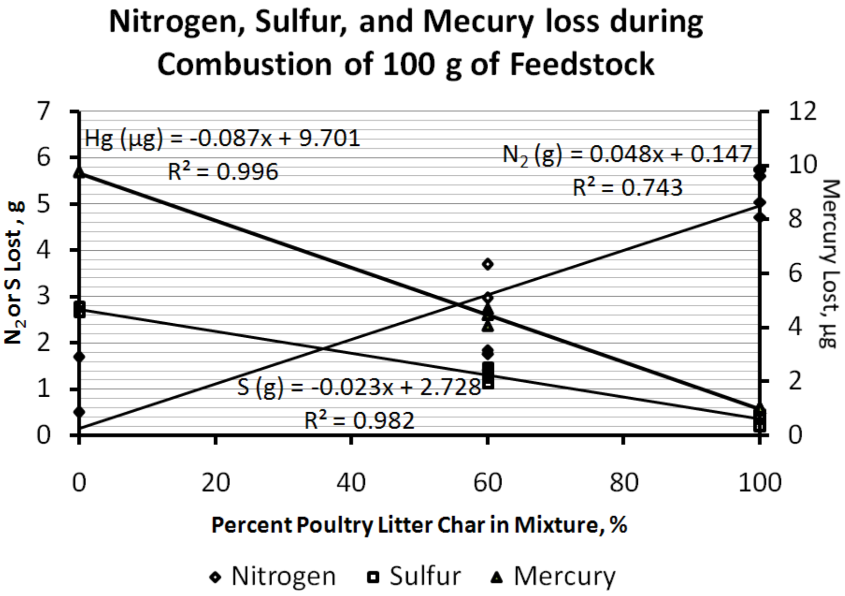

Figure 7.2 Relationship between amount of nitrogen, sulfur, or mercury lost and percent poultry litter char in the mixture due to its combustion.

The high content of minerals like calcium in poultry litter retains a significant amount of sulfur, resulting in less SOx emissions (Abelha et al., 2003). The nitrogen is released in the form of ammonia and NOx and the proportion of the two depends on the combustion temperature and air fuel ratio (oxygen availability) (Zhu and Lee, 2005). At high temperatures, the nitrogen is released from ammonia and combines with oxygen to generate NOx (Zhu and Lee, 2005). The linear relationship between the amount of nitrogen emissions and the amount of poultry litter char in the mixture is shown in figure 7.2. Theoretically, burning 0.6g poultry litter char and 0.4g standard coal individually would give 3.70 g nitrogen, 1.31g sulfur, and 4.51 μg mercury in emissions; however, nitrogen emissions measured under conditions described here was only dropped to 2.24g when poultry litter char and standard coal were co-fired.

A similar relationship for sulfur and mercury emission is also shown in the same figure. Based on this analysis, co-firing of poultry litter char with coal was recommended to reduce sulfur, and mercury emissions from coal fired electricity plants.

Conclusion

The following conclusions were drawn based on the experiment and analysis conducted in this research:

1. A mixture of 60% poultry litter char and 40% standard coal yielded a calorific value of 21.36 ± 0.22 MJ/kg and its combustion resulted in 19.46 ± 1.90% ash.
2. The nitrogen (ammonia and NOx) emissions for the mixture reduced to half compared to poultry litter char; however, the sulfur (SOx) and mercury emissions increased slightly.

Further research is required to see individual ammonia, nitrogen oxide, nitrous oxide, sulfur dioxide and mercury emissions due to combustion of this mixture.

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CHAPTER 8

SUMMARY AND CONCLUSIONS

Summary

This dissertation investigated the pyrolysis, pelletizing, and co-firing of fractionated poultry litter to develop value-added products from poultry litter. The goal was divided into five research studies. The first study ("fractionation and decomposition kinetics") not only explained the decomposition behavior of poultry litter under pyrolysis conditions but also proved that the differences in calorific values for poultry litter can be explained by proximate analysis. Therefore, ultimate, compositional, and mineral analysis are not needed to explain these differences. The second study ("screening and pyrolysis") confirmed that a coarse fraction obtained from screen #20 gave high calorific value and low ash char. The third study ("screening and pyrolysis parameter") showed that char prepared from the coarse fraction of poultry litter at 300°C was the best char for energy production. The fourth study ("compression behavior") explained the compression mechanism of the fine fraction (particle size < 0.85 mm) and the efficiency of pyrolysis bio-oil as binder. The fifth study ("Co-firing poultry litter char with coal") quantified calorific values and ash content of poultry litter char and standard coal mixtures and nitrogen, sulfur, and ammonia lost during its combustion. The following sections summarize the conclusions drawn from each study.

Fractionation and Decomposition Kinetics Study

In this study, poultry litter was divided into coarse and fine fractions using a # 20 screen. The following analyses were performed on the raw poultry litter and its coarse and fine fractions:

higher heating value, proximate, ultimate, compositional, mineral, thermogravimetric (TGA), and differential scanning calorimeter (DSC) analysis. The major conclusions drawn from the study were:

- The coarse fraction is a better source of energy than raw poultry litter or the fine fraction due to its high heating value and volatile content and low ash content.
- Pyrolysing the coarse fraction of poultry litter to achieve high fixed carbon and in turn high heating value is a good option because not only does the high sodium (Na) and potassium (K) content cause a catalytic effect on prolysis reaction, but also the exothermic nature of the pyrolysis reaction would consume less heat energy.
- Pyrolysis of the coarse fraction should be carried out at the peak temperature of 350°C to 400°C to make it feasible.
- High protein and mineral content of the fine fraction makes it more suitable for fertilizer production.

Screening and Pyrolysis Study

This study focused on the combined effect of screening and pyrolysis treatments for value added utilization. Poultry litter was sampled from three commercial farms and given nine treatments: one control, four coarse fractions, and four fine fractions obtained by using each of the four screens # 5, 10, 18, and 20. All the treated samples were pyrolyzed in a batch reactor to produce char and condensate at 500°C under a nitrogen flow rate of 2 lpm. The condensate was separated into three fractions based on density. The bomb calorimeter, proximate, and ultimate analysis were performed on un-pyrolysed but screen-treated samples, char, and three phases of condensate. The following major conclusions were drawn from the study:

- Although both screens #18 and #20 concentrated the energy into a coarse fraction, screen #20 was more effective, and thus should be used to separate an energy rich coarse fraction.
- The pyrolysis of the coarse fraction from screen #20 retained 44.47% of the feedstock dry matter in the char but retained only 43.53% of total feedstock energy.
- The fixed carbon yield was 19.0 to 20.0 % and independent of screen size.
- The pyrolysis process captured 57.23% of total feedstock energy and 53.86% of the total feedstock carbon in char, heavy phase, medium phase and light phase of condensate.
- Pyrolysis of poultry litter removed approximately 75% of the volatiles from poultry litter but increased ash content and fixed carbon content by two and three folds respectively.
- The light phase condensate (4.94 ± 2.70% of the dry biomass) had calorific value 34.83 ± 0.91 MJ/kg and could be further refined as low grade fuel.

Screening and Pyrolysis Process Parameter Study

This study presented the effect of the fractionation and pyrolysis process parameters on the calorific value of char and on the characterization of bio-oil. Poultry litter samples collected from three commercial poultry farms were divided into ten treatments which included two controls (raw poultry litter and its coarse fraction having particle size greater than 0.85 mm) and other eight treatments which were combination of three factors: Type (raw poultry litter or its coarse fraction), heating rate (30 ºC/min or 10 ºC/min), and pyrolysis temperature (300 ºC or 500 ºC). After the screening process, the poultry litter samples were dried and pyrolyzed in a batch reactor under nitrogen atmosphere and char and condensate yields were recorded. The condensate was separated into three fractions based on its density: heavy, medium, and light phase. Calorific value, proximate and nutrient analysis were performed for char, condensate and feedstock. Some of the major conclusions drawn from this study are:

- The highest calorific value of the char (17.39 ± 1.27 MJ/kg) was made from the coarse fraction pyrolyzed at 300°C at the heating rate of 30°C/min which captured 68.71± 9.37% of the total feedstock energy.
- The pyrolysis process doubles the ash content in char but increases fixed carbon by 2.42 times that of the original feedstock.
- Poultry litter must be heated above 500°C if the preferred product is the light phase of the condensate to produce low grade liquid fuel but it would only capture 4.90 ± 3.91% of the feedstock carbon.
- The medium fraction (68.65 ± 15.35% and 84.62 ± 2.25% yield at 300 and 500°C) captured 13.02 and 27.54% of the total feedstock nitrogen at two temperatures and may be used as fertilizer.

Compression Behavior Study

This study explained the compression behavior of the fine fraction of poultry litter. Pyrolysis condensate (aqueous phase and bio-oil phase) from the pyrolysis of coarse fraction (particle size > 0.85 mm) of poultry litter was studied for its binding properties. To study the compaction behavior, the fine fraction of poultry litter was pelletized into a single pellet making unit at 100°C and compressive load of 500, 1000, 2000, 4000, 6000, and 8000N. The compressive pressure versus density data obtained from this experiment was fitted with Heckel, Jones, Walker, Cooper Eaton, and Kawakita and Ludde models to explain the compression behavior. To test the binding properties of pyrolysis condensate, the aqueous and bio-oil phase were mixed with fine fraction in 5% and 10% amounts to make pellets from a single pelleter under the same set of loads. These pellets were tested for hardness. The study concluded following:

- Among five compaction models fitted to the compression data, the Kawakita and Ludde and Cooper Eaton model gave the best fit.
- The compaction of the fine fraction of poultry litter started by particle rearrangement at 0.06 MPa followed by elastic deformation at 4.87 MPa and plastic deformation at 26.32 MPa achieving pellet density equal to 1.04 times that of true density.
- Pelletizing the fine fraction of poultry litter increased bulk density from 466.65 ± 14.25 kg/m^3 to 1537.37 kg/m^3 (3.3/1 compression ratio) at 4000 N compressive load or 124.965 ± 0.844 MPa.
- Although pyrolysis oil is used to make phenolic resin (a binding glue), neither aqueous phase or bio-oil phase possess binding properties; however, inclusion of 5% aqueous phase would provide lubrication to densify the fine fraction of poultry litter at 138.805 ± 5.678 MPa pressure instead of 186.973 ± 1.052 MPa pressure giving maximum achievable density with lower energy input, but at the cost of reduced hardness.

Co-firing Study

This study quantified calorific values and ash content of screened poultry litter char and standard coal mixtures. Char was prepared from a coarse fraction (particle size > 0.85 mm) at 300°C in a batch reactor. The poultry litter char was mixed with standard coal at the inclusion rates of 0, 20, 40, 60, 80, and 100% and calorific value and ash content of the mixtures were measured. The following conclusions were drawn from the study:

- A mixture of 60% poultry litter char and 40% standard coal gave a calorific value of 21.36 ± 0.22 MJ/kg and its combustion resulted in 19.46 ± 1.90% ash.
- The nitrogen (ammonia and NOx) emissions for the mixture reduced to half compared to poultry litter char; however, the sulfur (SOx) and mercury emissions reduced to half compared to standard coal.

Scope for Future Research

The results of this dissertation will not only benefit the poultry industry by reducing storage and transportation costs and generating income from poultry litter through value added products, but also supply important information to industries working in pelletizing poultry litter and generating energy from poultry litter. Some additional work may broaden its impact. Energy consumption during the pelleting process (compression and extrusion) and complete feasibility analysis for the pelleting process is required. Flow properties of poultry litter and its fractions posed operation challenges in pellet mill and must be investigated to improve its design. Pilot scale co-combustion of poultry litter char with coal for its sustainability and economic feasibility is also recommended. In addition, some fundamental research will improve the efficiency of the pyrolysis process: e.g. 1. to develop a thermo-chemical kinetic model to predict decomposition and energy consumption, and 2. Develop a catalytic process to improve high energy bio-oil (light phase) yield. Benefits of land application of char and nutrient release rate from fertilizer pellets needs to be investigated. Complete energetics of poultry litter utilization using fractionation, pyrolysis, and pelletizing must be investigated. Finally, sustainability analysis of poultry litter utilization for the state of Georgia should be investigated considering environmental, economic, and social bottom lines.