Influence of a Biodegradable Litter Amendment on the Pyrolysis of Poultry Litter

Ryan Carl Allen Tarrant

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Foster A. Agblevor
Justin R. Barone
Doug Nelson

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ABSTRACT

The effects of adding a biodegradable litter amendment (AmmoSoak), developed from steam exploded corncobs, to poultry litter prior to pyrolysis on the product yields and qualities were investigated. Mixtures of litter and AmmoSoak were pyrolyzed in a bench-scale fluidized bed reactor. The objective of the second phase was to start-up a pilot-scale fluidized bed reactor unit.

The poultry litter had a lower higher heating value (HHV), higher moisture, ash, nitrogen, sulfur, and chlorine contents than AmmoSoak. Analysis of the poultry litter indicated a mixture of volatiles, hemicelluloses, cellulose, lignin, ash, and proteins. AmmoSoak had a simpler composition than the litter; mainly hemicelluloses, cellulose, and lignin. Bench-scale studies indicated that adding AmmoSoak affected the yields and characteristics of the products.

Addition of Ammosoak increased the bio-oil and syngas yields and decreased char yields. Adding AmmoSoak to the feed decreased the pH, water contents, initial viscosity, and the rate at which the viscosity increased with time, while densities and HHVs increased. The addition of Ammosoak to poultry litter also increased the carbon and oxygen contents of the boi-oils while nitrogen, hydrogen, sulfur, chlorine and ash contents decreased.

A pilot-scale fluidized bed reactor was designed, constructed, installed and investigated for the pyrolysis of poultry litter. Fluidization and thermal equilibrium of the reactor were successfully demonstrated. The reactor was heated by combustion of propane. To ensure complete combustion, the combustion water was collected and compared to the

stoichiometric yield. Complete combustion was achieved. Bio-oil yields on the pilot scale were lower than those obtained on the bench-scale pyrolysis unit. The water soluble fractions of the bio-oils were rich in oxygen. Water insoluble fractions were rich in carbon and ash.

DEDICATION

I dedicate this research to my family, near and far, who have provided me with the wisdom, love, and motivation necessary to achieve anything in life. I also dedicate this work to Annie Liberati and Julia Pryde; two friends who inspired me as much in their lives as they inspire me now.

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CHAPTER 1

INTRODUCTION

1.0 Background

Throughout the world, the poultry industry is one of the largest and fastest growing areas of livestock production (Sims and Wolf, 1994). In the United States alone, there are approximately 7 billion birds raised a year amounting to $22 billion in cash receipts (USDA-ERS, 2001). According to the Virginia Poultry Federation, there were 1180 poultry operations in the state in 2007, raising more than 272 million birds (Virginia Poultry Federation, 2007). In the same year, the poultry industry in Virginia accounted for approximately $937 million of the state's livestock revenue (Virginia Poultry Federation, 2007).

Any livestock industry of this magnitude is destined to create a large amount of litter by-product. In the U.S., the United States Department of Agriculture estimates that in 1997 alone, 17.9 million dry tons of poultry manure resulted from the industry (USDA-ERS, 2001). It is estimated that 400,000 tons of litter is produced from poultry production in Virginia annually (Mullins et al., 2002). The Virginia Poultry Federation estimates that in 1997, 50,000 tons of this poultry litter was exchanged between growers and those who use the litter for other applications.

Poultry litter is comprised of more than manure; it also contains avian urine, bedding material, mortal birds, feathers, spilt feed, and rocks and dirt from the floor of the house (United States Department of Energy, 2004). For generations, poultry litter has been seen as "grower's gold" because of its value as an organic fertilizer substitute and a supplemental protein source in animal feed. Poultry litter's traditional land application

stems from its nitrogen and phosphorous content. The problem of land application lies in the disproportionate ratio of N/P in the litter and the N/P demand of most agricultural crops. According to a University of North Carolina study, litter from the typical poultry house contains N/P ratios of 1.1 for broilers and 0.9 for turkeys (Barker et al., 2002). The nutrient needs for many forage grasses (i.e. rye, fescue, Sudan grass, wheat, Bermuda grass, and Bahia grass) require N/P of 2.4 to 3.9 (United States Department of Energy, 2004). Over application and disproportionate N/P supply/demand result in run-off of nutrients that can cause environmental issues such as contamination of water-sheds and eutrophication of major bodies of water (Harper, 1992). In July of 2003, the Chesapeake Bay experienced its largest "dead zone" since the federal government began monitoring oxygen levels 20 years prior (Chesapeake Bay Foundation, 2003). Bio-security issues also arise from the transportation involved with the land application of poultry litter (Maryland Department of Agriculture, 2002). The other traditional use of poultry litter is as a livestock feed. However, in response to the increased concern over bovine spongiform encephalopathy (BSE), also known as mad cow disease, the Federal Food and Drug Administration has placed bans on the use (Herson et al., 2004).

Considering the importance of the poultry industry to both the United States and Virginia as well as the environmental and biological effects involved with the disposal of the litter associated, there is increased desire to develop alternative uses or disposal methods. It is important that proposed alternative methods for the disposal of poultry litter don't cost growers more than traditional methods, while maintaining the integrity of the environment and human health. Proposed methods vary from processes as simple as aerobic digestion (composting) to thermo-chemical conversion processes: combustion,

gasification, and pyrolysis. There are advantages and disadvantages to each process. Composting is a very energy non-intensive technology. When litter is composted its volume is decreased and the nutrient density is increased (Holden, 1990). The major disadvantages of composting are the loss of nutrients, labor and material costs, odor, and the availability of land (Kelleher et al., 2002). Although thermo-chemical processes are greater in complexity, they offer many distinct advantages. Combustion technologies have potential as a disposal method for litter able to produce carbon neutral energy, but it is difficult to obtain stable combustion because of high water content and pollution controls to meet EPA standards are expensive (Yaman, 2003). Because the energy product is heat, it must be used immediately for heat and/or power generation (Bridgwater, 1999). Gasification produces high levels of gas capable of being converted into liquid fuels or other products but requires large amounts of energy to achieve necessary reaction temperatures and the gas can be very costly to store or transport (Gerods et al., 2008). Pyrolysis, with lower reaction temperatures than gasification, has the potential of producing both liquid and gaseous fuels and a value added char or fertilizer. Because one of the direct products of pyrolysis is a liquid fuel, transportation and storage is easier and more cost affective than the gaseous products from gasification (Bridgwater et al., 1999).

Development of thermo-chemical processes to dispose of poultry litter will be beneficial to growers, farmers, the environment, and future generations alike. These are very non-specific technologies that could be applied on medium to large scale applications, utilizing a variety of biomass feedstock without adding to water or air pollution. Extensive research has been conducted on the pyrolysis of mostly plant based materials.

These studies have analyzed the oils for both their fuel properties and for their chemical compositions. At Virginia Tech, in Blacksburg, VA, researchers have used pyrolysis to convert poultry litter into a bio-oil (energy) and char (fertilizer) (Agblevor et al., 2007). If scaled up, poultry litter pyrolysis could provide growers with energy in the form of liquid bio-oil and a slow-release fertilizer in the form of char while minimizing the health and environmental risks involved with current applications. However, poultry litter releases ammonia gas which can be very displeasing and harmful to those who work around the litter.

To meet the aesthetic and health requirements of the community, an amendment could be applied to the litter to control the odor and ammonia emissions during storage and processing. Dr. Foster Agblevor, at Virginia Tech, has developed a biodegradable litter amendment known as AmmoSoak that has proven to be successful in both reducing odors from poultry litter and in limiting the emission of harmful ammonia gasses. AmmoSoak is added to poultry litter as soon as it is removed from the poultry house, thus minimizing the discomfort and health affects associated with the litter. However, pyrolysis of AmmoSoak has never been studied. Adding AmmoSoak to poultry litter before the pyrolysis process will likely change the product yields, qualities, and chemical compositions. I, therefore, propose to investigate the affect of adding AmmoSoak to poultry litter on the product yields, fuel qualities, and chemical compositions of the pyrolysis oils. Once the effects are established, I propose to demonstrate the technology on a larger scale: up to 5 tons dry litter/ day.

1.1 Research Objectives

The pyrolysis of poultry litter has been studied on two different scales. It has proven to be a possible technology for the conversion of poultry litter into two valued products; liquid energy and slow-release fertilizer. However, the affects of adding a biodegradable litter amendment to help reduce odor and ammonia emissions are not known on the resulting product yields, qualities, and composition of the final products. The overall aim of this research will be to establish these affects and then demonstrate the ability to scale-up the pyrolysis of poultry litter.

The specific objectives of this research are:

1. Establish the physiochemical characteristics of poultry litter gathered from the Shenandoah Valley of Virginia and AmmoSoak produced at Virginia Tech.

2. Determine the affect of adding AmmoSoak to poultry litter on the pyrolysis yields, oil qualities (i.e. viscosity, HHV, pH, density, water content), and product chemical compositions.

3. Shake-down and start-up a pilot-scale pyrolysis unit built in the Shenandoah Valley.

4. Demonstrate pyrolysis of poultry litter on a large-scale.

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CHAPTER 2

LITERATURE REVIEW

2.1 Poultry Industry in the United States

According to the United States Department of Agriculture (USDA) Economic Research Service, the United States is the world's largest producer of poultry and the world's second largest exporter of poultry meat. Over 40 million pounds of meat is produced in the U.S. annually, of which 80% is broiler meat (USDA-ERS, 2008). In 2006, the value of sales in the American poultry industry was $26.8 billion (USDA-NASS, 2007). Poultry farms in the U.S are concentrated in the Southeast. Georgia, Arkansas, Alabama, Mississippi, and North Carolina are the top five broiler producing states. The five leaders in turkey production are Minnesota, North Carolina, Missouri, Arkansas, and Virginia (USDA-ERS, 2008).

2.2 Poultry Industry in Virginia

Poultry is the leading agricultural industry in Virginia. The state ranks 9th in broiler production and 4th in turkey production, supporting 1,200 farm families in Virginia. About 10,000 people are employed directly by the poultry industry with an additional 36,000 jobs indirectly supported by the industry. About half of the jobs directly provided by the industry are employed through 6 major companies all within the Shenandoah Valley, the state's leading production region. These six companies (Cargill, George's Foods, Pilgrim's Pride Corporation, Perdue Farms, Tyson Foods and Virginia Poultry Growers Cooperative, Inc) employ over 5,000 people (Virginia Poultry Federation, 2007).

2.3. Poultry Production

Poultry production is generally a two party system; there are the processors and the growers. Processors typically provide the birds (chicks), feed, and veterinary supplies, while growers are responsible for providing the growout houses fit with all the feeding, heating, cooling, and watering systems needed to raise the birds as well as the labor involved. Once raised, the processor schedules pickup and delivery from the farm to the processing plant (USDA-ERS, 2008). This system applies to approximately 85% of all broiler chicken production farms (USDE, 2004).

There are 4 houses, 40x400 ft each, on a typical broiler production farm (USDE, 2004). A variety of biomass sources are used as an absorbent placed on the house floor to help control moisture. These range from pine shavings to peanut hulls. Each house houses between 20 and 25 thousand birds at a time. With an average of 5.5 flocks raised per year in six week cycles, a typical farm raises about 440,000 birds per year (USDE, 2004). According to the Foundation for Organic Resources Management (FORM), about 130 tons of litter is produced on an average poultry production facility annually. Table 2.1 summarizes data collected at the University of North Carolina concerning poultry house litter characteristics. According to Table 2.1, 0.90 tons/1000 birds of dry litter is produced in a typical broiler house annually. This is equal to 1.8 lbs/bird.

Table 2.1 Poultry House Litter Characteristics, Summary of UNC Data

Manure Source	Assumed House Capacity	Manure + Litter Accumulation (tons/house/yr)	Dry Solids Content (%w.b.)	Dry Litter Accumulation (tons/house/yr)	Birds/House Annual	Dry Litter Accumulated Per Bird (tons/1000)
Broiler Chicken	20,000	126	78.6	99.0	110,000	0.90
Broiler Roaster	20,000	200	76.2	152.4	110,000	1.38
Turkey Grower Hen	10,000	200	73.2	146.4	175,000	4.18
Grower Tom	10,000	410	73.2	300.1	175,000	8.57

Source: (Barker et al., 2002)

The amount of litter that is legally allowed to be land applied is about 50% of the litter generated at a poultry production facility. This results in about 65 tons of surplus litter per farm per year (FORM, 2002).

2.4 Characteristics of Poultry Litter

Poultry litter is comprised of manure, avian urine, bedding material, mortal birds, feathers, spilt feed, and rocks and dirt from the floor of the house (United States Department of Energy, 2004). Because of the many constituents of poultry litter and variations in poultry diets from farm to farm, the composition varies greatly with each production facility and house. Table 2.2 shows the proximate analysis of poultry litter collected in Alabama.

Table 2.2 Proximate Analysis of poultry litter collected in Alabama

Component	Minimum	Maximum	Mean (SE)
Dry Matter (%)	61	95.3	80.5 (0.58)
% of Dry Matter			
Nitrogen	2.3	6	4.0 (0.72)
Crude Protein	14.4	37.5	24.9 (0.45)
Acid Detergent			
Fiber	18	69.1	41.1 (1.08)
Insoluble Nitrogen	0.1	3.4	0.6 (0.05)
Soluble Nitrogen	1.6	5.7	3.4 (0.02)
Crude Fiber	10.8	51.6	23.6 (0.81)
Ash	8.9	54.4	24.7 (0.89)
Bound Nitrogen	5.5	64.3	15.0 (1.06)

Source: (Stephenson et al., 1990)

Studies performed on poultry from Arkansas by the United States Department of Energy provide representative nitrogen, phosphorous, and potassium values for broiler litter. This data is provided in Table 2.3.

Table 2.3 Nitrogen, Phosphorous, and Potassium Values for AR Broiler Litter

	Total N (lb/ton)	P_2O_5 (lb/ton)	K_2O (lb/ton)	Ca (lb/ton)
Minimum	22	18	23	18
Maximum	98	96	80	108
Mean	60	58	52	45

Source: (USDE, 2004)

2.4.1 Moisture

In a broiler house that has properly functioning heating and ventilating systems, the moisture content of the litter will typically be between 25 and 35%. This value will increase if the birds have diarrhea, which can be caused by nutrition or infectious diseases. If birds eat too much of certain minerals such as potassium, sodium,

magnesium, sulfate or chloride, they can begin to consume much more water, leading to watery droppings (Butcher and Miles, 1995). The moisture content of the litter is very important in pyrolysis in terms of controlling reaction conditions and the properties of pyrolysis products. Litter with moisture contents greater than 25% will not move through an auger easily, but litter with less than 12% moisture will be undesirably dusty (McKinley, 2000).

2.4.2 Crude Protein, Bound Nitrogen, and Crude Fiber

On average, the crude protein content of broiler litter is 24%, ranging from 15 to 38%. Non-protein nitrogen can comprise more than 40% of the crude protein found in the litter. Most of the non-protein nitrogen in the litter is uric acid excreted by the birds. Nitrogen can become bound and insoluble as the litter is overheated. Typically, the bound nitrogen content of litter is 15% but can be as high as 50% in overheated litters. As this level increases, the digestibility of the dry matter decreases, limiting the litter's value as a fertilizer and as a feed. The crude fiber content of poultry litter is contributed mainly by the bedding applied to the floor. Crude fiber constitutes 24% of the litter on average (McKinley, 2000).

2.4.3 Minerals

The mineral content of poultry litter can vary greatly depending on the bedding used and diet of the birds, but litter is a good source for a number of macro and micro nutrients. Table 2.4 summarizes the macro and micro nutrients present in broiler litter collected in Alabama.

Table 2.4 Macro and Micro nutrient content of broiler litter collected in Alabama

Component	Minimum	Maximum	Mean (SE)
Minerals			
% of Dry Matter			
Ca	0.81	6.13	2.31 (0.082)
K	0.73	5.17	2.32 (0.059)
Mg	0.19	0.88	0.52 (0.014)
P	0.56	3.92	1.56 (0.047)
S	0.22	0.83	0.50 (0.013)
Ppm of Dry Matter			
Cu	25	1003	473 (22.7)
Fe	529	12604	2377 (262.7)
Mn	125	667	348 (12.9)
Zn	106	669	315 (13.0)
B	23	125	54 (1.7)

Source: (Stephenson et al., 1990)

2.4.4 Ash Content

The ash content of litter depends on the type of bedding, frequency of litter removal, diet, and how much soil or dirt is removed from the house floor (McKinley, 2000). Cleaning a house out more often reduces the ratio of excrement to bedding, therefore, decreasing the ash content. According to studies performed in Alabama, the average ash content of broiler litter is about 25% with a standard error of less than 1% (Stephenson et al., 1990). About 12% of the ash found in litter will be in the form of calcium, phosphorus, potassium, and other trace minerals (McKinley, 2000).

2.5 Traditional Applications of Poultry Litter

2.5.1 Land Application as an Organic Fertilizer

If used properly, poultry litter can be an inexpensive, effective fertilizer for farmers and growers. It gains its value as a fertilizer from its contents of N, P, and K, as well as other nutrients such as calcium, magnesium, and sulfur (Zhang et al, 1996). Litter is also

beneficial in terms of adding organic matter to the soil. Increased levels of organic matter in soil have positive effects on soil structure, tilth, water-holding capacity, aeration, cation exchange capacity, and microbial activity. Calcium carbonate in poultry feed can impact soil pH and liming of soil (Mullins et al., 2002). Table 2.5 compares the effects of using poultry litter as a fertilizer to those of no treatment and commercial nitrogen fertilizers.

Table 2.5 Average Forage Yield and Crude Protein Content of Bermuda Grass in Southeastern Oklahoma at Four Nitrogen Treatments.

Treatment	Forage Yield Tons/Acre	Crude Protein %
No N	2.77	8.0
300 lbs/Acre Ammonium Nitrate (96 lbs Total N/Acre)	3.44	8.8
2 Tons/Acre Poultry Litter (app. 130 lbs Total N/Acre)	3.54	11.4
4 Tons/Acre Poultry Litter (app. 260 lbs Total N/Acre)	4.82	12.6

Source: (Zhang et al, 1996)

The increase in forage yields and crude protein levels could be a combined effect of the litter providing a slow-release nitrogen supply and improving soil pH and quality (Zhang et al, 1996).

It is important, however, that application rates be set based on the nutritional requirements of the crops. Typically, crops are fertilized to increase the nitrogen value in the soil, which leads to an excess of phosphorous (Baker et al., 2006). Adding too little will not suffice the nutrient needs of the crop while too much application is a waste of

resources and can lead to a run-off of nutrients in the soil (Zhang et al, 1996). It has been shown that excess phosphorous levels in litter lead to water quality issues (Sims, 2000). These quality issues stem from the fact that in many areas, phosphorous is the limiting nutrient for much of aquatic plant life. Typical broiler litter contains 2-3 g/kg of water soluble phosphorous when removed from the house (Sistani et al., 2003). This could easily be washed into groundwater during a large rainfall event. When large amounts of phosphorous are present in the water, large algae blooms are possible, creating "dead-zones" or areas of depleted oxygen (Sistani et al., 2006). These blooms of microbial life deplete the waters of dissolved oxygen (DO) which is needed by all animal life in the waters to survive. Low DO levels, or hypoxia, can restrict growth and reproduction of aquatic species and increase vulnerability to diseases. For these environmental reasons, disposal methods other than land application need to be investigated. The Chesapeake Bay exhibited its largest areas of oxygen depletion in July of 2003; approximately 40% of the bay's mainstem (Chesapeake Bay Foundation, 2003). Figure 2.1 shows the 2008 hypoxia forecast for the mainstem of the Chesapeake Bay (www.eco-check.org/.../indicators/hypoxia/). In addition to environmental issues, Stevenson has shown that excess nitrate concentrations in drinking water can cause methaemoglobinaemia (blue baby syndrome), cancer, respiratory illness in humans, and fetal abortions in livestock (1986).
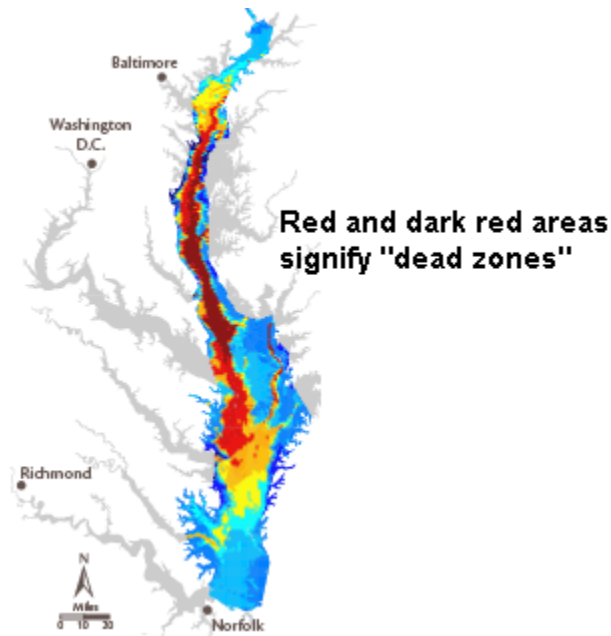
Figure 2.1 2008 hypoxia forecast for the mainstem of the Chesapeake Bay.

Source: www.eco-check.org/.../indicators/hypoxia/

2.5.2 Poultry Litter as Livestock Feed

Poultry litter has been used as a feedstock for ruminant animals such as beef cattle, sheep, and goats because of its crude protein, mineral, and energy content (Barnes et al., 1997; Rossi et al., 1999; Van Ryssen and Mavimbela, 1999). Based on a nutrient analysis, broiler litter is comparable to good quality alfalfa hay but not as palatable (Bagley and Evans, 1998). McCaskey et al. (1994) reported that steers fed on a concentrated diet of broiler litter had gains greater than those fed on a 50/50 blend of litter and corn. The growth rate for those fed on pure litter was 2.53 pounds per day while the steers on the 50/50 diet grew 2.12 pounds per day. For ewes, a 30% poultry litter-based diet is comparable to a traditional soy-bean meal-based diet (Muwalla et al., 1995). Studies have shown that goats fed a low-quality forage diet supplemented with poultry litter exhibited greater weight gain than goats fed on forage alone (Mekasha et al., 2004).

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In 2003, the first case of bovine spongiform encephalopathy (BSE) in the United States was reported. To give the Food and Drug Administration (FDA) time to inspect the risks associated with feeding poultry litter to ruminant animals, a temporary ban was placed on poultry litter based feed. Since then, the FDA has set mandates that allowed them to lift the ban in 2005, deeming there is no risk to human or animals from using poultry litter as a feed. There are other risks and popular conceptions that motivate research into other uses for litter. Because the risk of transmitting pharmaceuticals used in the raising of poultry, litter should not be fed to cattle within 21 days of slaughter (Daniel and Olsen, 2005). Even if all necessary precautions for safety are taken, cattle numbers are limited and another disposal method would still be needed (Brake, 1992).

2.5.3 Composting Poultry Litter

Raw manure and other forms of organic matter have been transformed successfully into soil amendments for many years. Pathogens present in the unprocessed poultry litter are killed by the heat generated during composting (Louisiana State University-Ag Center, 2005). Once composted, poultry litter is safer, takes up less volume, is more nutrient dense, and emits fewer odors. It is also more stable and homogenous than fresh litter (Holden, 1990). Although composting is an effective and inexpensive method of poultry litter disposal, it has drawbacks. The heat involved in composting has the ability to change the nature of nitrogen in the litter, affecting its use as a soil amendment (Tiquia and Tam, 2000). Losses of nitrogen due to nitrogen mineralization, ammonia volatilization, and denitrification can range from 21 to 77% (Martins and Dewes, 1992; Rao Bhamidimarri and Pandey, 1996). Composting is one of the leading disposal methods of animal manure, however, it has proven to be very labor intensive and causes

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air pollution through dust and odor and requires large amounts of space (Tiquia and Tam, 2002). Other disadvantages of composting are the loss of nutrients and high material costs (Kelleher et al., 2002). Due to these disadvantages, anaerobic and thermochemical conversion processes are receiving more attention.

2.6 Energy and Thermo-chemical Conversion of Poultry Litter

Anaerobic digestion and thermo-chemical conversion processes provide potential disposal methods for poultry litter. Both technologies produce energy, but there is a difference in the amount and state of nitrogen removed during processing. Anaerobic digestion typically results in an effluent of the same N concentration as the untreated manure. On the other hand, thermo-chemical processes, represented by combustion, gasification, and pyrolysis, result in nitrogen emissions and little ash (Chiumenti et al., 2007). This makes a significant difference in terms of nitrogen load on the land.

2.6.1 Anaerobic Digestion

Anaerobic digestion is advantageous because it reduces pathogens and increases fertilizer properties compared to raw manure (Chiumenti et al., 2007). Marketable methane gas and digestate can be produced from the degradation and stabilization of poultry litter through anaerobic digestion (Collins et al., 2000). The methane produced by this process can be used as a fuel for boilers, as a replacement for natural gas or fuel oil and can also be fired in engine-generators to produce electricity for on-farm use or sale to electricity companies. The residual digestate is stable and can be used as a soil fertilizer (Kelleher et al., 2002). Anaerobic digestion of farm residues began to gain popularity in the 1980's. In Italy alone, more than 50 plants were built and today more than 2,800 exist in Germany.

Plants range from 60 kW to 2 MW with the higher energy output achieved by adding other biomass such as corn silage (Chiumenti et al., 2007).

Although anaerobic digestion has potential as a litter disposal method, there are several challenges that must be addressed before commercialization will be possible. According to Collins et al. (2000), the litter and any other biomass added to the litter must be supplied free or there must be a tipping fee charged. In addition, digestion of poultry litter doesn't significantly reduce the volume of the litter, adding to the need for a market for the digestate (PPRP, 2004). There are also problems in terms of nitrogen reduction. The nitrogen content is not decreased through digestion, and for maximum power output from a plant, other biomasses must be combined with the litter, only increasing the nitrogen content. Finally, anaerobic systems typically require moisture contents of 84-85%, and litter typically only contains 30% water, therefore additional water must be supplied (Chiumenti et al., 2007).

2.6.2 Combustion of Poultry Litter

The essential process steps of combustion include drying, devolatilization, gasification, char combustion, and gas phase reactions (Khan et al., 2008). Combustion technologies can produce several forms of useful energy from biomass such as poultry litter, including hot air, hot water, steam, and electricity. The conversion efficiencies of steam-driven turbine electricity generators powered by the combustion of biomass generally range from 17-25%, while cogeneration can increase this to 85% (Cihan et al., 2009). The first commercial poultry-litter fired power plant in the world was opened by Fibropower, Page and Allen in 1993 in Suffolk UK. Since then, two more have opened in the United Kingdom in Glanford and Thetford (Anonymous, 1996). Also in the last twenty years,

attention has been put into developing on farm poultry-fired energy systems for heating poultry houses (FORM, 2002).

There are design, economic, and environmental issues associated with the combustion of poultry litter. Combustion technologies can produce two classes of pollutants: unburnt pollutants and pollutants created by combustion. The combustion-derived pollutants include CO, HC, tar, PAH, and C_XH_Y. The other class of pollutants includes ash, particulate matter, and oxides. Physical properties such as bulk density, moisture content, homogeneity, and particle size will all influence the efficiency of power production from combustion and the character of emissions (Khan et al., 2009). Slagging and corrosion also present challenges to operating a poultry litter-fired power plant. Slagging refers to the deposits on the furnace walls or other surfaces, which reduce heat transfer in the furnace. Corrosion is the deteriation of the physical properties of a material due to reactions with its environment and can be caused by gas phase species, slagging or a combination of both (Nielson et al., 2000). Deposition processes are influenced greatly by alkali compounds, potassium, and sodium (Baxter, 1998).

Research into the co-firing of biomass with other feed stocks has shown an increase in efficiency. Co-firing with coal, for example, has proven to increase energy conversion (Mitsui Babcock, 1997; Aston University and DK Teknik, 1993; Warren Spring Laboratory, 1993a,b; EU, 1999; Aston University, 1986). In particular, the co-firing of poultry litter and coal has been studied by Li et al. (2008). Henihan et al. have performed studies on the co-combustion of poultry litter with peat (2003). The co-combustion of poultry litter with natural gas has also been studied (Zhu, 2005).

2.6.3 Gasification of Poultry Litter

Gasification uses air, oxygen, or steam as a reaction medium to convert the organic portion of a dry or wet feedstock into the minor by-product char and primarily non-condensable, permanent gases, CO, CO_2, H_2, and low molecular weight hydrocarbon gases (Bridgwater, 2003; McKendry, 2002a; McKendry, 2002b). The gas mixture is known as synthesis gas or syngas and can be burned for its heating value. Gasification takes place at very high temperatures, thus requiring great energy input. The Community Power Corporation demonstrated a small modular biopower system using poultry litter gasification (USDE, 2004). Like combustion, the co-gasification of poultry litter has also been studied. Priyadarsan et al. (2005) have studied the co-gasification of poultry litter and coal.

2.7 Pyrolysis

Pyrolysis can be described as the thermal degradation of the organic matter in the absence of oxidizing agents into three components: solid (char), liquid (bio-oil), and gas (Yaman, 2004). Typical reaction temperatures are between 350 and 650°C (Bridgwater and Bridge, 1991). The solid or char fraction typically contains inorganic materials ashed to varying degrees, any unconverted organic solid and carbonaceous residues. The liquid or bio-oil is made up of a complex mixture of water and organic chemicals. Usually these are acids, alcohols, aldehydes, ketones, esters, heterocyclic derivatives and phenolic compounds (Klass, 1998). Pyrolysis has gained much attention in terms of producing energy from biomass because the process conditions can be manipulated to maximize yields of liquid, solid, or gaseous products (Horne and Williams, 1996). Pyrolysis studies

have been performed on a number of materials including: Acacia wood (Ahuja, 1996), agricultural residues (Blasi et al., 1999; Zanzi et al., 1996; Agblevor and Besler, 1996), almond shell (Blesa et al., 2001; Savova et al., 2001; Caballero et al., 1997; Rapagna and Latif, 1997), apple pulp (Suarez-Garcia et al., 2002), apricot stones (Savova et al., 2001), Arbutus Unedo (Zabaniotou, 1999), Argentinean hardwood species (Della Rocca et al.,1999), ash free cellulose (Antal et al., 1998), Aspidosperma Australe (Della Rocca et al.,1999), Aspidosperma Quebracho Blanco Schlecht (Della Rocca et al.,1999), Austrian pine (Ingemarsson et al., 1998), automobile shredder residue (ASR) (Shen et al., 1995), bagasse (Zandersons et al., 1999; Ahuja et al., 1996; Morris, 2001; Minkova et al., 2000), bales (Agblevor et al., 1996), beech wood (Blasi et al., 2000), birch bark (Murwanashyaka et al., 2001), birch sapwood (Murwanashyaka et al., 2001), birch wood (Minkova et al., 2000), black liquor Demirbas, 2002), cellulose (Boutin et al., 2002; Yoshida and Matsumura, 2001), cherry stones (Savova et al., 2001), chip piles (Agblevor et al., 1996), chlorogenic acid (Bassilakis et al., 2001), coir pith (Raveendran et al., 1995), corn stover (Agblevor et al., 1996), corn–potato starch gel (Antal et al., 2000), corn stalk (Kim et al., 1998; Lanzatta and Blasi, 1998), cotton cocoon shell (Caglar and Demirbas, 2002); Demirbas, 2001; Caglar and Demirbas, 2001), cotton gin wastes (Zabaniotou et al., 2000), cotton stalk (Putun, 2002), cotton straw (Putun, 2002), cottonseed cake (Ozbay et al., 2001; Putun et al., 1997), *Cynara cardunculus* L. (Encinar et al., 2002), D-glucose (Bassilakis et al., 2001), eucalyptus wood (Rocha et al., 1999), *Euphorbia rigida* (Putun et al., 2001; Ozcan et al., 2000; Putun et al., 1996), extracted oil palm fibers (Guo and Lua, 2000), filter pulp (Jakab et al., 1997), forest wood (Reina et al., 1998), grape (Encinar et al., 1997), grape residue (Blasi et al., 1999), grape seeds

(Savova et al., 2001), grass (Piskorz et al., 1998), ground nut shell (Raveendran et al., 1995), hardwoods (beech, chestnut) (Sipila et al., 1998; Blasi et al., 2001), hazelnut (*Corylus avellans*) shells (Putun et al., 2001; Demirbas, 2001; Kockar et al., 2000; Putun et al., 1999; Rao and Sharma, 1998; Demirbas, 1998; Demirbas et al., 1996), herbaceous feedstocks (Agblevor et al., 1996), herbaceous residues (Agblevor and Besler, 1996), hybrid poplar (Agblevor et al., 1996), Italian sweet sorghum (Piskorz et al., 1998), kraft lignin (Ferdous et al., 2001), lignin (Yoshida et al., 2001), Lodgepole pine (Ingemarsson et al., 1998), lucerne (Bjorkman and Stromberg, 1997), maize (Encinar et al., 1997), Miscanthus pellet (Minkova et al., 2000), mixed wood waste (Williams and Horne, 1996; Horne and Williams, 1996), municipal solid waste (Sebghati and Eley, 1997; Garcia et al., 1995; Gharieb et al., 1995), natural rubber (Kawser and Farid, 2000), Norway spruce (Ingemarsson et al., 1998), nut shells (Savova, et al., 2001), oil palm shell (Islam et al., 1999), old furniture (Reina et al., 1998), olive husk (Blasi et al., 1999; Demirbas, 2001; Rao and Sharma, 1998; Caglar and Demirbas, 2002; Demirbas et al., 2000; Zabaniotou, 2000), olive stone (Blesa et al., 2001; Caballero et al., 1997; Minkova et al., 2000; Caballero et al., 1997), petroleum residue (Garcia-Perez et al., 2001), pine (Ingemarsson et al., 1998; S̲ipila et al., 1998; Williams and Besler, 1996), pine sawdust (Garcia et al., 1999), pinus insignis sawdust (Olazar et al., 2001; Aguado et al., 2000), Ponderosa pine (Ingemarsson et al., 1998), poplar oil (wang et al., 1998), pulp black (Kim et al., 1998), rape plant (Karaosmanoglu and Tetik, 1999), rape seed (Sensoz et al., 2001; Karaosmanoglu and Culcuoglu, 2001; Onay et al., 2001; Sensoz et al., 2000; Predel and Kaminsky, 1998), rice husks (Ahuja et al., 1996; Blasi et al., 1999; Raveendran et al., 1995; Rao and Sharma, 1998; Williams and Nugranad, 2000; Islam and Ani, 2000;

Mansaray and Ghaly, 1999; Islam and Ani, 1998; Mansaray and Ghaly, 1998; Teng et al., 1997; Wang et al., 1995), safflower seed (Beis et al., 2002), sawdust (Blessa et al., 2001; Antal et al., 2000; Koullas et al., 1998; Dai et al., 2000; Aguado et al., 2000), Scotch pine (Ingemarsson et al., 1998), sewage sludge (Ahuja et al. 1996), silver birch (Drummond and Drummond, 1996), sitka spruce (Ingemarsson et al., 1998), soft woods (Douglas fir, redwood, pine) [59], soft wood bark residue [104], spruce (Ingemarsson et al., 1998), stalk of rape seed plant Karaosmanoglu et al., 2000), straw (Blessa et al., 2001; Sipila et al., 1998; Karaosmanoglu et al., 2000; Blasi et al., 2000), straw pellet (Minkova et al., 2000), straw rape Bjorkman and Stromberg, 1997), straw stalk (Karaosmanoglu and Tetik, 1999), sugar cane bagasse (Rocha et al., 1999; Bjorkman and Stromberg, 1997; Garcia-Perez et al., 2001; Drummond and Drummond, 1996; Pindoria et al., 1999; Bilba and Ouensanga, 1996), sun flower (*Helianthus annulus* L.) pressed bagasse (Putun et al., 2001; Ozcan et al., 2000; Encinar et al., 1997; Yorgun et al., 2001), sun flower press oil cake (Yorgun et al., 2001), sun flower oil (Marqeuvich et al., 2000), sweet sorghum bagasse (Piskorz et al., 1998), swine manure (He et al., 2001), switch grass Bjorkman and Stromberg, 1997; Agblevor et al., 1996), synthetic biomass (raveendran et al., 1995), tea waste (Demirbas, 2001; Caglar and Demirbas, 2001), tobacco (Bassilakis et al., 2001; Encinar et al., 1997; Sharma et al./, 2002), tobacco dust (Valverde et al., 2000), used pallets (Reina et al., 1998), waste paper (Demirbas, 2001), waste wood chips (Horne and Williams, 1996), wheat straw (blasi et al., 1999; Bassilakis et al., 2001; Lanzetta and Blasi, 1998; Demirbas, 2001; Stenseng et al., 2001; Olsson et al., 1997), white birch wood (Jakab et al., 1997), white spruce (Ingemarsson et al., 1998), wood (Zanzi et al., 1996; Raveendran et al., 1995; Demirbas, 2001; Rao and Sharma, 1998; Rustamov et al.,

1998; Yu et al., 1997; Miller and Bellan, 1996; Ahuja et al., 1996; Brage et al., 1996), wood chips (Blasi et al., 1999; Wang et al., 1995), wood cylinders (Blasi et al., 2001), wood waste (Horne et al., 1995), and xylan (Yoshida and Matsumura, 2001; Bassilakis et al., 2001).

2.7.1 Types of Pyrolysis

Among other factors, temperature, heating rate, and residence time have noticeable effects on the product yields, qualities, and compositions (Horne and Williams, 1996). Pyrolysis can be broken down into two main types, depending on these three conditions. Fast or flash-pyrolysis is characterized by high heating rates, temperatures between 450 and 600°C, and short residence times of less than one second. These conditions prevent cracking of the vapors into non-condensable gases, maximizing the liquid product yield (Bridgwater and Bridge, 1991). Pyrolysis liquid yields can reach 80% (64 wt% organics and 16 wt% water) wt dry biomass feed through fast pyrolysis. To achieve maximum liquid production, temperatures should be around 500°C with residence times no longer than 1 second (Bridgwater, 1999).

Slow-pyrolysis would be utilized in the maximum production of solids or char. Slow-pyrolysis is characterized by higher residence times and slower heating rates to lower temperatures than fast pyrolysis (Horne and Williams, 1996). Other factors that affect the pyrolysis process include heat transfer, heat supply, feed preparation, vapor residence time, secondary vapor cracking, and reactor configuration (Bridgwater, 1999).

2.7.2 Fast Pyrolysis Reactors

According to Bridgwater et al. (2002) the reactor is at the heart of the pyrolysis process but only constitutes about 20% of the total capital cost. Aside from factors such as particle size and reaction temperature, The Biomass Pyrolysis Network (PyNe) has compiled an overview of several of the main fast pyrolysis reactor configurations used in the production of bio-oil (Table 2.6).

Table 2.6 Overview of Fast Pyrolysis Reactor Characteristics for Bio-oil Production

Property	Status#	Bio-oil wt%	Complexity	Feed size	Inert gas need	Specific size	Scale up
Fluid bed	Demo	75	Medium	Small	High	Medium	Easy
CFB	Pilot	75	High	Medium	High	Large	Easy
Entrained	None	65	High	Small	High	Large	Easy
Rotating cone	Pilot	65	High	V small	Low	Small	Hard
Ablative	Lab	75	High	Large	Low	Small	Hard
Vacuum	Demo	60	High	Large	Low	Large	Hard

White cells show desirable characteristics	# Demo = demonstration (200 - 2000 kg h^{-1})
Black cells show undesirable characteristics	# Pilot = pilot plant (200 - 200 kg h^{-1}
Grey cells show moderate characteristics	# Lab = laboratory (1 - 20 kg h^{-1})

Source: (Reactors, PyNe, 2009)

Fluid bed and circulating fluid bed (CFB) reactors have become the most popular reactor configurations for the production of liquid products.

2.7.2.1 Fluid Bed Reactors

In a fluid bed reactor, a gas is passed through a fluidizing medium, commonly sand, at great enough velocity to overcome the weight of each particle and suspend the particles

in the gas. Several companies have developed fluid bed reactors including Union Fenosa with a 200 kg/h pilot plant in Spain (Cuevas et al., 1995), Dynamotive with a 75 kg/h unit in Canada (PyNe, 1997), and Wellman with a 250 kg/h unit in the UK (Dynamotive, 2000). Because of their relative ease to build and operate, many research units have also been constructed (Bridgwater and Peacocke, 1999). Below is a list of beneficial factors of fluid bed systems:

- Simple construction and operation

- Good temperature control

- Efficient heat transfer to biomass particles due to high solids density

- Easy scaling

- Well understood technology

- Good and consistent performance with high liquid yields 70-75%wt. from wood on a dry feed basis

These features make fluid beds popular for research and development (Bridgwater et al., 2002). The heat for a fluid bed can be provided by several ways. The reactor can be heated by heated recycle gas, hot inert gas, partial gasification, or fire tubes (Bridgwater, 1999). One drawback to fluid bed reactors is the necessity for small particle sizes (<2-3 mm) to achieve high heating rates (Bridgwater et al., 2002).

2.7.2.2 Circulating Fluid Beds (CFB) and Transported Bed Reactors

Circulating beds contain a fine fluidizing medium which is blown out of the reactor by high gas velocities and must be replaced by recycled or new fluidizing medium (Kunii and Levenspiel, 1997). Like bubbling fluid beds, circulating fluid and transported beds have been scaled to commercial sizes by several companies. Red Arrow (WI, U.S.A.) produces food flavorings from biomass pyrolysis liquids. Their reactor handles a rate of 1 to 1.5 tons/h (Underwood, 1992). ENEL in Italy has a 650 kg/h system (Rossi and Graham, 1997) and VTT in Finland has a 20 kg/h system (PyNe, 1997). Each of these units is based on a design and process developed by Ensyn. Liquid yields are reported between 60 and 70% wt on a dry feed basis. In reactors of this type, the sand alone or the sand and char can be recycled for process energy. If the char is recycled, a second reactor might be needed to burn the char and collect the heat or this can occur in the lower part of the pyrolyser (Bridgwater et al., 2002). The latter method is utilized by CRES, where a char combustor is integrated into the base of the CFB (Boukis, 2001). Table 2.7 presents some of the advantages and challenges of CFB and transported bed reactors.

Table 2.7 Advantages and Challenges of CFB and Transported Bed Reactors

Advantages	Challenges
Good temperature control in reactor	Hydrodynamics are more complex
Residence time is nearly the same for all product phases	Char is more attrited due to higher gas velocities
Suitable for very large throughputs	Closely integrated char combustion in second reactor requires careful control
Well understood technology	Heat transfer at large scale has to be proven

Source: (Bridgwater et al., 2002)

2.7.2.3 Ablative Reactors

Ablation is the process in which a solid material, subjected to a high external heat flux density undergoes superficial melting and/or sublimation reactions, with rapid elimination of the products (Lede, 2003). Ablative reactors are unique in their mode of heat transfer. In other reactor configurations, the limiting factor to the rate of reaction is heat transfer through a particle. In ablative pyrolysis, particles are forced against the wall of the reactor under pressure and "melted" like butter on a frying pan so the limiting factor is the heat transfer to the reactor and not the biomass. Ultimately the rate of reaction is strongly influenced by pressure, the relative velocity of biomass on the heat exchange surface and the reactor surface temperature (Bridgwater, 2002). Ablative pyrolysis makes it possible to reach fast pyrolysis reactions with the use of lower temperatures and larger pieces of biomass than other methods (Lede, 2003). Scale-up is a challenge with ablative pyrolysis. The process is controlled by surface area and the ratio of surface area to reactor volume decreases as reactor size increases. Additionally, the process is driven mechanically so the system is more complex (Bridgwater, 2002). The National Renewable Energy Laboratory (NREL) has achieved liquid yields of 60-65% wt on dry feed basis using an ablative vortex reactor. A prototype rotating blade reactor at Aston has been developed that has resulted in liquid yields of 70-75% wt on a dry feed basis (Bridgwater and Peacocke, 1999).

2.7.2.4 Rotating Cone Reactors

In a rotating cone reactor, a heated rotating cone spins at around 600 rpm, driving hot sand and biomass up the heated cone and vapors are collected and processed conventionally (Bridgwater, 2002). This reactor was first invented at the University at

Twente (Prins and Wagenaar, 1997). The char is combusted in a secondary fluid bed combustor and the sand is recirculated to the pyrolyser. This requires the complex integrated operation of three subsystems: rotating cone pyrolyser, fluid bed char combustor, and riser for recycling the sand. Typical liquid yields are 60-70% wt on a dry feed basis (Bridgwater, 2002).

2.7.2.5 Vacuum Reactors

Some say that vacuum pyrolysis is not a true fast pyrolysis process because the heat transfer rate to and through the solid is not as fast as typical fast pyrolysis but the vapor residence time is comparable (Bridgwater, 2002). The process has been scaled-up by Pyrovac at Jonquiere in Canada. This unit processes 3.5 tons/h of biomass feedstock (Yang et al., 2001). Three distinct advantages to vacuum pyrolysis include the ability to process larger particles than most reactors, less char in the liquid because of lower gas velocities, and there is no requirement for a carrier gas. Liquid yields of 35-40% wt on a dry feed basis are typically obtained (Bridgwater, 2002).

2.7.3 Pyrolysis Liquid – Bio-oil

Crude pyrolysis liquid is a dark brown free flowing substance and is referred to by many names including pyrolysis oil, bio-oil, bio-crude-oil, bio-fuel-oil, wood liquids, wood oil, liquid smoke, wood distillates, pyroligneous tar, pyroligneous acid, and liquid wood. The color and chemical composition of the liquid can change depending on the initial feedstock and mode of fast pyrolysis (Bridgwater, 2002). The liquids are multi-component mixtures of different size molecules derived from depolymerization and fragmentation of cellulose, hemicellulose and lignin (Zhang et al., 2007). Tables 2.8 and

2.9 show representative chemical compositions and typical physiochemical properties of

wood derived bio-oil.

Table 2.8. Representative chemical composition of fast pyrolysis liquid

Major Components	Mass %
Water	20-30
Lignin fragments: insoluble pyrolytic lignin	15-30
Aldehydes: formaldehyde, acetalhyde, hydroxyacetalhyde, glyoxal,	10-20
methylglyoxal	10-15
Carboxylic acids: formic, acetic, propionic, butyric, pentanoic, hexanoic,	
glycolic, hydroxy acetic	5-10
Carbohydrates: cellobiosan, α-D-levoglucosan, oligosaccharides, 1.6	
anhydroglucofuranose	2-5
Phenols: phenol, cresols, guaiacols, syringols	1-4
Furfurals	2-5
Alcohols: methanol, ethanol	1-5
Ketones: acetol (1-hydroxy-2-propanone), cyclo pentanone	

Source: (Bridgwater, 2002)

Table 2.9. Typical properties and characteristics of wood derived crude bio-oil

Physical Property	Typical Value	Notes
Moisture	25%	Water comes from moisture in the feed and reaction. Values can range from 15 to 35%
pH	2.5	The low pH comes from organic acids
Density	1.2	Very high at around 1.2 kg/l compared to light fuel oil at around 0.85 kg/l. Bio-oil has about 40% of the energy content of fuel oil on a weight basis, but 60% on a volumetric basis
Elemental analysis		Typically: C: 57%, H: 6.0%, O: 37%, N: trace; Ash; trace depending on char content
Ash	0%	All ash is associated with the char
HHV as produced (depends on water)	18 MJ/kg	Bio-oil has a higher heating value of about 18 MJ/kg as produced with about 25% wt. water that cannot be separated
Viscosity (at 40 °C and 25% water)	50 cP	Viscosity as produced can vary from 20 cSt to as high as 1000 cSt (measured at 40 °C) depending on feedstock, water content, light and ageing
Solids (char)	0.20%	0.1 wt.% is a good level and 1% is often encountered
Vacuum distillation residue	50%	Cannot be completely vaporized. Heating to 100 °C causes production of a solid residue of around 50 wt.% of the original liquid and distillate containing volatile organics and water
Appearance		Typically a dark brown free flowing liquid
Odor		A distinctive smoky smell
Miscibility		Water addition can be tolerated up to about 35% wt. Bio-oil is miscible with polar solvents such as methanol, but totally immiscible with petroleum-derived fuels

Source: (Bridgwater, 2002)

Bio-oils from pyrolysis can substitute for conventional fuels and have a heating value about 40% of the value of fuel oil or diesel. The oil does not mix with hydrocarbon fuels and is not as stable as fossil fuels (Bridgwater, 2002). The presence of oxygen in bio-oils is the main cause for differences in the properties and behavior between hydrocarbon

fuels and biomass pyrolysis oils (Oasmaa and Czernik, 1999). Because of the complexity and nature of bio-oil, some properties change with time. The viscosity increases, volatility decreases, and phase separation and deposition of gums can occur. These changes are due to interactions of physical and chemical processes including polymerization/condensation, esterification and etherification, and agglomeration of oligomeric molecules (Bridgwater, 2002).

2.8 Pyrolysis of Poultry Litter

Most research into pyrolysis for the production of liquid fuels is focused on wood and other planty biomass. Kim and Agblevor (2007) have studied the pyrolysis of poultry litter through thermal gravimetric analysis (TGA). The TGA allows researchers to recognize the major decomposition characteristics of the biomass. Figure 2.2 displays a TGA analysis of poultry litter compared to that of wood alone.
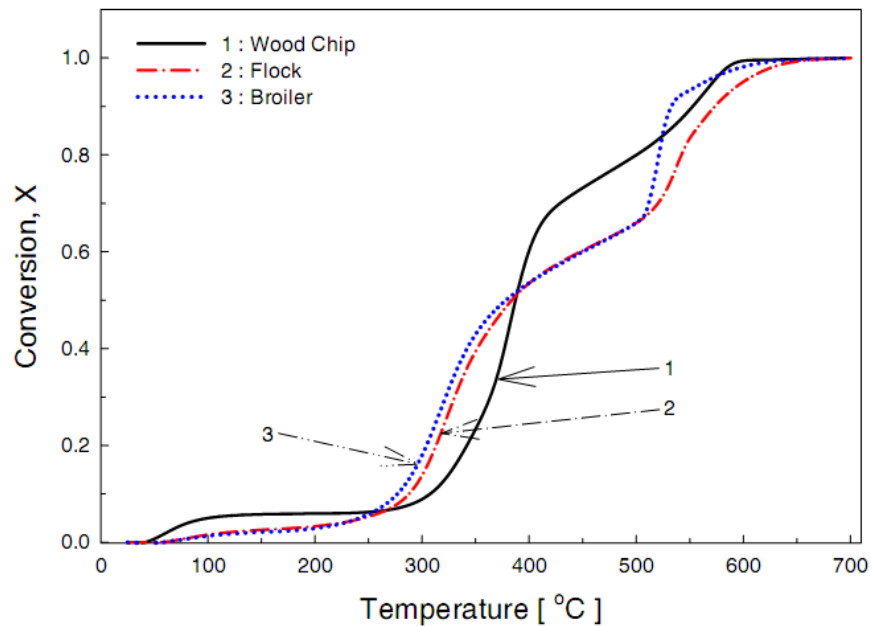
Figure 2.2. TGA of wood chips, flock and broiler at heating rate of 10°C/min.

Source: Kim and Agblevor, 2007.

The decomposition of the litter took place in three main regions of weight loss. The first occurred between 270 and 370°C is attributed to the decomposition of mostly cellulose and hemicelluloses. The second region between 375 and 500°C is due to the decomposition of manure and lignin. The third region between 500 and 550°C results from the decomposition of charcoal produced in the first two regions (Kim and Agblevor, 2007). According to Agblevor et al., bio-oil yields ranged from 30 to 50 percent by weight, depending on the age and the bedding content of the litter. Bedding material that was mostly hardwood shavings yielded bio-oil as high as 62 percent by weight. The higher heating value of the poultry litter bio-oil ranged from 26 to 29 MJ/kg while bio-oil from bedding material was only 24 MJ/kg. The bio-oils had relatively high nitrogen content of 4-7% by weight, very low sulfur content, <1% by weight, and were very viscous. The char yield ranged from 30 to 50 % by weight, depending on the source, age, and composition of the poultry litter. The char also had a high ash content, ranging from 30 to 60 % by weight, depending on the age and source of litter (Abglevor et al., 2007).

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CHAPTER 3

CHARACTERIZATION OF POULTRY LITTER AND BIODEGRADABLE LITTER AMENDMENT (AMMOSOAK)

Broiler litter is a mixture of avian urine and manure, mortal birds, bedding material, insects, and spilled feed. The bedding material is typically a cellulosic material ranging from wood shavings to pine needles to peanut shells. In order to ensure the health of a grower's birds, the grower will clean out the houses periodically. Traditionally, a total clean out of the litter is carried out every 8-10 flocks, but recently, more conventional methods aimed at cutting costs and labor have been used. Most growers today practice "decaking" in which only the fresh manure mixed with bedding and spilled feed are removed. This "cake" is usually a layer 5-10 cm thick and varies greatly in composition throughout the house (Sistani et al., 2003). This practice allows the growers to only add enough fresh bedding material to make up for the cake removed. The composition of broiler litter varies greatly. Whether a traditional or modern approach is taken to cleaning the litter from houses affects the composition of the litter. It was recognized as far back as 1967 that nitrogen (N), phosphorous (P), and potassium (K) levels depended on the number of flocks raised between cleanouts and also what type of bedding was used (Hileman, 1967). Other factors that affect the composition of poultry litter include the age and breed of birds, density of confinement, feed conversion rate, feed ration, moisture content of bedding material, type of floor (dirt, concrete, etc.), climatic conditions during litter accumulation, and any organic matter and N losses (Perkins et al., 1964).

AmmoSoak is a biodegradable litter amendment used to reduce odor and ammonia emissions. It is prepared by steam-exploding corn cobs and other agricultural residues.

Steam explosion is a thermomechanochemical process. Decomposition of the material is assisted by heat in the form of steam (thermal), shear forces from the expansion of moisture (mechanical), and hydrolysis of glycosidic bonds (chemical) (Overend and Chornet, 1987). The final product from a steam explosion process is strongly influenced by time, temperature, pressure, particle size, and moisture content (Saddler et al., 1993). The corn cob used in this study refers to the material left after the kernels are removed from the ear of corn. One kg of untreated corn cob on a dry basis will typically contain 391 g of cellulose, 421 g of hemicelluloses, 91 g of lignin, 17 g of protein, and 12 g of ash (Barl et al., 1991). Once steam exploded the AmmoSoak is dark brown in appearance and looks very much like dark soil.

3.1 Materials and Methods

3.1.1 Materials

Poultry litter for this experiment was collected from the floor of a broiler poultry house in Dayton, Virginia located in the Shenandoah Valley. AmmoSoak was prepared from steam explosion experiments on corn cob performed at the Thomas M. Brooks Forest Products Center (Virginia Tech). All materials were air dried and ground in a knife mill to pass a 1 mm mesh.

3.1.2 Methods

3.1.2.1 Moisture Content

Prior to pyrolysis, all samples were analyzed for their moisture content using an HG53 Halogen Moisture analyzer (Mettler Toledo, Greifensee, Switzerland). The HG53 heats 1

g of sample to 105°C over a time of 30 minutes and records the weight loss. The analyzer then displays the moisture content as percent moisture. The moisture contents were measured twice to ensure repeatability.

3.1.2.2 Analysis of Feedstock

The elemental composition and higher heating value of each material were determined by Galbraith Analytical Laboratory (Knoxville, Tennessee). The ash content of the broiler litter and AmmoSoak was determined using ASTM E1755 standard method. 1 g of sample was dried at 105ºC. The mass after drying was recorded as the mass of total solids in the sample. The sample was then placed in a porcelain crucible and the total mass recorded. The sample and crucible were then placed in a Thermolyne 1400 muffle furnace (Barnstead International, Dubuque, Iowa, USA) at 575°C for 8 h. At that point the crucible and sample were massed again. The difference between the masses before and after the furnace, divided by the mass of total solids, equaled the mass percentage of ash in the sample.

3.1.2.3 Bulk Density

The bulk density of the broiler litter and AmmoSoak was determined by ASTM method D1895B. This involved pouring the material to be measured through a funnel supported on a ring stand into a 100 mL graduated cylinder until the level reached 100mL. The cylinder was weighed before and after filling and the difference recorded as the mass per 100 mL. The bulk density was then calculated by dividing the mass by the volume. The bulk densities were measured in triplicate to ensure repeatability.

3.1.2.5 Thermogravimetric Analysis

Thermogravimetric analysis (TGA) was conducted on the broiler litter and AmmoSoak using a TA Instruments Q600 SDT (TA Instruments, New Castle, DE, U.S.A.). 20 mg of sample was placed in an alumina crucible and was subjected to thermogravimetric analysis with 50 ml/min of nitrogen as a carrier gas. The heating rate was at 5ºC/min from 25ºC to 700ºC.

3.1.2.6 Odor Evaluation

To determine the minimum proportion of AmmoSoak that would be effective in reducing the odor of the litter to a level acceptable by workers, five human subjects were exposed to samples with increasing proportions of AmmoSoak until they felt comfortable working in the environment. The samples began with 0% AmmoSoak and increased in increments of 5 wt.% AmmoSoak on a dry basis.

3.2 Results and Discussion

3.2.1 Bulk Density, Moisture Content, and Materials Composition

Table 3.1 shows the ultimate analysis of the broiler litter and AmmoSoak used in the pyrolysis experiments. The moisture content of the litter (11.3±0.48%) was very close to the minimum moisture content (12%) suggested by McKinley (2000) to prevent the litter from being excessively dusty during handling and processing, however, is was more than 100% greater than that of the AmmoSoak (4.9±0.38%). Adding AmmoSoak to the broiler litter reduced the overall moisture content of the feed and should have reduced the moisture content of the oils as well. The bulk densities of the two feeds were practically

identical at 0.43 kg/L. This is the same bulk density as that reported for oats (K-Tec, 2009). The fact that they were equal would mean that they shouldn't have separated too much in the storage and feeding processes, ensuring a consistent feed into the reactor. The ash content of the broiler litter (17.35±0.27%) was much greater than that of the AmmoSoak (1.11±0.07%) but 25% less than the average for broiler litter reported by Stephenson et al. (1990). The broiler litter had a much greater ash content than the AmmoSoak due to the fact that a certain amount of soil is collected when cleaning out a house as well as the mineral content of the poultry manure in the form of Ca, K, and P. The carbon (C) content of AmmoSoak (35.62%) was 22% greater than that of the broiler litter (29.16%). The nitrogen (N) content of the broiler litter (3.76%) was equal to the average nitrogen content reported by Stephenson et al. (1990) for broiler litters. This was significantly greater than that of the AmmoSoak (<0.5%). The greater nitrogen content was a result of uric acid in the broiler litter as well as other proteins from the manure and mortal bird content of the broiler litter. Broiler litter had lower carbon, hydrogen (H), and oxygen (O) levels than the AmmoSoak due to its relatively high ash content (Table 3.1). The oxygen content of this broiler sample (41.95%) was greater than those reported in other literature (34.05%) probably leading to the lower higher heating value as well (Kim et al., 2009). On the other hand, the sulfur and chlorine levels of the broiler litter were much greater than those of the AmmoSoak (Table 3.1).

Table 3.1 Materials characterization of broiler litter and AmmoSoak

	Material	
Composition	Litter	AmmoSoak
C (wt.%)*	29.16	35.62
H (wt.%)*	4.64	5.51
N (wt.%)*	3.76	<0.5
O (by diff.) (wt.%)*	41.95	57.52
S (wt.%)*	0.854	<0.05
Cl (wt.%)*	0.817	0.128
HHV (MJ/kg)	14.32	12.98
Ash (wt.%)	17.35±0.27	1.11±0.08
Moisture (wt.%)	11.3±0.48	4.9±0.38
Bulk Density (kg/L)	0.43±0.06	0.43±0.03

* Moisture free basis

3.2.2 Thermogravimetric Analysis

Thermogravimetric analyses were performed on each feedstock using a TA Instruments Q600 SDT. Figures 3.1 and 3.2 show the TG and DTG curves for each feedstock. The analysis showed that broiler litter exhibited several regions of weight loss between 84°C and 706°C. The first weight loss at 84.8°C was attributed to the evaporation of water and the decomposition of light volatile compounds, one of which was probably ammonia. The weight loss region between 141°C and 190°C was most likely due to the decomposition of hemicelluloses. Cellulose from the bedding material in the litter is most likely represented by the peaks between 311°C and 323°C (Guar and Reid, 1994). The decomposition of manure and lignin probably accounted for the weight loss region between 405°C and 464°C. The region from 465°C and 706°C was attributed to charcoal formed by the pyrolysis of the litter and proteins from the manure (Kim and Agblevor, 2007).

The decomposition of AmmoSoak occurred in three main stages. The first weight loss region occurred at about 190°C due to the decomposition of hemicelluloses. Some of the less thermally stable hemicelluloses were probably hydrolyzed and removed in the steam explosion process, resulting in the much smaller peak than might be expected and a hemicellulose peak at greater temperature than that of the ltter. The second stage of maximum weight loss occurred at 323°C and was most likely due to cellulose. The third, which was rather broad, occurred between 400 and 600°C and was attributed to further devolatilization of residual charcoal.

Figure 3.3 shows the TG curves of broiler litter, AmmoSoak, and a 50/50 blend of the two. The peak at 84.7°C, which was attributed to the evaporation of water and decomposition of light volatile compounds, was much more pronounced in the broiler litter than the AmmoSoak and the peak of the 50/50 blend was in between the other two. This could have arisen from the fact that the moisture and ammonia contents of the litter were greater than that from AmmoSoak. The contribution more thermally stable hemicelluloses to the mixture from AmmoSoak can be seen in the peak at 190°C. The broiler litter contributed to the cellulose shoulder in the 50/50 blend at 248°C. All three exhibited the strong peaks between 311 and 323°C, indicating high cellulose contents. It is worth noting that the differences in these peak temperatures could be attributed to a difference in the crystallinity of the cellulose. The cellulose peak of the blend shifted from 311°C for broiler litter alone to 314°C. It is known that the steam explosion of biomass increases its crystallinity. Very small contributions of the more thermally stable proteins in the litter could be seen at temperatures greater than 400°C. The addition of

AmmoSoak to broiler litter created a complex mixture of carbohydrates, lignin, and proteins.
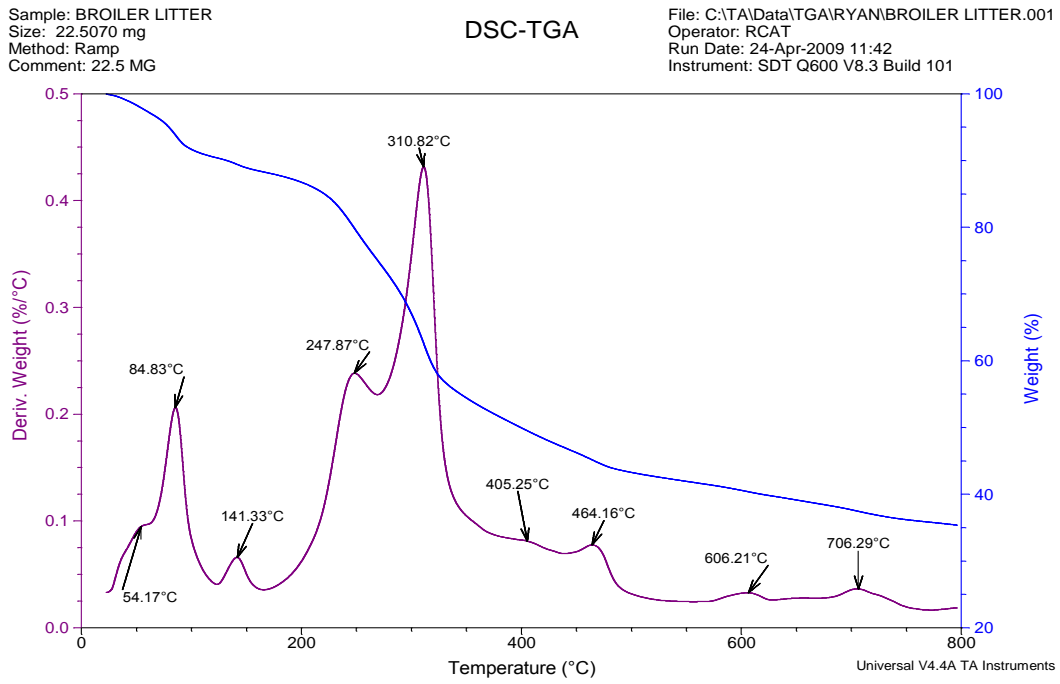
Figure 3.1 Thermogravimetric curve of broiler litter

Sample: AmmoSoak
Size: 21.5060 mg
Method: Ramp
Comment: 21.5 mg

DSC-TGA

File: C:\TA\Data\TGA\RYAN\AmmoSoak.001
Operator: RCAT
Run Date: 27-Apr-2009 16:41
Instrument: SDT Q600 V8.3 Build 101
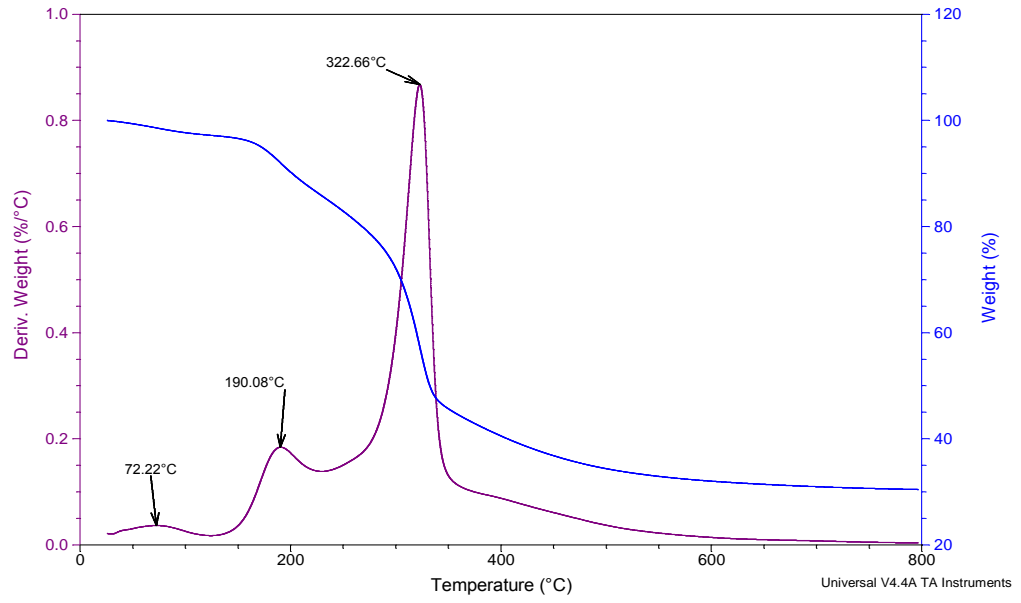
Figure 3.2 Thermogravimetric curve of AmmoSoak
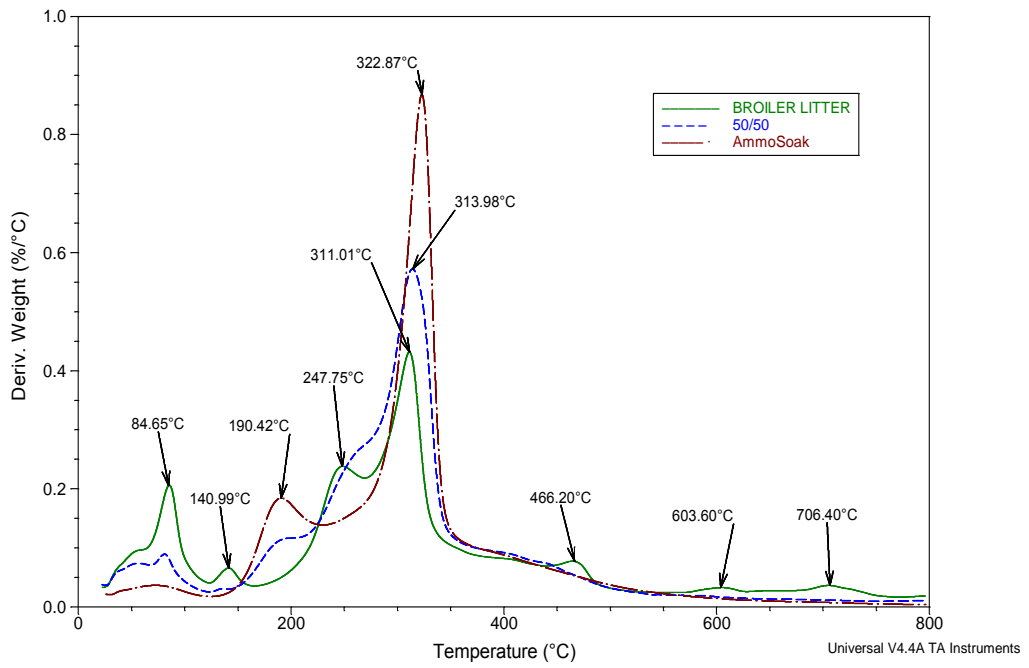
Figure 3.3 Thermogravimetric curve of broiler litter, AmmoSoak, and a 50/50 blend

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3.2.3 Odor Evaluation

Table 3.2 shows the results from the odor evaluation. For each proportion of AmmoSoak, the subject responded with a yes or no indicating whether or not they would feel comfortable working in that environment. Although a majority of the five subject tested were not comfortable until 15 dry wt.%, two subject were comfortable at 10 dry wt.%. Therefore, the minimum proportion of AmmoSoak tested in the pyrolysis experiments was 10 dry wt.%.

Table 3.2 Results of the odor evaluation. A yes indicates an acceptable proportion for reducing odor emissions.

Subject	Proportion of AmmoSoak					
	0	5	10	15	20	25
1	NO	NO	NO	YES	YES	YES
2	NO	NO	NO	YES	YES	YES
3	NO	NO	YES	YES	YES	YES
4	NO	NO	NO	YES	YES	YES
5	NO	NO	YES	YES	YES	YES

3.3 Conclusions

The characterization of broiler litter and AmmoSoak by means of ultimate analysis and thermogravimetric analysis of differential scanning calorimetry showed that the two had very different elemental compositions and ash contents. Broiler litter had greater amounts of proteins and therefore nitrogen, and inorganic compounds. On the other hand, AmmoSoak was composed mainly of carbohydrates. This suggested that the pyrolysis

and the resulting product compositions would be different for the two feedstocks and their mixtures. The addition of the carbohydrate content of lignin should result in greater amounts of alcohols, phenols, and aliphatic carbonyl/carboxyl groups in bio-oils with greater AmmoSoak contents. On the other hand, the proteins in the manure of the broiler litter should lead to the production of amides and other nitrogenous compounds.

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CHAPTER 4

INFLUENCE OF AMMOSOAK ON THE PYROLYSIS OF POULTRY LITTER

Diminishing supplies of fossil fuels are spurring interest in alternative sources of fuel. Biomass can provide an alternative and more environmentally friendly fuel source (Acikgoz and Kockar, 2006). Energy utilization from biomass poses less environmental pollution and health risk than fossil fuel utilization due to the lower levels of nitrogen and sulfur in the biomass (Tsai et al., 2007). At the same time, traditional uses of poultry litter have raised concerns over bio-security and other environmental issues, motivating alternative disposal methods to be used (Kelleher et al., 2002). Studies have already shown that waste from the poultry industry could be a feasible source for renewable energy (Graham, 1999). Thermochemical conversion technologies are receiving the most attention for the utilization of biomass to produce fuels and chemicals. There are four main categories of thermochemical conversion: pyrolysis, liquefaction, gasification and combustion (Bridgwater and Peacocke, 2000). Amongst these, pyrolysis is attractive because the process conditions can be optimized to maximize yields of liquid, solid, or gaseous products (Acikgoz and Kockar, 2006). Pyrolysis liquids are also known as bio-oils. Bio-oil yields from wood pyrolysis can be as high as 75%. Bio-oil yields from poultry litter pyrolysis are lower because of the greater ash contents in the litter. Bio-oils from pyrolysis are a complex mixture of oxygenated hydrocarbons with a noticeable moisture content arising from the original moisture in the biomass and water produced during the reaction (Bridgwater et al., 2002). The oxygen in bio-oils has been found in more than 200 compounds identified (Soltes and Elder, 1981).

Many bio-oils have been evaluated for applications including boilers, furnaces, engines, and turbines for generation of electricity or heat (Bridgwater et al., 2002). Unlike wood, poultry litter contains large amounts of inorganic material such as potassium (K), calcium (Ca) and phosphorous (P) that affect the pyrolysis. The bio-oil yields and compositions vary with the age and bedding material content of the litter (Agblevor et al., 2007). If poultry litter pyrolysis is to be applied on a large-scale for production of renewable energy, the influence of a biodegradable litter amendment (AmmoSoak) to reduce ammonia and odor emissions on the pyrolysis product yields and qualities must be studied.

4.1 Materials and Methods

4.1.1 Materials

4.1.1.1 Feedstock Preparation

Poultry litter for this experiment was collected from the floor of a broiler poultry house in Dayton, Virginia located in the Shenandoah Valley. AmmoSoak was obtained from steam explosion experiments on corn cob performed at the Thomas M. Brooks Forest Products Center (Virginia Tech). Steam explosion of the corn cob was performed at 212ºC with a residence time of 2.5 minutes. All materials were dried at ambient air conditions to moisture contents of 4.9±0.38% for AmmoSoak and 11.3±0.48% for broiler litter. The samples were ground in a knife mill to pass a 1 mm mesh. Mixtures of litter and AmmoSoak were prepared in fractions of 100:0, 90:10, 85:15, and 0:100 wt/wt.

4.1.2 Methods

4.1.2.1 Pyrolysis of Feedstocks

Fast pyrolysis was performed on a bench-scale fluidized bed reactor unit at the Biological Systems Engineering Bioresource Engineering Laboratory, Virginia Tech, Virginia. A schematic diagram of the unit is shown in Figure 4.1. The unit comprised of a K-Tron volumetric feeder, 50 mm bubbling fluidized bed reactor equipped with a 100 μm porous metal gas distributor, hot gas filter, two chilled glycol/water cooled condensers, an electrostatic precipitator, and a packed column. The reactor was externally heated by a three-zone clam-shell electric furnace (Thermcraft, Winston-Salem, NC). 100 g of silica sand was used as the fluidizing medium and the bed was fluidized with nitrogen gas at 11 L/min. The sand particles had a surface mean diameter of 391μm. 650 g of feedstock mixture was pyrolyzed at 445°C at a feed rate of 350 g/h. The feedstock was moved from a feed hopper to an entrainment zone by means of a screw conveyer. A nitrogen sweep gas at 9 L/min entrained the feed particles from the entrainment zone through an air-cooled feed tube into the bubbling fluidized bed reactor. The reactor temperature, feed rate, and gas flow rates were kept constant during each experiment. Reaction products were separated and collected after leaving the reactor. A hot-gas filter operating at an average temperature of 360°C separated and collected the solid char fraction. The remaining mixture of condensable vapors and non-condensable gases were separated using two glycol/water cooled condensers in series, an electrostatic precipitator (ESP), and a packed column of glass beads. The condensers were maintained at -10°C with a 50/50 cooling mixture of ethylene glycol and water from an 18-liter A82 refrigerated

circulating bath (Haake, Karlsruhe, W. Germany). The ESP voltage was maintained at 20 kV.
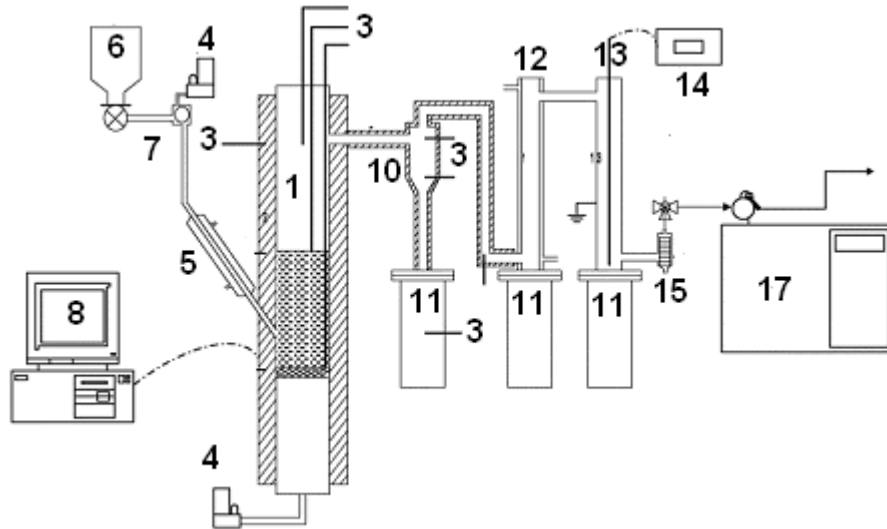
Figure 4.1 Schematic diagram of fluidized bed reactor unit

(1-Fluidized bed, 3- Thermocouple, 4-Mass flow controller, 5- Jacketed air-cooled feeder tube, 6-Hopper, 7-Screw feeder, 8-Computer, 10-Hot gas filter, 11-Reservoir, 12-Condenser, 13-ESP, 14-AC power supply, 15-Packed column filter, 17-Gas Chromatograph)

4.1.2.2 Pyrolysis Product Yields

The mass of char and bio-oil was determined gravimetrically. The char was determined by massing the reactor and hot-gas filter before and after each experiment. The difference was the mass yield. Bio-oil yields were determined with the same method using each of the condensers, the ESP, and the packed column. The gas yield was then calculated as the difference from 100%. Each yield was expressed in weight percentage on a moisture free basis.

4.1.2.3 pH, Density, Water Content, Viscosity, and Elemental Analysis and Higher Heating Value (HHV)

The pH of the oil was measured using a Corning 440 pH Meter equipped with an F-55500-10 Accumet pH probe (Cole-Parmer Instrument Company, Vernon Hills, IL, USA). The meter was frequently calibrated using standard pH solutions (MicroEssential Lab Inc., N.Y., U.S.A.).

The density of the oils was determined using a 2mL Gay-Lussac specific gravity bottle calibrated to ASTM Test Reference D-369. The specific gravity bottle was massed and the scale tared. The bottle was then filled with oil and a glass stopper inserted to seal the bottle. The stopper had a capillary that allowed excess volume of oil to escape the specific gravity bottle. The bottle and oil were then massed again. The density was then calculated by dividing the mass of oil by the volume of the bottle (1.98mL). All measurements were taken at 23°C.

To determine the water content of the oils, volumetric Karl Fischer titration was performed utilizing a Metrohm 701KF Titrino (Brinkmann Instruments, Inc, N.Y, U.S.A) and a 703 titration stand. The titration reagent used was Hydranal® Composite 5. 40 mL of methanol was placed in the titration vessel and conditioned. A plastic hypodermic syringe was used to draw about 1 g of oil sample and massed. The sample was injected into the titration solvent. The syringe was massed again and the difference was recorded as the mass of sample. The water content was expressed as a percentage of the amount of sample used.

Dynamic viscosities were measured using a Brookfield DV-II+Pro viscometer (Brookfield Engineering laboratories, Inc. MA, USA.) and a programmable thermosel

temperature controller. All measurements were made at 60ºC. A sample volume of 7 mL was used and the viscometer was allowed to stabilize before a reading was taken.

Elemental analysis (C, H, N, O, S, and Cl), ash, and HHV of the oils collected from the ESP were determined by Galbraith Analytical Laboratory (Knoxville, TN, USA).

4.1.2.4 Thermogravimetric Analysis, FT-IR, and Carbon-13 Nuclear Magnetic Resonance Spectrometry (^{13}C-NMR)

Thermogravimetric analysis (TGA) was conducted on the oil using a TA Instruments Q600 SDT (TA Instruments, New Castle, DE, U.S.A.). 20 mg of sample was placed in an alumina crucible and was subjected to thermogravimetric analysis with 50 ml/min of nitrogen as a carrier gas. The heating rate was 5ºC/min from 25ºC to 700ºC.

FT-IR analyses were performed on the oils using an IR spectrometer (Nicolet Avatar, 370 DTGS) equipped with a DTGS-KBR detector in multi-bounce horizontal attenuated total reflectance (HATR) mode. The spectrum was collected over a range of 4000-650 cm^{-1}. A 4 cm^{-1} resolution was used over 64 scans. A background gain of 4.0 was used. Data analysis was performed using the OMNIC 7.3 (Thermo Electron Corporation) software package.

^{13}C-NMR spectrometry was performed by the Chemistry Department at Virginia Tech using a Varian Unity 400 MHz NMR spectrometer. In a 10 mm sample tube, 2 g of oil was dissolved in 2.5 mL of dimethyl sulfoxide (DMSO). The observing frequency was 100.58 MHz. The pulse width, acquisition time, and recycle delay were 8.5 μs, 1.31 s, and 1 s, respectively. 1000 scans were taken at a sweep width of 25.0 MHz.

4.2 Results and Discussion

4.2.1 Pyrolysis of AmmoSoak

The product yields from the pyrolysis of AmmoSoak can be seen in Table 4.1. The product yields were all very similar to those reported in literature for the fast pyrolysis of corn cobs in a fluidized bed reactor (Yanik et al., 2007). The average oil yield was 45.2 wt.%, which is only 1.8% lower than that reported in literature (47 wt.%). The reported char yield of corn cobs was 23 wt.%, while the char yield from the pyrolysis of AmmoSoak was 27 wt.%. The gaseous product yield from AmmoSoak (28 wt.%) was only 2% lower than that reported in the literature (30 wt.%) (Yanik et al., 2007). These differences could be explained by some of the physicochemical changes that occur in biomass when subjected to steam-explosion including increased surface area, enhanced pore volume due to xylan removal, reduced cellulose degree of polymerization, increased biomass crystallinity, and melting and relocation of lignin (Grous et al., 1986), (Michalowicz et al., 1991), and (Wong et al., 1988).

Table 4.1 Summary of Product Yields from the Pyrolysis of AmmoSoak

Yield (wt.%)*		
Oil	**Char**	**Gas****
45.2±1.25	26.8±1.07	28.0±1.17

* Moisture free basis

**By difference

4.2.1.1 Physicochemical Properties of AmmoSoak Bio-oil

The physicochemical properties of AmmoSoak bio-oils are shown in Table 4.2. Bio-oils from the pyrolysis of AmmoSoak were acidic with a pH of 4.53. An acidic oil could prove to be corrosive to equipment used in certain applications such as pumps and boilers. The density of the oils was 1.16 g/mL. This was slightly greater than those of crude oils (0.80-1.0 g/mL), fuel oil (0.90 g/mL), and gasoline (0.75 g/mL) (Walker, 2007). The viscosity of the oils was rather high. The viscosity of olive oil at 60ºC is 19 cP while that of the AmmoSoak bio-oil was nearly twice that at 33.4 cP (Hansen, 1986). Both the density and viscosity could pose challenges to the utilization of AmmoSoak bio-oils. Table 4.2 shows that the ash content of the oil was very low, less than 0.09% because the low ash content of AmmoSoak and the use of the hot gas filter. Pyrolysis of the AmmoSoak almost doubled the energy density. Prior to pyrolysis, the HHV of the AmmoSoak was 13.0 MJ/kg while that of the resulting oil was 25.3 MJ/kg. The bio-oils from AmmoSoak were composed mainly of carbon (C) and oxygen (O) (Table 4.2), resulting in an average chemical composition of $CH_{1.28}N_{0.007}O_{0.32}$.

Table 4.2 Summary of Physicochemical Properties of AmmoSoak Bio-oils

Property	
Water Content (wt.%)	4.53
pH	3.56
Density @ 23C (g/mL)	1.16
Dynamic Viscosity @ 60C (cP)	33.4
Ash Content (wt.%)	<0.09
High Heat Value (MJ/kg)	25.3
Elemental Composition (wt.%)*	
C	65.15
H	6.70
N	0.61
O**	27.32
S	<0.05
Cl	<0.08
H/C molar ratio	1.24
O/C molar ratio	0.31
N/C molar ratio	0.01
Average Chemical Composition	$CH_{1.28}N_{0.007}O_{0.32}$

*Moisture free basis

**By difference

4.2.1.2 Thermogravimetric Analysis of AmmoSoak Bio-oil

Thermogravimetric (TG) and differential thermogravimetric (DTG) analyses were performed on each bio-oil. All analyses were performed under nitrogen at a heating rate of 5°C/min. The nitrogen flow rate was 50 ml/min. The TG and DTG plots are shown in Figure 4.2. The TG curve shows that the weight loss of the oil was a gradual process with no clear steps. The oils showed small peaks below 81°C. These peaks were attributed to the decomposition of light volatile compounds such as acetic acid, methanol, etc. (Lu et al., 2008). A major weight loss occurred at 126°C. This peak was most likely caused by the degradation of monolignols which are source materials for the biosynthesis of both

lignans and lignin. The peaks between 200°C and 310°C were probably from the degradation of cellulose degradation products such as levoglucosan (Mante, 2008). Any remaining peaks at temperatures greater than 335°C were attributed to the degradation of heavy non-polar compounds such as hydrocarbons and ethers (Garcia et al., 2007).
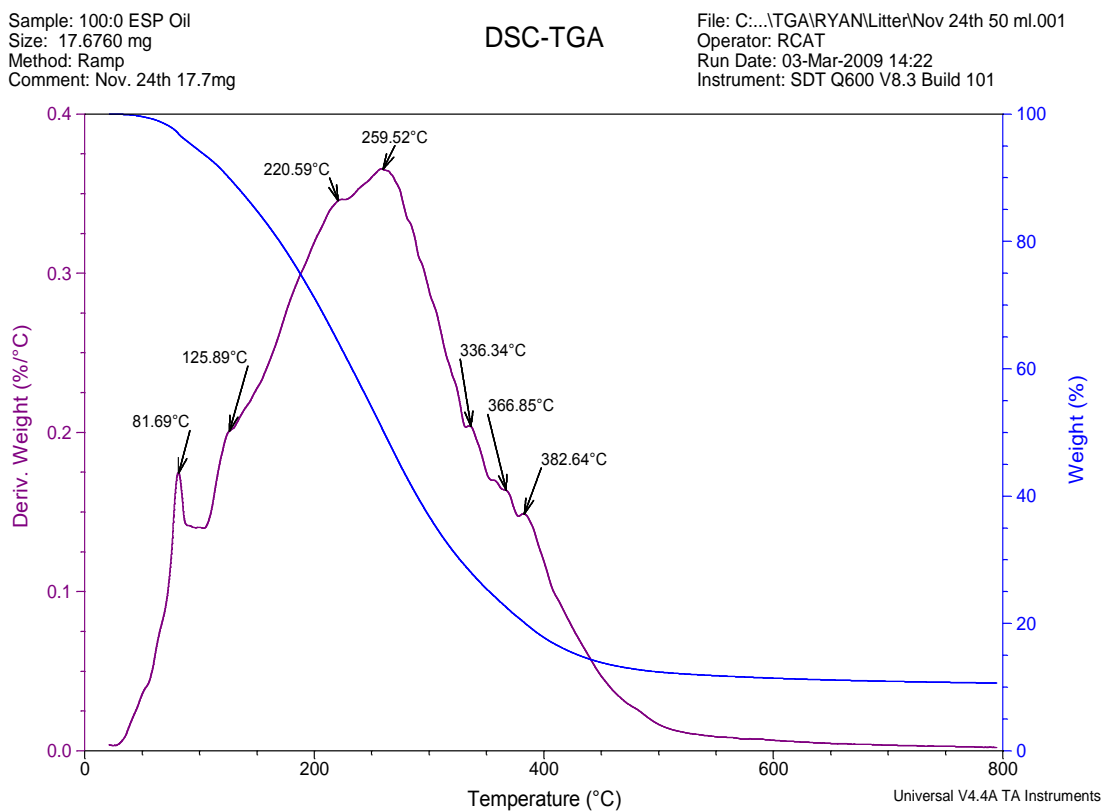
Figure 4.2 Thermogravimetric and differential thermogravimetric curves of AmmoSoak bio-oils

4.2.1.3 FT-IR Analysis

Because the absorption band at 1512cm^{-1} (aromatic skeletal vibration) was relatively constant throughout the spectra, it was used to calculate the relative intensities of the other peaks. The peak intensities were divided by the intensity of the peak at 1512cm^{-1} to determine the relative intensity. The bio-oils are a very complex mixture of many

different organic compounds, making it difficult to interpret the spectra. All interpretations of the FT-IR spectra were based on literature by Gigliotti (2001), Smidt and Meissl (2007), and Sellami (2007).

Figure 4.3 shows the FT-IR spectra of the bio-oil produced by the pyrolysis of AmmoSoak and Table 4.3 shows the FT-IR assignments and relative intensities for the oils. The peak at 3365 cm^{-1} was representative of the O-H stretching of alcohols and phenols. The peaks at 2924 and 2963 cm^{-1} were probably from CH aliphatic stretching. Peaks between 1600 and 1705 cm^{-1} were attributed to alkenes, aromatics, and carboxylic acids. Alkanes could account for the peaks between 1360 and 1456 cm^{-1}. The remaining peaks between 1033 and 1241 cm^{-1} were attributed to alcohols, phenols, carboxylic acids, and ethers. The alcohols and phenols most likely resulted from the decomposition of lignin.
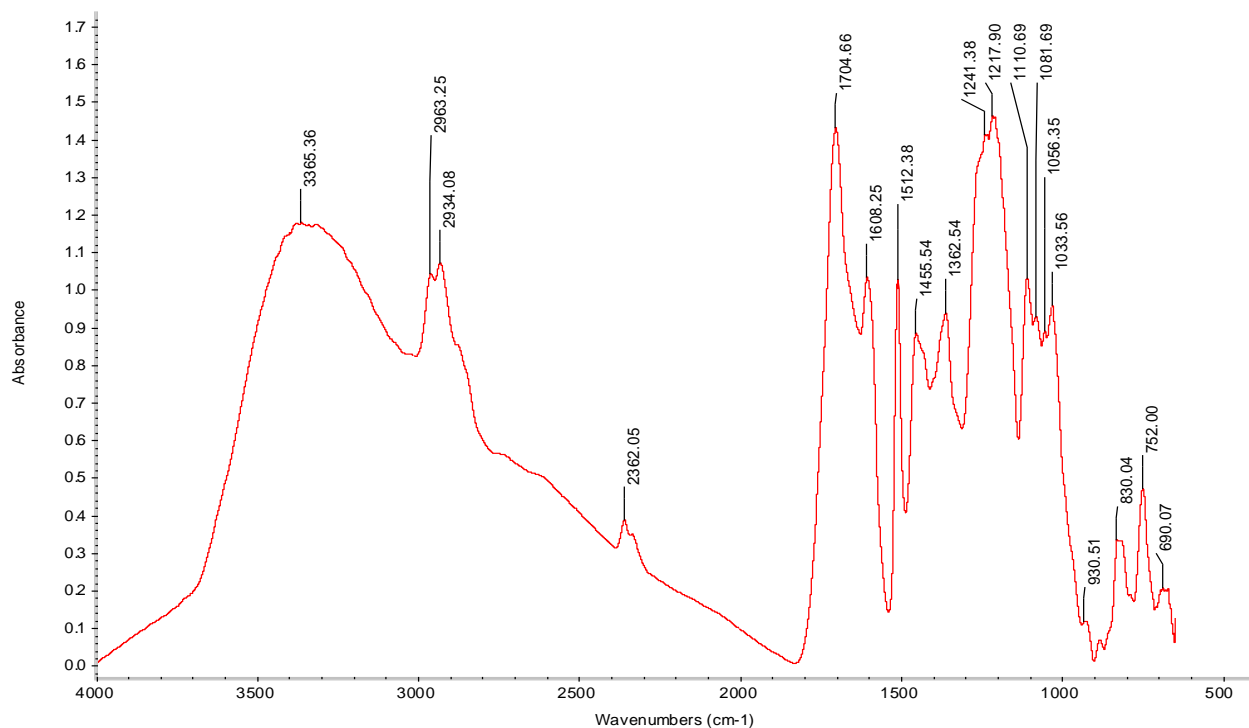
Figure 4.3 FT-IR spectra of AmmoSoak bio-oil

Table 4.3 Summary of FT-IR assignments and relative intensities for AmmoSoak bio-oils

Assignment	Wave number (cm-1)	Relative Intensity
O-H stretch, N-H stretch	3365	1.15
Methylene CH2 asymmetric stretch	2934-2963	1.04
Carbonyl C=O stretch, unconjugated C=O in xylans (hemicellulose)	1705	1.40
Aromatic skeletal vibration with C=O stretch	1608	1.01
Aromatic skeletal vibration	1512-1513	1.00
C-H deformation (asymmetric)	1455	0.86
C-H deformation (symmetric)	1363	0.91
Symmetric C-O-C stretch	1218	1.43
Secondary aliphatic alcohol C-O stretch	1111	1.00
Primary aliphatic alcohol C-O stretch	1082	0.93
CH vibration coupled with C-OH related modes	830	0.32
NH2 out-of-plane bend	752	0.46
NH2 wagging	691	0.20

4.2.1.4 ^{13}C-NMR Analysis

Figure 4.4 shows the ^{13}C-NMR spectra of bio-oils from the pyrolysis of AmmoSoak. The

tentative assignments of signals in these spectra are shown Table 4.4. Assigned to 0-25

ppm were methyl groups bound to carbon. Methylene groups in aliphatic rings and chains

were assigned to 25-45 ppm. It is worth noting that the peak at 30 ppm was most likely

from the internal methylene carbon in long-chain alkyl hydrocarbons. The smaller peak at

14 ppm originated from terminal methyl groups and supported the presence of long-chain

alkyl hydrocarbons (Almendros et al., 2003). There are established empirical rules which

state methyl groups usually appear at 14 ppm, α-methylene next to methyl at 23 ppm, and

β-methylene at 32 ppm. The peak at 23 ppm was assigned to C(1) of acetic acid, which was complimented by the peak at 172 ppm (Mante, 2008). The region represented by 45-60 ppm was assigned to methoxyl groups, C-6 of some polysaccharides, and Cα- of some amino acids. The peak at 56ppm was from methoxyl carbon groups in lignin (Almendros et al., 2003). The peak at 62ppm derives from levoglucosan. The peaks in the range of 60-80 ppm were assigned to C-2 to C-5 in hexoses, Cα- of some amino acids, or aliphatic part of lignin structures. This region is also the normal alcohol region (Jacobsen, 2007). Anomeric carbon of carbohydrates, C-2, and C-6 of syringyl units were assigned to the range of 80-110 ppm. Signals in the range of 110-160 ppm were assigned to aromatic carbons. The peaks at 116, 121, 130, and 146 ppm corresponded to aromatic carbon of lignin and carbon in N-heterocyclic structures (Schnitzer et al., 2007). Indications of the presence of lignin-derived structures were given by the signals in the region of O-substituted aromatic carbon between 160 and 140 ppm (Almendros et al., 2003). The signals at 150 and 155 ppm corresponded to lignin or tannins (Waite). The signal at 148 ppm could be assigned to C_3/C_4 in guiacyl units (Liidemann and Nimz, 1973). The region from 160-220 ppm was assigned to carboxylic-, carbonylic-, and amide- carbons. The signal at 172 ppm was assigned to the acetyl carbonyl group of hemicellulose components. Carboxylic signals evident at 173 ppm and 21 ppm were attributed to acetic acid (Waite). The signal at 174.8 ppm was attributed to the presence of amides and was supported by the signals at 29.7 ppm (CH_2) and 23 ppm (CH_2 or CH_3) which were assigned to methylene groups in proteins (Vane et al., 2003). The signal at 203 ppm in the ^{13}C NMR spectrum could be assigned to an α/β-unsaturated ketone functionality (Wilton et al., 1985).

Figure 4.4 ^{13}C-NMR of bio-oils from the pyrolysis of AmmoSoak

Table 4.4 Tentative assignments of ^{13}C-NMR spectra signals of bio-oils

Chemical Shift Range (ppm)	Assignment
220-160	Carboxylic-, carbonylic-, amide-C
160-140	Aromatic C-O-R or C-N-R
140-110	Aromatic C-H
110-80	Anomeric carbon of carbohydrates, C-2, C-6 of syringyl
80-60	C-2 to C-5 in hexoses, Cα- of some amino acids, higher alcohols, aliphatic part of lignin structures
60-45	Methoxyl groups, C-6 of some polysaccharides, Cα- of some amino acids
45-25	Methylene groups in aliphatic rings and chains (lipids or proteins)
25-0	Methyl groups bound to carbon

Source: (Liidemann and Nimz, 1973; Hatcher et al., 1980; Wilson, 1987)

4.2.2 Pyrolysis of Broiler Litter

The product yields from the pyrolysis of broiler litter can be seen in Table 4.5. The average oil yield was 38.8 wt.%, which is much lower than that reported in literature for most woods (up to 80 wt.%) (Bridgwater et al., 1999). It is only slightly lower than that reported for manure with no bedding (43.3 wt.%). The reported char yield of manure (43.1 wt.%), is about the same as that found for broiler litter (42.7 wt.%). The gaseous product yield from broiler litter (18.5 wt.%) was about 5% greater than that reported in the literature for manure (13.6 wt.%) (Mante, 2008). These differences could be explained by the number of flocks raised between cleanouts, density of confinement, feed conversion rate, feed ration, type of floor (dirt, concrete, etc.), climatic conditions during litter accumulation, and any organic matter and N losses (Perkins et al., 1964).

Table 4.5 Summary of Product Yields from the Pyrolysis of Broiler Litter

Yield (wt.%)*		
Oil	**Char**	**Gas****
38.8±0.61	42.7±0.42	18.5±0.51

* Moisture free basis

**By difference

4.2.2.1 Physicochemical Properties of Broiler Litter Bio-oil

The physicochemical properties of broiler litter bio-oils are shown in Table 4.6. Bio-oils from the pyrolysis of broiler litter were almost neutral with a pH of 7.31. This is good because an acidic oil could prove to be corrosive to equipment used in certain applications such as pumps and boilers. The density of the oils was 1.04 g/mL. This was

slightly greater than those of crude oils (0.80-1.0 g/mL), fuel oil (0.90 g/mL), and gasoline (0.75 g/mL) (Walker, 2007). The viscosity of the oils was rather high. The viscosity of olive oil at 60ºC is 19 cP (Hansen, 1986) while that of the broiler litter was nearly nine times that at 185.7 cP. Both the density and viscosity could pose challenges to the utilization of broiler litter oils. Table 4.6 shows that the ash content of the oil was very low, less than 0.1% because of use of the hot gas filter. Pyrolysis of the broiler litter more than doubled the energy density. Prior to pyrolysis, the HHV of the litter was 14.3 MJ/kg while that of the resulting oil was 29.7 MJ/kg. The bio-oils from broiler litter were composed mainly of carbon (C) and oxygen (O) (Table 4.2), resulting in an average chemical composition of $CH_{1.78}N_{0.12}O_{0.28}S_{0.002}Cl_{0.0001}$.

Table 4.6 Summary of Physicochemical Properties of Broiler Litter Bio-oils

Property	
Water Content (wt.%)	8.96
pH	7.31
Density @ 23C (g/mL)	1.04
Dynamic Viscosity @ 60C (cP)	185.7
Ash Content (wt.%)	<0.1
High Heat Value (MJ/kg)	29.7
Elemental Composition (wt.%)*	
C	60.16
H	8.90
N	8.30
O**	22.10
S	0.37
Cl	0.17
H/C molar ratio	1.78
O/C molar ratio	0.28
N/C molar ratio	0.12
Average Chemical Composition	$CH_{1.78}N_{0.12}O_{0.28}S_{0.002}Cl_{0.0001}$

*Moisture free basis
**By difference

4.2.2.2 Thermogravimetric Analysis of Broiler Litter Bio-oil

Thermogravimetric (TG) and differential thermogravimetric (DTG) analyses were performed on each bio-oil. All analyses were performed under nitrogen at a heating rate of 5°C/min. The nitrogen flow rate was 50 ml/min. The TG and DTG plots are shown in Figures 4.5. The TG curves show that the weight loss of the oil was a gradual process with no clear steps. The oils showed small peaks below 85°C. These peaks were attributed to the decomposition of light volatile compounds such as acetic acid, methanol, etc. (Lu et al., 2008). The major weight loss at 186°C was most likely caused by the degradation of monolignols which are source materials for the biosynthesis of both lignans and lignin. The peaks between 222°C and 281°C were probably from the degradation of cellulose degradation products such as levoglucosan (Mante, 2008). Any remaining peaks at temperatures greater than 307°C were attributed to the degradation of heavy non-polar compounds such as hydrocarbons and ethers (Garcia et al., 2007).

Sample: 0:100 ESP Oil
Size: 22.4600 mg
Method: Ramp
Comment: Apr. 3rd 22.5mg

DSC-TGA

File: C:...\TGA\RYAN\AmoSoak\Apr 3rd 50 ml.001
Operator: RCAT
Run Date: 03-Mar-2009 16:22
Instrument: SDT Q600 V8.3 Build 101
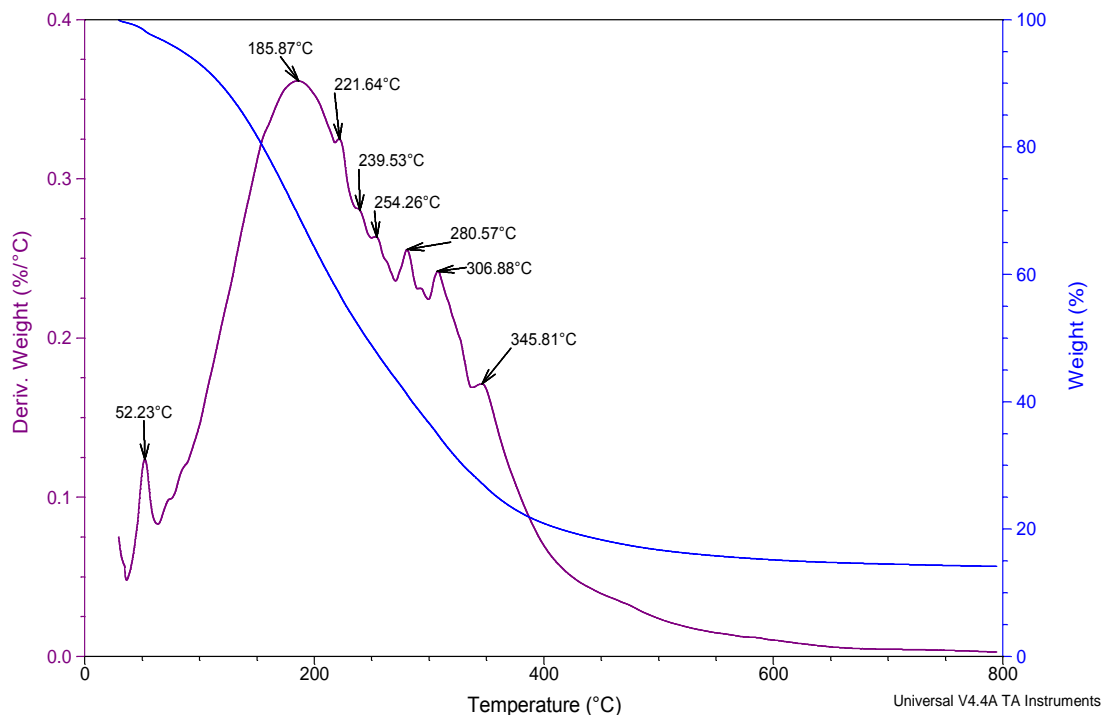
Figure 4.5 Thermogravimetric curve of broiler litter bio-oils

4.2.2.3 FT-IR Analysis of Broiler Litter Bio-oil

Because the absorption band at $1512cm^{-1}$ (aromatic skeletal vibration) was relatively constant throughout the spectra, it was used to calculate the relative intensities of the other peaks. The peak intensities were divided by the intensity of the peak at `$1512cm^{-1}$ to determine the relative intensity. The bio-oils are a very complex mixture of many different organic compounds, making it difficult to interpret the spectra. All interpretations of the FT-IR spectra were based on literature by Gigliotti (2001), Smidt and Meissl (2007), and Sellami (2007).

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Figure 4.6 shows the FT-IR spectra of the bio-oil produced by the pyrolysis of broiler litter and Table 4.7 shows the FT-IR assignments and relative intensities for the oils. The peak at 3207 cm^{-1} was representative of the O-H stretching of alcohols and phenols. The peaks at 2926 and 2960 cm^{-1} were probably from CH aliphatic stretching. Peaks between 1597 and 1659 cm^{-1} were attributed to alkenes, aromatics, and amide carbonyls. Alkanes could account for the peaks between 1385 and 1452 cm^{-1} which complement the peaks at 2926 and 2960 cm^{-1}. The remaining peaks between 1049 and 1269 cm^{-1} were attributed to alcohols, phenols, carboxylic acids, and ethers. The alcohols and phenols most likely resulted from the decomposition of lignin.
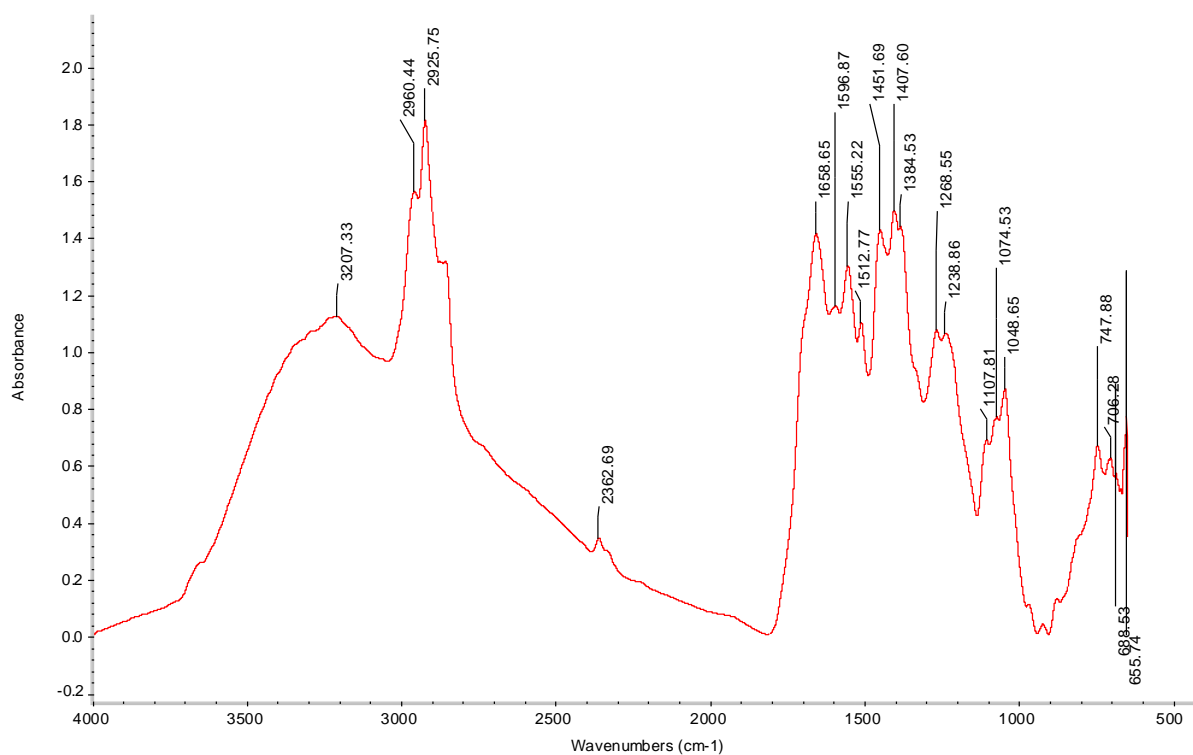

Figure 4.6 FT-IR spectra of broiler litter bio-oil

Table 4.7 Summary of FT-IR assignments and relative intensities for broiler litter bio-oils

Assignment	Wave number (cm-1)	Broiler Litter
O-H stretch, N-H stretch	3207	1.18
Methylene CH2 asymmetric stretch	2926	1.65
Amide Carbonyl C=O	1659	1.28
Amide II, N-H bending vibration	1555	1.18
Aromatic skeletal vibration	1513	1.00
C-H deformation (asymmetric)	1451	1.29
C-N stretch of primary amides	1408	1.36
Aromatic ether C-O-C	1269	0.98
Secondary aliphatic alcohol C-O stretch	1108	0.62
Primary aliphatic alcohol C-O stretch	1049	0.79
NH2 out-of-plane bend	748	0.61
NH2 wagging	689	0.57
O-C=O in-plane deformation	656	0.70

4.2.2.4 ^{13}C-NMR Analysis

Figure 4.7 shows the ^{13}C-NMR spectra of bio-oils from the pyrolysis of broiler litter. The

tentative assignments of signals in these spectra are shown Table 4.8. Assigned to 0-25

ppm were methyl groups bound to carbon. Methylene groups in aliphatic rings and chains

were assigned to 25-45 ppm. It is worth noting that the peak at 30 ppm was most likely

from the internal methylene carbon in long-chain alkyl hydrocarbons. The smaller peak at

14 ppm originated from terminal methyl groups and supported the presence of long-chain

alkyl hydrocarbons (Almendros et al., 2003). There are established empirical rules which state methyl groups usually appear at 14 ppm, α-methylene next to methyl at 23 ppm, and β-methylene at 32 ppm. Similarly, the pair at 23 ppm was assigned to C(2) and C(28) and the pair at 32 ppm to C(3) and C(27) (Nakai et al., 1999). The region represented by 45-60 ppm was assigned to methoxyl groups, C-6 of some polysaccharides, and Cα- of some amino acids. The peak at 56ppm was from methoxyl carbon groups in lignin (Almendros et al., 2003). The peak at 62ppm derives from levoglucosan. The peaks in the range of 60-80 ppm were assigned to C-2 to C-5 in hexoses, Cα- of some amino acids, or aliphatic part of lignin structures. This region is also the normal alcohol region (Jacobsen, 2007). Anomeric carbon of carbohydrates, C-2, and C-6 of syringyl units were assigned to the range of 80-110 ppm. Signals in the range of 110-160 ppm were assigned to aromatic carbons. The peaks at 116, 121, 130, and 146 ppm corresponded to aromatic carbon of lignin and carbon in N-heterocyclic structures (Schnitzer et al., 2007). Indications of the presence of lignin-derived structures were given by the signals in the region of O-substituted aromatic carbon between 160 and 140 ppm (Almendros et al., 2003). The signals at 150 and 155 ppm corresponded to lignin or tannins (Waite). The signal at 148 ppm could be assigned to C_3/C_4 in guiacyl units (Liidemann and Nimz, 1973). The region from 160-220 ppm was assigned to carboxylic-, carbonylic-, and amide- carbons. The signal at 172 ppm was assigned to the acetyl carbonyl group of hemicellulose components. Carboxylic signals evident at 173 ppm and 21 ppm were attributed to acetic acid (Waite). The signal at 174.8 ppm was attributed to the presence of amides and was supported by the signals at 29.7 ppm (CH_2) and 23 ppm (CH_2 or CH_3) which were assigned to methylene groups in proteins (Vane et al., 2003). The signal at 203 ppm in

the 13C NMR spectrum could be assigned to an α/β-unsaturated ketone functionality (Wilton et al., 1985).

Figure 4.7 ^{13}C-NMR of bio-oils from the pyrolysis of Broiler Litter

Table 4.8 Tentative assignments of ^{13}C-NMR spectra signals of bio-oils

Chemical Shift Range (ppm)	Assignment
220-160	Carboxylic-, carbonylic-, amide-C
160-140	Aromatic C-O-R or C-N-R
140-110	Aromatic C-H
110-80	Anomeric carbon of carbohydrates, C-2, C-6 of syringyl
80-60	C-2 to C-5 in hexoses, Cα- of some amino acids, higher alcohols, aliphatic part of lignin structures
60-45	Methoxyl groups, C-6 of some polysaccharides, Cα- of some amino acids
45-25	Methylene groups in aliphatic rings and chains (lipids or proteins)
25-0	Methyl groups bound to carbon

Source: (Liidemann and Nimz, 1973; Hatcher et al., 1980; Wilson, 1987)

4.2.3 Effect of AmmoSoak on Pyrolysis of Poultry Litter

Table 4.9 and Figure 4.8 show the product yields from pyrolyzing mixtures of poultry litter and AmmoSoak. It can be seen that adding AmmoSoak to the litter had an effect on the pyrolysis yields. As the content of AmmoSoak increased the liquid and gas yields increased while the char yield decreased. The liquid content of the litter alone was 39 wt.%. When 15 wt.% AmmoSoak was added, the liquid yield increased to 41 wt.%. The char yield decreased from 43 wt.% to 40 wt.%. AmmoSoak had the highest liquid yield (45 wt.%) and the lowest char yield (27 wt.%). On the other hand, broiler litter had the lowest oil yield (39 wt.%) and the highest char yield (43 wt.%). The decrease in char yield with increase in AmmoSoak content was most likely attributed to the low ash content of the AmmoSoak which diluted the ash content of the mixture. In other words, as AmmoSoak (1.22 wt.% ash) was added to the litter (18.82 wt.% ash) the ash content of the feed mixture decreased and, therefore, the char yield decreased.

Table 4.9 Summary of Pyrolysis Results

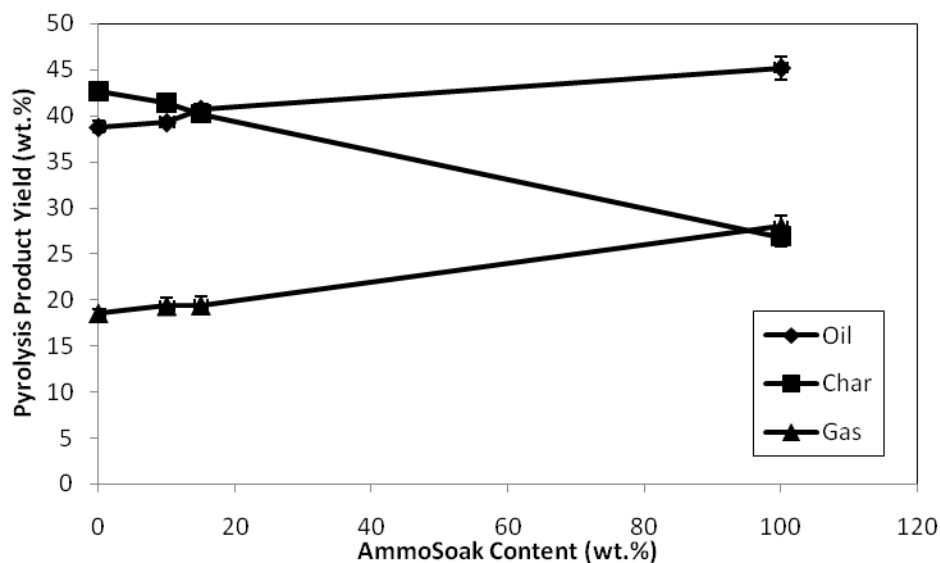| Feedstock			Pyrolytic Yields (wt.%)		
Litter (wt.%)	AmmoSoak (wt.%)	Mean Reactor Temperature (ºC)	Total Liquid	Char	Gas*
100	0	450±7	38.8±0.61	42.7±0.42	18.5±0.51
90	10	442±4	39.3±0.39	41.4±0.73	19.3±0.92
85	15	432±3	40.7±0.56	40.2±0.54	19.4±0.96
0	100	443±2	45.2±1.25	26.8±1.07	28.0±1.17

- By difference

Figure 4.8 Yields of pyrolysis products of poultry litter and AmmoSoak

4.2.3.1 Physicochemical Properties

Table 4.10 shows a summary of the physicochemical properties of bio-oils with different AmmoSoak contents. All the oils were dark brown to black in appearance and smoky in odor much like liquid smoke. The smell was most likely due to the low molecular weight aldehydes and acids (Bridgwater et al., 2002). Depending on the AmmoSoak content, the oils flowed somewhere between heavy motor oil and honey. The differences in appearance, odor, and composition were related to the initial feedstock and the interaction of intermediate degradation products of hemicelluloses, cellulose, lignin, and manure.

The broiler litter oil had the highest water content, pH, initial viscosity and higher heating value (HHV) and the lowest density. Adding 15 wt.% AmmoSoak reduced the water content from 8.96 to 7.41 wt.%. The pH dropped from 7.31 to 6.64 when 15 wt.% AmmoSoak was added to the feedstock as a result of the release of carboxylic acids from the decomposition of carbohydrates in the AmmoSoak. The HHV of the oil also decreased from 29.7 MJ/kg to 27.6 MJ/kg with the addition of 15 wt.% AmmoSoak. The lower HHV was most likely caused by the increased oxygen levels in the oils with a

greater AmmoSoak content. On the other hand, the density of the oils increased when the amount of AmmoSoak increased. The density rose from 1.04 g/mL to 1.07 g/mL with 15 wt.% AmmoSoak was added to the broiler litter.

Elemental analysis of the oils show that hydrogen (H), nitrogen (N), sulfur (S), and chlorine (Cl) all decreased as AmmoSoak content increased. The broiler litter oil had 8.90% H, 8.30% N, 0.37% S, and 0.17% Cl. When 15 wt.% AmmoSoak was added to the feed the resulting bio-oils only had 7.80% H, 5.79% N, 0.33% S, and 0.13% Cl. Carbon content increased from 60.16% to 62.79% with 15 wt.% AmmoSoak.

Table 4.10 Summary of physicochemical properties of broiler litter and AmmoSoak mixtures (100/0 = 100% broiler litter, 90/10 = 90% broiler litter / 10% AmmoSoak, 85/15 = 85% broiler litter / 15% AmmoSoak, 0/100 = 100% AmmoSoak)

| Property	Feedstock Ratio			
	100/0	90/10	85/15	0/100
Water Content (wt.%)	8.96	8.27	7.41	4.53
pH	7.31	6.97	6.64	3.56
Density @ 23°C (g/mL)	1.04	1.06	1.07	1.16
Dynamic Viscosity @ 60°C (cP)	185.7	163.2	85.6	33.4
Ash Content (wt.%)	<0.1	<0.1	<0.1	<0.09
High Heat Value (MJ/kg)	29.7	28.1	27.6	25.3
Elemental Composition				
C (%)	60.16	62.48	62.79	65.15
H (%)	8.90	8.20	7.80	6.70
N (%)	8.30	6.81	5.79	0.61
O* (%)	22.10	22.01	23.16	27.32
S (%)	0.37	0.37	0.33	<0.05
Cl (%)	0.17	0.13	0.13	<0.08
H/C molar ratio	1.78	1.58	1.49	1.24
O/C molar ratio	0.28	0.26	0.28	0.31
N/C molar ratio	0.12	0.09	0.08	0.01
Average chemical Compositions	$CH_{1.78}N_{0.12}O_{0.28}$	$CH_{1.57}N_{0.093}O_{0.26}$	$CH_{1.49}N_{0.079}O_{0.28}$	$CH_{1.23}N_{0.0080}O_{0.31}$

* By difference
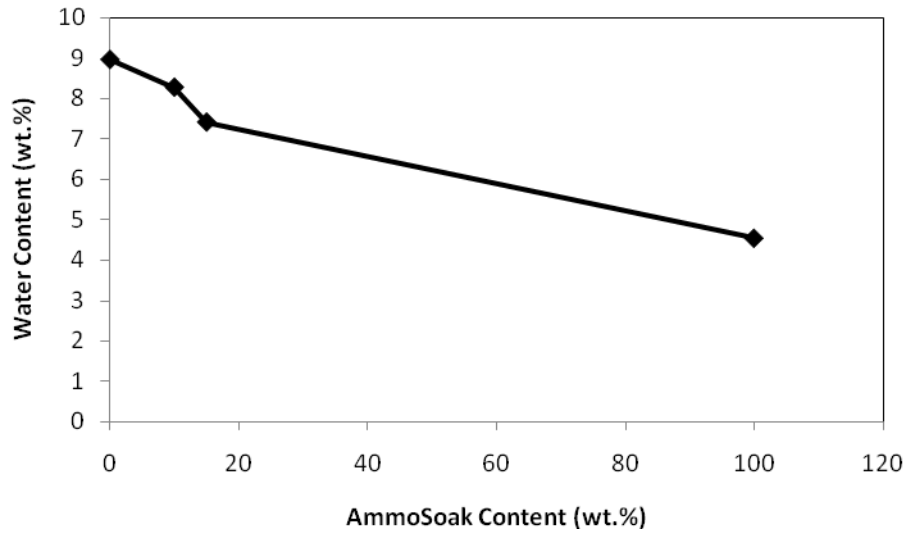
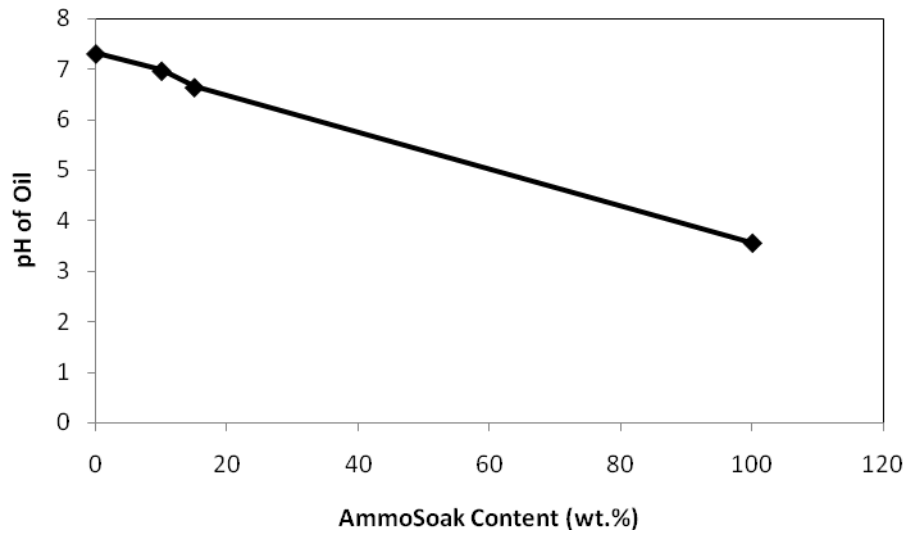Figure 4.9 Effect of AmmoSoak addition to broiler litter on water content of bio-oils

Figure 4.10 Effect of AmmoSoak addition to broiler litter on pH of bio-oils
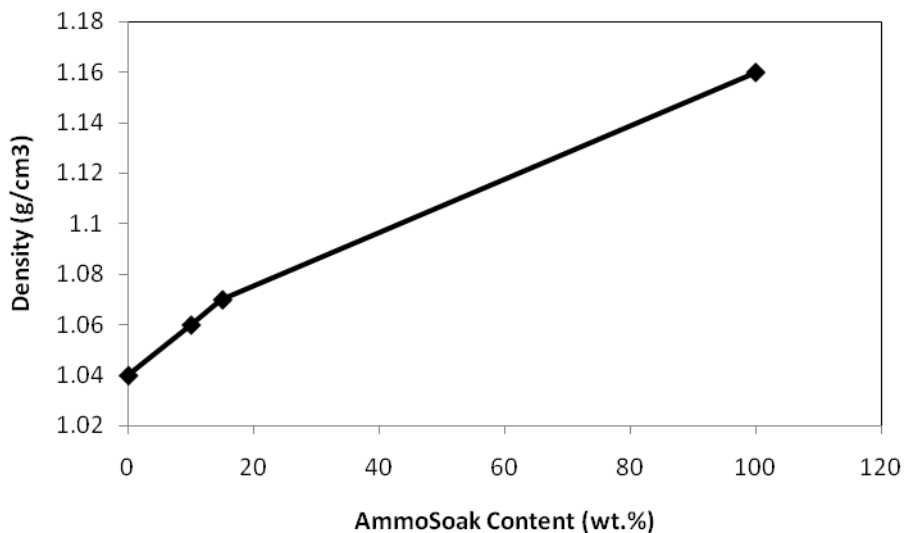
Figure 4.11 Effect of AmmoSoak addition to broiler litter on density of bio-oils
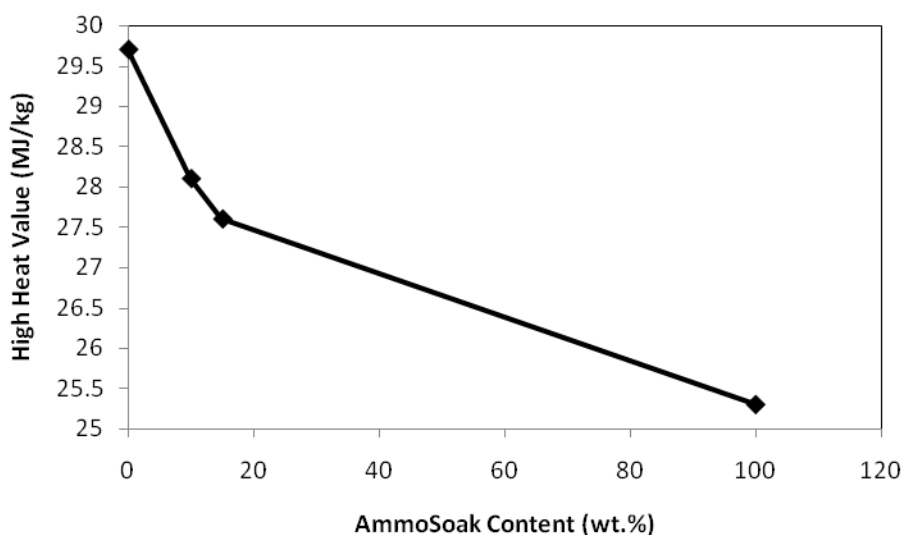
Figure 4.12 Effect of AmmoSoak addition to broiler litter on HHV of bio-oils

4.2.3.2 Viscosity of Bio-oils

The initial viscosities of the oils were determined immediately after collection from the pyrolysis unit. In addition to the initial viscosities, the viscosities of the oils were measured every 10 days for 180 days to study the effect of aging on the viscosity of the oils. All viscosities were taken at 60°C. Figure 4.13 shows the effect of adding AmmoSoak to the feed on the initial viscosity of the bio-oils. The initial viscosity of the

oils decreased significantly as the AmmoSoak content increased. The viscosity of the litter oil decreased from 185.7 cP to only 85.6 cP with 15 wt.% AmmoSoak added. Figure 4.14 shows the effect of age on the viscosities of each oil. Table 4.11 summarizes the findings from the aging study. The addition of AmmoSoak at all levels influenced the aging rate of the oils (Figure 4.14). As the amount of AmmoSoak in the litter increased, the rate of aging decreased. Adding 15 wt.% AmmoSoak to the feed resulted in an oil that had an initial dynamic viscosity (94.1 cP) nearly one-half that of broiler litter oils (180.0 cP). Adding 15 wt.% AmmoSoak also decreased the rate at which the dynamic viscosities of the oils increased over time. Bio-oils from 100% broiler litter increased at a rate of 1.71 cp/day compared to 1.38 cP/day for those with 15 wt.% AmmoSoak and 0.45 cP/day for 100% AmmoSoak. Thus, the addition of AmmoSoak prior to pyrolysis has several beneficial and non-beneficial effects on the broiler litter. Addtion of AmmoSoak mitigates the odor of the broiler litter. The addition of AmmoSoak to broiler litter also reduces the water content, initial viscosity, and increase in viscosity with age. On the other hand, the addition of AmmoSoak decreases the pH and increases the density of the resulting bio-oils.
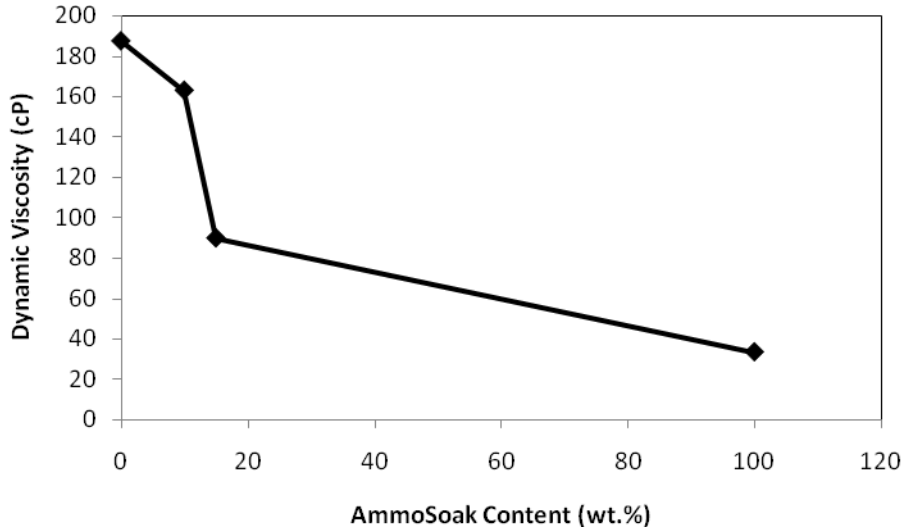
Figure 4.13 Effect of AmmoSoak addition to broiler litter on the initial dynamic viscosity
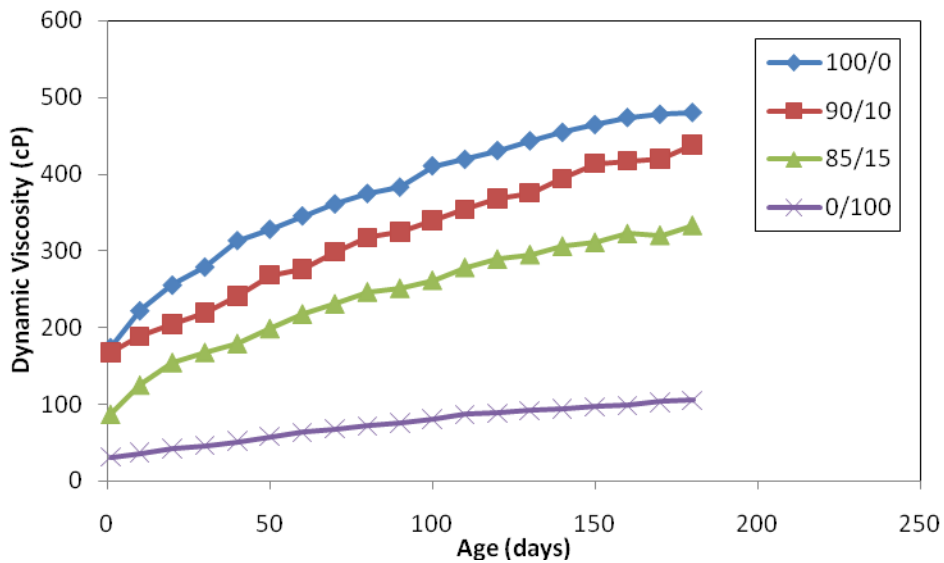
of bio-oils

Figure 4.14 Effect of age on the dynamic viscosity of broiler litter / AmmoSoak bio-oils

(100/0 = 100% broiler litter, 90/10 = 90% broiler litter / 10% AmmoSoak, 85/15 = 85%

broiler litter / 15% AmmoSoak, 0/100 = 100% AmmoSoak)

Table 4.11 The effect of age on the dynamic viscosity of bio-oils

	Feedstock Ratio			
Property	100/0	90/10	85/15	0/100
Initial Dynamic Viscosity (cP) (0 days)	180.0	173.3	94.1	36.5
Final Dynamic Viscosity (cP) (180 days)	487.4	434.1	341.6	118.3
Rate of Change in Dynamic Viscosity (cP/day)	1.71	1.45	1.38	0.45

4.2.3.3 Thermogravimetric Analysis of Bio-oils

Thermogravimetric (TG) and differential thermogravimetric (DTG) analyses were performed on each bio-oil. All analyses were performed under nitrogen at a heating rate of 5°C/min. The nitrogen flow rate was 50 ml/min. The TG and DTG plots are shown in Figures 4.15 and 4.16, respectively. The TG curves show that the weight loss for the oils was a gradual process with no clear steps. All the oils showed small peaks below 85°C. These peaks were attributed to the decomposition of light volatile compounds such as acetic acid, methanol, etc. (Lu et al., 2008). The maximum rates of decomposition for the oils occurred between 185.5 and 273.5°C. The peaks on the curves between 170 and 215°C were most likely due to the degradation products of monolignols which are source materials for the biosynthesis of both lignans and lignin. The peaks between 235 and 300°C were probably from the degradation of cellulose and proteins. The remaining peaks at temperatures greater than 345°C are attributed to the degradation of heavy non-polar compounds such as hydrocarbons and ethers (Garcia et al., 2007).

The bio-oils from 100% litter exhibited a peak at 80.7°C. When 10% and 15% AmmoSoak was added, this peak shifted to 75.8°C for both oils. The maximum degradation rate for broiler litter oil occurred at 258.6°C. When 10% AmmoSoak was added, this peak shifted to 231.0°C and new peaks due to sugars and monolignols in the

AmmoSoak evolved at 273.5°C and 182.5°C, respectively. Figure 4.17 shows the DTG curve of bio-oil from a 50/50 mixture of litter and AmmoSoak. When 50% AmmoSoak was added the maximum degradation peak was shifted from that of broiler litter (258.6°C) to 191.7°C. It is clear that the addition of AmmoSoak to poultry litter reduced the thermal stability of the resulting bio-oils.
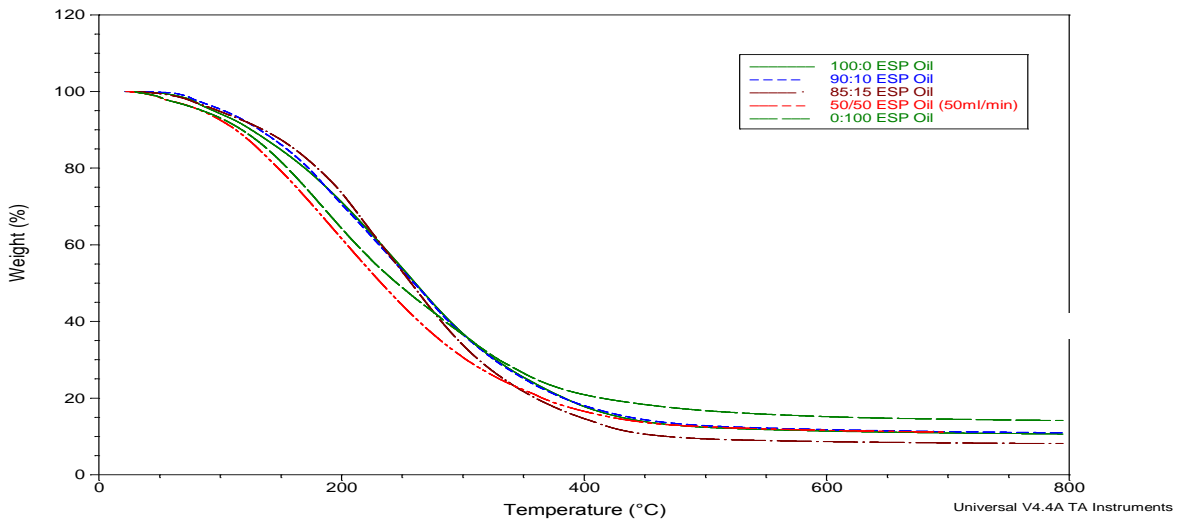

Figure 4.15 TG plot of bio-oils
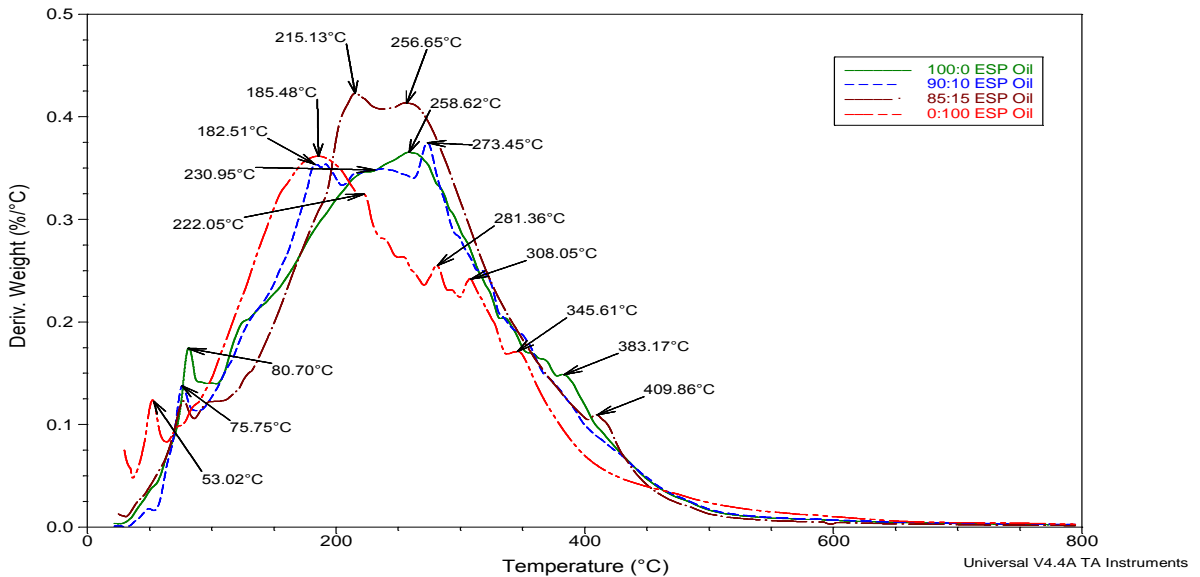
Figure 4.16 DTG plot of bio-oils
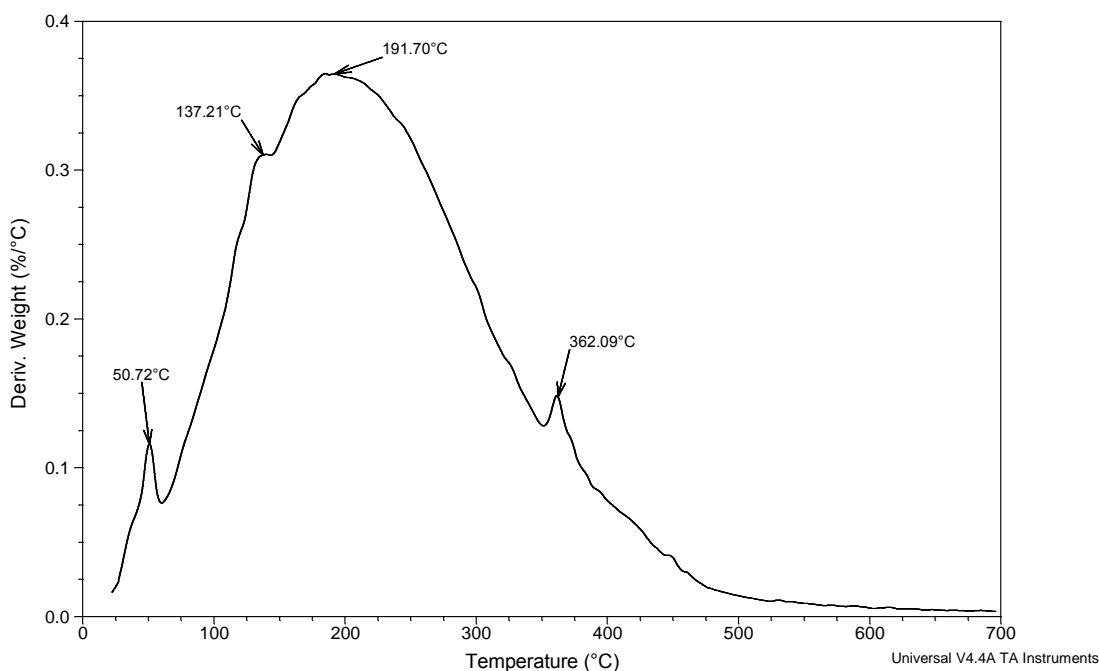
Figure 4.17 DTG plot of 50/50 pyrolyis oil

4.2.3.4 FT-IR Analysis

The FT-IR spectra of the bio-oils are shown in Figures 4.18-4.21. Table 4.12 shows a summary of the FT-IR assignments and their relative intensities of each bio-oil. Because the absorption band at $1512cm^{-1}$ (aromatic skeletal vibration) was relatively constant throughout the spectra, it was used to calculate the relative intensities. The peak intensities were divided by the intensity of the peak at `$1512cm^{-1}$ to determine the relative intensity. The bio-oils are a very complex mixture of many different organic compounds, making it difficult to interpret the spectra. All interpretations of the FT-IR spectra were based on literature by Gigliotti (2001), Smidt and Meissl (2007), and Sellami (2007). The 100% litter bio-oil was rich in methyl groups, amides, and other hydrocarbons. The 100% AmmoSoak bio-oils were rich in aromatics, alcohols, phenols and other oxygenated compounds. The alcohols and phenols most likely resulted from the decomposition of

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lignin. The relative intensities of peaks at 2925-2934cm^{-1} (aliphatic hydrocarbons, methylene CH$_2$ asymmetric stretch) 1655-1659cm^{-1} (amide carbonyl C=O), 1555-1557cm^{-1} (amide II, N-H bending vibration), and 1404-1408cm^{-1} (C-N stretch of primary amides) all decreased as the AmmoSoak content increased (Figure 4.22). On the other hand, relative intensities of peaks at 1240-1269cm^{-1} (Aromatic ether C-O-C), 1034-1073cm^{-1} (primary aliphatic alcohol C-O stretch), and 1107-1112cm^{-1} (secondary aliphatic alcohol C-O stretch) increased as the AmmoSoak content increased (Figure 4.23). The relative intensities of peaks at 3207-3365cm^{-1} (O-H stretch, N-H stretch) decreased until the AmmoSoak content reached 15%. After this the relative intensities increased. This could have been due to reaction of the amide groups with the phenolic O-H. When 15% AmmoSoak is added, there were no amide groups to react with the phenolic O-H, thus resulting in the increase in peak intensity.

The difference in the oil compositions was most likely due to chemical reactions than a dilution effect. The decrease in amides could have resulted from reactions with the acidic components from the AmmoSoak decomposition. This was also supported by the decrease in the peak at 1704 cm^{-1} and the change in pH of the oils as the AmmoSoak content was increased. If the interaction was completely additive, the relative intensity of the C-N stretch of primary amides of a 50/50 blend would be one-half of that of 100% litter. Instead, the relative intensity at 50% AmmoSoak was nearly 75% of that for litter alone. The same applies for the amide II. The relative intensity of litter alone was 1.18 while there was no peak in the 50/50 blend.
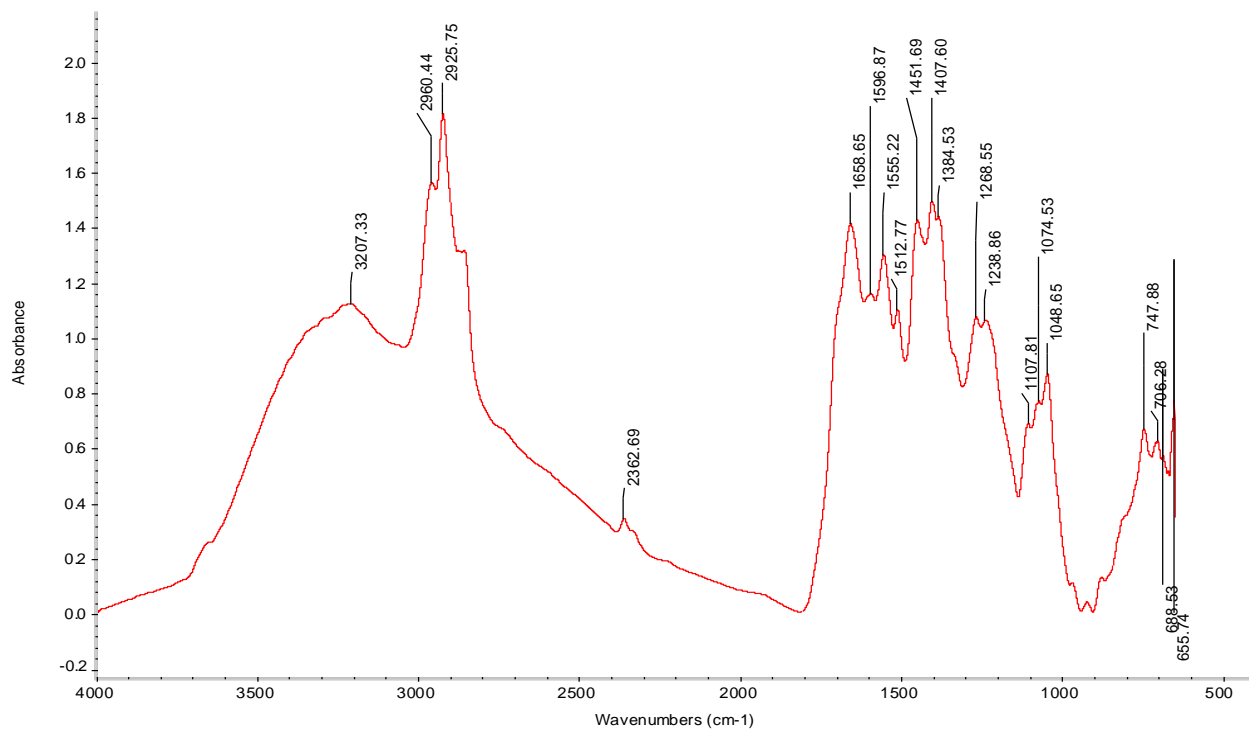
Figure 4.18 FT-IR spectra of 100% broiler litter bio-oil

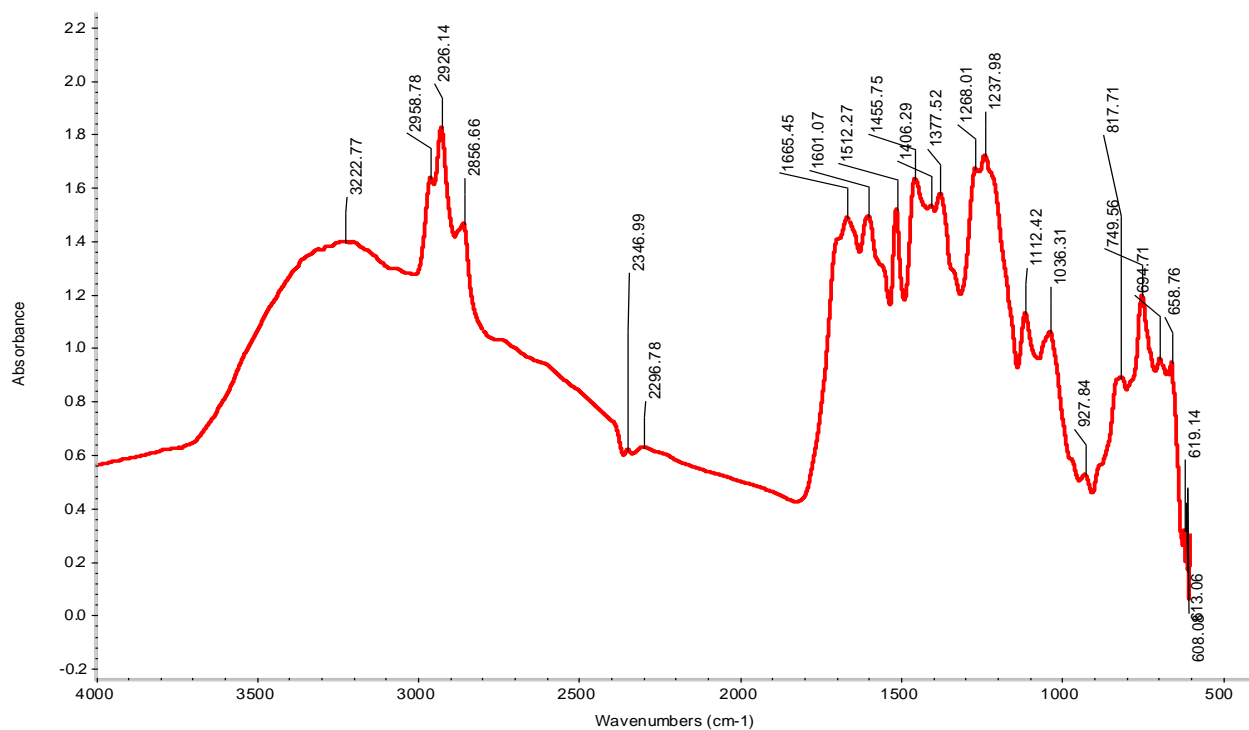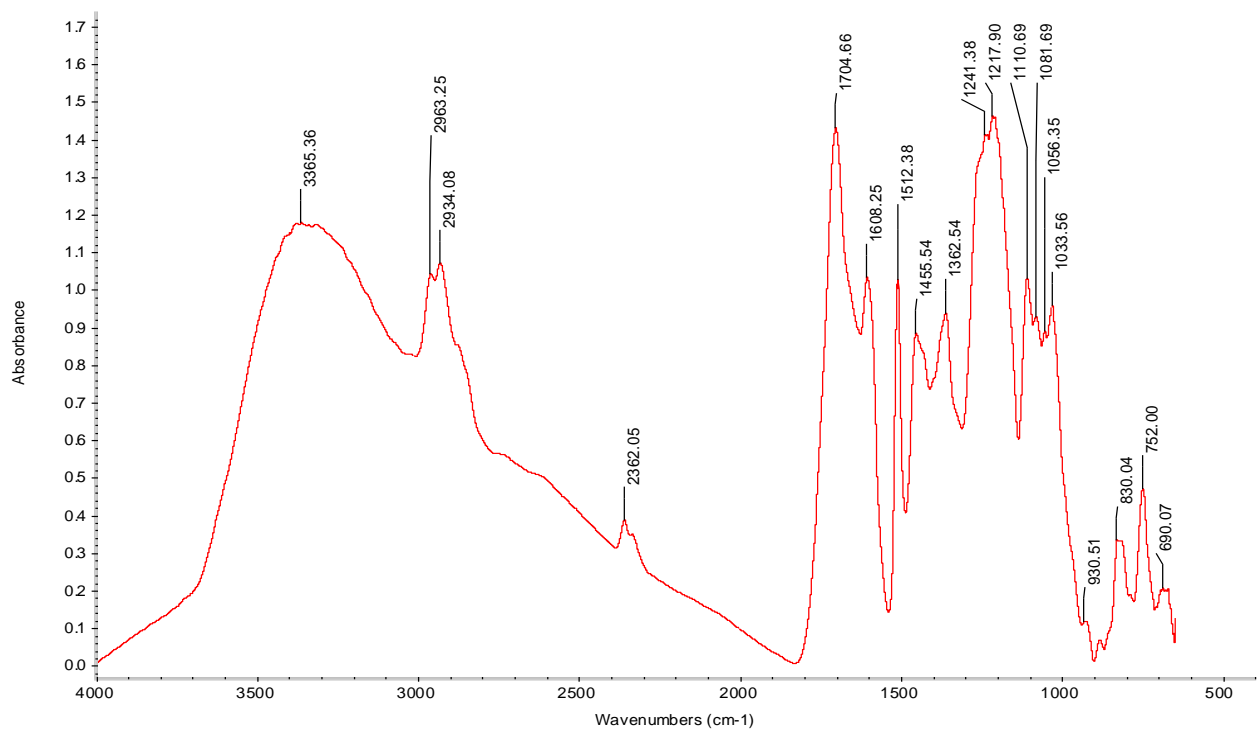Figure 4.19 FT-IR spectra of 50/50 bio-oil
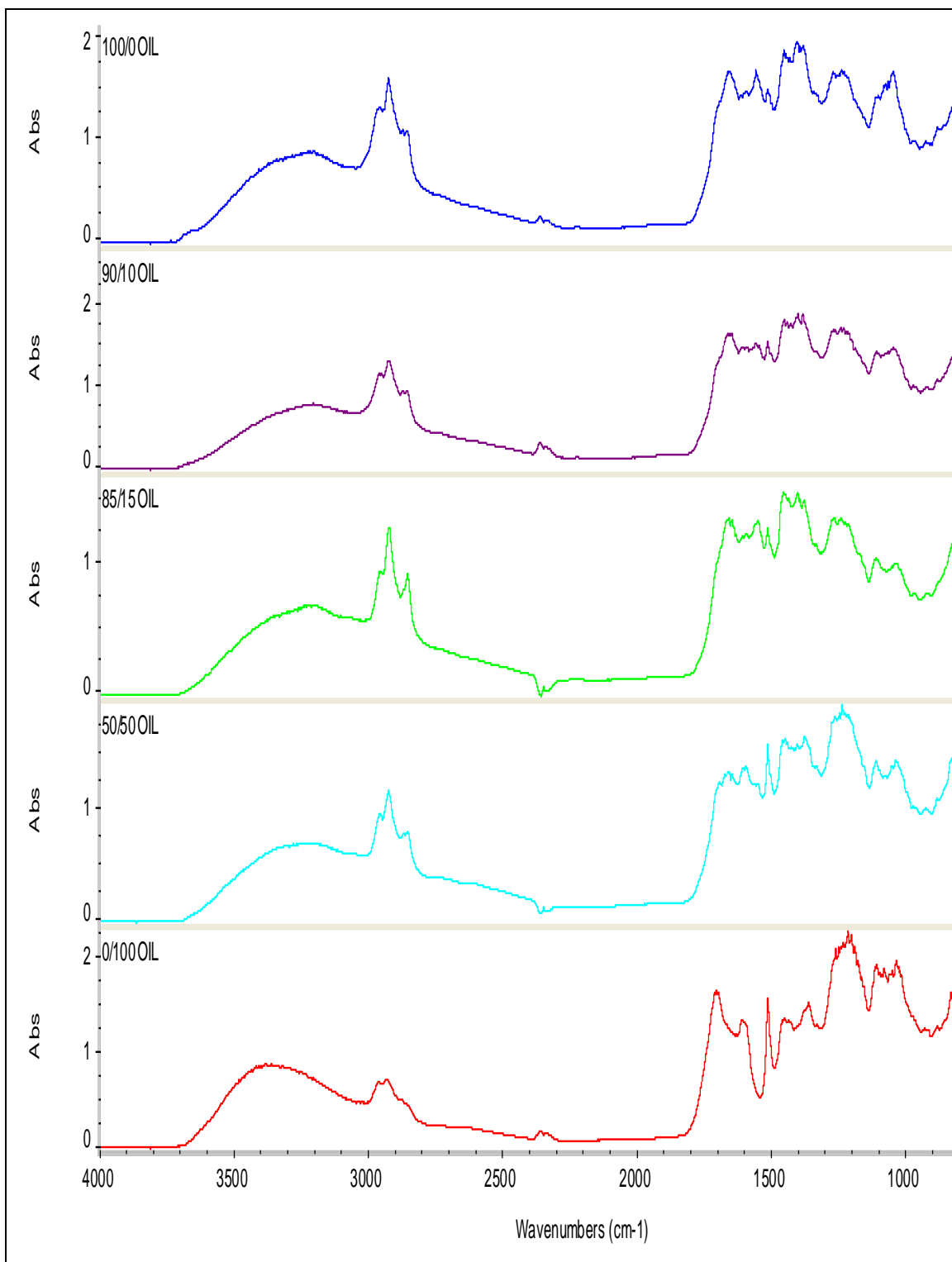
Figure 4.20 FT-IR spectra of 100% AmmoSoak bio-oil

Figure 4.21 FT-IR spectra of bio-oils. (100/0 = 100% litter. 90/10 = 90% litter. 85/15 = 85% litter. 50/50 = 50% litter. 0/100 = 100% AmmoSoak)
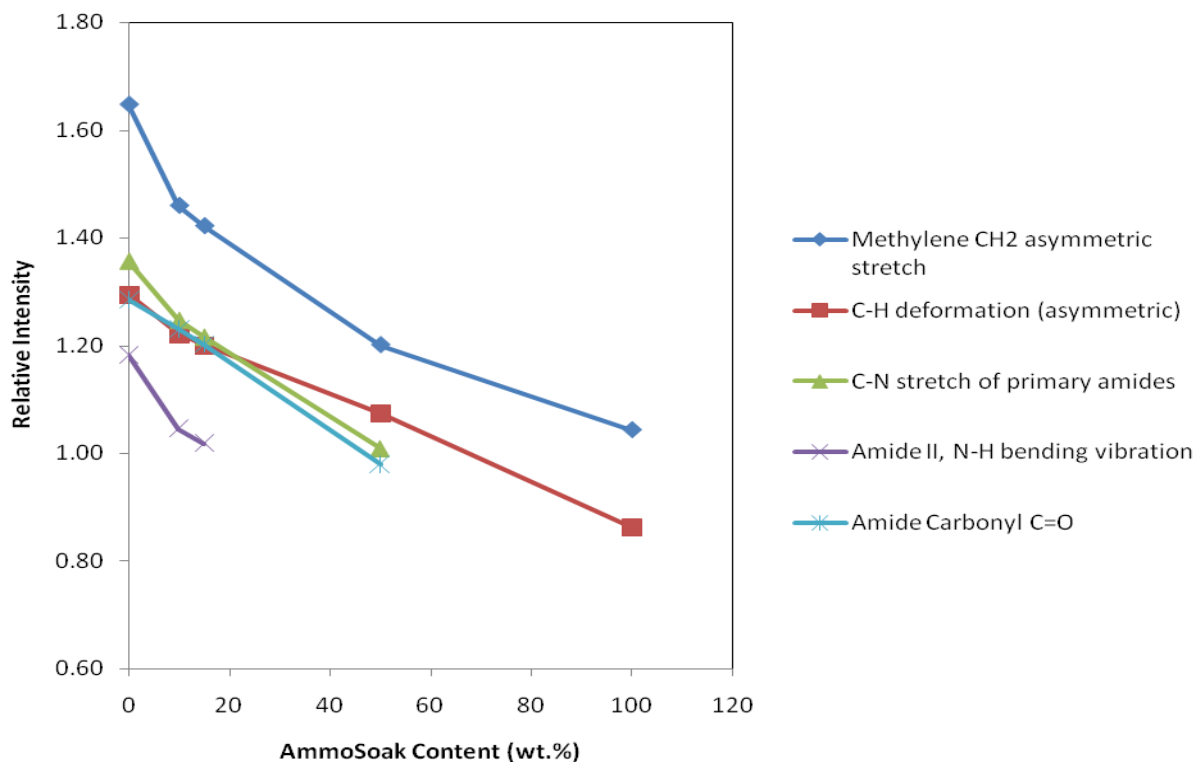
Figure 4.22 FT-IR relative intensities of decreasing absorption bands in bio-oils
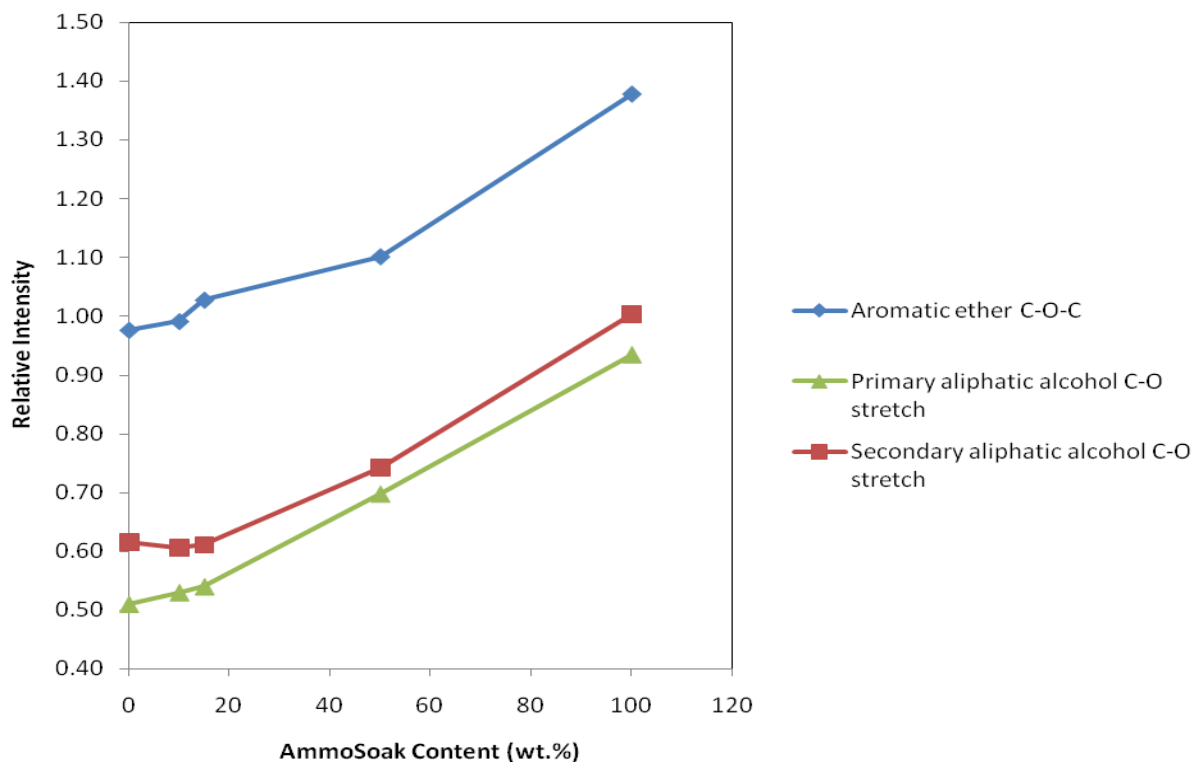
Figure 4.23 FT-IR relative intensities of increasing absorption bands in bio-oils

Table 4.12 Summary of FT-IR assignments and relative intensities for bio-oils

Assignment	Wave number (cm-1)	Relative Intensity				
		100% Litter	90/10	85/15	50/50	100% AmmoSoak
O-H stretch, N-H stretch	3207-3365	1.18	0.90	0.89	0.92	1.15
Methylene CH_2 asymmetric stretch	2925-2934	1.65	1.46	1.42	1.20	1.04
Carbonyl C=O stretch, unconjugated C=O in xylans (hemicellulose)	1705	-	-	-		1.40
Amide Carbonyl C=O	1655-1659	1.28	1.23	1.20	0.98	-
Aromatic skeletal vibration with C=O stretch	1601-1608	-	-	-	0.98	1.01
Amide II, N-H bending vibration	1555-1557	1.18	1.05	1.02	-	-
Aromatic skeletal vibration	1512-1513	1.00	1.00	1.00	1.00	1.00
C-H deformation (asymmetric)	1451-1456	1.29	1.22	1.20	1.07	0.86
C-N stretch of primary amides	1404-1408	1.36	1.25	1.22	1.01	-
C-H deformation (symmetric)	1363-1378	-	-	-	1.04	0.91
Aromatic ether C-O-C	1240-1269	0.98	0.99	1.03	1.10	1.38
Symmetric C-O-C stretch	1218	-	-	-	-	1.43
Secondary aliphatic alcohol C-O stretch	1107-1112	0.62	0.60	0.61	0.74	1.00
Primary aliphatic alcohol C-O stretch	1034-1073	0.51	0.53	0.54	0.70	0.93
CH vibration coupled with C-OH related modes	818-830	-	-	-	0.58	0.32
NH_2 out-of-plane bend	744-752	0.61	0.64	0.78	0.79	0.46
NH_2 wagging	691-706	0.57	0.51	0.78	0.63	0.20
O-C=O in-plane deformation	651-670	0.70	0.89	0.71	0.62	-

4.2.3.5 ^{13}C-NMR Analysis

Figure 4.24 shows the ^{13}C-NMR spectra of bio-oils from the pyrolysis of poultry litter and varying contents of AmmoSoak. The tentative assignments of signals in these spectra are shown Table 4.13. Assigned to 0-25 ppm were methyl groups bound to carbon. Methylene groups in aliphatic rings and chains were assigned to 25-45 ppm. It is worth noting that the peak at 30 ppm was most likely from the internal methylene carbon in long-chain alkyl hydrocarbons. The smaller peak at 14 ppm originated from terminal methyl groups and supported the presence of long-chain alkyl hydrocarbons (Almendros et al., 2003). There are established empirical rules which state methyl groups usually appear at 14 ppm, α-methylene next to methyl at 23 ppm, and β-methylene at 32 ppm. The closely located pair at 14 ppm was thus assigned to C(1) and C(29). Similarly, the pair at 23 ppm was assigned to C(2) and C(28) and the pair at 32 ppm to C(3) and C(27) (Nakai et al., 1999). The region represented by 45-60 ppm was assigned to methoxyl groups, C-6 of some polysaccharides, and Cα- of some amino acids. The peak at 56 ppm was from methoxyl carbon groups in lignin (Almendros et al., 2003). The peak at 62 ppm was attributed to methoxyl aryl ethers (eg. syringyl) (Waite). Any peaks in the range of 60-80 ppm were assigned to C-2 to C-5 in hexoses, Cα- of some amino acids, or aliphatic part of lignin structures. This region is also the normal alcohol region (Jacobsen, 2007). There were nearly no peaks in this region until 50% AmmoSoak was added to the litter. Anomeric carbon of carbohydrates, C-2, and C-6 of syringyl units were assigned to the range of 80-110 ppm. It can be seen that the entire carbohydrate region increased as the AmmoSoak content increased. Signals in the range of 160-110 ppm were assigned to aromatic carbons. The peaks at 116, 121, 130, and 146 ppm corresponded to aromatic

carbon of lignin and carbon in N-heterocyclic structures (Schnitzer et al., 2007). Indications of the presence of lignin-derived structures were given by the signals in the region of O-substituted aromatic carbon between 160 and 140 ppm (Almendros et al., 2003). The signals at 150 and 155 ppm corresponded to lignin or tannins (Waite). The signal at 148 ppm could be assigned to C_3/C_4 in guiacyl units (Liidemann and Nimz, 1973). The region from 220-160 ppm was assigned to carboxylic-, carbonylic-, and amide- carbons. The signal at 172 ppm was assigned to the acetyl carbonyl group of hemicellulose components. Carboxylic signals evident at 173 ppm and 21 ppm were attributed to acetic acid (Waite). The signal at 174.8 ppm was attributed to the presence of amides and was supported by the signals at 29.7 ppm (CH_2) and 23 ppm (CH_2 or CH_3) which were assigned to methylene groups in proteins (Vane et al., 2003). The signal at 203 ppm in the ^{13}C NMR spectrum could be assigned to an α/β-unsaturated ketone functionality (Wilton et al., 1985).

The methyl groups (14 ppm), α-methylene (23 ppm), and β-methylene (32 ppm) all decreased as AmmoSoak content increased. The peak at 29.7 ppm (CH_2), indicative of methylene groups in proteins, decreased as the content of AmmoSoak increased. Internal methylene carbons in long alkyl chains (30 ppm) decreased with the addition of AmmoSoak. The methoxyl carbon groups in lignin (56 ppm) remained relatively constant as AmmoSoak was increased. The methoxyl aryl ethers (62 ppm) decrease until the AmmoSoak content reaches 50%. This supported the finding from the FT-IR analysis that methylene groups decreased as AmmoSoak increased. The olefinic peak at 118 ppm decreases as AmmoSoak content increased. This could explain the decrease in C-H deformations noticed in the FT-IR analysis. The peaks at 116, 121, 130, and 146ppm

(aromatic carbon of lignin and carbon in N-heterocyclic structures) decreased slightly with an increased AmmoSoak content, contradicting the FT-IR analysis. The FT-IR analysis found that a rise in aromatics occurred with a rise in AmmoSoak content, which makes more sense since aromatics would result from the breakdown of lignin. Increasing the AmmoSoak content increased the amount of carbohydrates and lignin in the feedstocks. The lignins or tannins represented by the signals at 150 and 155 ppm, increased slightly until 50% AmmoSoak where they increased sharply. The amides at 174.8 ppm decreased as the AmmoSoak content increased, supporting the FT-IR findings and the assumption that amides would result from the degradation of proteins in the litter. The carboxylic acid peak at 173 ppm increased as the AmmoSoak content increased supporting the decrease in pH. The increase in carboxylic acid probably resulted from the degradation of hemicelluloses. Finally, the peak at 203ppm (α/β-unsaturated ketone) remained fairly constant as the AmmoSoak content increases.

100%

90/10

85/15
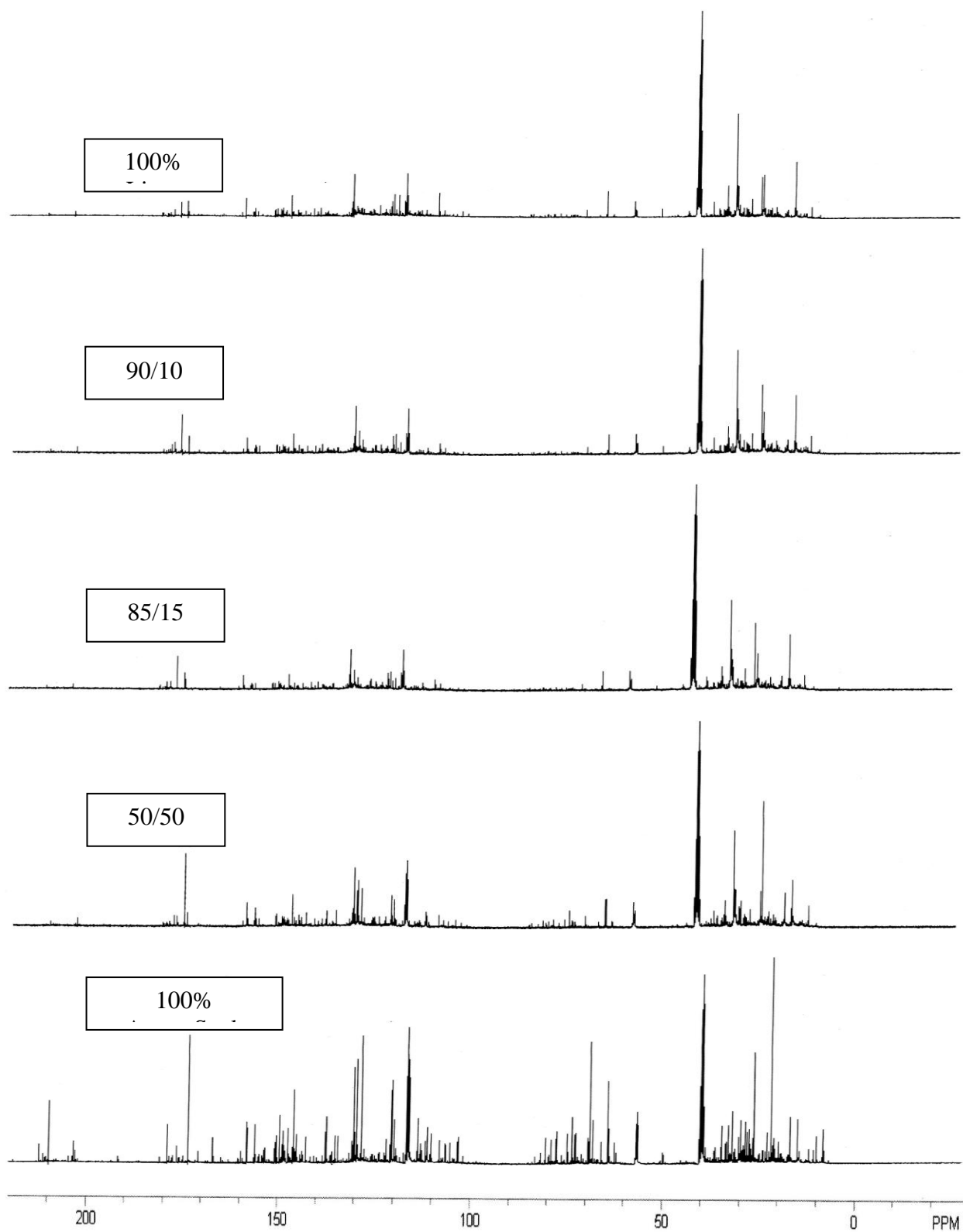
50/50

100%

200 150 100 50 0 PPM

Figure 4.24 ^{13}C-NMR of bio-oils from poultry litter and varying contents of AmmoSoak

Table 4.13 Tentative assignments of ^{13}C-NMR spectra signals of bio-oils

Chemical Shift Range (ppm)	Assignment
220-160	Carboxylic-, carbonylic-, amide-C
160-140	Aromatic C-O-R or C-N-R
140-110	Aromatic C-H
110-80	Anomeric carbon of carbohydrates, C-2, C-6 of syringyl
80-60	C-2 to C-5 in hexoses, Cα- of some amino acids, higher alcohols, aliphatic part of lignin structures
60-45	Methoxyl groups, C-6 of some polysaccharides, Cα- of some amino acids
45-25	Methylene groups in aliphatic rings and chains (lipids or proteins)
25-0	Methyl groups bound to carbon

Source: (Liidemann and Nimz, 1973; Hatcher et al., 1980; Wilson, 1987)

4.3 Conclusions

The addition of AmmoSoak to poultry litter prior to pyrolysis had an effect on the product yields, compositions, and qualities. Both liquid and gaseous product yields increased at the expense of solid products. This was most likely caused by the "dilution" of ash contents as the AmmoSoak content increased. Adding AmmoSoak to the feed also decreased the initial viscosity and the rate at which the viscosity increased with age. The pH and water contents of the oils also decreased with an increase in AmmoSoak content. Densities of the oils increased with the increase in AmmoSoak content. The addition of AmmoSoak affected the elemental compositions of the oils as well. Carbon and oxygen contents increased while nitrogen, hydrogen, sulfur, chlorine and ash contents decreased.

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CHAPTER 5

START-UP AND DEMONSTRATION OF A PILOT-SCALE POULTRY

PYROLYSIS UNIT

5.1 Pilot-Scale Start-Up

The pilot-scale pyrolysis unit was converted from an existing poultry litter gasification system by Hazen Research, Inc. (Golden, CO, U.S.A.). The existing system was developed under a Department of Energy (DOE) Small Business Innovative Research (SBIR) grant by Community Power Corporation (CPC) in 2003. The skid-mounted system employed a poultry litter feed system, a fluidized bed gasifier followed by a moving bed granular filter (MBGF), heat recuperators to cool the gas, and catalytic tar reformer to produce a synthetic gas (syngas) intended for on-site heating or electric power production.

The conversion of the existing CPC gasifier to a bio-oil pyrolysis unit involved replacing the MBGF, heat recuperators, and tar reformer with a three step gas filter and condensing system used to recover bio-oil separated from pyrolyzed poultry litter. Figure 5.1 shows the process flow for the pyrolysis unit. A high-temperature filter (HTF) with ceramic filter elements and temperature adjusted back pulse replaced the MBGF to filter the gas and vapor stream. Gas and vapor temperatures were cooled to recover the bio-oil in a multistage condensing process that included two tube-in-shell heat exchangers, a wet electrostatic precipitator (WESP), and a final coalescing cartridge filter. A non-condensable gas (syngas) compressing system controled system pressures and re-circulated syngas into the fluidized bed gas heater to recuperate its heat content and

provide gas flows necessary for fluidization of the reactor bed. Syngas was also recycled into the fluidized bed windbox to provide additional fluidizing gas and heat.

National Instruments Fieldpoint embedded controller and input/output (I/O) modules were used to monitor and control the process instrumentation. The controller contained its own processor, operating system, RAM and flash memory. Logic software created in LabVIEW could be downloaded to the controller and run independent of the control, ensuring reliable operation. The controller communicated with the control computer through standard TCP/IP communication over an Ethernet network. A Human-Machine Interface (HMI) graphic containing the process values, trends, alarms, and controls provided an interface between the control computer and the controller.
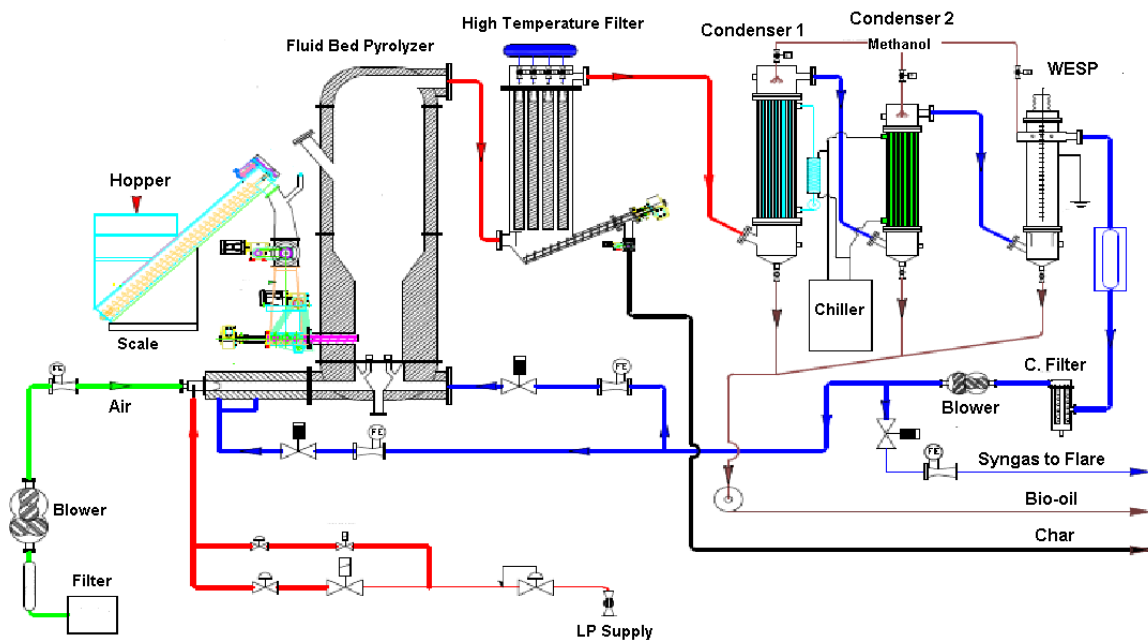

Figure 5.1 Process flow diagram of pilot-scale pyrolysis unit

5.2 Demonstration of Fluidization

Nitrogen gas in addition to recycled syngas was used as the fluidizing gas and 200 lbs of silica sand was the fluidizing medium. Fluidization of the sand was achieved with a

fluidizing flow rate of 18 standard cubic feet per minute (SCFM). Figure 5.2 shows the bed temperature profile at fluidization. It can be seen that prior to fluidization, the bed was packed to a height between the second (Bed 2) and third (Bed 3) thermocouples from the bottom in the reactor bed zone, because they were at much higher temperatures than the other two thermocouples (Bed 3 and Bed 4). As fluidization neared, Bed 3 temperature increased as the bed began to bubble. At fluidization, Bed 1, Bed 2, and Bed 3 temperatures quickly approached an equilibrium point. The Bed 4 temperature also quickly changed but to a slightly lower temperature than the others, suggesting that the fluidized bed height was between the third and fourth thermocouples.

Figure 5.3 shows the reactor pressure profile at fluidization. Distinct evidence of fluidization can be seen in the bed pressure drop and freeboard pressure. As fluidization was approached, the bed pressure drop increased very gradually and at fluidization suddenly decreased. The freeboard pressure also rose gradually, but as the bed fluidized there was a sudden increase. Figure 5.4 shows the superficial space velocity (SSV) at fluidization. The SSV gradually increased leading to fluidization. At fluidization the SSV had a quick drop from about 2.45 ft/sec to nearly 1.8 ft/sec and then instantly up to about 2.6 ft/sec. Rises in the condensation train temperatures at fluidization can be seen in Figure 5.5. Figures 5.6 and 5.7 both show a sudden increase of pressure and then fluctuations of consistent magnitude at fluidization.
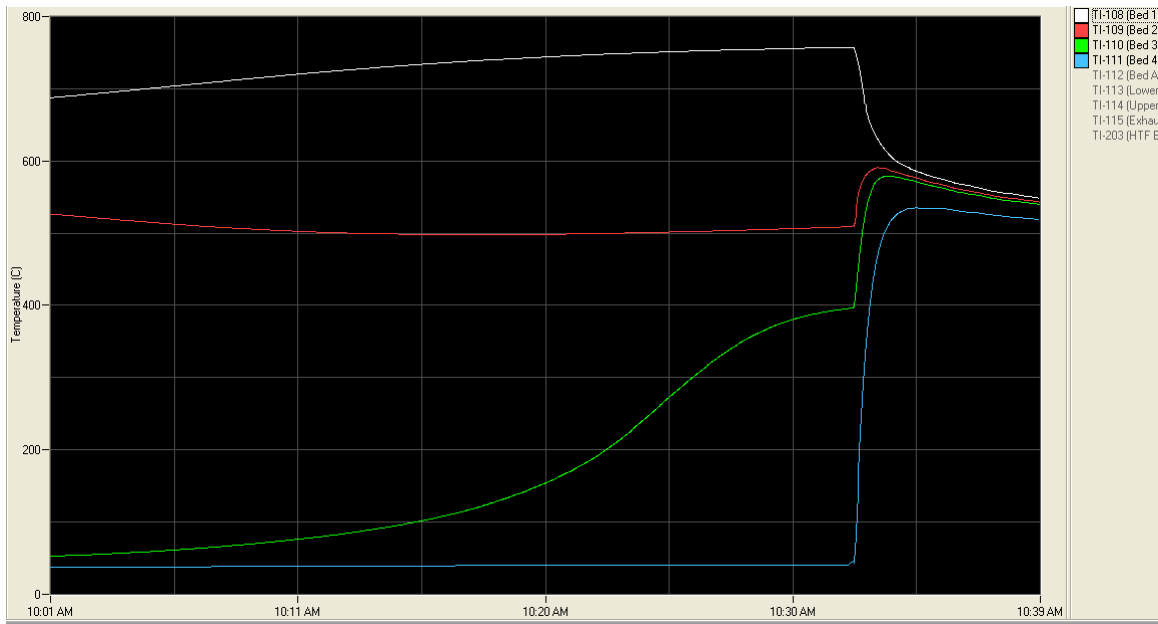
Figure 5.2 Pyrolysis reactor bed temperatures before and at fluidization. TI-108 = Temperature of bottom of reactor bed (Bed 1). TI-109 = Temperature of second thermocouple from bottom of reactor bed (Bed 2). TI-110 = Temperature of third thermocouple from bottom of reactor bed (Bed 3). TI-111 = Temperature of top of reactor bed (Bed 4).
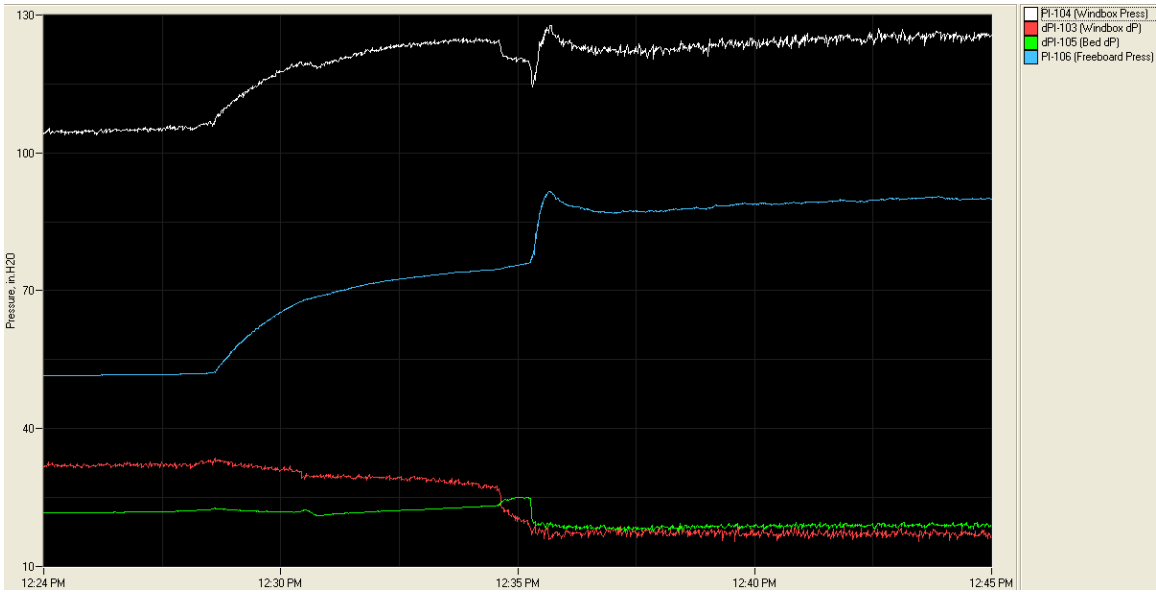
Figure 5.3 Reactor pressure profile at fluidization in in. H$_2$O. PI-104 = Windbox pressure.

dPI-103 = Pressure drop across windbox. dPI-105 = Pressure drop across bed. PI-106 =

Freeboard pressure.
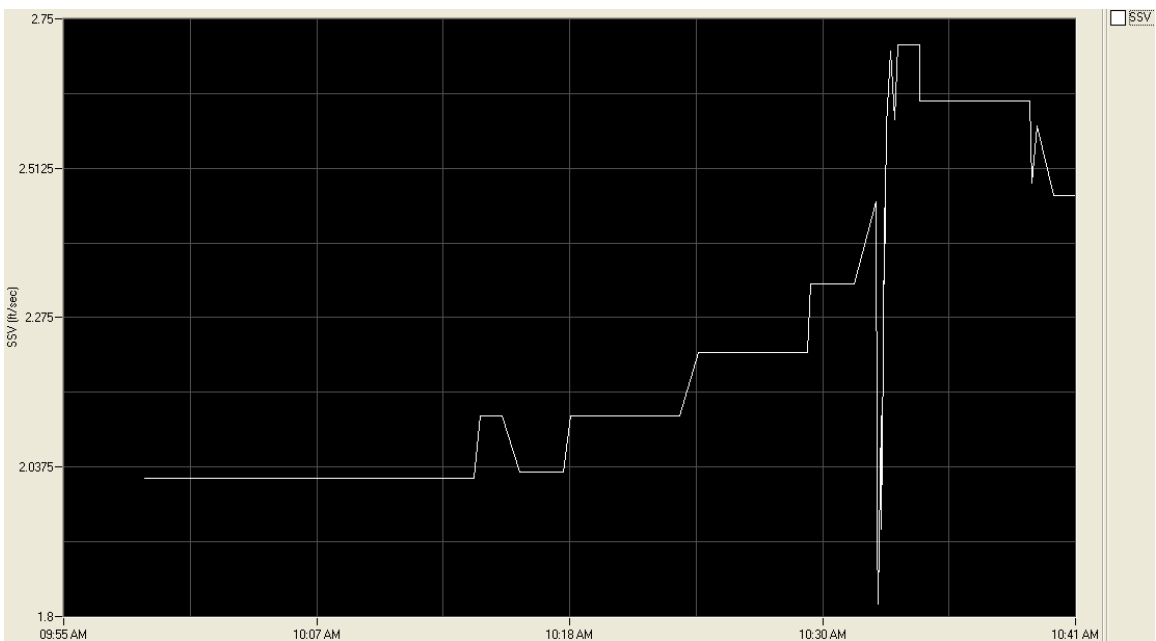
Figure 5.4 Superficial space velocity (SSV) at fluidization in ft/sec.
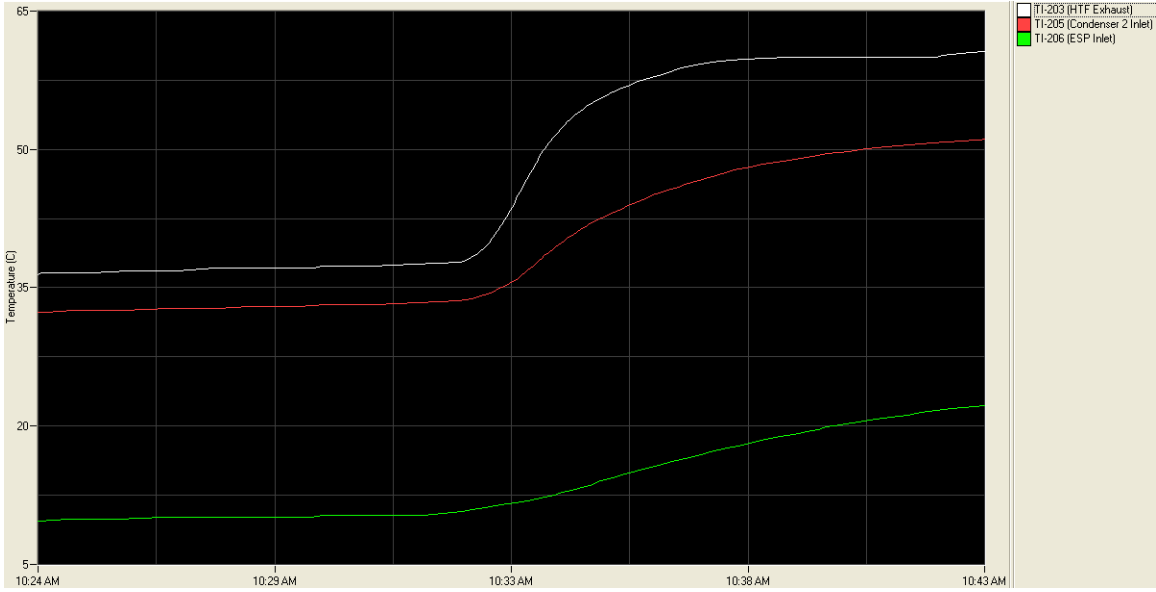
Figure 5.5 Bio-oil condensation train temperature profile at fluidization in ºC. TI-203 = High temperature filter exhaust temperature. TI-205 = Condenser 2 inlet temperature. TI-206 = ESP inlet temperature.
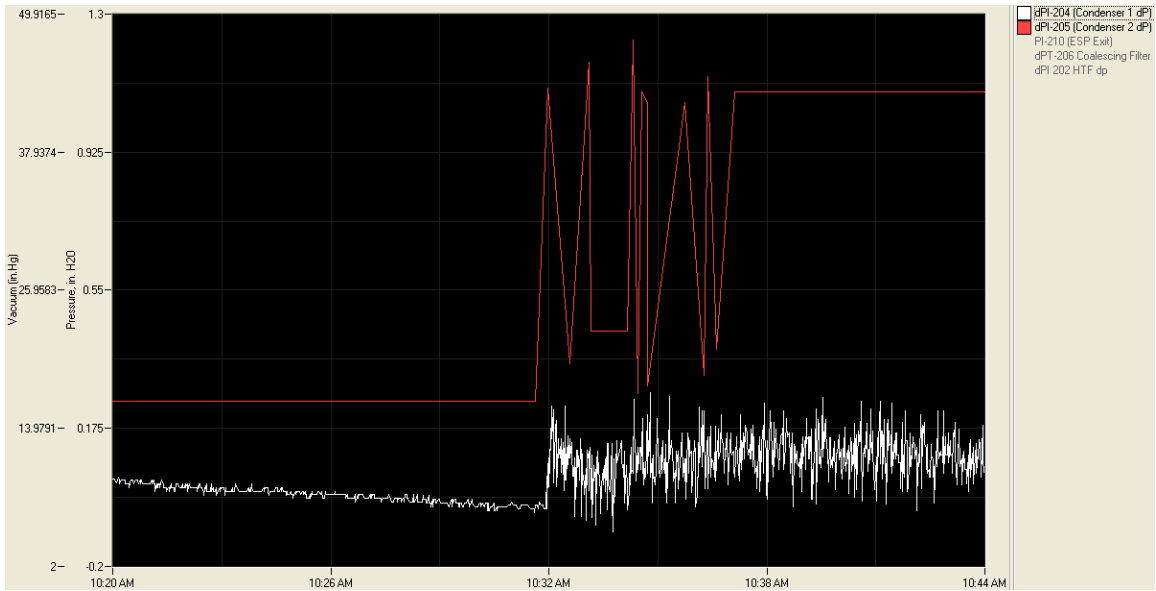
Figure 5.6 Condenser 1 and 2 pressure drops at fluidization in in. H_2O. dPI-204 = pressure drop across condenser 1. dPI-205 = pressure drop across condenser 2.
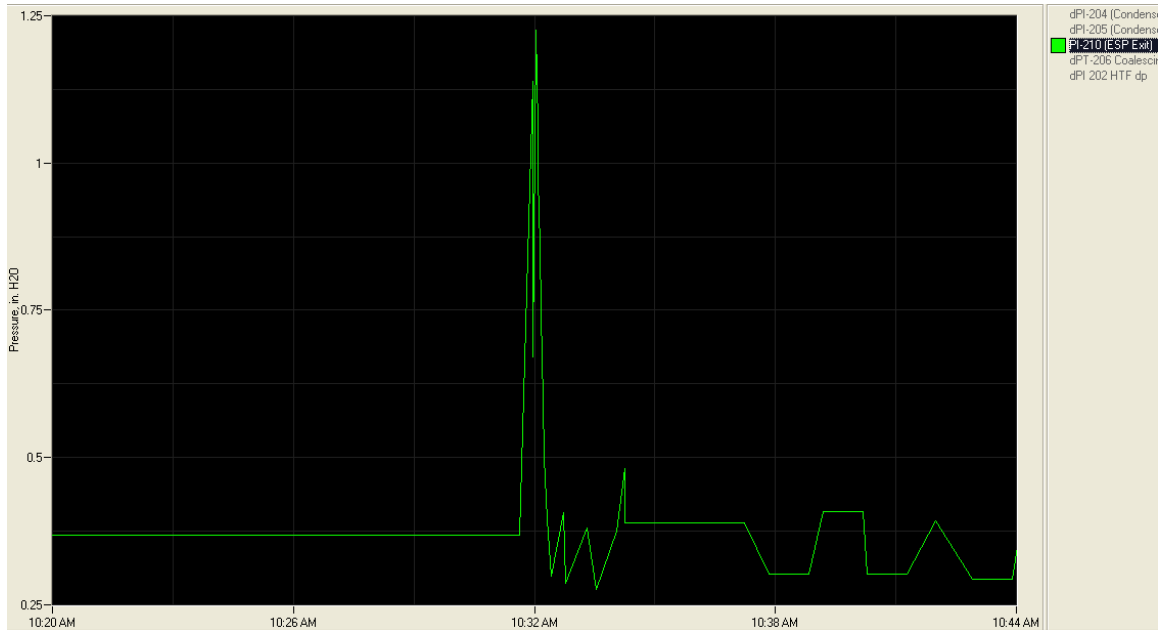
Figure 5.7 Wet electrostatic precipitator (WESP) pressure at fluidization. PI-210 = WESP

pressure in in. H$_2$O.

5.3 Pilot-Unit Operation

5.3.1 Start-up Procedures

Before heating the reactor unit, a specific set of start-up procedures had to be followed in order to ensure safety and a steady-flow through the system. The first thing to do was to turn on the power, nitrogen, instrument air, propane, and the process chiller. The nitrogen was used as a purge gas to loosen the char from the filter elements in the high temperature filter. The propane was set to flow at 0.85 SCFM but was not allowed to flow until an ignition switch was turned on later. Once these were on, the blowers and motors were set to auto so that they could be controlled from the computer. From the computer, PCV-106 (relief valve to flare) was set to maintain the freeboard pressure in the reactor at 8 in. H$_2$O. At this point, the air blower (MB-107) was set to provide ideal stoichiometric air (24 parts air:1 part propane) for the combustion of propane, ensuring

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complete combustion without excess oxygen. The syngas blower was then activated to provide 11 psig. At this point, the burner flow control was set at 10 SCFM and the bed flow control to 3 SCFM. When these values were reached, the burner control switch was turned on and the propane was ignited. To maintain an average bed temperature of 467ºC, the reactor bed was heated to nearly 500ºC before feeding began.

5.3.2 Feed System

Approximately one ton of poultry litter and 10 wt.% AmmoSoak was loaded into the industrial tumbling feed mixer at a time via front end loader. The litter/AmmoSoak mixture was mixed for about thirty minutes. At this time the front end loader was used to transfer 600 lb of feed into the primary hopper that sat upon a scale. From the hopper, the feed was transferred by auger to a secondary auger. The feed rate was controlled by adjusting the set point on the feed screw speed control (M-101) and was determined by the rate of weight loss from the primary hopper. The secondary auger (M-102) transferred the feed into the feed metering bin sealed from the atmosphere by a rotary valve (M-103). Once in the metering bin, the feed fell onto three live bottom screws (M-104) that could be adjusted to maintain a steady feed level in the bin. The live bottom screws fed the feed into the injection screw (M-105), which transferred the feed into the fluidized bed. To achieve thermal equilibrium in the bed M-101 and M-104 were set at 10% and 15%, respectively. This resulted in a dry feed rate of about 1.25 lbs/min.

5.4 Wet Electrostatic Precipitator (WESP) Operation

A diagram of the WESP is shown in Figure 5.8. The wet electrostatic precipitator was a pipe design that included inlet and outlet bustle distributors, a quartz glass high voltage

insulator, and collection sump for collection and draining of the bio-oil. The inlet and outlet were 2" diameter pipes. Materials of construction were 316SS for resistance to corrosion. A 30 kilovolt, 30 milliamp power supply was used to generate a corona on the central electrode. The central electrode had a ¼" diameter threaded rod to promote corona discharge.

The WESP was monitored for voltage and current feedback, and the voltage output was controlled by an operator set point. The power supply was self-protecting against short circuiting, and would shut down if a short circuit was detected.
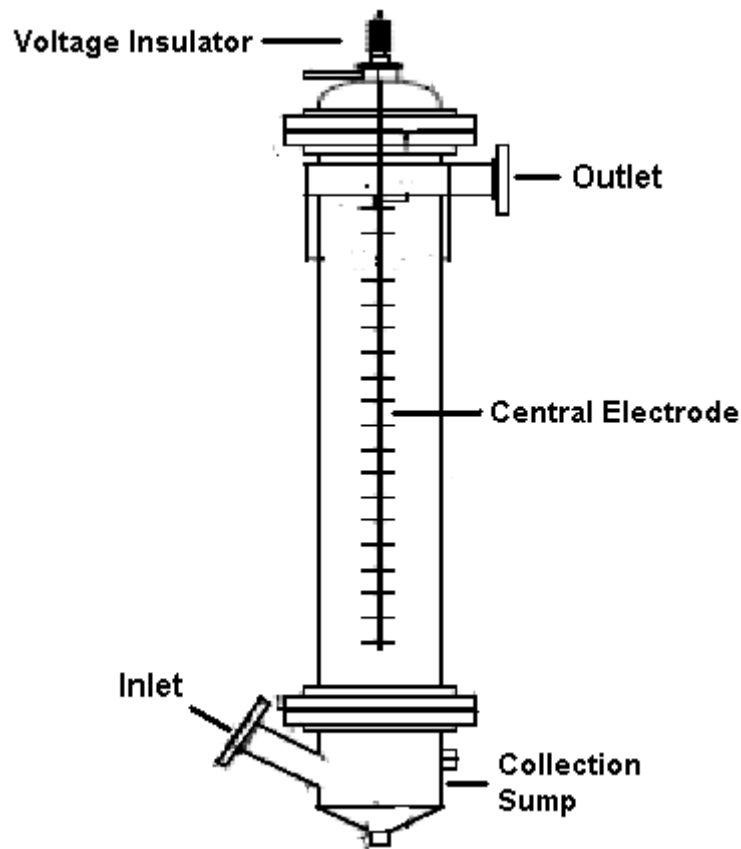
Figure 5.8 Diagram of the wet electrostatic precipitator (WESP)

5.4.1 Arcing Relative to Voltage and Current

Figure 5.9 shows the relationship between voltage and current applied to the WESP. The plot was recorded in a dry atmosphere with no pyrolysis gases traveling through the WESP. It can be seen that there is a direct relationship between the applied voltage and the resulting ionization current within the WESP. As the applied voltage decreased, the resulting ionization current decreased as well. This phenomenon can be used by active voltage controllers to apply the maximum voltage to the electrode without creating a breakdown of current in the WESP. It was discovered that if the resulting ionization current reached 0.52 mA, the resistance of the gases broke down and arcing occurred. Figure 5.10 shows an experiment demonstrating the ability to prevent arcing by reducing the applied voltage as the current approached 0.52 mA. In this experiment, the voltage set point was reduced manually as the current reached or exceeded 0.50 mA. It is clear that each time the voltage was decreased, the resulting current also decreased, preventing the occurrence of arcing. This was a clear demonstration of Ohm's law (V = IR). Because the resistance of the air (R) was constant, the voltage (V) was directly proportional to the current (I). It is important to apply the maximum allowable voltage without breakdown for several reasons: high applied voltages produce high electric fields which in turn charged more particles and created higher migration velocities of the particles to the collection surface (McDonald et al., 1982).
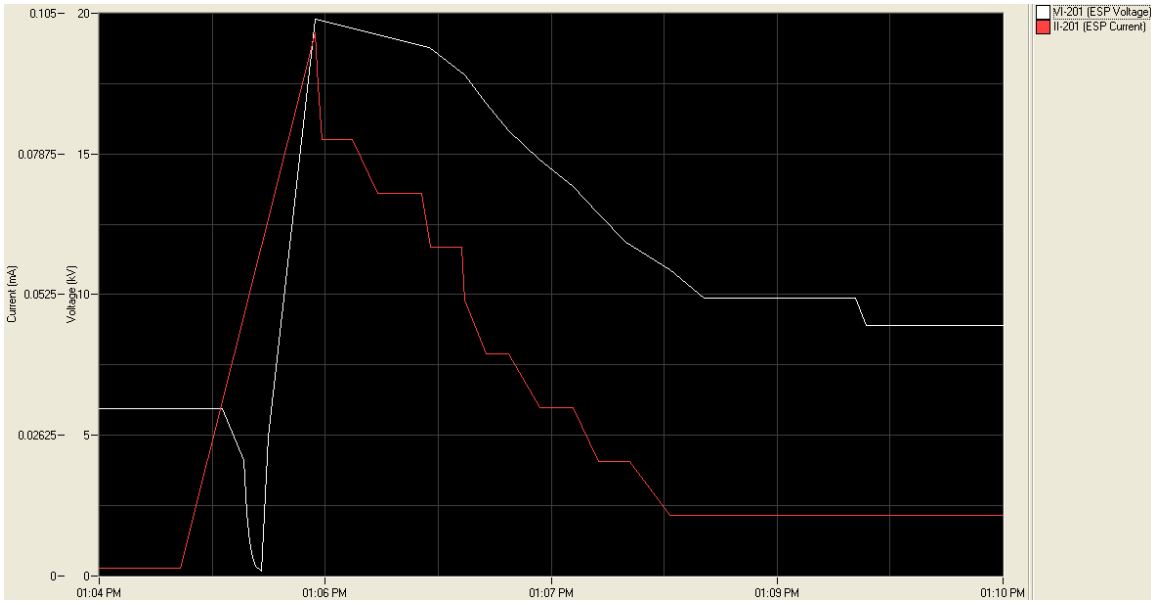
Figure 5.9 Direct relationship between WESP voltage and current. VI-201 = WESP

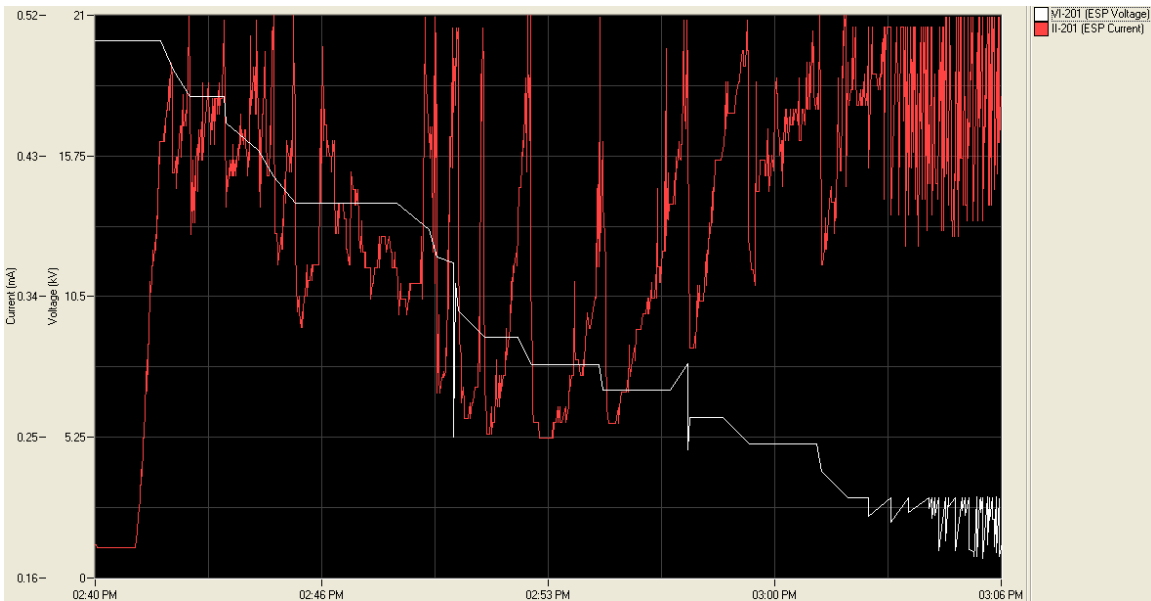Voltage in kV. II-201 = WESP current in mA.

Figure 5.10 Prevention of arcing by reducing voltage as current approached 0.52mA. VI-

201 = WESP Voltage in kV. II-201 = WESP current in mA.

There are a number of factors that could lead to the inefficiency of this WESP. One very

important factor in the design of any electrostatic precipitator is the presence of uniform

flow of low turbulence through the WESP. The main reason for this is due to the exponential nature of the collection mechanism, uneven treatment of the gas lowers collection efficiency in the high velocity zones to the extent that can not be compensated by collection in the areas of low velocity. To help achieve uniform, low velocity flow, several devices can be employed. Turning or guiding vanes help maintain low turbulence through duct work prior to the WESP inlet and plenum chambers and/or diffusion screens can be utilized at the inlet to slow the flow. Build-up of a product layer on the collection surface can also cause arcing in the WESP, reducing the efficiency of the unit. This reduces the distance between the electrode and collection surface, reducing the maximum allowable voltage (McDonald et al., 1982).

Another factor that affected the performance of this WESP in particular was the performance of the condenser system prior to the WESP inlet. The high moisture content of the feed and combustion gases put a strain on the system to collect the moisture and reduce the WESP inlet temperature. Increasing the moisture content of the process gases entering the WESP reduced the resistance of the gases to arcing (Schmidt, 1949). Increasing the temperature of the gases also reduce the resistance by effects of Brownian motion (Porle and Parker, 1997). It was observed that arcing could be prevented by reducing the applied voltage until the inlet temperature of the WESP exceeded 42ºC. At this point, no voltage no matter how low could be held without the WESP arcing. It was assumed that a combination of moisture content and Brownian motion contributed to this behavior.

5.5 Pyrolysis Product Collection

The high temperature filter had a heated nitrogen purge system designed to purge any char build up on the filter elements if the pressure drop across the filter exceeded 2 in. H_2O. Char was collected from the bottom of the unit by means of a screw auger. The auger carried the char to the top of a rotary air lock. Below the rotary air lock was a 50 gallon steel drum to store the char. The rotary air lock allowed the char to be collected without allowing any excess air into the system. A six inch hole was cut into the lid of the drum and a six inch sleeve placed over the exit of the rotary air lock and down into the hole to ensure collection of the char. It was important that the collection drum be metal because the char had a tendency to oxidize when exposed to air and generated a large amount of heat, hot enough to melt plastic containers such as low-density polyethylene.

The oils were collected from condensers 1 and 2 and the WESP. At the bottom of each unit was a collection sump with a ball-valve to open and close the drain. The original collection system designed utilized steel braided hose to connect the drain of the WESP to the drain of condenser 2 by way of T-valve and then to the drain of condenser 1 likewise. A pump was used to draw the products out of the system and pump them into a collection tank. This system did not work, however, because of the two fractions of liquid collected, the less viscous fraction (high water content) was successfully pumped into the tank, but the viscous fraction would slowly accumulate in the pump until it would overheat. A new system was introduced that worked better. Instead of having all three lines connected into one line and using a pump, the new system only utilized gravity for collection and collected from all three units into separate containers allowing for collection of individual samples.

The unit had an ethanol flush system attached to the top of each condenser unit to help collect the more viscous oils. The flush system proved unnecessary for condenser 1 and condenser 2 because the liquids collected in these units were more than 95% water. On the other hand, the WESP collected more viscous oils that drained very slowly from the unit requiring the solvent to lower the oil viscosity. The ethanol flush on the WESP wasn't a spray like the condensers, but instead was designed to drip down the wall to help minimize the influence on arcing in the unit. However, every time the ethanol was activated in the WESP, an increase in the WESP current was noticed, causing more frequent arcing. The high velocities of gas traveling through the WESP were probably enough to entrain the ethanol from the wall and into the gas stream, thus lowering its resistance to arcing.

5.6 Pyrolysis Experiment

5.6.1 Materials

Starter turkey and broiler litter for this experiment were collected from HideAway Farm of the Rohrer family in Dayton, Virginia located in the Shenandoah Valley. The broiler litter was collected from a house which changed its bedding once per year. On the other hand, the starter turkey litter came from a house in which the litter was changed every six weeks. The more frequent changing of the starter turkey litter resulted in less manure in the litter. Less manure resulted in lower levels of ash and proteins in the litter. AmmoSoak was obtained from steam explosion experiments on corn cob performed at the Thomas M. Brooks Forest Products Center (Virginia Tech). 10 wt.% AmmoSoak was mixed with broiler litter in an industrial tumbling feed mixer.

5.6.1.1 Moisture Content

Prior to pyrolysis, all samples were analyzed for their moisture content using an HG53 Halogen Moisture analyzer (Mettler Toledo, Greifensee, Switzerland). The HG53 heats 1 g of sample to 105°C over a time of 30 minutes and records the weight loss. The analyzer then displays the moisture content as percent moisture.

5.6.1.2 Higher Heating Value (HHV), Ash Contents, and Elemental Compositions

The HHV, ash content, and elemental compositions of each feed stock were determined by Galbraith Analytical Laboratory (Knoxville, TN, U.S.A.).

5.6.2 Methods

5.6.2.1 Pyrolysis of Poultry Litter

Before pyrolysis, the mass of the char collection drum and the three oil collection containers were recorded along with the mass of litter in the hopper. To pyrolyze the poultry litter, the reactor and high temperature filter were heated to 500 and 250ºC, respectively. Once these temperatures were achieved, the feed system was activated for a feed rate of 1.1 lb/min. This resulted in a reactor temperature of about 467ºC. Litter was then fed for at least one hour. At this point, the feed system was shut down and the system allowed to run for ten minutes to ensure all reaction products went through the filter and condensation train. Once the system was clear and the heat shutdown, the high temperature filter and condensers were emptied into their individual collection vessels and the vessels were massed again. The differences in mass before and after were recorded as the yields of char and oil.

5.6.2.2 Separation into Water Soluble and Insoluble Fractions

The water soluble and insoluble fractions of the bio-oils were separated using suction filtration. A Büchner funnel was connected to a side-arm flask by means of a neoprene adapter to an aspirator for vacuum filtration. The filtration paper was placed on the plate, and the filter paper was moistened with 5 mL of water to prevent initial leakage. The liquids were then poured into the cylinder and drawn through the perforated plate by vacuum suction.

5.6.2.3 Higher Heating Value (HHV), Ash Contents, and Elemental Compositions

The higher heating values, ash contents, and elemental compositions of each sample were determined by Galbraith Analytical Laboratory (Knoxville, Tennessee).

5.6.2.4 Thermogravimetric Analysis of Differential Scanning Calorimetry and FT-IR Analysis

Thermogravimetric analysis (TGA) was conducted on the oil using a TA Instruments Q600 SDT (TA Instruments, New Castle, DE, U.S.A.). 20 mg of sample was placed in an alumina crucible and was subjected to thermogravimetric analysis with 50 ml/min of nitrogen as the carrier gas. The heating rate was 5ºC/min from 25ºC to 800ºC. FT-IR analyses were performed on the oils using an IR spectrometer (Nicolet Avatar, 370 DTGS) equipped with a DTGS-KBR detector in multi-bounce horizontal attenuated total reflectance (HATR) mode. The spectrum was collected over a range of 4000-650 cm^{-1}. A 4 cm^{-1} resolution was used over 64 scans. A background gain of 4.0 was used.

5.6.3 Results and Discussion

A bed temperature profile of a typical run is shown in Figure 5.11. Pyrolysis runs were limited in time by constant issues with the WESP. A typical experiment lasted about 95 minutes with a feed rate of 1.25lb/min. Differences in product yields and compositions from those found on the bench-scale could result from differences in bedding, the age and breed of birds, density of confinement, feed conversion rate, feed ration, moisture content of bedding material, type of floor (dirt, concrete, etc.), climatic conditions during litter accumulation, and any organic matter and N losses (Perkins et al., 1964).
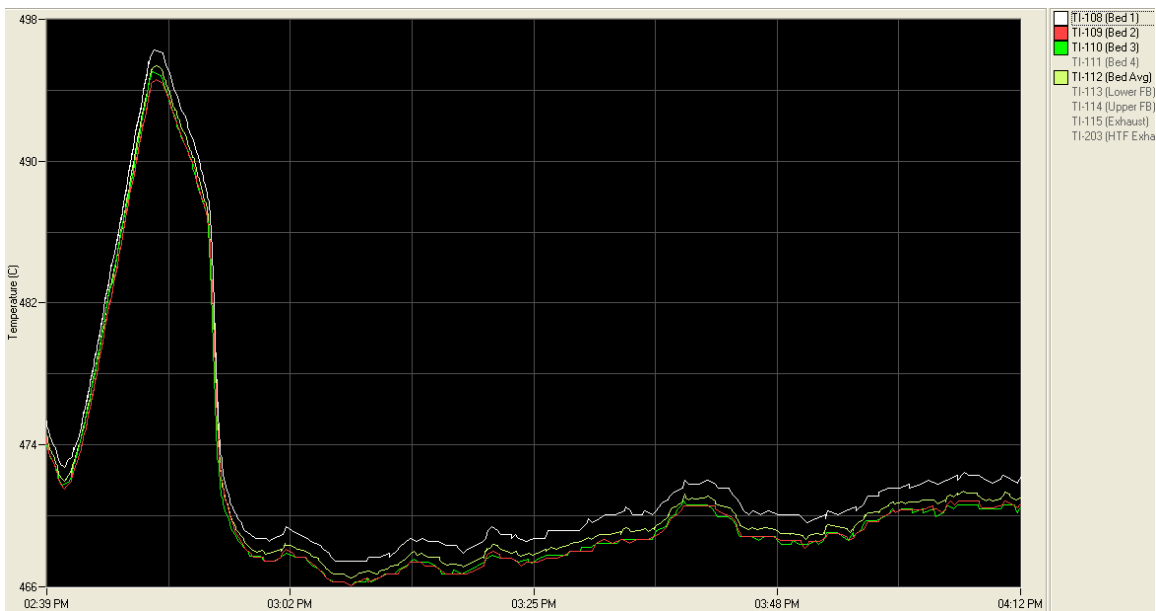
Figure 5.11 Bed temperature profile for a typical run in ºC. TI-108 = Temperature of bottom of reactor bed (Bed 1). TI-109 = Temperature one thermocouple from bottom of reactor bed (Bed 2). TI-110 = Temperature two thermocouples from bottom of reactor bed (Bed 3). TI-112 = Average bed reactor temperature (Bed Ave.).

Table 5.1 shows the ultimate analysis of the broiler and starter turkey litter and AmmoSoak used in the experiments. The moisture content of the litter is very close to the

minimum moisture content (12%) suggested by McKinley to prevent the litter from being excessively dusty during handling and processing. The starter turkey litter had a greater moisture content than both the broiler and AmmoSoak, but still less than that reported as too great by McKinley (25%) (2000). The ash content of the broiler (18.82%) and the starter turkey (13.86%) were much greater than that of the AmmoSoak (1.22%) but less than the average of 24% for broiler litter reported by Stephenson et al.. (1990). The litters had a much greater ash content than the AmmoSoak due to the fact that a certain amount of soil was collected when cleaning out a house as well as the mineral content of the poultry manure in the form of Ca, K, and P. The carbon content of AmmoSoak (35.62%) was 22% greater than that of the broiler (29.16%) but less than that of the starter turkey (41.68%). The nitrogen content of the broiler litter (3.76%) was equal to the average nitrogen content reported by Stephenson et al. (1990) for broiler litters and that of the starter. The starter turkey litter had a lower nitrogen content (2.83%) than the broiler, as was expected. This was significantly greater than that of the AmmoSoak (<0.5%). The greater nitrogen content is a result of uric acid in the litter as well as other proteins. Broiler litter had lower carbon, hydrogen, and oxygen contents than the AmmoSoak due to its relatively high ash content (Table 5.1). The oxygen content of this broiler sample was greater than those reported in literature probably leading to the lower higher heating value as well. On the other hand, the sulfur and chlorine levels of the litter were much greater than those of the AmmoSoak (Table 5.1).

Table 5.1 Ultimate analysis of broiler and starter turkey litter and AmmoSoak

Elemental Composition (wt.%)	Broiler	Starter Turkey	AmmoSoak
C	29.16	41.68	35.62
H	4.64	3.56	5.51
N	3.76	5.8	<0.5
O (by diff.)	41.95	30.43	57.52
S	0.854	0.64	<0.05
Cl	0.817	0.26	0.128
Ash	18.82	13.86	1.22
Moisture	11.3±0.48	18.47±1.02	4.9±0.38
HHV (MJ/kg)	14.32	17.63	12.98

5.6.3.1 Liquid Yields

Collecting the liquid product was the biggest challenge to the pilot-scale reactor. The total liquid yield collected was only 9.3 wt.%. This is particularly disappointing because a 95 minute run should result in 12.7 lb of water from the combustion of propane alone, but only 9.1 lb of liquid were collected. Figure 5.12 shows the distribution of water soluble and insoluble fractions gathered in each unit. It shows that condensers 1 and 2 were almost solely collecting water soluble fractions. They were not cooling the stream enough to condense all of the water. A majority (69%) of what the WESP collected was also water solubles. It was obvious that the condenser system wasn't sufficiently cooling the vapors. Figure 5.13 shows the temperature profile of the condenser train before at and after fluidization. Only ten minutes after fluidization the inlet temperature to condenser 2 and the WESP were already 52ºC and 24ºC, respectively. Within 27 minutes of feeding, the inlet temperature to the WESP was 46ºC. By the end of a run this temperature would exceed 64ºC.
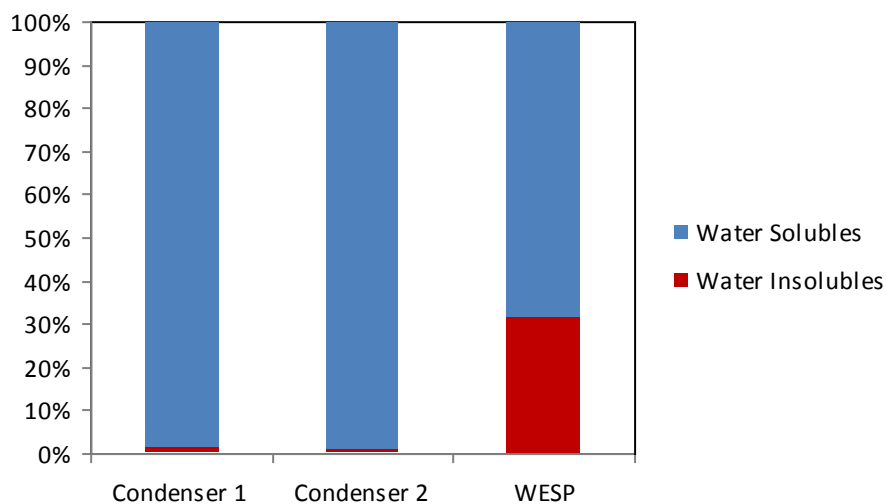
Figure 5.12 Fraction of water solubles and insolubles collected in each unit
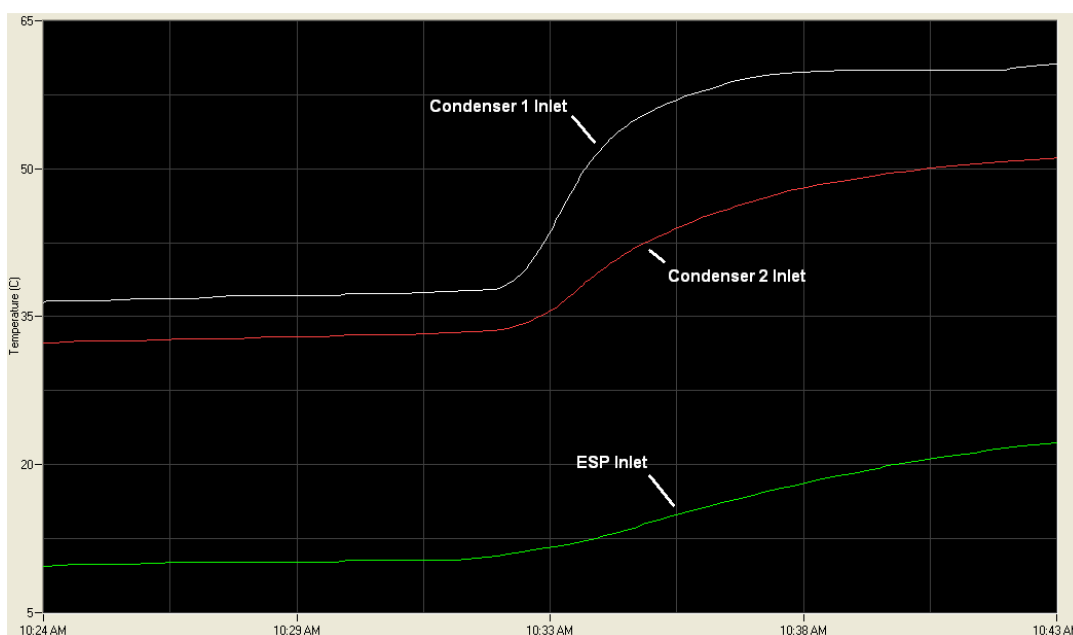
Figure 5.13 Temperature profile of condenser train before and after fluidization

5.6.3.2 Liquid Composition

Results from the elemental analysis of the water soluble and insoluble fractions are shown in Tables 5.2 and 5.3, respectively. The relatively high levels of carbon, nitrogen, sulfur, and chlorine are probably a result of fine char passing through the high temperature filter into the first condenser. This was supported by the elevated levels of

ash in the first condenser as well. As for the high levels of the same elements in the WESP, these could be attributed to ultra fine particles of char trapped in smoke. Condenser 2 had the highest level of oxygen in the water solubles, possibly in the form of hydroxyl units in alcohols and phenols. The average chemical compositions show that the water solubles collected in condenser 2 were significantly different from those in the other units.

Unlike the water solubles, the water insolubles in condenser 2 had the highest amount of carbon (59.01%). The high levels of ash in the insoluble fractions of all three units further support the presence of char. It is worth noting the much higher concentrations of chlorine in condenser 1 and the WESP. The high carbon content and lower oxygen content in condenser 2 insolubles probably resulted in the highest HHV of the three units (26.1 MJ/kg). All three of the insolubles from the pilot-scale had lower carbon, hydrogen, and nitrogen than the samples produced on the bench-scale. The bench-scale also had a higher HHV. This is to be expected from the results of the AmmoSoak study; decreasing the amount of manure in the feed lowered the HHV.

Table 5.2 Elemental composition of water soluble fractions

Elemental Composition (wt.%)	Unit		
	Condenser 1 Water Solubles	Condenser 2 Water Solubles	WESP Water Solubles
C	5.66	1.70	6.17
H	10.68	10.36	9.96
N	1.15	<0.5	1.44
O (by diff.)	59.98	65.45	51.62
S	0.079	<0.05	0.091
Cl	192 (ppm)	75 (ppm)	672 (ppm)
Ash (wt.%)	0.308	0.123	0.584
Moisture (wt.%)	88.01	87.83	82.56
H/C molar	22.64	73.12	19.37
O/C molar	7.94	28.87	6.27
N/C molar	0.17	0.20	0.20
Average Chemical Composition	$CH_{22.72}O_{7.98}N_{0.17}$	$CH_{74.00}O_{29.22}N_{0.26}$	$CH_{19.53}O_{6.33}N_{0.20}$

Table 5.3 Elemental composition of water insoluble fractions

Elemental Composition (wt.%)	Condenser 1 Water Insolubles	Condenser 2 Water Insolubles	WESP Water Insolubles	Bench Scale
C	46.86	59.01	54.54	62.48
H	4.30	7.02	7.60	8.20
N	4.03	3.13	4.04	6.81
O (by diff.)	16.25	17.86	25.50	22.01
S	0.43	0.39	0.24	0.37
Cl	542 (ppm)	173 (ppm)	556 (ppm)	0.13%
Ash	14.57	10.70	7.45	0.26
Moisture	17.26	15.11	16.24	8.27
HHV (MJ/kg)	25.8	26.1	25.4	28.1
H/C molar	1.10	1.43	1.67	1.57
O/C molar	0.26	0.23	0.35	0.26
N/C molar	0.07	0.05	0.06	0.09
Average Chemical Composition	$CH_{1.10}O_{0.26}N_{0.074}$	$CH_{1.43}O_{0.23}N_{0.045}$	$CH_{1.67}O_{0.35}N_{0.063}$	$CH_{1.57}O_{0.26}N_{0.093}$

5.6.3.3 Thermogravimetric Analysis of Bio-oils

Thermogravimetric (TG) and differential thermogravimetric (DTG) analyses were performed on each pyrolysis oil. All analyses were performed under nitrogen at a heating rate of 5°C/min. The nitrogen flow rate was 50 ml/min. The TG and DTG curves are shown in Figures 5.14-5.16, respectively. The TG curves show that the weight loss of the oils was a gradual process with no clear steps. All of the oils showed peaks below 148°C. These peaks were most likely attributed to the decomposition of light volatile compounds such as acetic acid, methanol, and maybe organic chlorine compounds such as methyl_3-chlrobenzoate or chlorobenzene which boil at 101°C and 132°C, respectively (Dreisbach, 1955). The peaks on the curves between 175°C and 250°C were most likely caused by the degradation of monolignols which are source materials for the biosynthesis of both lignans and lignin. The remaining peaks at temperatures greater than 380°C were attributed to the degradation of heavy non-polar compounds such as hydrocarbons and ethers. The DTG thermogram in Figure 4.14 suggests that the water-insoluble fraction of the bio-oil from the WESP contained a high-temperature polymeric material. The monomeric material degraded at 225ºC, the dimeric material, which is more crystalline, degraded at 431ºC, while the cross-linked polymers degraded from 640ºC to 728ºC.
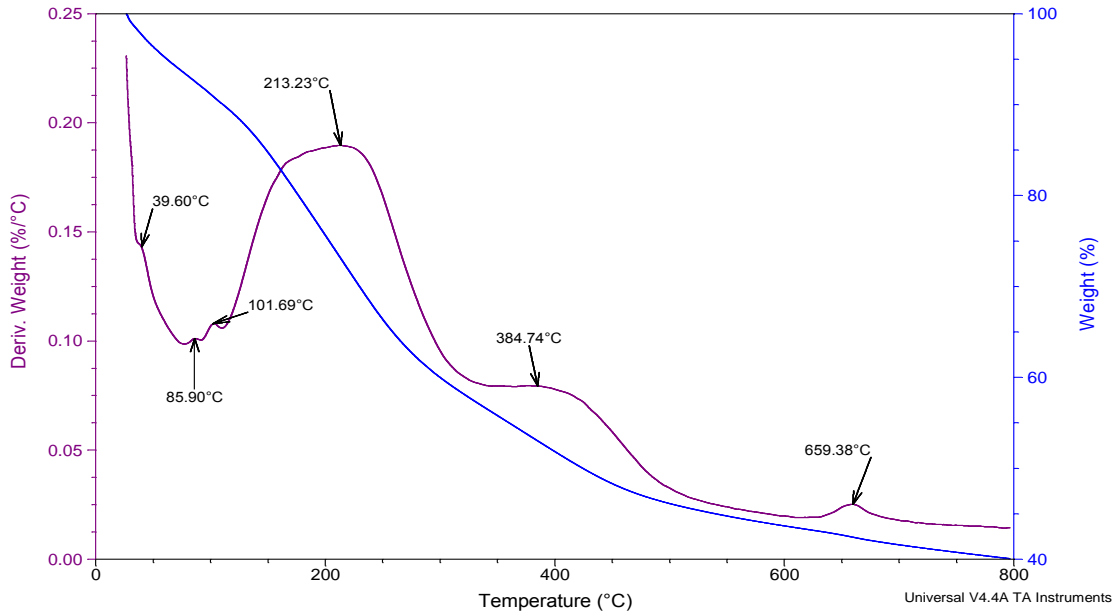
Figure 5.14 TG and DTG curve for water insolubles from condenser 1
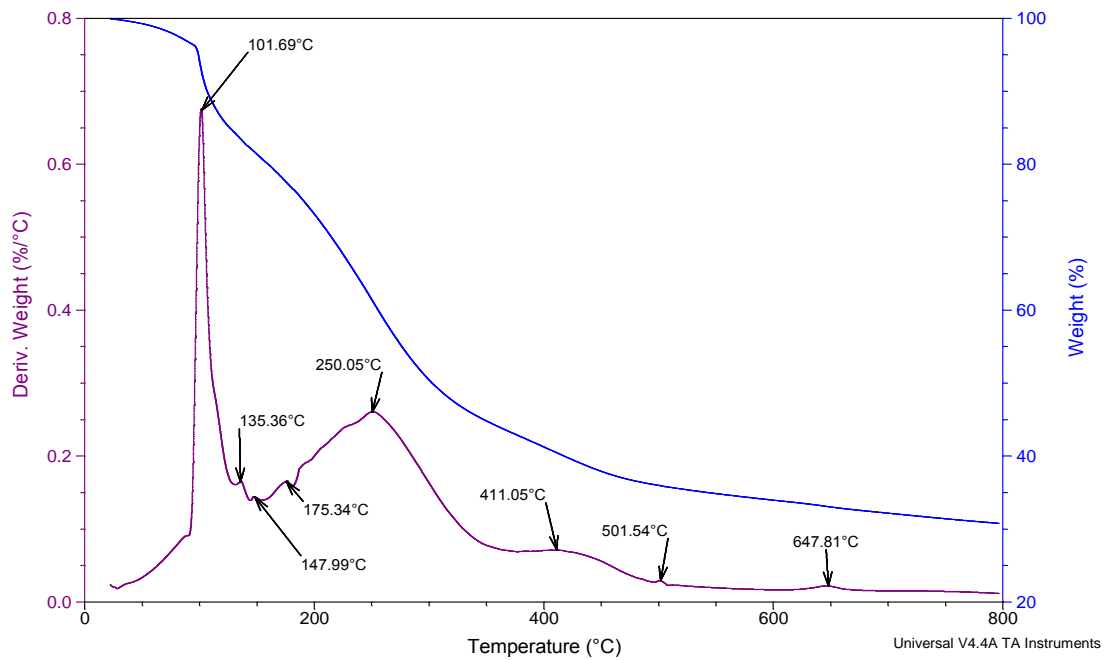

Figure 5.15 TG and DTG curves of water insolubles in condenser 2

Sample: ESP SOLIDS
Size: 19.6850 mg
Method: Ramp

DSC-TGA

File: C:\TA\Data\TGA\RYAN\LARGE\ESP_SOLIDS.C
Operator: RCAT
Run Date: 20-Apr-2009 13:38
Instrument: SDT Q600 V8.3 Build 101
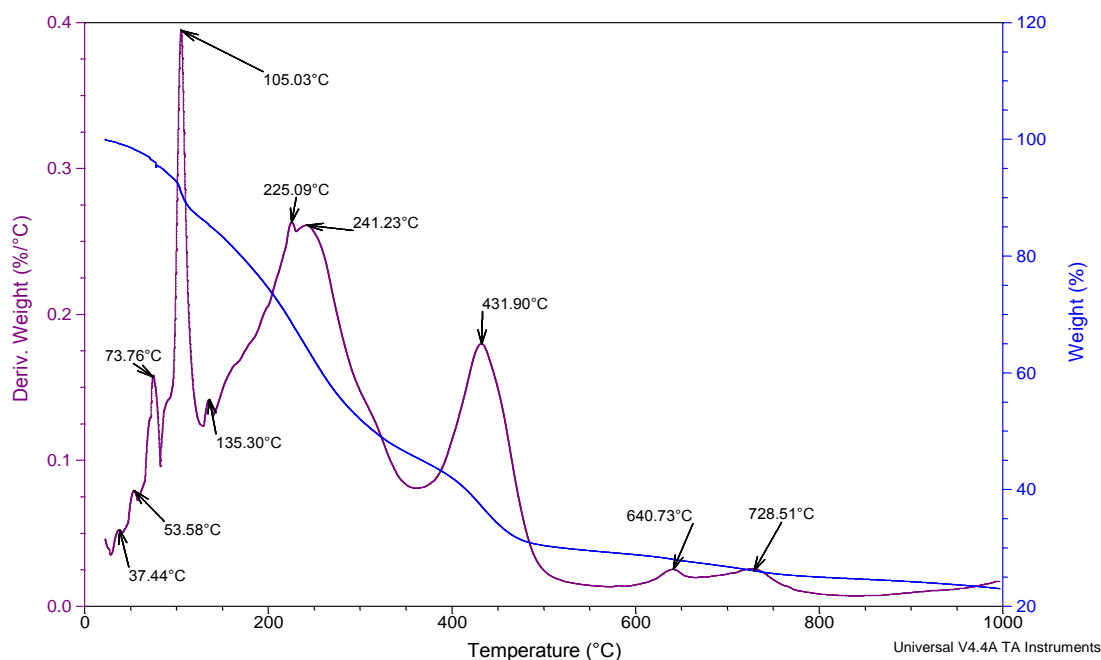
Figure 5.16 TG and DTG curves of water insolubles in the WESP

5.6.3.4 FT-IR Analysis

The FT-IR spectra of the water soluble fractions are shown in Figure 5.17. It is clear that this fraction is composed mainly of alcohols and phenols (3500-3000 cm^{-1}) and aromatics and alkenes (1640-1400 cm^{-1}). The water solubles from condenser 2 had a greater content of alcohols and phenols than the other two units. This could be a result of the greater oxygen content in the condenser 2 solubles allowing for more hydroxyl units or from the hydration of alkenes in a slightly acidic environment into alcohols and phenols. The lower content of alkenes and aromatics in condenser 2 supports the latter.

Figure 5.18 shows the FT-IR spectra of the water insolubles collected in the WESP. Much like the oils collected from broiler litter on the bench-scale, those collected from the pilot-scale were composed of aliphatic hydrocarbons, amides, other nitrogenous compounds, alkenes, aromatics, alcohols, and phenols. They were particularly rich in

aliphatics, hydrocarbons, amides, and alcohols. When compared to the oils with 10% AmmoSoak content from the bench-scale they were richer in aromatics, alkenes, alcohols, and phenols (Table 5.4). This was expected because this spectrum was a fraction of the total oils, whereas the spectrum from the bench-scale unit represents the total oil without fractionation. Since the turkey samples had less manure and nitrogen than the broiler samples, they also had less aliphatic hydrocarbons, amides, and other nitrogenous compounds.
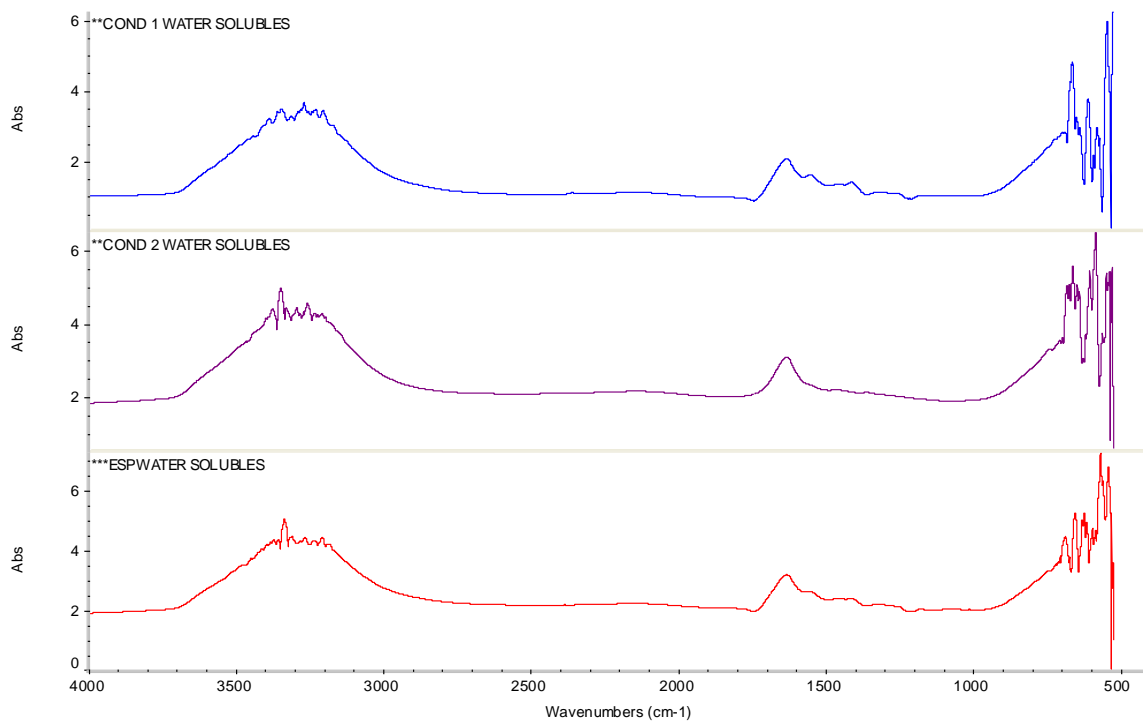
Figure 5.17 FT-IR spectra of water soluble fractions of starter turkey litter
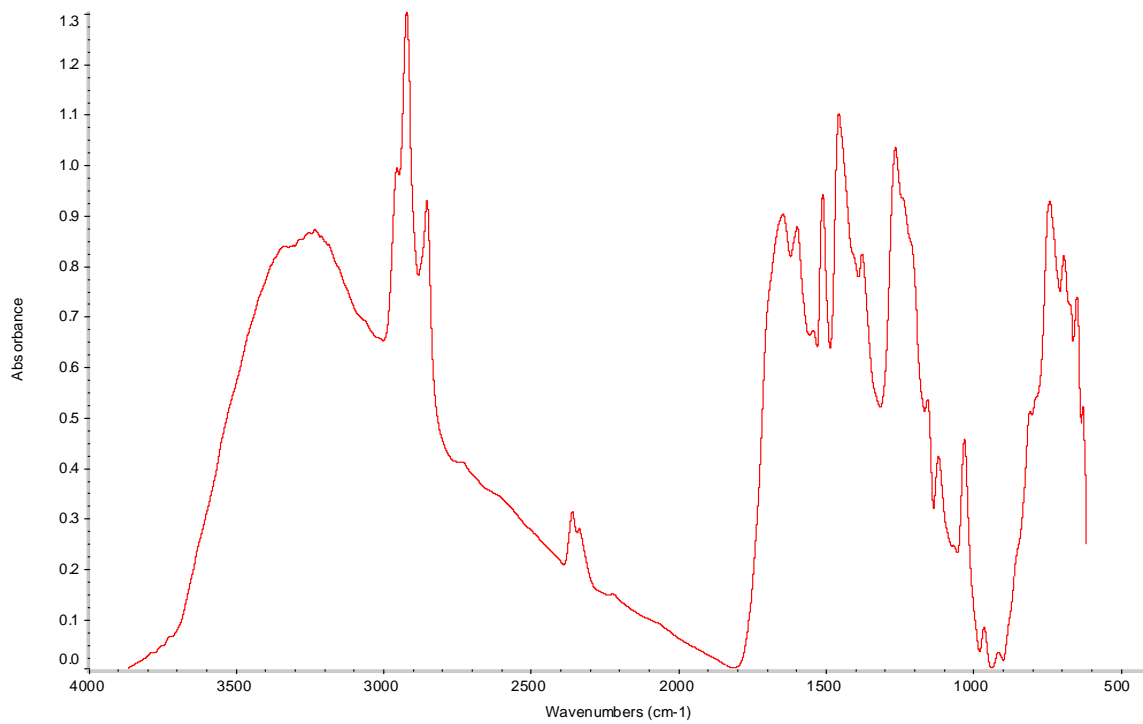
Figure 5.18 FT-IR spectra of WESP water insoluble fraction of bio-oil from starter turkey

litter.

Table 5.4 Relative intensities of absorption bands of water insolubles

	Relative Intensity			
Assignment	**Wave number (cm-1)**	**Bench**	**Pilot**	**Percent Difference**
O-H stretch, N-H stretch	3234	0.90	0.93	2.7
Methylene CH2 asymmetric stretch	2924	1.37	1.06	-23.1
Amide Carbonyl C=O	1648	1.23	0.96	-22.0
Aromatic skeletal vibration with C=O stretch	1600	-	0.93	-
Amide II, N-H bending vibration	1544	1.05	0.71	-31.7
Aromatic skeletal vibration	1513	1.00	1.00	0.0
C-H deformation (asymmetric)	1458	1.22	1.17	-4.1
Alcohols and Phenols	1267	0.99	1.10	11.0
Secondary aliphatic alcohol C-O stretch	1119	0.60	0.64	5.8
Primary aliphatic alcohol C-O stretch	1033	0.59	0.63	6.5
NH2 out-of-plane bend	742	0.64	0.56	-12.2
NH2 wagging	695	0.59	0.51	-13.6
O-C=O in-plane deformation	651	0.89	0.78	-11.6

5.6.3.5 Char Yields

Table 5.5 summarizes the char yields from the pilot-scale pyrolysis experiments. Using broiler as a feed, the average moisture free char yield was 32.2% and 42.9% on a moisture and ash free basis. Compared to a feed mixture with 10wt.% AmmoSoak

pyrolyzed on the bench-scale unit, these yields are about 9% less. This could be explained by two factors. First, the mean reactor temperature for the pilot-scale reactions (~467ºC) was about 25ºC greater than those on the bench-scale unit (442ºC). It has been shown that the char yield decreases as the reactor temperature increases (Demirbas, 2004). Second, char particles were found in the bio-oil collected from the first condenser. This suggests that the high temperature filter was either not performing to specification or had some sort of damage.

Table 5.5 Summary of pilot-scale char experiments

Run	Feed	Mass Feed (lb)	Feed Ash Content	Mass Char (lb)	Moisture Free Yield	Moisture and Ash Free Yield
1	1 yr Broiler	100.0	19.0	26.0	34.2	45.5
2	1 yr Broiler	87.0	19.0	19.0	28.7	38.2
3	1 yr Broiler	100.0	19.0	24.0	31.5	42.0
4	1 yr Broiler	187.0	19.0	49.0	34.4	45.9
5	St. Turkey	116.0	13.6	20.5	20.5	25.1
Average*		118.5	19.0	29.5	32.2	42.9
Standard Error*		23.0	0	6.7	0.013	0.018

* Excludes Run 5

5.6.3.6 Char Composition

Table 5.6 shows the elemental compositions for chars produced on the pilot and bench-scales from litter with 10 wt.% AmmoSoak. The chars were fairly similar, which can be seen in the average chemical compositions. The biggest difference was in the H/C molar

134

ratio. Its worth noting that although the pilot-scale feed had less nitrogen and hydrogen than the bench-scale feed, a greater amount of the elements were concentrated in the char. Otherwise, the two samples compared very closely.

Table 5.6 Elemental compositions of pyrolysis chars from broiler litter

Elemental Composition (wt.%) *	Pilot-Scale	Bench-Scale
C	41.06	36.29
H	2.26	1.10
N	3.59	2.25
O (by diff.)	4.42	5.98
S	1.25	1.43
Cl	1.34	2.41
Ash	46.08	50.54
Moisture	2.76	2.06
H/C molar ratio	0.66	0.36
O/C molar ratio	0.08	0.12
N/C molar ratio	0.08	0.05
Average Chemical Composition	$CH_{0.66}O_{0.08}N_{0.08}$	$CH_{0.36}O_{0.12}N_{0.05}$

*Moisture free

5.7 Potential Applications of Poultry Litter Pyrolysis Products

Any commercial applications of pyrolysis bio-oils from poultry litter will depend on many factors and will vary with scale, location, and its associated economic and logistical factors (Brammer, 2005). Three of the most promising applications of bio-oil are combustion for the production of heat in poultry houses as a substitute for liquid propane or for the production of electricity by engine or turbine, power generation by diesel engine, or the as a feedstock for chemical production. Chemicals that have been reported as recovered include polyphenols for resins with formaldehyde, calcium and/or magnesium acetate for biodegradable de-icers, fertilisers, levoglucosan,

hydroxyacetaldehyde, and a range of flavourings and essences for the food industry (Bridgwater, 1999). The DTG thermogram of the water-insoluble fraction suggests that this material could be a source of high-temperature polymeric material.

In 1999, Diebold et al. proposed specifications for biomass derived oils. The oils produced on the pilot scale reactor met some of the specifications but also failed to meet others. The less viscous (1.1cSt), water soluble fractions met the requirements for maximum viscosity, which is 4.1 cSt at 40ºC. On the other hand, the water insoluble fractions were very thick tars and too thick to measure the viscosity even at 60ºC. Ash was a major concern. The maximum acceptable ash content is 0.10 wt.%. All water soluble and insoluble fractions contained greater ash contents than this. The minimum was in the condenser 2 solubles (0.123 wt.%) and the maximum in the condenser 1 insolubles (14.57 wt.%). All fractions but the condenser 1 water insolubles met the specifications for maximum sulfur content (0.4 wt.%). A particular challenge to meeting these requirements was the high nitrogen content in the feed. None of the fractions meet the maximum specifications for nitrogen content (0.4 wt.%) (Diebold et. al, 1999). Many of these specifications could be met if the char was collected more efficiently and not allowed to collect in the oil fractions.

Potential applications for the char produced in the pyrolysis of poultry litter exist too. At the local scale, soil organic carbon levels shape agro-ecosystem function and influence soil fertility and physical properties, such as aggregate stability, water holding capacity and cation exchange capacity (CEC) (Milne et al., 2007). Chars from the pyrolysis of biomass have been shown to improve the ability of soils to retain nutrients in cation form that are available to plants (McHenry, 2009). The char collected from the pyrolysis of

poultry litter showed promise as a fertilizer and soil conditioner. Table 5.6 shows that the chars poses a high nitrogen (3.59 wt.%) and ash (46.08 wt.%) contents. These together with the relatively high carbon content (41.06 wt.%) support the use as a fertilizer or soil conditioner.

In addition to a fertilizer or soil conditioner, bio-char itself may be sold as is, or activated with steam to produce activated carbon. The highly developed internal surface area and porosity of activated carbon results in considerable adsorptive abilities. Activated carbon has a wide range of high value uses that include water and gas treatments, material recovery, catalysts and gas storage applications (Zanzi et al., 2001).

5.8 Challenges to Further Development of Pilot-Scale Pyrolysis Unit

There were several challenges to operating the pilot-scale pyrolysis unit that must be addressed for further development. The first issue was caused by rocks that were sometimes collected in the litter when cleaning out the poultry houses. These rocks caused the feed augers to jam when fed. A simple screening process would not work because the rocks nor the litter were of uniform size. Another issue lied in maintaining an air tight seal between the outside environment and the feed metering bin. Pyrolysis vapors and gases tended to escape from the rotary air lock atop the metering bin. These vapors rapidly increased the moisture content of the feed entering the bin, ultimately causing the feed to cake in the vanes of the rotary lock. This clogging of the vanes reduced the possible feed rate and sometimes caused the rotary air lock to cease completely. An air purge was implemented directly below the rotary air lock to prevent the pyrolysis vapors and gasses from infiltrating the vanes, but it was not possible to ensure air was not entering the reactor and causing combustion of the feed. The air purge

could have been replaced with a nitrogen purge to ensure no combustion was possible, but using more nitrogen requires more money. The condenser cooling capacity was another issue with the system. The two condensers were unable to sufficiently cool the pyrolysis vapors. A significant amount of moisture was left in the vapors entering the WESP, causing a major loss of collection efficiency. It was observed that once the inlet temperature of the WESP exceeded 42ºC, arcing occurred very frequently and even a reduction of voltage couldn't prevent the breakdown. Developing solutions for these challenges would help ensure a more consistent feed rate into the reactor and improve the collection efficiency of the product collection train.

5.9 Conclusions

A pilot-scale fluidized bed reactor was started and shaken down for the pyrolysis of poultry litter. Fluidization of the reactor bed was successfully demonstrated by evidence of the bed temperature and reactor pressure profiles. A stable reactor temperature of about 470ºC within the reactor was achieved with a biomass feed rate of 1.1 lb/min. The reactor was heated by the combustion of liquid propane, so to ensure complete combustion was achieved, the combustion water was collected to compare to the stoichiometric yield of water. Complete combustion was in fact achieved. The bio-oil yields were very low compared to those on the bench-scale. Yields of only 9% were achieved. This was attributed to inefficiencies of the condensation train and electrostatic precipitator. These could result from under-sizing of the equipment, insufficient insulation of the condensers, too high of an operating temperature at the high temperature filter, or too short of a residence time in the condensers. The water soluble fractions of the bio-oils were rich in oxygen, while the water insoluble fractions were rich in carbon

and ash. The high contents of carbon and ash in the water insoluble fraction were attributed to damage or inefficiencies of the high temperature filter in collecting the char product. Even with these inefficiencies, the average char yield achieved was 32%.

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CHAPTER 6

SUMMARY AND RECOMMENDATIONS

The feedstocks were analyzed for elemental composition, higher heating value and by thermal gravimetric (TG) analysis. The product yields were determined gravimetrically. Solid (char) products were collected in a high temperature filter. Liquid (bio-oil) samples were collected in a series of two ethylene glycol cooled condensers and an electrostatic precipitator. Gaseous products (syngas) were determined by the difference from 100% and not collected on the bench-scale. On the pilot-scale, the Syngas was recycled and combusted to supplement the heat requirements of the system. In addition to the yields, the liquid products were analyzed for elemental composition, pH, higher heating value (HHV), viscosity and viscosity versus age, density, moisture content, and by thermal gravimetric analysis, Fourier Transform Infrared, FTIR, spectroscopy, and ^{13}C-nmr analysis. The char was also analyzed for elemental composition.

Poultry litter had a greater HHV, moisture content, ash content and nitrogen, sulfur, and chlorine contents. Thermal gravimetric analysis of the litter indicated poultry litter was a mixture of light volatiles, water, hemicelluloses, cellulose, lignin, and proteins. AmmoSoak had greater carbon, hydrogen, and oxygen contents. It had a simpler composition of hemicelluloses, cellulose, and lignin. Results from the bench-scale studies indicated that the addition of AmmoSoak had an effect on the yields and all studied characteristics of the products. The pyrolysis bio-oils were rich in carbon and oxygen and these contents increased with the addition of AmmoSoak to the feed. As the AmmoSoak content of the feed was increased bio-oil and syngas yields increased and char yields decreased. This was most likely from the "dilution" effect on the ash and mineral

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contents of the feed by the addition of AmmoSoak. The pH of the resulting bio-oils decreased as the AmmoSoak content of the feed increased, most likely resulting from the release of carboxylic acids from the carbohydrate content of the AmmoSoak. With an increase of AmmoSoak content, the density of the oils increased. This was attributed to the fact that the moisture content of the oils decreased and to potential non-degraded oligomeric carbohydrates. The addition of AmmoSoak to the feed decreased the initial viscosity as well as the rate at which the viscosity increased with age. The increase of acids most likely catalyzed hydrolysis reactions in the oils and prevented repolymerization reactions that would increase the viscosity. The higher heating value of the oils decreased with the addition of AmmoSoak. This was attributed to the increased oxygenation of the oils. Thermal gravimetric analyses of the oils showed contents of light volatiles, hemicelluloses, cellulose, and lignin degradation products, and heavy non-polar compounds. The TG curves showed that the thermal stability of the oils was decreased with the addition of AmmoSoak. FT-IR analyses showed that bio-oils from poultry litter alone were rich in methyl groups, amides, and other hydrocarbons. The addition of AmmoSoak increased the aromatic, alcohol, and other oxygenated compound contents of the oils. ^{13}C-nmr analyses indicated that the methyl and methoxyl groups decrease with the addition of AmmoSoak. The spectrums also indicated the presence of anomeric, aromatic, and carboxylic carbons.

In the second phase of the research, the pilot-scale reactor was started up, shaken down and pyrolysis products were collected and analyzed for their elemental compositions. Fluidization of the reactor bed was successfully demonstrated by evidence of the bed temperature and reactor pressure profiles. A stable reactor temperature of about 470°C

within the reactor was achieved with a biomass feed rate of 1.1 lb/min. The reactor was heated by the combustion of liquid propane, so to ensure complete combustion was achieved, the combustion water was collected to compare to the stoichiometric yield of water. Complete combustion was in fact achieved. The bio-oil yields were very low compared to those on the bench-scale. Yields on only 9% were achieved. This was attributed to inefficiencies and under-sizing of the condensation train and electrostatic precipitator. The water soluble fractions of the bio-oils were rich in oxygen, while the water insoluble fractions were rich in carbon and ash. The high contents of carbon and ash in the water insoluble fraction were attributed to damage or inefficiencies of the high temperature filter in collecting the char product. Even with these inefficiencies, the average char yield achieved was 32%.

Because the higher heating value of the oils decreased with an addition of AmmoSoak because of the increased oxygen content, pyrolysis reactions at higher temperatures should be studied to attempt to free more of the oxygen content into the non-condensable vapors. This could help to increase the HHV as well as the thermal stability of the oils. In order to improve the performance of the pilot-scale reactor, the sizing of the condensation train and wet electrostatic precipitator should be reconsidered as well as the vapor residence times in the condensers. Currently evidence shows that they are too inefficient to effectively condense and collect the water and oils. The feed system of the pilot-scale reactor also presented challenges. Rocks collected with the litter from the poultry houses caused the feed augers to jam when fed. A simple screening process would not work because neither the rocks nor the litter were of uniform size. Another issue lied in maintaining an air tight seal between the outside environment and the feed metering bin.

Pyrolysis vapors and gases tended to escape from the rotary air lock atop the metering bin. These vapors rapidly increased the moisture content of the feed entering the bin, ultimately causing the feed to cake in the vanes of the rotary lock. This clogging of the vanes reduced the possible feed rate and sometimes caused the rotary air lock to cease completely. An air purge was implemented directly below the rotary air lock to prevent the pyrolysis vapors and gasses from infiltrating the vanes, but it was not possible to ensure air was not entering the reactor and causing combustion of the feed. The air purge could have been replaced with a nitrogen purge to ensure no combustion was possible, but using more nitrogen requires more money.