INFLUENCE OF WOOD ON THE PYROLYSIS OF POULTRY LITTER

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ABSTRACT

Pyrolytic oils produced from poultry litter differ in physico-chemical properties and the chemical composition. The litter is composed of manure and bedding material with traces of spilled feed and feathers. The type and amount of bedding material was varied to investigate its influence on the pyrolysis of layer manure. 400g of each feedstock: manure, wood (pine and oak), and mixtures of manure and wood in proportions (75:25 50:50, and 25:75 w/w %) respectively were subjected to fast pyrolysis at 450°C in a fluidized bed reactor. The total pyrolytic oil yield ranged from 43.3% to 64.5 wt%. The highest bio oil yield and the lowest char yield were obtained from oak wood. The manure oil had the highest HHV of 29.7 MJ/kg, the highest pH (5.89), the lowest density (1.14 g/cm^3) and a relatively low viscosity of 130cSt. The oils had relatively high nitrogen content ranging from 5.88wt% to 1.36 wt%; low ash content (approximately <0.07wt %) and low sulfur content (<0.28wt %). FT-IR, ^{13}CNMR, and ^{1}HNMR analysis showed that manure oil was rich in aliphatic hydrocarbon and primary and secondary amides and the addition of wood introduced oxygenated compounds like aliphatic alcohols, phenols, aromatic ethers, and carbonyl/carboxylic groups into the oil. TG/DTG analysis also showed that the thermal decomposition of the oils were different depending on the amount and the type of wood in the manure/wood mixture.

The parametric variables used for the mixture of 50% manure and 50% pine wood shavings study were; temperature (400-550°C), nitrogen gas flow rate (12-24 L/min), and feed rate (160-480 g/h). The results showed that the pyrolysis product yields, physical properties and the chemical composition of the oil were influenced by all parameters. Temperature was the most influential factor and its effect on the liquid, char and gas yields were significant. It was evident that depending on the gas flow rate and the feed rate, a maximum oil yield (51.1wt.%) can be achieved between 400-500 ^{o}C. Also an increase in temperature significantly increased the oil viscosity and decreased the carbonyl/carboxylic and the primary aliphatic alcohol functional groups in the oil.

The study on the influence of wood on the stability of the oils when stored at ambient conditions for 8 months in a 30ml glass bottle showed that the viscosity of the oils increases when stored, however the manure oil was relatively more stable and the oil from the 50/50 mixture for both pine and oak was the least stable. It was found that the stability of the oils from the manure and wood mixtures were dependent on the amount and the type of wood (pine or oak) added to the manure. Also the addition of 10% solvent (methanol/ethanol) to the oil from 50% manure and 50% pine reduced the initial viscosity of the oil and was also beneficial in slowing down the increase in viscosity during storage.

DEDICATION

I dedicate this research work to the entire Mante family, for their unconditional support, encouragement and love. I also want to dedicate this to Pearl Golder Appiah for been supportive of me in every step of the way. I also dedicate this research work to all my lab mates for their help and suggestions through out my research work.

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CHAPTER ONE

INTRODUCTION

1.0 Background

Poultry litter is produced from the normal operation of hatcheries, broiler, turkey and egg laying. The industry is one of the largest and fastest growing sectors of livestock production in the world (Sims and Wolf, 1994). The poultry industry consists mainly of chickens, but also includes significant production of turkeys, with limited production of other poultry. The United States Department of Agriculture (USDA) estimated that in 1997, 17.86 million tons (dry matter) of manure was generated by poultry operations in the USA (USDA-ERS, 2001). In Virginia, the Poultry Federation estimated that 50,000 tons of poultry litter was brokered from poultry growers to other users in 1997. Virginia also has 880 chicken farms which produce 256 million birds and ranks tenth in the country in broiler production (Virginia Poultry Federation, 2007).

Poultry litter consists of droppings, bedding (usually wood shavings, peanut, and rice hulls), feathers and waste feed. The litter is considered a valuable source of plant nutrients which can be used as a substitute for inorganic fertilizers in agriculture and also as a protein source in animal feed. Litter-derived phosphorus and nitrogen production in Virginia were respectively 16 million pounds and 59 million pounds (VDEQ, 1998). Land application of poultry litter can result in runoffs rich in nutrients which can impair water resources. Land application may also result in the spread of pathogens, the production of phytotoxic substances, air pollution and emission of greenhouse gases (Kelleher et al., 2002). Furthermore, excessive land application of poultry litter can result in nitrate (NO_3) contamination of groundwater which can cause methaemoglobinaemia (blue baby syndrome), cancer, and respiratory illness in humans and fetal abortions in livestock (Bitzer and Sims, 1988). Poultry litter is also used as a feed supplement in ruminant, but concerns about bovine spongiform encephalopathy (BSE), commonly known as mad cow disease has resulted in the Food and Drug Administration (FDA) ban on this application (Herson et al., 2004).

The above environmental implications have stimulated interest in the development of alternative disposal methods to replace the traditional ones. Kelleher et al., (2002) reviewed other methods of poultry litter disposal; which include composting (aerobic digestion), anaerobic digestion, and direct combustion. However the major disadvantages of compositing are loss of nitrogen and other nutrients, equipment and labor cost, odor, and availability of land. Direct combustion for heat and power generation is currently being investigated. The United Kingdom has poultry litter combustion plants with capacities ranging from 13.5MW to 38.5MW (www.eprl.co.uk). In the USA, Fibrowatt LLC is constructing combustion plants that will generate 30-55MW of electricity from 200,000-700,000 tons of poultry litter per year in Minnesota, Maryland, and Mississippi (www.fibrowattusa.com). Unfortunately, this method causes air pollution and would require efficient pollution abatement equipments to meet EPA standards.

A potential method of solving the poultry litter disposal is to convert it into a useful renewable source of energy or a chemical byproduct with no net increase in carbon dioxide or greenhouse gas equivalents. Fast pyrolysis can be used to convert biomass into fuels and chemicals. Studies conducted by Agblevor et al., (2007) showed that fast pyrolysis technology can be used to convert poultry litter into energy (bio oil) and fertilizer (char). Another study by Schnitzer et al., (2007) also used fast pyrolysis to convert chicken manure into bio oil. Koutcheiko et al., (2007) pyrolyzed chicken litter char in the presence of NaOH to produce activated charcoal. The thermo-chemical conversion of poultry litter to biofuels will contribute to the development of the new-bio-based economy as a result of going green, improving the sustainability of rural communities and the health of humans and wildlife. The oil produced from the litter can be used as a substitute for fossil fuels to generate heat, power and/or chemicals. In developing the application of these oils, a thorough understanding of the physico-chemical properties is crucial. Mohan et al., (2006) reviewed recent developments in wood/biomass pyrolysis and reported the characteristics of the bio oils. However, these studies are lignocellulosic biomass consisting of lignin, hemicellulose, and cellulose, which are nearly free of protein, sulfur (S), phosphorus (P), and metallic compounds. In contrast, poultry litter is rich in protein, P, and trace metals that could influence the bio oil properties. Additionally, poultry litter has a wide variation in composition due to different growing practices and the number of flocks raised on the litter before cleaning the house. This variable composition could influence the composition and properties of the bio oil. Thus, it is proposed to investigate the influence of wood shavings (one of the major components of the litter) on the composition and properties of poultry litter bio oils.

1.1 Research Objectives

Although poultry litter pyrolysis has been reported in published literature, the influence of the individual components of this heterogeneous mixture on the pyrolysis products properties has not been reported. Wood shavings is one of the major components of poultry litter whose specific influence on the pyrolysis products composition, litter decomposition mechanism, and influence on products stability are not known. Thus the overall goal of this research is to investigate the influence of wood on the pyrolysis of poultry litter.

The specific objectives include;

1. Collect and characterize layer manure, pine and oak wood shavings from a poultry farm in the Shenandoah Valley.

2. Determine the effect of addition of pine and oak wood shavings on the pyrolysis of layer manure.
3. Determine the effect of temperature, gas flow rate and feed rate on product yield and composition.
4. Determine storage stability of poultry litter pyrolysis oils.

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CHAPTER TWO

LITERATURE REVIEW

2.0 Poultry Industry in Virginia

Poultry production is one of the most important industries in Virginia. Virginia has 300 turkey farms which produce about 21.5 million birds per year and ranks fourth in the country (Virginia Poultry Federation, 2007). Virginia also has 880 chicken farms which produce 256 million birds and ranks tenth in the country in broiler production (Virginia Poultry Federation, 2007). The Shenandoah Valley is Virginia's top poultry producing region with approximately 900 farms and 6 poultry processing companies (Cargill, George's Foods, Pilgrim's Pride Corporation, Perdue Farms, Tyson Foods and Virginia Poultry Growers Cooperative, Inc). Rockingham County is the nation's second-largest turkey producing county (Virginia Poultry Federation, 2007).

2.1 Poultry litter Production

Poultry litter is produced during the normal operation of hatcheries, broiler, turkey, and egg laying . In Virginia, growers own the poultry houses and manage bird production whereas the companies typically own the birds and the feed. The growers are responsible for purchasing bedding material and disposing of dead birds and litter. Almost all poultry operations grow the birds on concrete, wooden, or earthen floors. The bedding material is usually laid down on the floor and the choice of material depends on the needed absorption and commercial availability (Overcash et al., 1983). A 2-6-inches layer of wood shavings, peanut hulls, or other bedding material is used as an absorptive base (Collins, 1996). Bedding material in Virginia typically consists of pine shavings or peanut hulls(Pelletier et al., 2001). Poultry litter produced from farm to farm may differ as the manure content of the litter varies depending on the number of birds raised and the number of flocks raised on the bedding material. Generally, one house contains

20,000-25,000 chickens, however recent housing trends carry 50,000-60,000 chickens(Virginia Department of Environmental Quality, 1998). The removal of the litter is done one or more times a year and replaced with fresh bedding material (Collins, 1996). However, this practice varies widely, and farmers in the Shenandoah Valley clean houses between once per flock to once every five years. Turkeys produce considerably more litter per bird than broilers, and this increased litter production also affects cleaning rates (Pelletier et al., 2001). About 1.1 to 1.4 tons of litter per 1,000 birds is generated for most broiler operations and for a flock of 18,000 to 20,000 birds, 22-34 tons of litter per flock is produced (Collins, 1996). A 20,000 bird broiler house will produce approximately 150 tons of litter per year (6 flocks) and a flock of 14,000 breeder hens will produce approximately the same about of 150 tons of manure (50 percent dry weight basis) in one year (Ritz and Merka, 2004). It has been estimated that more than 400,000 tons of poultry litter are produced annually in Virginia (Mullins et al., 2002).

2.2 Composition of Poultry Litter

Poultry litter comprises of poultry manure, feed spilled from feeders, feathers, bedding material, and dirt from the floor of the poultry house (Cross, 1995). The chemical composition of poultry manure has been extensively studied. Poultry litter varies in composition due to variations in the amount and type of bedding material placed on the floor, the amount of dirt removed with the litter, the number of flocks raised on the litter, water system used, method of clean-out, storage time, etc (Jacob et al., 1997). Table 2.1 shows a summary of the chemical composition of a typical broiler litter.

Table 2.1 Average chemical composition of broiler litter

Component	**Average**	**Range**
Dry matter (DM), %	80.5	61-95
Composition of DM:		
Total Digestible Nutrient (TDN) , %	50.0	36-64
Crude protein, %	24.9	15-38
Crude fiber, %	23.6	11-52
Ash, %	24.7	9-54
Calcium, %	2.3	0.81-6.13
Phosphorus, %	1.6	0.56-3.92
Copper, ppm	473	25-1,003
Magnesium, ppm	348	125-667
Iron, ppm	2377	529-12,604

Source : (Jacob et al., 1997)

2.2.1 Moisture

The significance of moisture content depends on the end application of the litter. Watering system management affects the amount of moisture in the litter(Jacob et al., 1997). Excessive litter moistures can also be caused by factors other than improper management. High intake of minerals such as potassium, sodium, magnesium, sulfate or chloride can lead to excessive water consumption and wet droppings(Butcher and Miles, 1995). The moisture content determines the physical quality of the feed. If the moisture content is more than 25 percent, the deep stack may generate too much heat and the excess heat may damage (denature) the protein in the litter. Poultry litter with moisture levels of 10 percent or less will also be excessively dusty.

2.2.2 Crude Protein

The crude protein consists of both true protein and non-protein nitrogen. Uric acid is the main source of non-protein nitrogen in the litter. More than 40% of the crude protein in litter can be non-protein nitrogen (Jacob et al., 1997). Broiler litter averages 24 percent crude protein and can range from 15 to 38 percent (Mckinley et al., 2000). Cross (1995) also found that the non-protein represent as high as half the total nitrogen content.

2.2.3 Crude Fiber

The average crude fiber in broiler litter is 24 percent (Mckinley et al., 2000). The bedding material (wood shavings, sawdust, or peanut hulls) are the main fiber source in the litter. As more flocks of broilers are raised on the litter, total fiber in litter decreases(Jacob et al., 1997).

2.2.4 Minerals

Broiler litter is an excellent source of macro and trace minerals(Mckinley et al., 2000). Trace minerals, such as copper, iron, and magnesium, are present in larger amounts in broiler litter (Jacob et al., 1997). Table 2.2 is a summary of some of the minerals found in egg layer and broiler litter.

Table 2.2 Composition of different types of poultry litter

Parameter	**Sample Type**	
	Egg layer litter	**Broiler litter**
Organic C (%)	15.3(4.7)+	32.5
pH	8.1	6.4
Salts (dS/m)	7.2	7.0
Macronutrients (%)		
Nitrogen	3.3	4.1
Phosphorus	2.9	2.1
Potassium	3.6	2.7
Sulfur	1.0	0.73
Calcium	17.9	4.0
Magnesium	0.8	0.7
Micronutrients (ppm)		
Boron	42.7	33.5
Copper	163	163
Iron	2,040	3,254
Manganese	647	444
Molybdenum	10.7	6.2
Zinc	403	383
+ Value in parenthesis is inorganic C as calcium carbonate		

Source : (Dick et al., 1998)

2.2.5 Ash Content

The ash content of poultry litter varies over a wide range depending on the kind of farming practice, clean out method and age of the litter. The high ash content primarily represents the amount of dirt contamination that has occurred in the litter (Cross, 1995). Ash content is one of the important measures of the quality of litter (Mckinley et al., 2000). Very high ash content is indicative of high mineral content or high soil content in the litter. Ash levels between 15% and 25% are acceptable (Jacob et al., 1997).

2.3 Composition of woody biomass

Woody biomass is a natural polymer complex of cellulose, hemicellulose, and lignin (Hon and Shiraishi, 1990). The major structural chemical components with high molar masses are carbohydrate polymers and oligomers (65%-75%) and lignin (18%-35%). Minor low molar mass extraneous materials are mostly organic extractives and inorganic minerals (usually 4%-10%) (Rowell, 1984). The weight percent of cellulose, hemicellulose, and lignin varies in different species of wood. Their distribution is determined by the species, geographical region and environmental stresses applied to the living tissue (Hon and Shiraishi, 1990).

2.3.1Cellulose

Cellulose is the most abundant organic material on earth (Hon and Shiraishi, 1990). It serves as the structural material and provides wood's strength and comprises (40-50 wt %) of dry wood (Rowell, 1984). Cellulose is a high-molecular-weight (10^6 or more) linear polymer of β-(1→4)-D-glucopyranose units in the $^4C_1$ conformation (Mohan et al., 2006). In vascular plants cellulose is synthesized by specialized cellular organelles and polymerized in the golgi apparatus or at the plasma membrane by rosette terminal complexes (Brown et al., 1996). The basic repeating unit of the cellulose polymer consists of two glucose anhydride units called cellobiose unit. The glucose anhydride is polymerized into long cellulose chains that contain 5000-10000 glucose units (Mohan et al., 2006). They are found predominantly in the primary and secondary cell walls of wood. Cellulose in woody cell walls occurs in crystalline form as the result of certain characteristic of the cellulose molecule itself: (1) the cellulose molecule is a uniform ribbonshaped structure, (2) the carbon-to-carbon bonding gives the chain great rigity and coherence, and (3) numerous hydroxyl (OH) groups (Panshin and Zeeuw, 1980). It is insoluble in typical solvents such as water, or alcohols. It is soluble in more exotic solvents, such as aqueous *N*-methylmorpholine-*N*-oxide (NMNO), CdO/ethylenediamine (cadoxen), or LiCl/*N,N'*-dimethylacetamide, or near supercritical water and in some ionic liquids (Swatloski et al., 2002; Turner et al., 2004).

2.3.2 Hemicellulose

Hemicellulose, a second major wood chemical constituent which is also known as polyose is the most abundant renewable organic material next to cellulose. A variety of hemicelluloses usually account for 25%-35% of the mass of dry wood, 28% in softwoods, and 35% in hardwoods (Rowell, 1984). Hemicellulose is a mixture of polymerized monosaccharides such as glucose, mannose, galactose, xylose, arabinose, 4-*O*-methyl glucuronic acid and galacturonic acid residues. Hemicelluloses exhibit lower molecular weights than cellulose. The number of repeating saccharide monomers is only ~150, compared to 5000 - 10000 in cellulose. Cellulose has only glucose in its structure, whereas hemicellulose has a heteropolysaccharide makeup. The hemicellulose found in hardwood and softwood varies both in structure and quantity. The predominant hardwood hemicellulose is a partly acetylated, glucuronoxylan (O-acetyl-4-O-methylglucuronoxylan), accounting for 20-35wt%, whereas softwoods contain glucuronoarabinoxylan (arabino-4-O-methylglucuronoxylan) in range in range of 10wt%. Hardwoods contain only a small quantity of glucomannan and softwood contain 18wt% partly acetylated galactoglucomanna (O-acetylgalactoglucomanna) (Hon and Shiraishi, 1990).

2.3.3 Lignin

Lignin is a characteristic fraction of the woody cell wall and is formed only in the walls of living plants in the spermatophytes (Panshin and Zeeuw, 1980). Lignin exists as one of the essential wood components ranging in amount from 10-30wt% (Hon and Shiraishi, 1990). Although the cellulose content is more or less the same in both hardwood and softwood, hardwood contains less lignin. The lignin content of hardwood is usually in the range of 18 -25wt%, whereas that of softwood is in the range of 25-35wt%(Hon and Shiraishi, 1990). The amounts of lignin found in other macrostructures such as bark and needles are dependant on the state of plant development (Ishii and Shimizu, 2001), and may show differences in properties as a result of the coupling-linkage characteristics. Unlike cellulose, the structure and exact composition of lignin is still not fully determined. Characterization of the chemical structure of lignin indicates its composition as being phenolic based, arranged in a 3-dimensional polymer network that spans the spaces in between cellulose fibers and hemicellulose providing rigidity and unification between adjacent cells (Hon and Shiraishi, 1990). It is thought that lignin is a polymer formed by the enzymatic dehydrogenation of the phenylpropanes followed by radical coupling. Softwood lignin is mainly composed of guaiacyl units originating from the predominant precursor, *trans*-coniferyl alcohol, while hardwood lignin is composed of both guaiacyl and syringyl units derived from *trans*-conferyl and *trans*-sinapyl alcohols (Sakakibara and Sano, 2001). Lignin is the most complex polymer among naturally occurring high-molecular-weight material. The phenolic hydroxyl groups in lignin are major functional groups affecting the physical and chemical characteristics of the lignin polymers (Lai, 2001). This functionality promotes alkali-catalyzed cleavage of the ether linkages and oxidative degradation of lignin. Other sites of reaction include aliphatic hydroxyl groups, uncondensed lignin units, unsaturated groups such as coniferyl alcohol end-groups, ester groups and methoxyl groups (Lai, 2001).

2.3.4 Extractives

Wood extractives represent extremely wide range of classes of organic chemicals. The most important groups that occur naturally in large amount are the polyphenols and oleoresin (Panshin and Zeeuw, 1980). Polyphenols include tannins, anthocyanins, flavones, catechins, and lignans. Extractives are in most cases, different between families, genuses, or even species of wood. The extractives provide a major contribution to many of the properties of wood (Panshin and Zeeuw, 1980). Some of the properties include, color, smell, and durability(Hon and Shiraishi, 1990).

2.4 Poultry litter disposal methods

2.4.1 Land application of poultry litter

The value of poultry manure/litter as an organic fertilizer has been recognized for centuries (Ritz and Merka, 2004). The valuable organic fertilizer can therefore substitute for the use of inorganic fertilizers in agriculture (Nicholson et al., 1996). Poultry litter is potentially used as fertilizer and soil amendment on crop, pasture, and hay lands; as topdressings for lawns, baseball fields, golf courses, and other landscapes (Mullins et al., 2002). However when poultry litter is applied to crop or pastureland, it has the potential to adversely impact water quality, both in the short-term and long-term (Collins and Basden, 2006). Although land application of poultry litter on farms has been in practice for years, improper management of litter applications may cause nutrient enrichment and/or contamination of surface and ground water resources with nitrate and bacteria (Collins, 1996; Marsh et al., 2003). Phosphorus and potassium are known to be readily available in the soil (Dick et al., 1998) and because nitrogen is often the limiting nutrient for crop production (Warren et al., 2006), attempts to meet the nitrogen requirement leads to over application of the litter and this result in elevated phosphorus levels in the soil. Increases in soil phosphorus correspond to increase in soluble phosphorus concentrations in surface water runoff (Sharpley, 1995). Phosphorus is the limiting nutrient in most aquatic systems; therefore, the addition of nonpoint-source phosphorus from application of litter can be a contributor to eutrophication of sensitive water bodies (Pote et al., 1996). With excessive phosphorus loading, large algal blooms can occur, resulting in degradation of water quality (Moore and Edwards, 2007). Recent outbreaks of the dinoflagellate *Pfiesteria piscicida* in the eastern United States, and Chesapeake Bay tributaries have been linked to excess nutrients (Sharpley et al., 2003). Finally high-rate of poultry litter applications may contribute to toxic concentrations of ammonia, nitrite, nitrate and soluble salts (Edwards and Daniel, 1992). Hence land application of poultry litter as fertilizer or soil conditioner is being regulated.

2.4.2 Poultry litter as ruminant feed supplement

Broiler litter is a good source of energy, nitrogen and minerals for ruminants (Jacob, Kunkle et al., 1997) and can be used as cattle feed (Mckinley et al., 2000) because they have the ability to utilize the nitrogen components in poultry litter to synthesize protein, along with its fiber-digesting ability (Cross, 1995). Poultry litter is more valuable as a feed ingredient than as a fertilizer. The economic value of broiler litter as a feed ingredient in balanced diets for several classes of ruminants is up to four times greater than its value as a fertilizer (Jacob et al., 1997).

Despite the good use of poultry litter for protein supplement and hay substitute, the outbreak of Bovine Spongiform Encephalopathy (BSE) in cattle in the United States raised concerns about the use of litter as feed. As a result of the first case of BSE in the United States in December 2003, the Food and Drug Administration (FDA) temporarily banned the feeding of poultry litter to beef cattle (Daniel and K.C., 2005). Later in 2004, the FDA announced a second interim rule to ban the use of poultry litter as a feed ingredient for ruminant (Hall, 2004).

2.4.3 Composting of Poultry litter

Land application of waste from the poultry industry and subsequent negative environmental impact has stimulated interests in the development of alternative disposal methods (Abelha et al., 2003). Environmental concerns on the use of poultry litter as fertilizer can be eased by composting. Composting has been recognized as an effective way of partially solving the growing concern of the effects of over application of poultry litter on lands. The process improves the handling characteristics of the manure by reducing its volume and weight, kills pathogens, and stabilizes the nutrients and organic matter. The composted material is odorless and fine textured with a low moisture content (Kelleher et al., 2002). Composting provides a beneficial alternative method for handling litter due to immobilization of nutrients (Preusch et al., 2002). Additionally the slow release of nutrients from composted poultry litter may lessen adverse environmental effects from leaching of phosphorous and nitrogen in runoff from farmlands (Chang and Janzen, 1996). It has been reported that composting of poultry manure in an aerated pile results in overheating and causing a rapid loss of total volatile solids and nitrogen (Kelleher et al., 2002). Composting also changes the nature of the waste and can affect its usefulness as a soil amendment due to the loss of nitrogen through mineralization, ammonia (NH_3) volatilization, nitrification, and denitrification (Tiquia and Tam, 2000). Composting has been found to be labor intensive and creates air pollution (e.g. dust and odour). Large space/land is also required for creating piles, spreading and stacking the layered manure into windrows (Tiquia and Tam, 2002).

2.4.4 Combustion of poultry litter

An alternative method of poultry litter disposal is direct combustion for cogeneration of heat and electricity. Currently this process is utilized by Fibrowatt, LLC (United Kingdom) in wall-water tube boilers and the steam is used to drive turbines. This process is currently used in three UK facilities and Benson, MN. Direct combustion of poultry litter has the potential to provide space heating for poultry houses and power generation or combined heat and power (Kelleher et al., 2002). Unfortunately this method causes air pollution as well as equipment problems due to the high concentration of alkali metals (sodium oxide (Na_2O), and potassium oxide (K_2O), nitrogen, sulfur, and ash (Bock, 2006). Therefore efficient pollution abatement equipment is required by these systems to meet EPA standards. The nitrogen, sulfur, chloride, and alkali contents in poultry litter are about ten times higher than that in wood and consequently, this increases the potential for NO_X and SO_X emissions. High alkali metal content, especially in conjunction with high silica levels, has a high potential for slagging, fouling, corrosion, particulate and acid gas emissions (Bock, 2006). Researchers have been studying the co-combustion/firing of poultry litter with fossil fuels (coal) and other forms of biomass to address energy supply issues and to reduce air pollution (Zhu and Lee, 2005).

Co-firing may reduce fuel costs, minimize waste and reduce soil and water pollution depending on the chemical composition of the biomass used (Demirbas, 2004). In order for this application to be harnessed in a more environmentally sound way, the combustion of poultry litter has to be controlled to minimize the formation of pollutants such as NOx, maximize the retention of SO_2, minimize ash sintering, fusion or eventual ash interaction from different wastes that can cause serious problems of fouling and slagging (Henihan et al., 2003).

2.5 Thermochemical conversion as a tool in poultry litter disposal

It cannot be over emphasized that more environmentally acceptable methods are needed to address the disposal of poultry litter. The traditional methods previously discussed attempted to provide solutions, however environmental problems such as water and air pollutions persists. Stringent regulations for litter disposal have motivated scientists to study the potential use of poultry litter as an economical source of energy. Novel technologies are needed to deal with chicken litter disposal since the traditional method of disposal is no longer suitable (Kim and Agblevor, 2007). A potential environmentally acceptable means of poultry litter disposal is to use more efficient energy conversion processes to produce energy-dense alternative fuels. Thermochemical processes are considered to offer a means of efficiently and economically converting biomass into higher value fuels (Antal, 1983). Poultry litter can be converted into producer gas, bio-oils, and char. These products can be upgraded and used for combined heat and power (CHP) or catalytically converted into liquid fuels and mixed alcohols (Cantrell et al., 2007). Studies have shown the feasibility of using poultry litter as an alternative, natural fuel source for power generation (Davalos et al., 2002). Pyrolysis technology can be used to solve the waste disposal and water pollution problems, and also convert a potential waste into a valuable product (Kim and Agblevor, 2007). The use of incineration/combustion for energy recovery from waste is well established in industry but pyrolysis offers potentially advantageous process.

2.5.1 Pyrolysis

Pyrolysis is one of the possible pathways to convert biomass to higher value products (Ringer et al., 2006) and it is considered as the heart of all thermochemical fuel conversion processes (Antal, 1983). Pyrolysis is the thermal decomposition of materials in the absence of oxygen or oxidizing agent (Bridgwater and Cottam, 1992; Demirbas, 2004; Yaman, 2004; Mohan et al., 2006; Boateng et al., 2007). It is also described as a process in which liquid oils are preferred products(Soltes and Milne, 1987). Pyrolysis converts the organic portion of the feedstock into a mixture of char and volatile gases containing noncondensable vapors and condensable tars (oxygenated hydrocarbons), which form a pyrolytic oil or bio-oil (Bridgwater, 2004). Pyrolysis offers the advantage of a liquid that can be stored, transported and used as alternative fuels after upgrading. The bio-oil can also be used as an energy carrier and as a source of valuable chemicals (Bridgwater, 2004; Bock, 2006) because it contains a wide variety of organic compounds (Li et al., 2005). Many researchers have employed pyrolysis in producing liquids from different kinds of biomass feedstock; from agricultural residues to municipal solid waste. Some of the feedstocks include grass (Agblevor et al., 1996; Debdoubi et al., 2006; Boateng et al., 2007), woody biomass (Agblevor et al., 1996; Oasmaa and Kuoppala, 2003; Oasmaa et al., 2003; Oasmaa et al., 2003; Sensöz, 2003; Demirbas, 2005; Li and Zhang, 2005; Garcìa-Pérez et al., 2007; Garcia-Perez et al., 2008), straws (Di Blasi et al., 1999; Lee et al., 2005), bagasse (Drummond and Drummond, 1996; Yorgun et al., 2001), seedcakes (Sensöz et al., 2000; Pütün et al., 2002; Onay and Mete Kockar, 2004; Nurgül Ozbay et al., 2006; Sensöz and Kaynar, 2006), municipal solid waste (Li et al., 2005; Nurul Islam et al., 2005; Changkook Ryu, 2007), and chicken litter (Agblevor et al., 2007; Schnitzer et al., 2007). The yield and composition of pyrolysis products depend on the composition of the feedstock, the pyrolysis technique used, and the operating conditions: temperature, residence time, and heating rate (Bridgwater and Cottam, 1992; Maschio et al., 1992; Klass, 1998; Meier and Faix, 1999).

2.5.2 Types of pyrolysis

Pyrolysis processes can be divided into conventional/slow and fast pyrolysis depending on the operating conditions (Maschio et al., 1992). Conventional pyrolysis produces more solid char, while fast pyrolysis yields more liquid and gas (Farag et al., 2002). Conventional pyrolysis consists of the slow, irreversible, thermal decomposition of the organic components in biomass and has traditionally been used for the production of charcoal (Klass, 1998; Demirbas, 2004). When the aim is the production of mainly liquid and/or gaseous products, a fast pyrolysis is recommended (Demirbas, 2004).

2.5.3 Fast Pyrolysis

Fast pyrolysis is the leading method for producing liquids from organic materials. The advantages include low production costs, high thermal efficiency, low fossil fuel input, and CO_2 neutrality (Mohan et al., 2006). Fast pyrolysis is characterized by high heating rates and rapid quenching of the liquid products to terminate the secondary reaction of the products (Klass, 1998; Bridgwater, 2004; Bock, 2006). Fast heating rates are achieved with high operating temperatures, very short contact times, and very fine particles (Demirbas, 2004). For maximum liquid yield, the temperature required should be approximately 500 °C, the biomass particle size (<2mm), biomass moisture content(<10%) and the vapors should be immediately separated from the char and condensed to prevent secondary cracking to gaseous products (Bridgwater, 2004; Kersten et al., 2005). The yield of fast pyrolysis processes are; 60-75 wt % bio-oil, 15-25 wt % solid char, and 10-20 wt % noncondensable gases, depending on the feedstock used (Mohan et al., 2006). Fast pyrolysis technology generates no waste since the bio-oil and the char can be used as a fuel and the gas can be recycled. Practically any form of biomass can be used for fast pyrolysis. Many feedstocks, ranging from agricultural residues (straw, olive pits and nut shells), forestry residues (wood chips and bark), energy crops (Miscanthus and Sorghum), and solid wastes such as sewage sludge and leather wastes have been tested using fast pyrolysis (Bridgwater, 2007). The type of reactor used in a fast pyrolysis process is of importance since the reactor configuration affects the production, separation, and recovery of pyrolysis products.

2.5.4 Fast Pyrolysis Reactors

Among many factors (feed drying, particle size, pretreatment, heat supply, heating rates, reaction temperature, vapor residence time, secondary cracking, char separation and liquid recovery method), reactor configuration constitutes the heart of the fast pyrolysis process (Mohan et al., 2006; Bridgwater, 2007). Several types of reactors can be used for fast pyrolysis. Meier and Faix (1999) reviewed the state-of-art of fast pyrolysis reactors used for lignocellulosic feedstock. They include; (1) fluidized bed, (2) circulating fluidized bed, (3) ablative pyrolysis, (4) rotating cone reactor, (5) vortex reactor, and (6) vacuum pyrolysis. Many scientists have used some of these various reactor designs for their research. Some used fluidized bed (Agblevor et al., 1996; Luo et al., 2004; Kersten et al., 2005; Lee et al., 2005; Agblevor et al., 2007; Boateng et al., 2007; Garcia-Perez et al., 2008), vacuum pyrolysis (Boucher et al., 2000; Ba et al., 2004; Darmstadt et al., 2004; Garcia-Perez et al., 2008), and others fixed bed (Yorgun et al., 2001; Pütün et al., 2002; Sensöz, 2003; Onay and Mete Kockar, 2004; Ates et al., 2005; Nurul Islam et al., 2005; Debdoubi et al., 2006; Nurgül Ozbay et al., 2006; Sensöz and Kaynar, 2006). The three main fast pyrolysis reactor configurations are: (1) Fluid bed and circulating fluid bed pyrolysis where the heat transfer to biomass is a mixture of convection and conduction, (2) Ablative pyrolysis in which biomass is pressed against a heated surface and rapidly moved during which the biomass melts at the heated surface and leaves oil film behind which evaporates, and (3) Vacuum pyrolysis uses slow heating rates but removes pyrolysis products rapidly (Meier and Faix, 1999; Ringer et al., 2006).

2.5.4.1 Fluidized Bed Reactor

Fluidized beds are simple in construction and operation; they have good temperature control with very efficient heat transfer to biomass particles. Fluid bed reactors give good and consistent performance with high liquid yields of typically 70-75wt% from wood (dry-feed basis). Small biomass particle sizes of less than 2-3 mm are needed to achieve high biomass heating rates (Bridgwater, 2007). Sand is often used as the solid phase of the bed. Fluidized beds produce good quality bio-oil with a high liquid product yield. The residence times of solids and vapors are controlled by the fluidizing gas flow rate and are higher for char than for vapors(Mohan et al., 2006). In fluidized beds, the char acts as an effective vapor cracking catalyst at fast pyrolysis reaction temperatures, therefore rapid and effective char separation is important. This is usually achieved by ejection and entrainment followed by separation in one or more cyclones. Hot gas filters can be used to achieve that. The earliest pioneering work on fast pyrolysis was carried out at the University of Waterloo. DynaMotive (Vancouver, Canada) have demonstrated the bubbling fluidized bed process at 10 t/day of biomass and commissioned their first 100 t/day in July 2004 in Ontario. The Dynamotive Energy System Corporation is an international company that focuses on biomass liquefaction technologies, currently their fluidized bed reactor at Ontario is the largest(Bridgwater, 2007). There are research units at universities and research institutions around the world including Virginia Tech, USA, Iowa State University, USA, RTI Canada, IWC

Germany, Aston University UK, VTT Finland, and the National Renewable Energy Laboratory (NREL), USA.

2.5.4.2 Circulating fluid bed Reactor

Circulating fluid beds (CFB) have many of the features of fluidized beds except that the residence time of the char is almost the same as that for vapors. Also the char is more attrited as a result of gas velocities, and could consequently lead to higher char deposits in the bio-oil. Their heat transfer rates are not high, because it is mostly convective. In circulating fluid beds such as the twin-bed reactor where a second vessel is used as a char combustor to reheat the circulating solids there is ash buildup in the circulating solids. However, an advantage of CFBs is that they are suitable for very large throughputs, even though the hydrodynamics are more complex. This technology is widely used for very high throughputs in the petroleum and petrochemical industries (Bridgwater, 2007).

2.5.4.3 Vacuum Pyrolysis Reactor

Vacuum pyrolysis involves the thermal decomposition of biomass under reduced pressure. Vacuum pyrolysis is generally conducted at 450 °C and 15 kPa. The heat-transfer rate is much lower than other types of reactors. The vaporized products are quickly withdrawn, condensed and recovered as pyrolytic oils. It is important to note that more rapid volatilization under pressure minimizes the extent of secondary decomposition reactions. The main feature of the vacuum pyrolysis process is that a short residence time for volatiles is easily achieved but suffers from poor heat and mass-transfer rates (Mohan et al., 2006).

2.5.4.4 Ablative pyrolysis

Ablative pyrolysis reactors have fundamentally different modes of heat transfer and biomass particle size requirement. During ablative pyrolysis the heat is transferred from the hot reactor wall to ‘melt’ the biomass that is in contact with it under pressure in the absence of fluidizing gas (Bridgwater, 2004). As the biomass is mechanically moved away, the residual oil film both provides lubrication for successive biomass particles and also rapidly evaporates to give pyrolysis vapors for collection in the same way as other processes (Bridgwater, 2007). The rate of reaction is strongly influenced by pressure, the relative velocity of the wood and the heat exchange surface, the reactor surface temperature and shear forces (Bridgwater, 2007). Recent developments include Aston University’s (UK) and Pytec’s pilot plant(Bridgwater, 2004). Ablative pyrolysis seems to be very promising for industrial application because of high heat and mass transfer and less dependence on particle size.

2.6 Properties of Pyrolytic Oil

Bio-oils are dark brown, free-flowing organic liquids composed of highly oxygenated compounds. The liquid has a distinctive odor - an acrid smoky smell due to the low molecular weight aldehydes and acids (Bridgwater, 2007). It is a complex mixture of water, guaiacols, catecols, syringols, vanillins, furancarboxaldehydes, isoeugenol, pyrones, acetic acid, formic acid, and other carboxylic acids (Mohan et al., 2006). The properties of the pyrolysis liquids depend on feedstock, the pyrolysis conditions, and the liquid recovery systems used. Physico-chemical properties reported for bio oils include; water, solid content, elemental analysis, acidity, viscosity, heating vale and stability among many others (Oasmaa et al., 1997; Oasmaa and

Peacocke, 2001). A summary of some of the physico-chemical properties of bio oils are shown in Table 2.3. These properties have significant impact on the application of the bio oils.

2.6.1 Water content

The water content of pyrolysis liquids ranged from 15-35wt% determined by Karl- Fischer method titration. Pyrolysis liquids contain low-boiling (below 100 °C) compounds and hence any drying method cannot be used. Pyrolysis liquids contain aldehydes, ketones and carboxylic acids that may form water by reaction with methanol in the solvent. Hence, two standard methods (ASTM E 203 and ASTM D 1744) for Karl Fischer titration were tested. It was concluded that both Karl-Fischer titration methods [ASTM E 203 and ASTM D 1744] can be used to determine water content in bio oils (Oasmaa et al., 1997).

2.6.2 Higher Heating Value (HHV)

The heat of combustion of a fuel is defined as the amount of heat released by a specified quantity (initially at 25 °C) when combusted and the products have returned to 25 °C. A bomb calorimetric technique is used in its determination. There are two values for the heat of combustion, or calorific value, for every fuel. They are referred as higher heating value (HHV) and lower heating value (LHV) of combustion. The difference between the two calorific values is equal to the heat of vaporization of water formed by combustion of the fuel. The heating value can be measured as calorimetric value (higher heating value, e.g. HHV) by ASTM D2015.

2.6.3 Stability

One of the primary attributes of converting solid biomass to a liquid bio-oil is the ability to store bio-oil until needed for immediate energy application. In the early development of this technology the long-term storability of bio-oils was plagued by major problems; the principal one being a gradual increase in the viscosity of the oil during storage. Due to the instability of the pyrolysis liquids special care has to be taken in handling, transporting, storing, and using the liquids(Mohan et al., 2006). When exposed to air in an open vessel, fast pyrolysis liquids change gradually to glue-like material (Diebold, 2000) The main reason for this is the evaporation of low-boiling dissolving compounds (alcohols, acids) including water. During a long-term storage the liquids tend to polymerize, which can be observed as an increase in average molecular-weight distribution in water and in viscosity (Agblevor and Besler, 1996; Diebold, 2000; Czernik and Bridgwater, 2004). The stability of the oil can therefore be measured as a change in viscosity over time.

Table 2.3 Summary of 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 cSt	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 ºC 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, 2004)

2.7 Pyrolytic Decomposition of Poultry litter

Poultry litter unlike wood has not been extensively studied. Poultry litter which is a composite mixture of microbially degraded wood, manure, feathers, and spilled feed is more complex than woody biomass. Wood is composed of lignin, cellulose, hemicellulose, extractives and trace amounts of elements such potassium, calcium, silicon and nitrogen. However, poultry litter has considerably large amounts of the inorganic elements. Whereas the ash content of woody biomass is 1-5 wt%, poultry litter ash is 15-20wt%. The trace elements in wood are known to influence the pyrolysis of wood and thus we will expect poultry litter to be also strongly influenced. The pyrolysis process and kinetic analyses of chicken litter by thermogravimetric analysis (TGA) were studied by (Whitely et al., 2006; Kim and Agblevor, 2007) to understand chicken litter decomposition. In their findings, the TG curves of flock and broiler showed three different weight losses suggesting decomposition in three stages compared to two in wood. The first stage was between 270 ^{o}C and 370 ^{o}C, at a 50% conversion and was attributed to the decomposition of mostly cellulose and hemicellulose. The second weight loss occurred between 375 ^{o}C and 500 ^{o}C was attributed to high manure. The third weight loss region 500 ^{o}C- 550 ^{o}C was due to the devolatilization of charcoal. It was also observed that the weight loss in the broiler was more rapid than the flock. This is because the broiler contains more manure than the flock litter (Kim and Agblevor, 2007) and also because poultry litter contains some wood, reactions likely corresponding to the decomposition of lignin and hemicellulose and cellulose, were observed (Whitely et al., 2006; Kim and Agblevor, 2007).

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CHAPTER THREE

CHARACTERIZATION OF LAYER MANURE AND PINE WOOD SHAVINGS

ABSTRACT

Poultry litter is a heterogeneous mixture of manure, bedding material (usually wood shavings, peanut and rice hulls), feathers and waste feed. Manure and wood shavings are the major components of the litter. In this study, layer manure, pine and oak wood shavings were characterized by ultimate analysis and FT-IR spectrometry. The nitrogen content was 6.42% in the manure and <0.5% in both pine and oak wood shavings. The carbon (C), hydrogen (H), and oxygen (O) contents were respectively 29.15%; 4.13%; 36.56% in the manure, 46.53%; 5.91%; 42.31% in the pine and 49.52%; 6.06%; 43.17% in oak shavings. The manure had high ash content (23.53%) and low HHV (14.79 MJ/kg) whiles the pine and oak respectively had low ash of 1.95% and 1.11%. The sulfur and chlorine contents were relatively higher in the manure than in the wood shavings. The manure also had a higher bulk density (0.41kg/L) than that of pine (0.24kg/L) and oak (0.23kg/L) wood shavings. Infrared spectrometry showed absorption bands associated with proteins and inorganic compounds in the manure and those indicative of carbohydrates and lignin in pine and oak wood shavings.

Keywords: Characterization; ultimate; proximate; FT-IR spectroscopy; manure; pine; oak; wood; protein; carbohydrate; lignin; inorganic

3.0 Introduction

Most poultry operations raise birds on concrete, wooden, or earthen floors with 2 to 6-inches layer of wood shavings, peanut hulls, or other bedding material as an absorptive base (Collins, 1996). Poultry growers periodically clean poultry houses to promote bird health and limit build up of wet manure (Sistani et al., 2003). The litter is removed one or more times a year and replaced with fresh bedding material (Collins, 1996). During clean outs, the entire bedding materials is not removed, instead small quantities of fresh bedding is added to compensate for the amount removed (Sistani et al., 2003). Poultry litter is highly variable in composition and physical characteristics within production facilities and between farms and regions (Dao and Zhang, 2007). The clean out methods influence the composition of the poultry litter because of incorporation of soil in the litter. The ash represents the inorganic compounds in poultry litter and ranges from 9% to 54% (Jacob et al., 1997). Other factors that affect poultry litter variability include; (1) age and breed of chickens, (2) density of confinement, (3) feed ration, (4) type and amount of bedding material, (5) moisture content of bedding material, and (6) type of floor (Edwards and Daniel, 1992). Feedstock characterization is important for both technical and economic success of a thermochemical conversion. The elemental composition and important parameters such as total solids, volatile solids, and ash content affect the efficiency of pyrolysis and its products. For example, high carbon content contributes to a higher higher heating value (HHV) (Cantrell et al., 2007). Also, high moisture and ash content reduce the usable fraction of the biomass available for thermal conversion and subsequently affect the yield and quality of products. To effectively examine how wood shavings bedding material influences the pyrolysis of poultry manure, their composition and physical characteristics have to be determined. The goal of this chapter of the study is to characterize the layer manure, pine and oak wood shavings used for the research.

3.1 Materials and Methods

3.1.1 *Materials*

The layer manure, pine and oak wood shavings were obtained from a local farm in Shenandoah Valley, Virginia. The manure, nearly free of bedding material, was collected from a concrete floor beneath layers kept in cages. Samples of clean pine and oak wood shavings bedding material were collected from a month old pile on the farm. All samples were ground in a Wiley mill to pass a 1 mm mesh screen.

3.1.2 Methods

3.1.2.1 *Moisture content*

The moisture content was determined using an HG53 Halogen Moisture analyzer (Mettler Toledo, Greifensee, Switzerland). 1g of sample was weighed into a tarred sampler pan and its moisture was determined by quickly heating it by the integral halogen dryer at 105^{o}C for 30 minutes. During the drying operation, the instrument continuously determined the weight of the sample and displayed the loss of moisture. On completion of drying, the moisture content of the sample was displayed as the final result.

3.1.2.2 *Elemental composition and HHV*

The elemental composition (C, H, N, O, S, and Cl) and the HHV of the layer manure and pine wood shavings were determined by Galbraith Analytical Laboratory (Knoxville, TN, USA).

3.1.2.3 *Ash Content*

The ash content of the layer manure, pine and oak wood shavings were determined using ASTM E1755-2002, standard method. 1.0g of each sample was weighed into a pre-weighed porcelain crucible. The crucible and its content were ashed at 575°C for 8 h in a Thermolyne 1400 muffle furnace (Barnstead International, Dubuque, Iowa, USA). The crucible was then removed and placed in a desiccator and weighed after cooling. The ash content on moisture free basis was calculated using Equation 3.1.

$$\%\mathrm{M}_{\mathrm{ash}} = \left[\frac{(m_{ash} - m_{cont})}{m_s}\right] \times 100 \qquad (3.1)$$

Where:

$\%m_{\mathrm{ash}}$ = mass percent of ash, based on 105°C oven dried mass of sample

m_{ash} = mass of ash and crucible, g

m_{cont} = mass of crucible, g, and

m_s = mass of moisture-free solids in the sample, g

3.1.2.4 *Bulk density*

The bulk density was determined using the method described in ASTM D1895B. A funnel was suspended above a tarred 100ml measuring cylinder on a Mettler Toledo Analytical Balance Model AX205 Delta Range. The funnel was filled with the sample and allowed to freely flow into 100ml measuring cylinder. The sample and the cylinder were then weighed. The bulk density was determined using Equation 3.2.

$$\text{Bulk density (g/cm}^3\text{)} = \frac{\text{Weight of sample(g)}}{\text{Volume of packed sample}(\mathrm{cm}^3)} \qquad (3.2)$$

3.1.2.5 *Infrared Spectroscopy*

Infrared spectroscopy has been used to measure the relative amounts of lignin, carbohydrate and protein in many samples (Calderon et al., 2006). 20mg of each sample was subjected to a Fourier-transform infrared (FTIR) analysis. The spectra were obtained over a range of 4000-550cm^{-1} by using an IR spectrometer (Nicolet Avatar, 370 DTGS) equipped with a DTGS-KBR detector in multi-bounce horizontal attenuated total reflectance (HATR) mode. 64 scans at a 4 cm^{-1} resolution and a background gain of 4.0 were used. Data analysis was performed using the OMNIC 7.3 (Thermo Electron Corporation) software package.

3.2 Results and Discussion

3.2.1 Feedstock composition

The manure had a higher bulk density (0.41kg/L) than that of pine (0.24kg/L) and oak (0.23kg/L) wood shavings. Additionally, the ash content of the layer manure was 23.53% compared to pine and oak wood shavings of 1.95% and 1.11% respectively. The high ash content of the manure was attributed to physically incorporated soil and intrinsic inorganic materials such as potassium (K), calcium (Ca) and phosphorous (P) present in manure. The nitrogen content of the pine and oak wood was less than 0.5%, compared to 6.42% for the layer manure. Manure was relatively rich in nitrogen because of its protein content. However the pine and oak shaving were higher in carbon (C), hydrogen (H) and oxygen (O) compared with the layer manure (Table 3.1). The low C and O content of the manure was due to the dilution effect of its high ash content. The ratio of H/C of the manure was 1.70 compared to 1.52 for pine and 1.47 for oak wood shavings. Between pine and oak, oak wood was relatively higher in C, O, H, S, Cl and higher heating value (HHV). Both wood shavings had higher heating value (HHV) approximately 21% higher than the manure. Since HHV relates to carbon content (Susott et al., 1975; Tillman, 1978; Demirbas, 2001), the low heating value of the manure was due to its high ash content. Finally, sulfur and chlorine contents in manure were over 100% higher than that found in the wood shavings (Table 3.1).

Table 3.1

Sample characterization of layer manure, pine and oak wood shavings

	Feedstock		
Elemental Composition (wt %)†	Layer manure	Pine	Oak
C	29.15	46.53	49.52
H	4.13	5.91	6.06
N	6.42	< 0.5	<0.5
O	36.56	42.31	43.17
S	0.36	< 0.05	<0.1
Cl	0.62	180ppm	0.032
HHV(MJ/kg)	14.79	18.02	19.50
Ash (wt %)[a]	23.53	1.95	1.11
Moisture (wt %)[b]	11.50	9.85	8.00
Bulk Density (kg/L)	0.41	0.24	0.23

[a] ASTM E1755, Standard test method for ash in biomass.
[†] Moisture free basis
[b] HR73 Halogen moisture Analyzer

3.3.2 Infrared Spectroscopy

3.2.2.1 Layer Manure

Figure 3.1 is an HATR spectrum of layer manure. Absorption bands due to secondary amides that are common in proteins were identified in the manure spectrum. The band at 3069 cm^{-1} was assigned to N-H stretch. The band at 1645 cm^{-1} was assigned to amide carbonyl (C=O) stretch and that at 1533 cm^{-1} was assigned to N-H in–plane bend. The additional band at 1267 cm^{-1} was assigned to C-N stretch, which complimented the above bands suggesting the presence of secondary amides in the manure protein. The peaks at 2916 cm^{-1} was assigned to methylene CH_2 asymmetric stretch of aliphatic hydrocarbon. The presence of phosphorus in the manure was confirmed by two strong bands at 1001 cm^{-1} and 595 cm^{-1} which are characteristic absorptions of inorganic phosphates that belong to PO_4^{-3} stretch and bend vibrations respectively. Furthermore, bands at 1421 cm^{-1}, 873 cm^{-1} and 711 cm^{-1} are indicative of the presence of inorganic carbonate which is most likely calcium carbonate (OMNIC 7.3 Software, 1991; Spectral Database for Organic Compounds, 2001). The FTIR analysis of the functional groups shows that the layer manure contains nitrogenous and inorganic compounds. The manure also lacks carbohydrate peaks possibly because the manure was almost free of any form of bedding material (wood shavings) or was degraded. The interpretations of the FTIR spectrum are based on data from (OMNIC 7.3 Software, 1991; Smith, 1998; Coates, 2000; Spectral Database for Organic Compounds, 2001; Silverstein et al., 2005; Calderon et al., 2006).

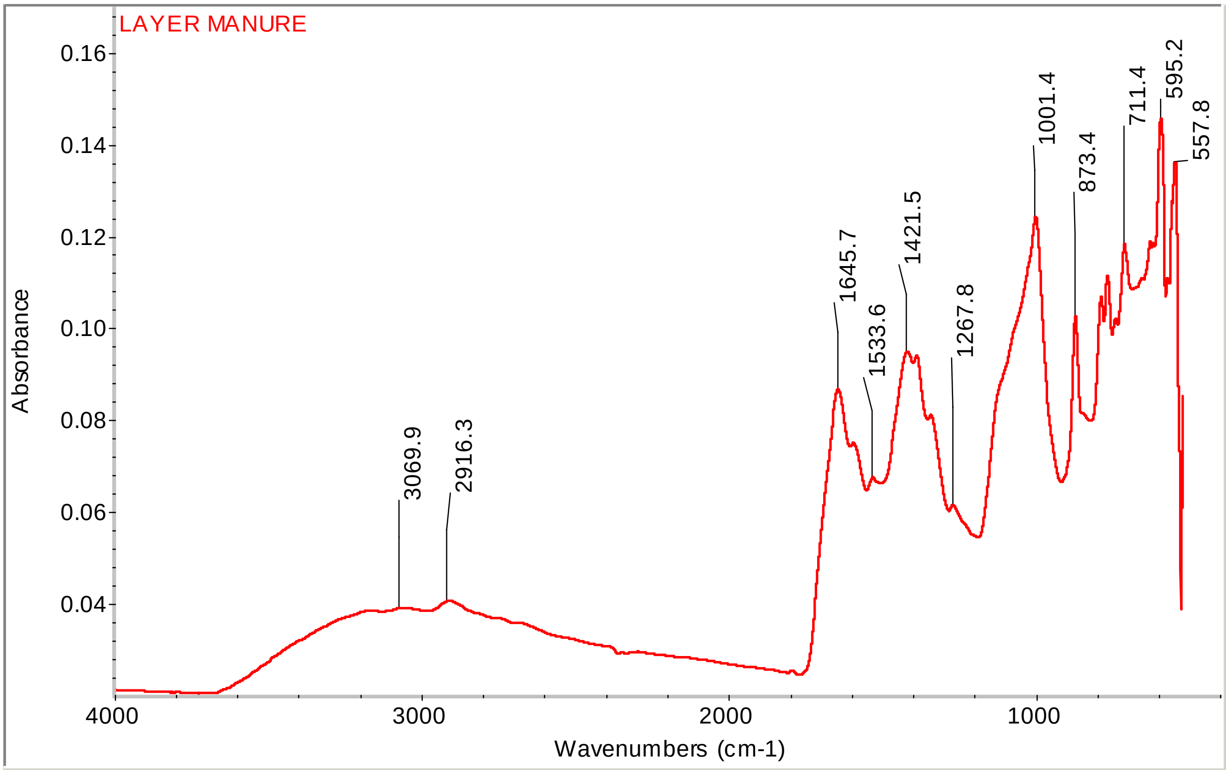

Figure 3.1 HATR spectrum of layer manure

3.2.2.2 Pine and oak wood shavings

Figure 3.2 and 3.3 is an HATR spectrum of pine and oak wood shaving respectively. There was no observable difference in the functional groups peaks in pine and oak wood spectra. The IR spectrum show strong hydrogen bonded O-H stretching absorption at 3323 cm^{-1} corresponding to the hydroxyl groups associated with cellulose (Hon and Shiraishi, 1990). The C-H stretching and bending vibrations of methylene (CH_2) of aliphatic hydrocarbons were assigned to bands at 2880 cm^{-1} and 1419 cm^{-1} respectively. The band at 1728 cm^{-1} was assigned to carbonyl stretching (C=O) in aldehydes, ketones, esters and carboxyl groups (El-Hendawy, 2006). The Peaks at 1506 cm^{-1} and 1600 cm^{-1} were identified as aromatic skeletal vibrations (ring modes). The 1506 cm^{-1} band was assigned to lignin (Pandey, 1999; Sun et al., 2001; Uçar et al., 2005). The C-O stretch of primary alcohol at 1026 cm^{-1} and secondary alcohol C-O stretch at 1151 cm^{-1} indicated the presence of carbohydrates. The band at 1260 cm^{-1} was assigned to Phenolic C-O-H in-plane bending (Hon and Shiraishi, 1990).

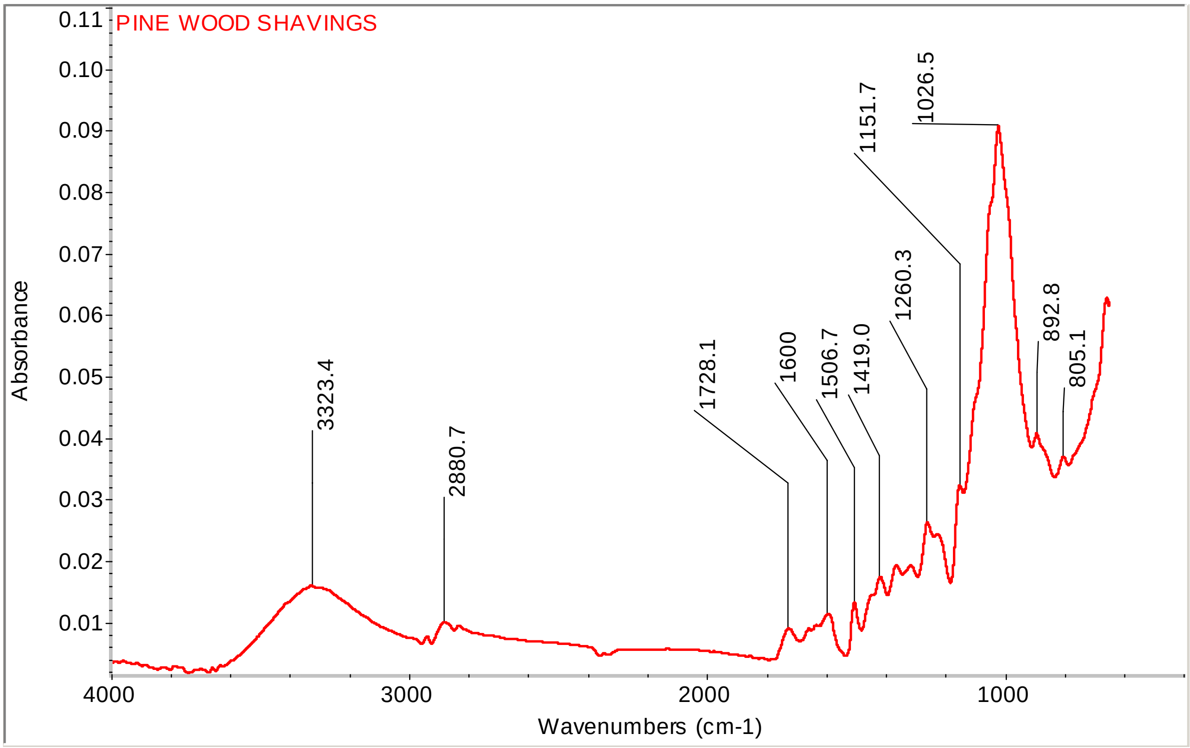

Figure 3.2 HATR spectrum of Pine wood shaving

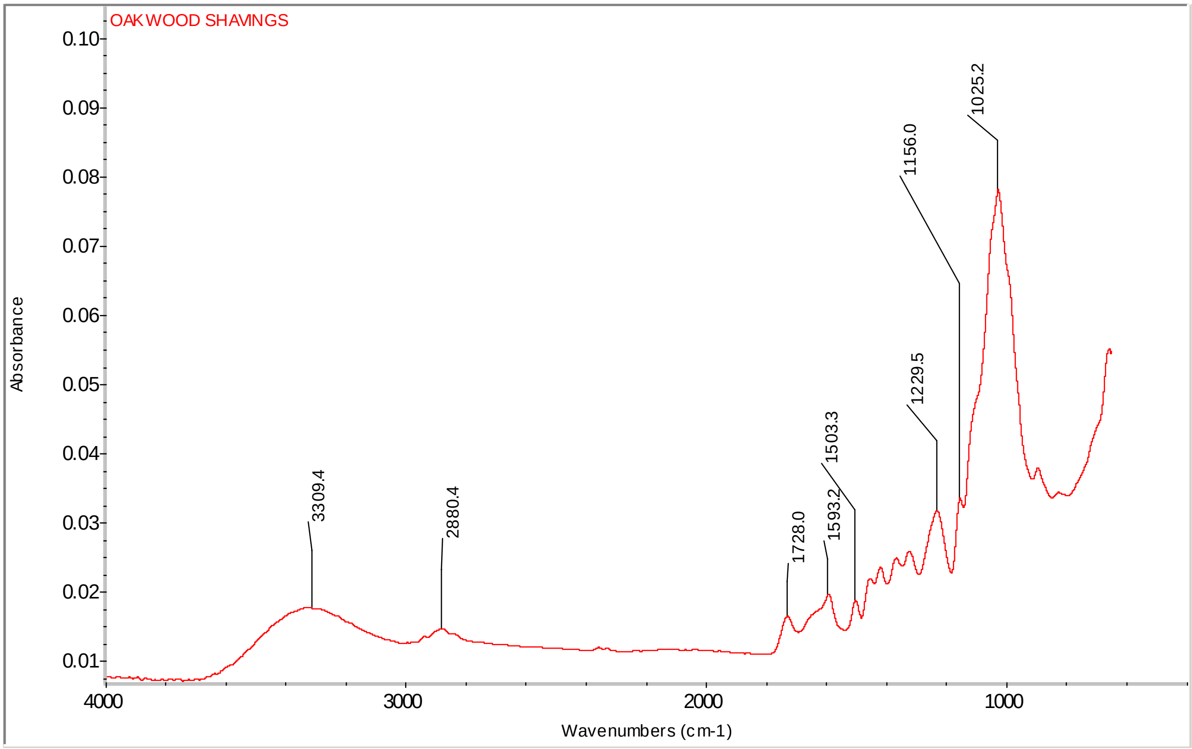

Figure 3.3 HATR spectrum of oak wood shaving

3.3 Conclusions

The characterization of the feedstocks using ultimate, proximate and FT-IR spectrometry showed that the chemical composition, ash content, and HHV of manure is very different from that of pine and oak wood shavings. The presence of large amount of protein and inorganic compounds in manure suggest that the pyrolytic chemistry may be different from pine and oak wood shavings which has low protein and ash contents but rich in carbohydrate polymers and lignin. This information will help to understand how wood influences the manure when pyrolyzed.

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CHAPTER FOUR

INFLUENCE OF WOOD SHAVINGS ON THE PYROLYSIS OF LAYER MANURE

ABSTRACT

The poultry litter composes mainly of manure and bedding material with traces of spilled feed and feathers. The type and amount of bedding material was varied to investigate its influence on the pyrolysis of the manure. 400g of each feedstock: manure, wood (pine and oak), and mixtures of manure and wood in proportions (75:25 50:50, and 25:75 w/w %) respectively were subjected to fast pyrolysis at 450°C in a fluidized bed reactor. The total pyrolytic oil yield ranged from 43.3% to 64.5 wt%. The highest bio oil yield and the lowest char yield were obtained from oak wood. The manure oil had the highest HHV (29.7 MJ/kg), the highest pH (5.89), the lowest density (1.14 g/cm^3) and a relatively low viscosity (130cSt). The physicochemical properties of the oils were strongly influenced by the amount and the type of wood in the mixture. The pH and HHV of the oils from the mixture decreased and density increased as the wood of the manure increased. The oils had relatively high nitrogen content ranging from 5.88wt% to 1.36 wt%. The ash (<0.07wt %) and sulfur (<0.28wt %) contents were very low. FT-IR, ^{13}CNMR, and ^{1}HNMR analysis showed that manure oil was rich in aliphatic hydrocarbon and primary and secondary amides. The addition of wood to the manure essentially changed the chemical composition of the pyrolytic oils and caused an increase in compounds with oxygen functionalities and a decrease in aliphatic hydrocarbons and nitrogenous compounds. The results reveal that during pyrolysis, not only does decomposition of manure and wood occur, but also reactions between their products take place and their reactivity depends on the amount and the type of wood in the manure.

Keywords: Layer manure; pine wood; oak wood; fast pyrolysis; pyrolytic oil; properties; FT-IR spectrophotometry; ^{13}CNMR spectrometry; ^{1}HNMR spectrometry.

4.0 Introduction

The high demand for energy and the depletion of fossil fuels suggests that source of energy supply in the future has to come from renewable sources (Demirbas and Arin, 2002). Furthermore, concerns about environmental degradation and the need for sustainability have led to the utilization of various forms of biomass as a renewable source of energy. Biomass potential includes wood, energy crops, agricultural and forestry residues and animal waste (Demirbas and Arin, 2002; Bridgwater, 2004). These renewable sources of energy offer the possibility of generating fuels that can partially substitute for fossil fuels and chemical feedstock for industries (Encinar et al., 2000). The environmental problems associated with the traditional methods of poultry litter disposal have spurred interest in its use as an energy source. Thermochemical conversion including combustion, gasification and pyrolysis are thought to have great promise as a means for efficiently and economically converting poultry litter to synthetic fuels (Çaglar and Demirbas, 2000; McKendry, 2002; Cantrell et al., 2007). Poultry litter has a unique fuel property that makes it a more challenging fuel than wood. The ash, nitrogen, sulfur, chlorine and alkali metals (sodium oxide, Na_2O, and potassium oxide, K_2O) concentrations are much higher in poultry litter than in wood. These characteristics of poultry litter affect the choice of the thermochemical process to be used. Pyrolysis is an efficient method that can be used to transform biomass and any organic waste into a product of high energy density and higher value chemicals. Moreover pyrolysis offers the advantage of a liquid product that can be stored, transported and used as alternative fuel and additionally as a chemical feedstock. Pyrolysis can be used to convert biomass into liquids, solids and gaseous products. The yield and composition of pyrolysis products depend on the composition of the feedstock, the pyrolysis reactor, and the operating conditions: temperature, residence time, and heating rate (Bridgwater and Cottam, 1992; Maschio et al., 1992; Klass, 1998; Meier and Faix, 1999). Pyrolysis oils from wood and herbaceous biomass are complex, acidic, viscous, reactive and thermally unstable. These properties of bio-oil result in several significant problems during its use as fuel in standard equipment such as boilers and engines. Poor volatility, high viscosity, corrosiveness and long term instability have limited the range of bio-oil applications (Czernik and Bridgwater, 2004). Poultry litter contains high amounts of inorganics such as K and Ca, which can catalyze pyrolytic reactions and lead to high char yields (Yaman, 2004). Research conducted by Agblevor et al.,(2007) on the thermochemical conversion of broiler chicken litter, turkey litter and bedding material in a fast pyrolysis fluidized bed reactor showed that the yield of pyrolysis products and the properties of the oils depend on the age and bedding material content of the litter. Another work by Schnitzer et al., (2007), on the chemical characterization of bio oil produced from fast pyrolysis of chicken manure showed that the bio oil contained nitrogenous compounds that were aliphatic, aromatic and heterocyclic. Although poultry litter pyrolysis has been reported in published literature, the influence of wood shavings on the pyrolysis product yields, products composition and properties has not been reported. Given the high levels of nitrogen, sulfur, alkalis, and chloride in poultry manure, it is important to know how they react under pyrolytic conditions with wood which is rich in cellulose, hemicelluloses, and lignin. The aim of this chapter is to investigate the influence of wood shavings on the pyrolysis of layer manure and examine its effects on the product yields, properties and compositions of the bio oils.

4.1 Materials and Methods

4.1.1 Materials

4.1.1.1 *Preparation of feedstocks*

Layer manure, pine and oak wood shavings were obtained from poultry growers in Shenandoah Valley, Virginia for this study. The layer manure and the wood shavings were air dried at ambient conditions to equilibrium moisture content (moisture content ranged from 8% to 10%) and ground in a Wiley mill to pass a 1mm mesh screen. Mixtures of (manure and pine) and (manure and oak) were prepared in a blender. In both type of mixtures, the manure and wood were mixed in the following ratios; 100:0, 75:25, 50:50, 25:75 and 0:100 w/w.

4.1.2 Methods

4.1.2.1 *Pyrolysis of feedstocks*

The fast pyrolysis was carried out in a bench-scale fluidized bed reactor unit located at the BSE Bioresource Eng. Lab, Virginia Tech, U.S.A (Figure 4.1). The unit comprised of a K-Tron volumetric feeder, 50mm bubbling fluidized bed reactor equipped with a 100µm porous metal gas distributor, hot gas filter, two chilled water condensers, an electrostatic precipitator and a packed column. The reactor was externally heated with a three-zone electric furnace (Thermcraft, Winston-Salem, NC). 100g of silica sand was used as the fluidizing medium and the bed was fluidized with nitrogen (12L/min). The silica sand particles had a surface mean diameter of 355µm. The static bed height of 31mm expanded to 40mm when it was fully fluidized. 400g of each feedstock: pure manure, pure wood (pine and oak), and mixtures of manure and wood in proportions (75:25 50:50, and 25:75 w/w %) respectively were pyrolyzed at 450°C. They were fed at a rate of 300-330 g/h from a feed hopper using a screw feeder to convey it into an entrainment zone. 6 L/min of nitrogen gas was used to entrain the feed through a jacketed air-cooled feeder tube into the fluidized bed. The K-Tron feeder was set on low speed between 36- 46 rpm depending on the bulk density of the feedstock. To prevent a blockage in the feeding tube during the transport of the feed from the feed hopper into the pyrolysis zone, all feed particle size was less than 1mm mesh, the moisture content was 8-10wt% and the feed tube was air-cooled. The reactor temperature, feed rate, and gas flow rate were kept constant for each run. During pyrolysis, the mixture of char, gases and vapors that exited from the reactor were separated by a hot gas filter maintained at 400^{o}C. The separated gases and vapors were then passed through two condensers connected in series. The condensers were maintained at -8^{o}C with a 50/50 cooling mixture of ethylene glycol and water from an 18-liter A82 refrigerated circulating bath (Haake, Karlsruhe, W. Germany). Any condensable gases and aerosols that escaped from the condenser were captured by an electrostatic precipitator (ESP) kept at 16-20 kV and a packed column of glass beads.

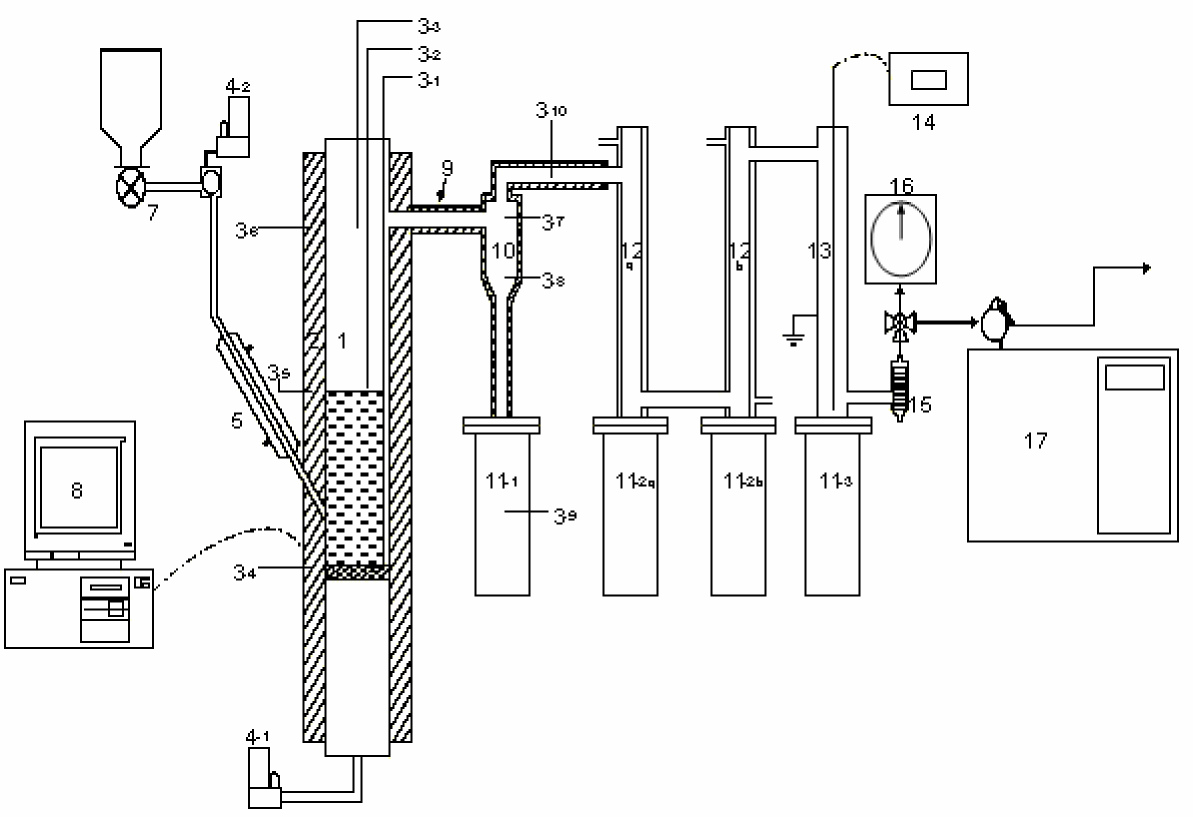


Figure 4.1 Schematic diagram of the fluidized bed reactor unit

(1-Fluidized bed, 3- Thermocouple, 4-Mass flow controller, 5- jacketed air-cooled feeder tube, 6-Hopper, 7-Screw feeder, 8-Computer, 9-Heating tape, 10-Hot gas filter, 11-Reservoir, 12-Condenser, 13-ESP, 14-AC power supply, 15-Filter, 16-Wet gas meter, 17-Gas Chromatograph)

4.1.2.2. *Pyrolysis Products*.

The mass of char was determined gravimetrically by weighing the hot gas filter and the reactor before and after each pyrolysis experiment. The total mass of bio oil was also determined gravimetrically by weighing the condensers, electrostatic precipitator and the packed column before and after each experiment. The total mass of the producer gas was calculated by difference. The yields were expressed in percentage on a moisture free basis.

4.1.2.3 *Acidity*

The pH was measured using a Corning pH Meter 440 equipped with F-55500-10 Accumet pH probe (Cole-Parmer Instrument Company, Vernon Hills, Illinois, USA). The pH data were obtained after 10 min stabilization of the mechanically stirred oil. The pH values were reported to two decimal places. The meter was frequently calibrated using standard pH solutions (Micro Essential Lab Inc., N.Y., U.S.A.).

4.1.2.4 *Viscosity*

The dynamic viscosities of the freshly produced oils were measured with a Brookfield DV-II+ Pro viscometer (Brookfield Engineering laboratories, Inc. MA, USA.) and a programmable thermosel temperature controller. The measurement was conducted at $60^{o}C$ with Spindle SC4-18 and speed ranging from 1-30 rpm depending on the viscosity of the oil. Sample volume of 7ml was used and the reading of the instrument stabilized within 5-15min. The dynamic viscosities were also converted into kinematic viscosities.

4.1.2.6 *Water content*

A Metrohm 701KF Titrino (Brinkmann Instruments, Inc, N.Y, U.S.A) and a 703 titration stand setup were used for the Volumetric Karl Fischer titration. Hydranal® Composite 5 reagent was used. A solvent mixture of 40 mL of methanol + 20mL of toluene were placed in the titration vessel and conditioned. About 1g of oil sample was loaded into a hypodermic plastic syringe and weighed. The sample was injected into the titration solvent and the syringe was weighed again. The mass of sample used was determined by difference. The mixture was stirred to dissolve the oil. The water content was titrated volumetrically and the resulting mass was recorded. The water content was expressed as a percentage of the amount of sample used (1.00g).

4.1.2.5 *Density*

The densities were determined at 23 °C using a Mettler Toledo DA-110M density meter (Greifensee, Switzerland) according to ASTM D4052. Calibrations were done prior to measurements with distilled water free from bubbles. The oil sample was introduced into an oscillating sample tube and the density was calculated from measured resonance frequency. The values were reported to 3 decimal places in g/cm^3.

4.1.2.6 *Elemental composition and Higher heating value (HHV)*

The elemental composition (C, H, N, O, S, and Cl), ash and HHV of the oils (pine, oak, manure and mixtures of both) collected from the ESP were determined by Galbraith Analytical Laboratory (Knoxville, TN, USA).

4.1.2.6 *FT-IR Spectrometry*

20mg of each sample was subjected to a Fourier-transform infrared (FTIR) analysis. The spectra were obtained over a range of 4000-650cm^{-1} using an IR spectrometer (Nicolet Avatar, 370 DTGS) equipped with a DTGS-KBR detector in multi-bounce horizontal attenuated total reflectance (HATR) mode. 64 scans at a 4 cm^{-1} resolution and a background gain of 4.0 were used. Data analysis was performed using the OMNIC 7.3 (Thermo Electron Corporation) software package.

4.1.2.7 *Carbon-13 nuclear magnetic resonance spectrometry (^{13}C-NMR)*

2.0g of oil was dissolved in 2.5ml of dimethyl sulfoxide (DMSO) and 0.25ml of tetramethylsilane (TMS) in a 10mm sample tube. The ^{13}CNMR spectra were recorded on a Varian Unity 400 MHz NMR spectrometer. The observing frequency for the ^{13}C nucleus was 100.58MHz. The pulse width was 8.5µs, the acquisition time was 1.31s, and the recycle delay was 1s. The spectra were obtained with 1000 scans and a sweep width of 25.0 MHz.

4.1.2.8 *Proton nuclear magnetic resonance spectrometry (^{1}H-NMR)*

The oil was weighed to 400mg and was dissolved in 0.5ml of dimethyl Sulfoxide (DMSO) and 0.05ml of tetramethylsilane (TMS) in a 5mm sample tube. The ^{1}HNMR spectra were recorded on a Varian Unity 400 MHz NMR spectrometer. The observing frequency for the ^{1}H was 400.0 MHz. The pulse width was 6.4µs, the acquisition time was 3.74s, and the recycle delay was 1s. The spectra were obtained with 32 scans and a sweep width of 6.4 MHz.

4.1.2.9 TG/DTG Spectrometry

TGA was conducted on the oil using a TA Instruments Q600 SDT. 20mg of sample was placed in an alumina crucible and was subjected to thermogravimetric analysis with 20ml/min of N_2 as a carrier gas. The heating rate was at 5°C/min from 25°C to 700°C. All the tests were repeated three times to ensure good reproducibility of the results.

4.2 Results and Discussion

4.2.1 Effect of Pine wood shavings on pyrolysis of layer manure

The yields of products obtained from the pyrolysis of layer manure and pine wood are shown in figure 4.1a and summarized in Table 4.2. It was evident that the amount of wood in the manure/wood mixture influenced the pyrolytic yields. An increase in wood content resulted in an increase in pyrolysis oil (organics + water) yield and a decrease in char yield. The oil yield for the pure manure was 43.3wt% and increased to 53.5wt% as the wood content in the mixture increased to 75wt% and the char yield on the other hand decreased from 43.1wt% to 29.5wt%. Additionally, the organic portion of the oil increased from 58.6wt.% to 66.1wt.% as the wood content increased to 75%. The gas yields did not show any strong difference. It is worth mentioning that, the pure wood had the highest oil yield (62.0wt %) and the lowest char yield of (22.9wt. %). The Pyrolysis product yields were influenced by the feedstock composition since the operating conditions were maintained constant for each run. The ash content of the feedstocks was consistent with the yields. High ash contents imply high inorganic contents in the feedstock. Alkali metals, especially K and Ca, are known to have a catalytic effect on biomass decomposition and lead to high char forming reactions and consequently low oil yield (Yaman, 2004). As can be seen in Table 4.1, the ash content of the manure was 23.5wt% compared to 1.95wt% of pine shavings. Therefore, one would expect that the quantity of the liquid product from pyrolysis of feedstock with high manure content would be less than that of those with high wood content.

Table 4.1

Properties of biomass feedstocks (Moisture free basis)

	Feedstock		
Elemental Composition (wt %)	Layer manure	Pine	Oak
C	29.15	46.53	49.52
H	4.13	5.91	6.06
N	6.42	< 0.5	<0.5
O	36.56	42.31	43.17
S	0.36	< 0.05	<0.1
Cl	0.62	180ppm	0.032
HHV(MJ/kg)	14.79	18.02	19.50
Ash (wt %)	23.53	1.95	1.11

Table 4.2

Summary of Pyrolysis Results

Feedstock			**Pyrolytic Yields (%)**		
Manure (wt. %)	Pine wood (wt. %)	**Mean Reactor Temperature (^{o}C)**	**Total liquid**	**Char**	**[†]Gas**
100.0	0.0	468.8±9	43.25±0.43	43.1±0.95	13.6±1.00
75.0	25.0	461.6±12	46.84±0.91	39.2±0.20	15.7±2.92
50.0	50.0	448.4±16	49.03±0.89	34.1±1.83	16.97±2.4
25.0	75.0	433.5±23	53.52±1.44	29.5±2.94	16.95±1.52
0.0	100.0	420.5±20	62.69±2.39	22.4±1.14	14.88±2.6

[†] By difference

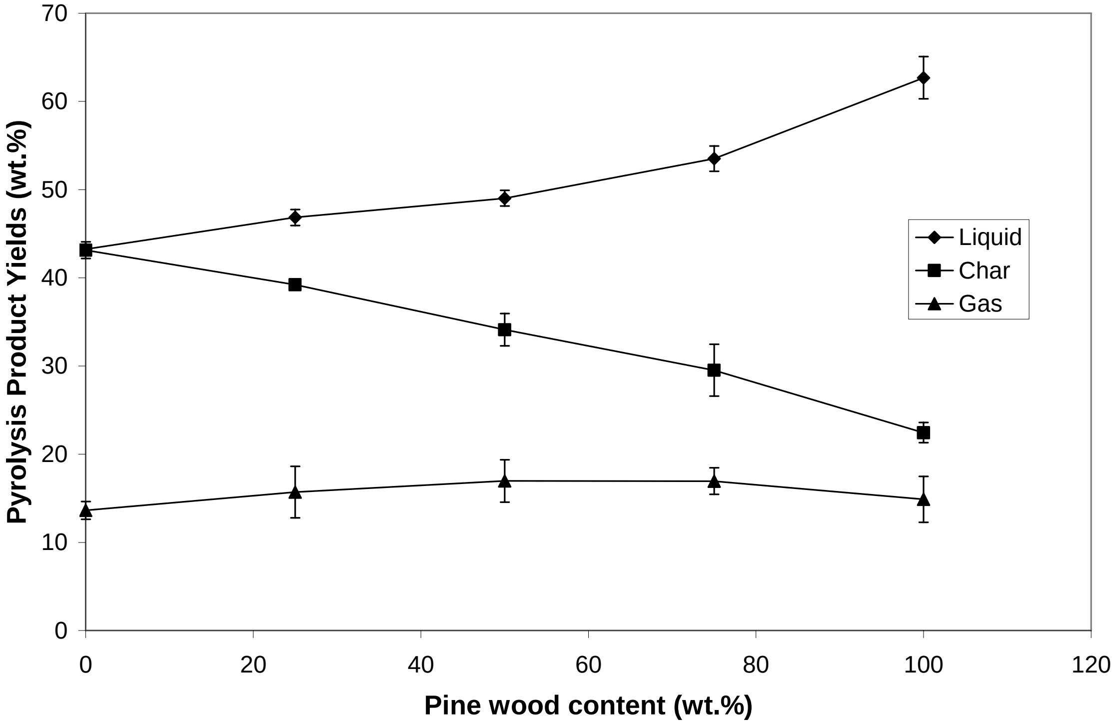


Figure 4.1a Yields of pyrolysis products of manure and pine wood

4.2.1.2 Physico-chemical properties

Table 4.3 shows a summary of the physico-chemical properties of the oil fractions from the ESP. Their physico-chemical properties differed as a result of feed composition and pyrolytic reactions between the decomposition products of manure and wood. The appearance of the bio oils were almost black or dark brown depending on the manure and wood content in the feedstock. Figure 4.1b and 4.1c are pictures respectively for both bio oil and char derived from a mixture of 50% manure and 50% pine wood. The oil was free flowing when freshly produced and had a smoky or barbecue smell.

The manure oil had the highest pH value and HHV and the lowest density. The pH decreased from 5.93 to 3.89, the HHV decreased from 29.7 to 26.15 MJ/kg whiles the density increased from 1.14 to 1.24g/cm^3 as wood content was increased to 75%. The pine wood initially did not have any significant effect on the water content of the whole bio oil, but when 75% of wood was added, it decreased the water content of the whole bio oil from 41.38 to 33.9wt%. The kinematic viscosity of the oils did not follow any specific trend. The manure oil had relatively low viscosity of 130 cSt at 60°C. When 25% and 50% of wood was added to the manure, the oil viscosity increased to 223 cSt and 225 cSt respectively, but when 75% of wood was added, the viscosity of the oil decreased to 97 cSt. The high viscosity measured for the 25% and 50% wood mixtures were attributed to the formation of compounds of higher molecular weight due to chemical reactions between the decomposition products of manure and wood. The influence of the wood on the viscosity of the pyrolysis was not due to physical interaction but rather a chemical reaction between the wood and manure degradation products. When manure oil and wood oil were mixed physically, the trends in oil viscosities were different (Table 4.4). Additionally the difference between the experimental values and values obtained by additivity rule of the pH of the oils from both 75/25 and 50/50 mixtures show that chemical reaction occurred between the decomposition products of the manure and wood.

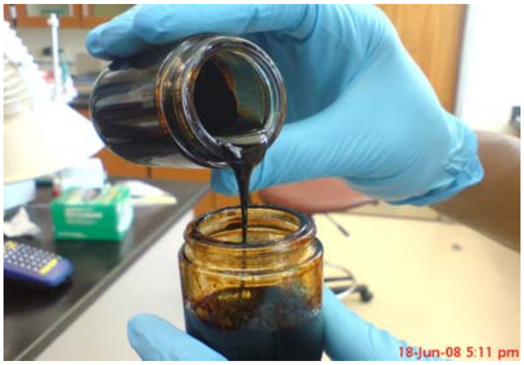


Figure 4.1b Bio oil

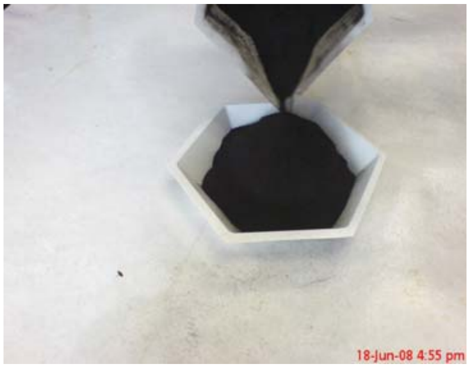


Figure 4.1c Char

Table 4.3

Summary of physico-chemical properties of manure and pine wood oils

Property	Analysis Method	Pyrolysis Oils (ESP)				
		100% M	M:P (75/25)	M:P (50/50)	M:P (25/75)	100% P
Moisture content (wt %)	Karl-Fischer titration	6.46	6.14	4.13	3.14	3.65
Water content of whole oil (wt %)	Karl-Fischer titration	41.38	37.61	38.13	33.93	25.84
pH	pH meter	5.93	4.47	4.29	3.87	3.04
Density @ 23^{o}C, g/m^{3}	ASTM D4052	1.14	1.20	1.21	1.24	1.26
Kinematic viscosity, at 60^{o}C (cSt)	Rotational Viscometer	130.0	223	225	97	86
Ash Content, (wt %)	ASTM D482	<0.08	<0.07	<0.06	<0.05	<0.08
Higher Heating Value (MJ/kg)	ASTM D5865	29.7	28.9	27.7	26.15	25.64
Elemental Composition	ASTM D3176					
C (%)		61.86	60.93	61.08	60.80	58.29
H (%)		8.02	7.56	7.11	6.86	6.71
N (%)		5.88	4.18	2.90	1.36	<0.5
O* (%)		23.93	27.10	28.75	30.75	34.99
S (%)		0.28	0.21	0.15	0.081	<0.05
Cl (ppm)		318	193	149	118	137
H/C molar ratio		1.56	1.49	1.40	1.35	1.38
O/C molar ratio		0.29	0.33	0.35	0.38	0.45
N/C molar ratio		0.08	0.06	0.04	0.02	0.01

* By difference, M= Manure, P=Pine

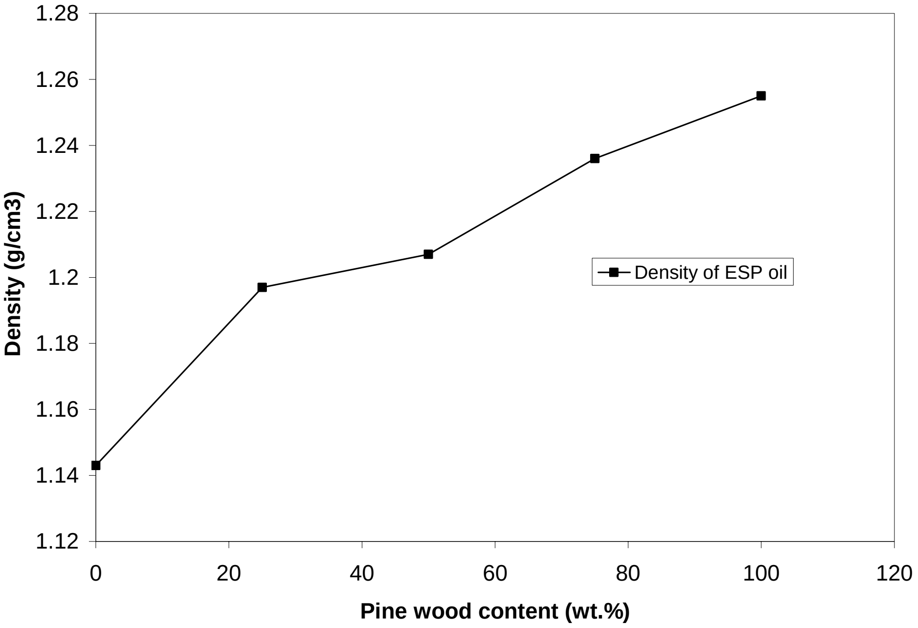


Figure 4.2 Density of ESP oils of manure, pine and their mixtures

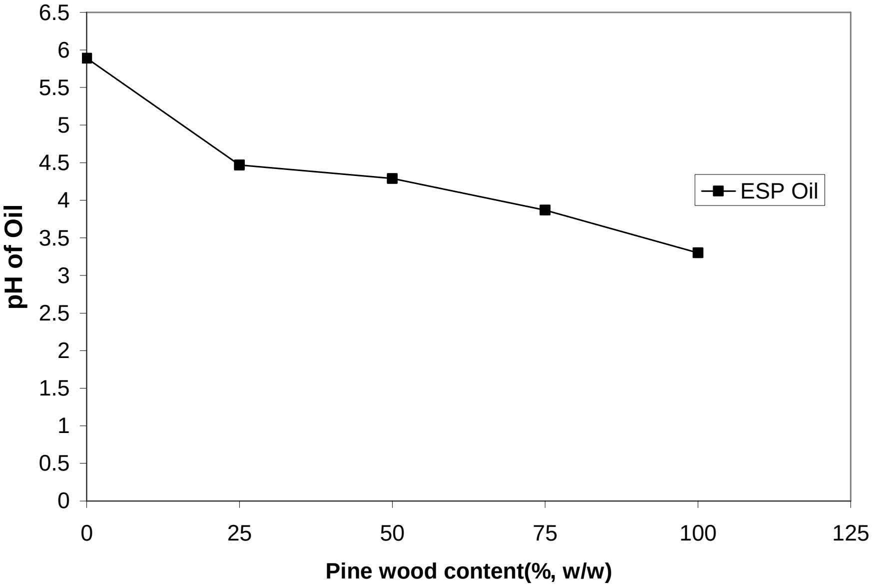


Figure 4.3 pH of ESP oils of manure, pine and their mixtures

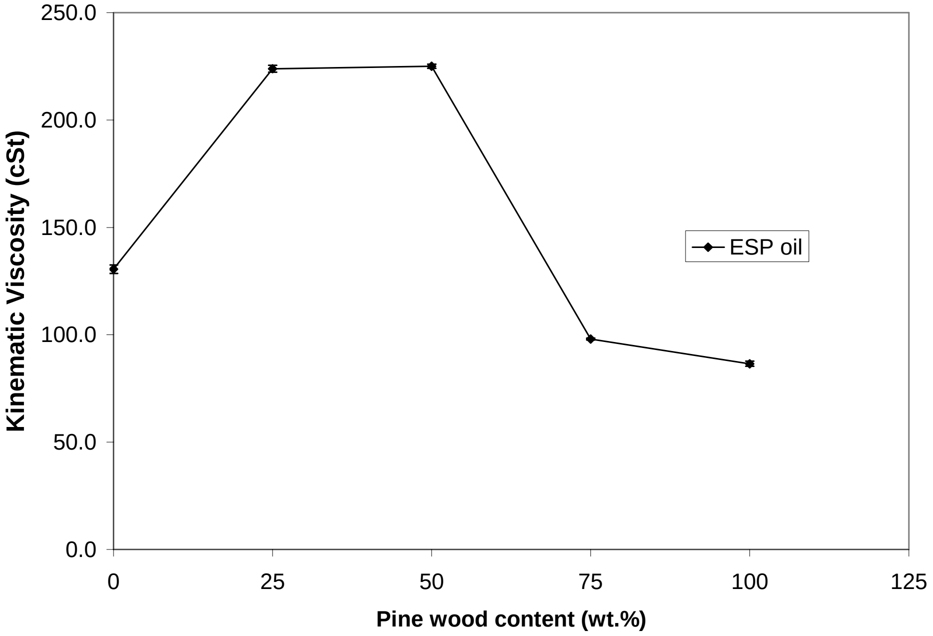


Figure 4.4 Kinematic viscosity of ESP oils from manure, pine wood and their mixtures

Table 4.4
Comparison of viscosity of oils from pyrolysis and physical mixtures

Manure (wt. %)	Pine wood (wt. %)	Age of Oil (Days)	Kinematic viscosity (cSt)	
			Original	Physical
75.0	25.0	1	223	147
50.0	50.0	1	225	146
25.0	75.0	1	97	130

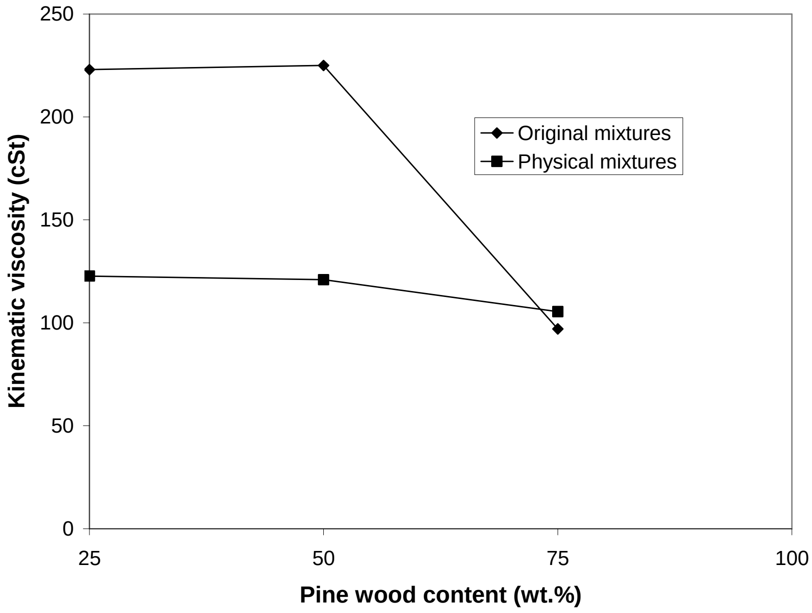


Figure 4.5 Kinematic viscosities of ESP oils from original and physical mixtures of manure and pine wood

4.2.1.3 Chemical composition of ESP oils

The elemental analysis showed that nitrogen (N), hydrogen (H), sulfur (S) and chlorine (Cl) decreased with increased in wood content. However, the oxygen (O) followed the opposite trend. As expected, the manure oil had higher N (5.93%), H (8.02%), O (23.93%), S (0.28), and Cl (318 ppm) compared with the mixture of 25% manure and 75% wood which had N (1.36%), H (6.86%), O (34.99%), S (0.081%) and Cl (137ppm). The average chemical compositions of the oils were $CH_{1.56}N_{0.08}O_{0.29}$, $CH_{1.49}N_{0.06}O_{0.33}$, $CH_{1.4}N_{0.04}O_{0.35}$, and $CH_{1.35}N_{0.02}O_{0.38}$, corresponding to wood composition of 0%, 25%, 50% and 75% respectively.

4.3.1.3.1 *FT-IR Analysis*

The FT-IR spectra of the ESP oils are presented in Figure 4.6 and their relative intensities summarized in Table 4.5. Most of the peaks observed were common to all the oils. However there were distinct differences in the spectrum of the pure manure and pure wood oils. Major peaks due to the decomposition products of protein were found in the manure oil and those due to carbohydrates and lignin decomposition were dominant in the wood oil. The absorption band at 1510cm^{-1}, which was attributed to aromatic skeletal vibration mode, was relatively stable and as a result all other bands were semi quantitatively analyzed by dividing their peak intensities by that at 1510cm^{-1}. Because bio oils are complex mixtures of many organic compounds it was not easy assigning functional groups to the bands observed since most of them appear at the same or similar wavelength. The interpretations of the FTIR spectra were based on data presented by Silverstein and Webster, (1998); Bellamy, (1956); Smith, (1998); and Coates, (2000). The IR spectra of all the oils showed hydrogen bonded O-H and N-H stretching absorption around 3300 cm^{-1} and C-H stretching around 2900 cm^{-1}. In the fingerprint region, between 1800 and 900 cm^{-1}, many sharp and discrete absorption bands due to various functional groups were observed. The bands observed above 1510 cm^{-1} were distinct, whereas other bands in the fingerprint region below 1460 cm^{-1} were complex, with contributions from various vibrational modes in carbohydrates, lignin and proteins. The absorption at 3209-3334 cm^{-1} was assigned to H-bonded OH groups and an N-H stretch. The bands at 2926 and 2853 cm^{-1} were assigned to the asymmetric and symmetric C-H stretches of methylene (CH_2) group, indicating the presence of aliphatic hydrocarbons. The band at 1705 cm^{-1} was assigned to carbonyl C=O stretching vibration of carboxylic acids and ketones from decomposition of carbohydrates. The carbonyl C=O stretch at 1656 cm^{-1} was attributed to amides from the decomposition of proteins in manure. The absorption bands at 1556 cm^{-1} and 1409 cm^{-1} which were indicative of the presence of secondary and primary amides were assigned to N-H in–plane bend and C-N stretch respectively. Peaks at 1512 and 1600 cm^{-1} were identified as aromatic skeletal vibrations (ring modes). The 1512 cm^{-1} band was assigned to lignin aromatic skeletal vibration (Faix, 1991; Faix

1992; Pandey, 1999). The bands at 1456 and 1369 cm^{-1} which assigned C-H bending vibrations of methylene (CH_2) and methyl (CH_3) respectively complemented the presence of aliphatic hydrocarbons. Phenolic C-O-H deformation (1209 cm^{-1}), aromatic ethers of C-O-C (1268 cm^{-1}), C-O stretch of primary alcohol (1034 and 1080 cm^{-1}) and secondary alcohol C-O stretch (1117) were also identified in the oils. The bands at 923, 856 and 808 cm^{-1} were indicative of γ -CH or β-ring modes of substituted furans. In figure 4.6, it can be seen in the pure manure spectrum that the most intense peaks were the aliphatic hydrocarbons (2926 cm^{-1}) and the amide groups (1660, 1556, 1406 cm^{-1}) from the decomposition of protein. However, the addition of 25% of pine wood to manure dramatically diminished the amide carbonyl (1660 cm^{-1}) and increased the carboxylic acid C=O stretch at 1705 cm^{-1}. The decrease in the amide carbonyl may be due to amide hydrolysis or chemical reactions leading to the formation of carboxylic acids or possible ketones. This explains the sharp drop in the pH of the oil from 5.89 to 4.47 when 25% of wood was added. The oil with 75% of wood did not differ much from the oil derived from 100% pine wood. They both had the C-O stretch due to aliphatic primary alcohol at 1035 cm^{-1} to be the most intense. It can be inferred that the amount of wood added to the manure resulted in oils with different chemical composition. The FT-IR analysis of the oils showed that the nitrogen and oxygen functionalities and hydrocarbons contents of the oils were highly dependent on the composition of the manure/wood mixture. It can generally be concluded that manure with increased amount of carbohydrate and lignin results in oils with low amount of protein decomposition product like hydrocarbons, amides and other nitrogenous compounds but contain high amount of aliphatic alcohols, phenolic compounds, carbonyl/carboxylic groups, aromatic compounds and ethers which are from the decomposition of carbohydrate and lignin.

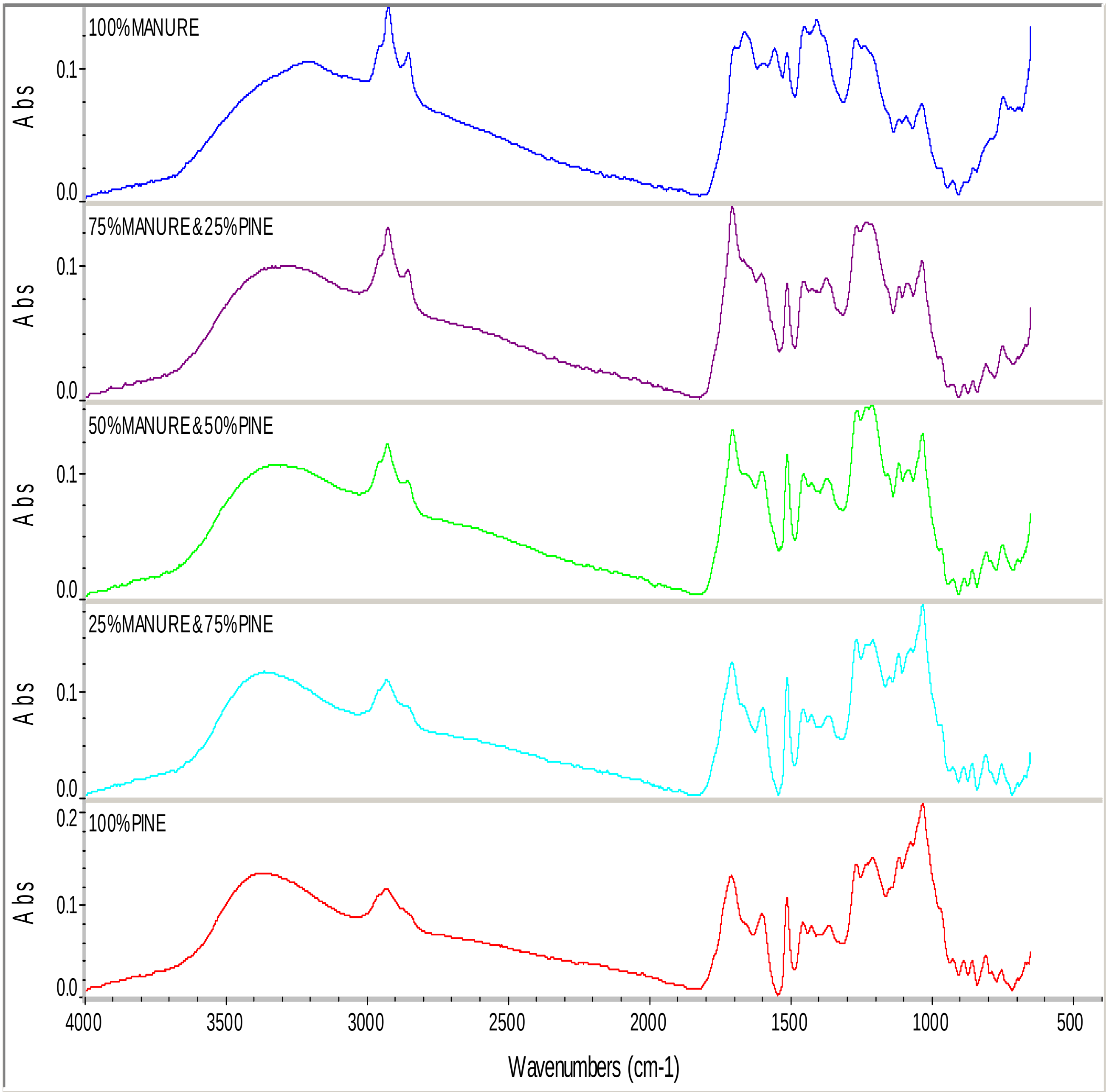


Figure 4.6 FT-IR spectra of oils from manure, pine wood and their mixtures.

Table 4.5
Summary of FT-IR assignment and their relative intensities

Functional Group	Wave number (cm^{-1})	Relative Intensity			
		100% Manure	75% Manure & 25% Pine	50% Manure & 50% Pine	25% Manure & 75% Pine
O-H stretch, N-H stretch	3363-3241	1.07	0.81	0.81	0.86
Methylene CH_2 asymmetric stretch	2929-2924	1.37	1.07	0.92	0.90
Methylene CH_2 symmetric stretch	2854	1.08	0.85	0.75	
Carbonyl C=O stretching: unconjugated ketone and carboxyl group	1702-1706	1.27	1.04	1.03	1.12
Amide Carbonyl C=O	1658	1.30	0.94	0.80	
Aromatic skeletal vibration with C=O stretching	1600	1.12	0.86	0.80	0.70
C-H deformation (asymmetric)	1451	1.20	0.94	0.78	0.69
C-N stretch	1427-1408	1.21	0.91	0.76	0.67
C-H deformation (symmetric)	1378-1362	1.19	0.93	0.77	0.70
Phenolic OH-deformations	1267	1.36	1.23	1.20	1.21
Aromatic ether C-O-C	1234-1208	-	1.19	1.19	1.22
Secondary aliphatic alcohol C-O stretch	1122-1112	-	0.71	0.75	0.81
Primary aliphatic alcohol C-O stretch	1085-1078	0.70	0.67	0.78	0.97
Primary aliphatic alcohol C-O stretch	1032-1034	0.88	0.89	1.06	1.26
Para substituted ring mode out-of-plane bending C-H	854	0.23	0.19	0.17	0.15
	752-745	0.79	0.48	0.31	0.22
Out –of plane N-H bend	600	1.14	0.61	0.49	0.43

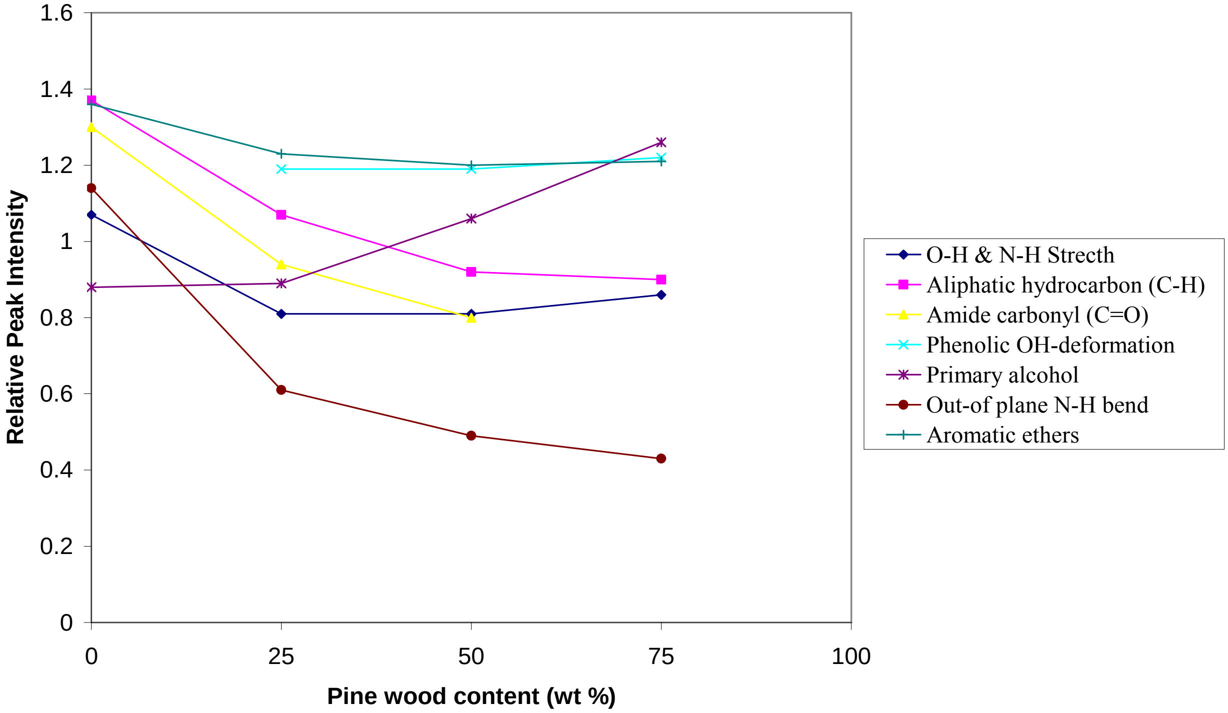


Figure 4.6 Relative intensities of absorption bands of manure and manure/wood mixture oils

4.2.1.3.2 ^{13}*C -NMR Analysis*

Figure 4.7a shows the ^{13}CNMR spectra of pyrolysis oil from manure, pine wood and their mixtures. The complex mixture of products from the decomposition of protein, carbohydrate and lignin in the oils is seen at various chemical shifts. It was difficult in assigning specific structures to the signals. The interpretations of the ^{13}CNMR spectra were based on data presented in literature. In the ^{13}CNMR spectrum of manure bio oil, the prominent signal at 174.8 ppm was indicative of the presence of amides (Vane et al., 2003). The complementary strong signals at 29.7(CH_2) and 23 ppm(CH_2 or CH_3) which can be assigned to methylene groups in proteins (Gutierrez et al., 1996; Vane et al., 2003) confirmed the presence of amides in the oil. The entire region between 5-36 ppm were attributed to methylene carbons of saturated n-alkyl groups (Veeken et al., 2001; Marche et al., 2003). The peak at 116, 121, 130 and 146 ppm in the aromatic region (105-160 ppm) were attributed to aromatic C of lignin and C in N-heterocyclic structures (Schnitzer et al., 2007). The signals at 103, 77, 74, 72 and 65 ppm were attributed to C in levoglucosan by comparing the signals in pure levoglucosan spectrum (Fig 4.7b). The signal at 56ppm (OCH_3) was assigned to methoxyl carbon in lignin (phenolmethoxyl of coniferyl and sinapyl moieties) (Kolodziejski et al., 1982). In comparison, the oil from pine wood shavings showed strong signals of C in levoglucosan (103, 77, 74, 72, and 65 ppm) and methoxyl (56 ppm). Also the aromatic region (105-160 ppm) indicating C in lignin and phenolic OH were also relatively intense. The signals that showed in the range between 160 and 180 ppm were generally attributed to carboxylic acids, amides, ester and nitriles. The signals in the region of 190-210 ppm were attributed to C in ketones and aldehydes (Silverstein et al., 2005). The changes due to the addition of wood in various chemical shifts were analyzed semi-quantitatively by integrating specific regions and signals in the ^{13}CNMR spectra with reference to TMS signal at 0 ppm with an integration value of 10. The amphoteric nature of amides enables it to act as a very feeble acid as well as base. An acid-base reaction is possible to occur between amides and decomposition products from carbohydrates and lignin in the wood. Depending on the reactants available and reaction conditions, amides are known to breakdown to yield products like carboxylic acids, amines, nitriles, carboxylate ion, imines, ammonia, nitrogen gas and etc. A careful analysis of the ^{13}CNMR spectra showed that the addition of 25% wood to manure caused a sharp decrease in the signals at 174.8 and 23 ppm and consequently increased distinctively the signals at 172.8 and 21.9 ppm (see fig 4.7a). The signals at 172.8 and 21.9ppm were identified as acetic acid (Silverstein et al., 2005). The results from the integration are summarized in Table 4.6. It was found that an increase in wood addition to manure decreased the methylene groups in protein (30ppm) and increased both the methoxyl group (56ppm) in lignin and the levoglucosan signals

(65, 72, 74, 77, and103ppm) from decomposition of cellulose. The signal at 172.8 which was assigned to acetic acid increased with 25% of wood addition but decreased gradually when more wood was added. The same holds for the acetyl group (21.7ppm). The aliphatic hydrocarbons assigned to 5-35pmm decreased with increase in wood up to 50% of wood and increased with further addition of wood. The region between 105-160 ppm which was attributed to C in lignin, N-heterocyclic and heteroaromatics also decreased with addition of wood up to 50% but increased with further addition of wood. The lack of trend in the intensities of some of the chemical groups identified indicated that chemical reactions between the decomposition product of protein, lignin and carbohydrates may have occurred. Also, the relative intensities presented in Table 4.6 shows that the signal at 173ppm due to acetic acid had a higher relative intensity in the 75% manure and 25% pine oil than 100% pine oil. This is indicative of some reactions between the decomposition products of protein in manure and carbohydrates and lignin in pine which lead to the generation/formation of acetic acid. The difference in value of the experimental measured pH (4.47) of the derived oil from 75% manure and 25% pine and the calculated value (5.2) using additivity rule confirmed the occurrence of chemical reactions.

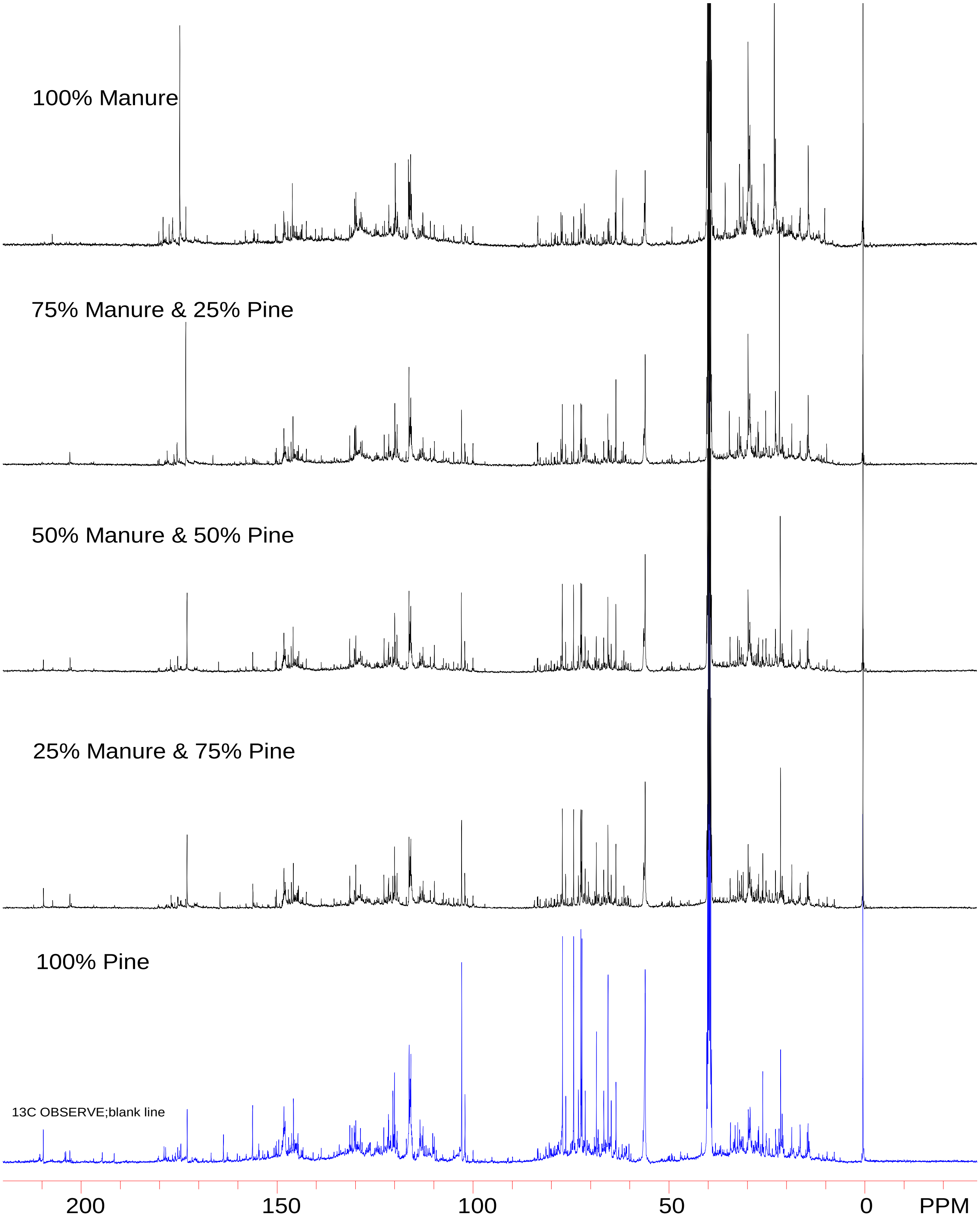
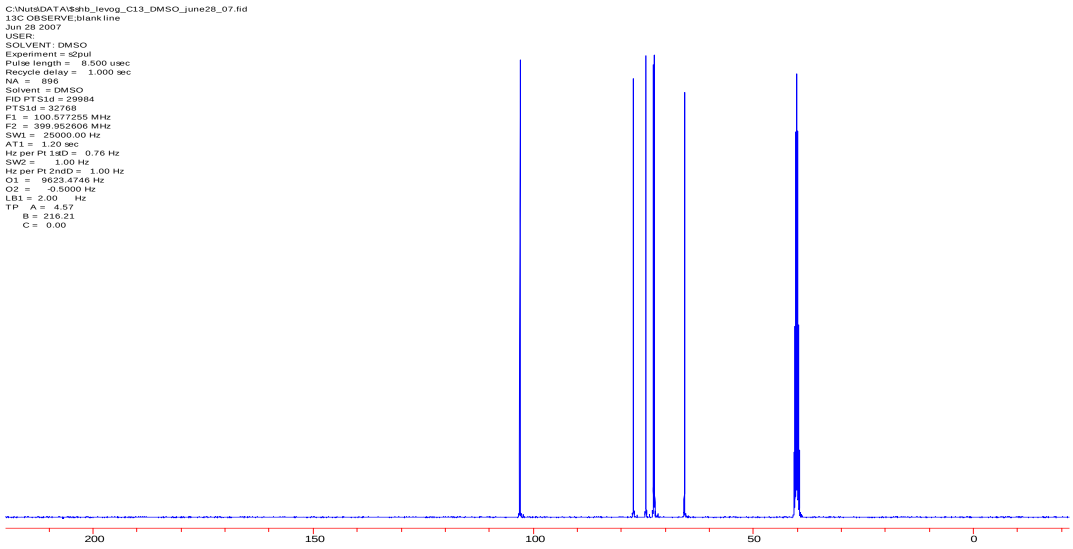


Figure 4.7a ^{13}CNMR of oils from manure, pine wood and their mixtures

Table 4.6

^{13}CNMR spectra relative intensity of the oils from manure, pine wood and their mixtures

Type of Carbon	Chemical Shift, δ (ppm)	Relative Intensity				
		100% Manure	M:P (75/25)	M:P (50/50)	M:P (25/75)	100% Pine
Acetyl (CH_3)	21.5-22	5.1	11.0	9.8	10.7	9.7
Methylene(CH_2) in Proteins	30	24.1	21.4	15.4	14.2	12.3
Methylene carbons of saturated n-alkyl groups	5-35	144	141	106	128	119
Methoxyl (-OCH_3) in lignin	55-56	5.6	11.4	14.8	17.5	23.0
(levoglucosan C) in carbohydrates	65, 72, 74 77, 103	6.2	14.7	21.3	26.6	45.9
Aromatic C in N-heterocyclic C in heteroaroamtic	105-160	154.0	128.0	125.0	171.5	210.0
Acetic Acid (C=O)	173.2-172.9	1.2	5.0	3.0	3.0	2.1
Amide (C=O)	174.8-175	4.77	0.1	0.07	0.14	0.21
C=O (carboxylic groups)	160-180	21.5	10.1	4.7	14.1	14.2



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Jun 28 2007
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Recycle delay =   1.000 sec
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F1  =  100.577255 MHz
F2  =  399.952606 MHz
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AT1 =   1.20 sec
Hz per Pt 1stD =   0.76 Hz
SW2 =       1.00 Hz
Hz per Pt 2ndD =   1.00 Hz
O1  =    9623.4746 Hz
O2  =      -0.5000 Hz
LB1 =  2.00      Hz
TP    A =   4.57
      B =  216.21
      C =   0.00
```

Figure 4.7b ^{13}CNMR of levoglucosan

4.2.1.3.3 ^{1}*H -NMR Analysis*

The ^{1}HNMR spectra of the bio oils are shown in figure 4.8. A semi-quantitative analysis was conducted by integrating specific regions and signals in the ^{1}HNMR spectra with reference to TMS signal at 0 ppm with integration value set to 10. The sharp decrease in the amide groups with the addition of 25% as already shown by FTIR and ^{13}CNMR was also evident in the ^{1}H –NMR spectra. The amide proton signal at 5.8 ppm (Silverstein et al., 2005) decreased immensely in intensity from 35.3 to 19.3 (see Table 4.7) with 25% pine in the mixture but a further increase in pine only resulted in a small decrease. Generally, it was found that an increase in pine continually decreased the protons in the amide region of 5.7-6.1 ppm and also increased the methoxyl and hydroxyl protons in 3.3-5.5 ppm (Schnitzer et al., 2007). There was also an increase in the aromatic protons as the pine content in the mixture increased from 25% to 75%. The oil from 75% manure and 25% pine had the highest intensity in the total aliphatic groups and both the pine and the 50/50 mixture had the least intensity. The variation in intensities and the lack of trend seen as well in the ^{1}H –NMR of the oil mixtures, especially the oil derived from 75% manure and 25% wood suggests the possible occurrence of chemical reactions between protein, carbohydrate and lignin decomposition products.

Table 4.7

Summary of ^{1}HNMR spectra relative intensity of the oils

Type of Hydrogen	Chemical Shift, δ (ppm)	Relative Intensity				
		100% Manure	M:P (75/25)	M:P (50/50)	M:P (25/75)	100% Pine
Aliphatic protons in CH_3, CH_2, & CH (further from an aromatic ring)	0.5-1.6	42.3	50.3	29.0	34.9	20.58
Aliphatic protons in CH_3, CH_2, & CH (Attached to an aromatic ring)	1.6-3.3	48.6	62.9	46.1	54.1	45.5
Protons in Methoxyl and Hydroxyl	3.3-5.5	24.6	49.5	44.8	54.6	77.1
Amide, N_2H groups	5.7-6.1	35.3	19.3	11.5	10.4	2.3
Aromatic protons (benzenoid & N-heterocyclics)	6.1-8.5	29.3	34.7	40.2	47.5	31.0

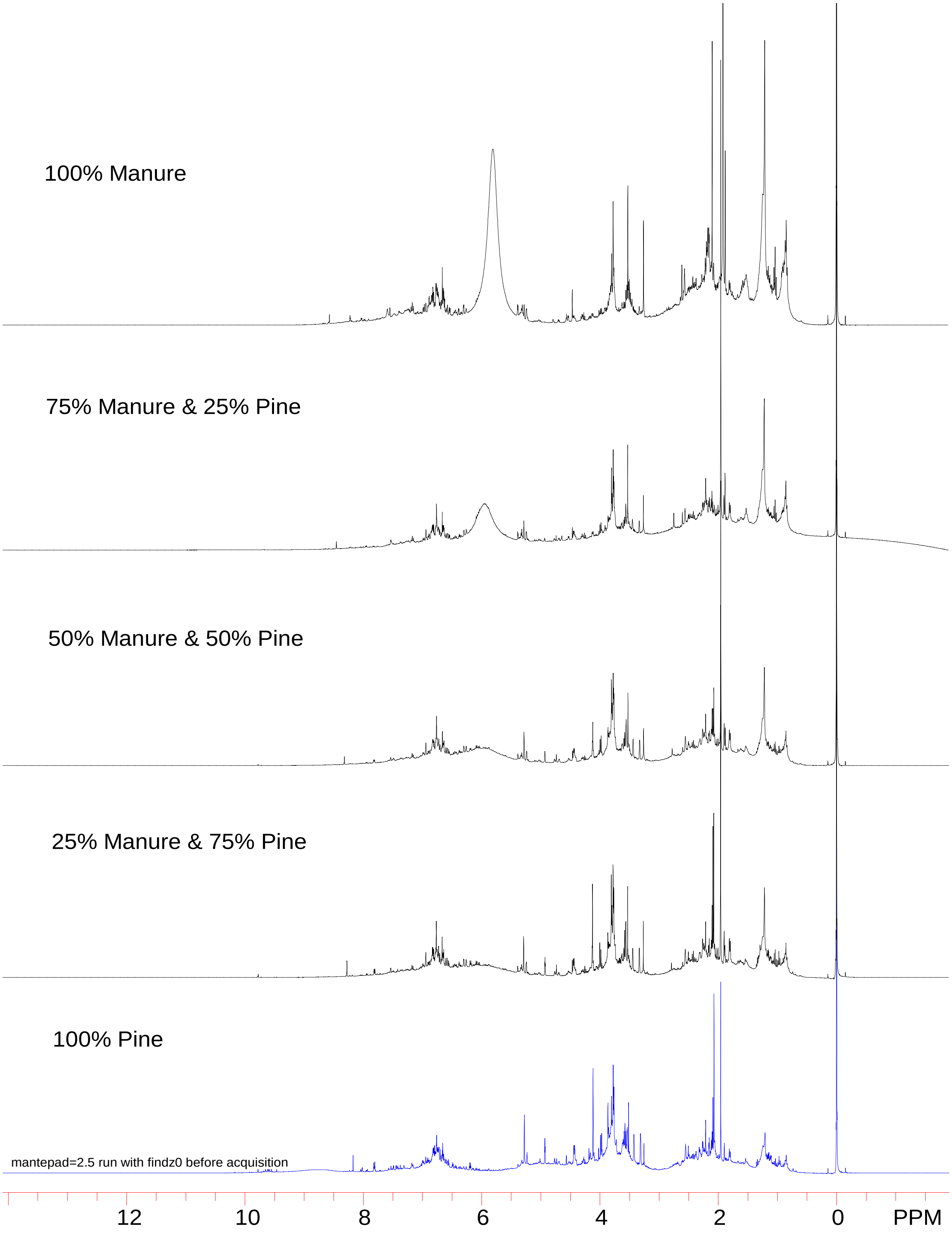

Figure 4.8 ^{1}HNMR of oils from manure, pine wood and their mixtures

4.2.1.3.4 *TG/DTG Analysis*

The thermal degradation of the pyrolysis oils from manure, pine, and their mixtures of 75:25 and 50:50 were performed under nitrogen at a heating rate of 5 °C/min. The thermogravimetry (TG) and differential thermogravimetry (DTG) plots are presented in Figure 4.8. The thermal decomposition of the bio-oils was a gradual process with no clear steps according to the TG curves. The thermograms of all the oils exhibited peaks below 150°C and a maximum rate of decomposition peak between 230°C and 250°C. The manure, 75:25 and 50:50 mixtures oils had additional peaks at 395°C, 272 and 350 °C respectively. The peaks below 150 °C in all the oils were attributed to the evaporation of water and the decomposition of light compounds which were thermally less stable. The major peaks between 230 °C and 250 °C corresponded to the degradation of sugars and hemicellulose derivatives (Ba et al., 2004). The last major peaks at 350 °C, 372 °C and 395 °C in the 50:50, 75:25 and the manure oil respectively were attributed to decomposition of heavy non-polar compounds (Ba et al., 2004; Garcia-Perez et al., 2007). The effect of pine addition to manure was evident in the decrease in the decomposition temperature of the manure decomposition peak at 395 °C to 350°C when the wood content was increased to 50wt.%. There was also a decrease in the sharp shoulder at 451 °C of the manure oil to 424 °C. The DTG curves indicated that the pine bio-oil consisted of two main groups of compounds compared to three main groups observed in the manure and the mixtures of 75:25 and 50:50. This means that oils with higher manure content contain compounds that are more thermally stable compared to oils with high pine wood content.

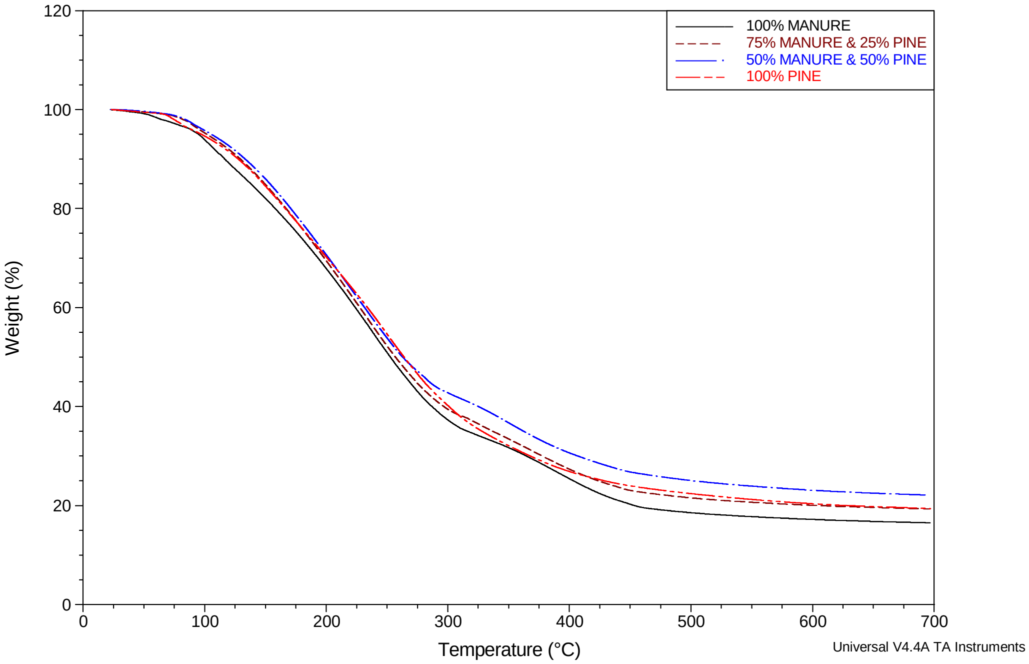

Figure 4.8a TG curves of manure and wood oils

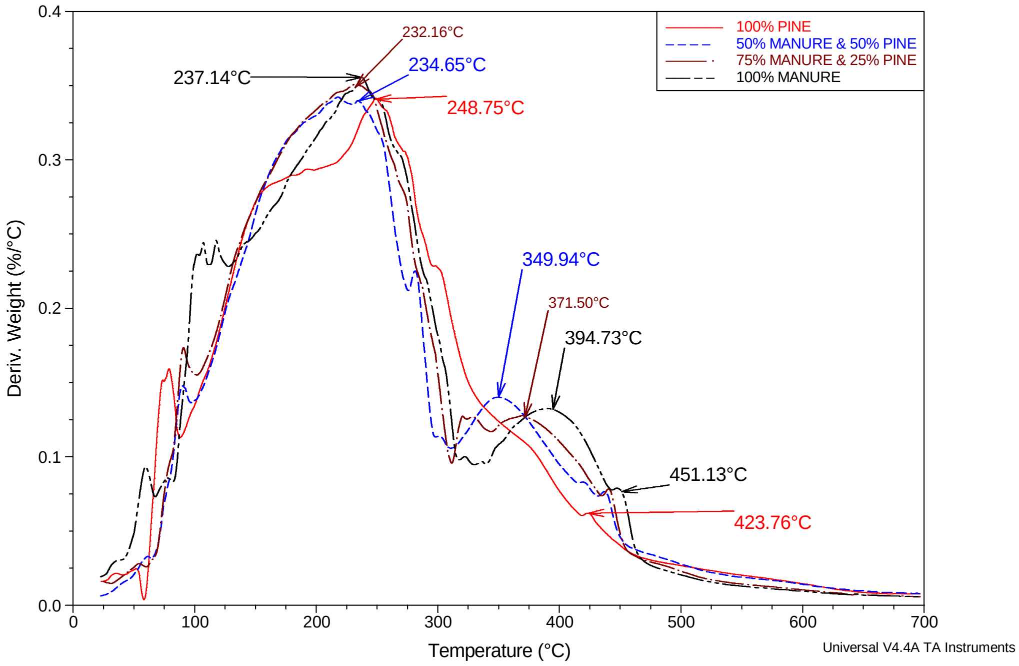

Figure 4.8b DTG curves of manure and wood oils

4.2.2 Effect of Oak wood shavings on pyrolysis of layer manure

The pyrolysis products yields of layer manure and oak wood are shown in figure 4.9 and summarized in Table 4.8. An increase in oak wood content in the mixture increased the pyrolysis oil (organics + water) yield and decreased the char yield. The oil yield for the manure was 43.3% and increased to 55.1% as the oak wood content in the mixture increased to 75% and the char yield on the other hand decreased from 43.1% to 23.8%. The organic portion of the oil increased from 58.6wt.% to 66.2wt.% as the wood content increased to 75%. The gas yield also increased as more oak wood was added. The oak wood had the highest oil yield (64.5wt %) and the lowest char yield (16.7wt. %). The feedstock composition influenced the pyrolysis product yields. One characteristic of the feedstock that is in consistent with the yields is the ash content. The manure feedstock had 23.53wt% ash as compared to 1.11 wt% ash in oak wood. As a result of effect of ash content, the quantity of the liquid product from pyrolysis of feedstock with high manure was less than that of those with high wood content.

Table 4.8 Yields of oak wood and manure pyrolysis products

Feedstock			**Pyrolytic Yields (%)**		
Manure (wt. %)	Oak wood (wt. %)	**Mean Reactor Temperature (^{o}C)**	**Total liquid**	**Char**	**[†]Gas**
100.0	0.0	468.8±9	43.25±0.43	43.1±0.95	13.6±1.00
75.0	25.0	435.0±11	45.68±1.05	37.29±0.30	17.04±1.39
50.0	50.0	427.0±21	50.03±2.33	29.48±0.73	20.44±2.19
25.0	75.0	403.5±18	55.05±2.29	23.78±1.01	21.8±2.44
0.0	100.0	420.5±25	64.50±0.30	16.72±2.65	18.78±2.36

[†] By difference

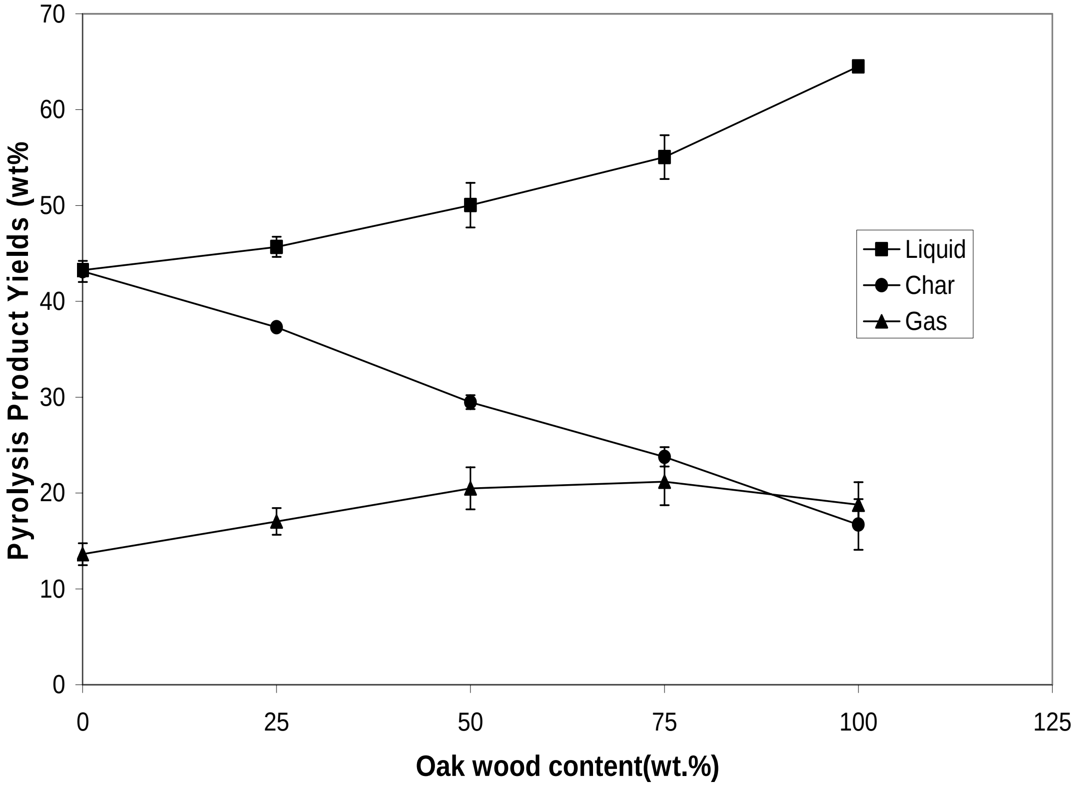

Figure 4.9 Yields of pyrolysis products of manure and oak wood

4.2.2.1 *Physico-chemical properties*

Table 4.9 shows a summary of the physico-chemical properties of the oil fractions from the ESP. Their properties differed as a result of feed compositions. The pH decreased from 5.89 to 3.72 and the density increased from 1.14 to 1.22g/cm^3 as oak wood content was increased to 75%. The higher heating value (HHV) of the oils also decreased as oak content in mixture increased, however the HHV values for the oils from both the 75/25 and the 50/50 mixtures were the same. The oak wood initially did not have any significant effect on the water content of the whole bio oil until 75% of wood was added, it decreased the water content of the whole bio oil from

41.38wt.% to 33.7wt.% (Table 4.9). The oak wood oil had the lowest water content (26.3wt.%). The kinematic viscosity of the oils increased from 130 cSt to 225 cSt when 50% of oak was added but decreased to 145.5 cSt when the oak content was 75%. The variation in the physico-chemical properties of the various oils may be attributed to dilution effect and possible chemical reactions between the decomposition products of manure and oak wood.

Table 4.9

Physical properties of manure and oak wood bio oils

Physical property	Analysis Method	Pyrolysis Oils				
		100% M	M:O (75/25)	M:O (50/50)	M:O (25/75)	100% O
Water content of whole oil (wt.%)	Karl-Fischer titration	41.88	41.88	39.54	33.76	26.27
pH	pH meter	5.93	5.31	4.31	3.72	3.31
Density @ 23^{o}C, g/m^3	ASTM D4052	1.14	1.16	1.21	1.22	1.26
Kinematic viscosity, at 60^{o}C (cSt)	Rotational Viscometer	130.0	143.9	226	145.5	99
Heating Value (MJ/kg)	ASTM D5865	29.7	26.82	26.88	25.09	24.00

M = Manure, O = Oak wood

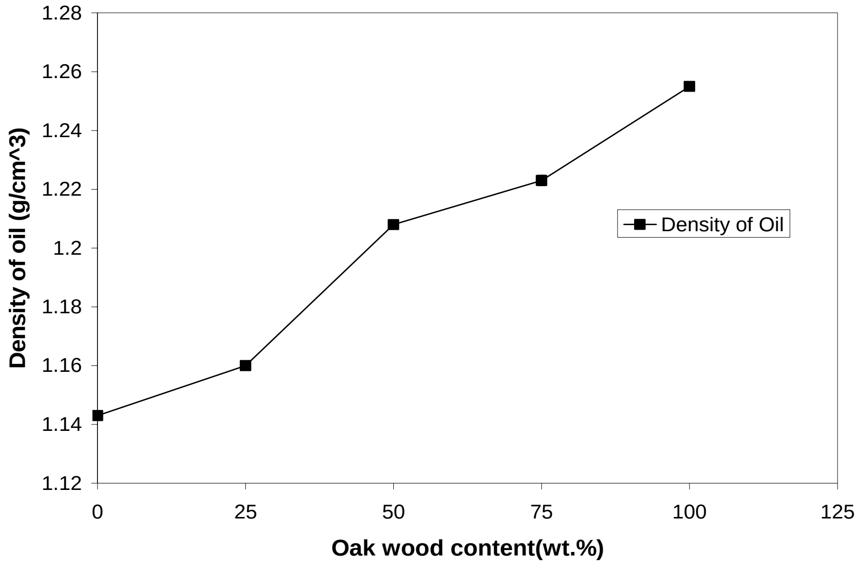

Figure 4.10 Density of ESP oils of manure, oak wood and their mixtures

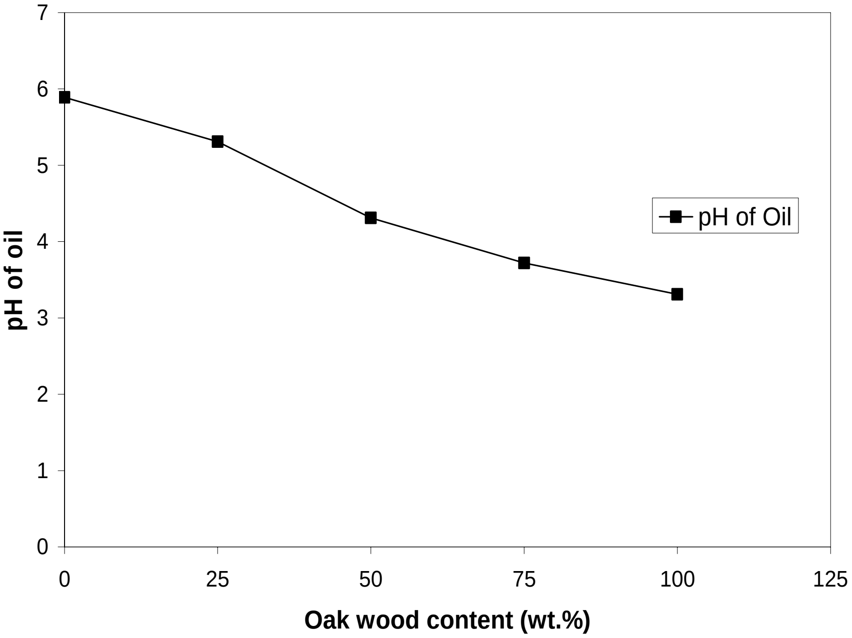

Figure 4.11 pH of ESP oils of manure, oak wood and their mixtures

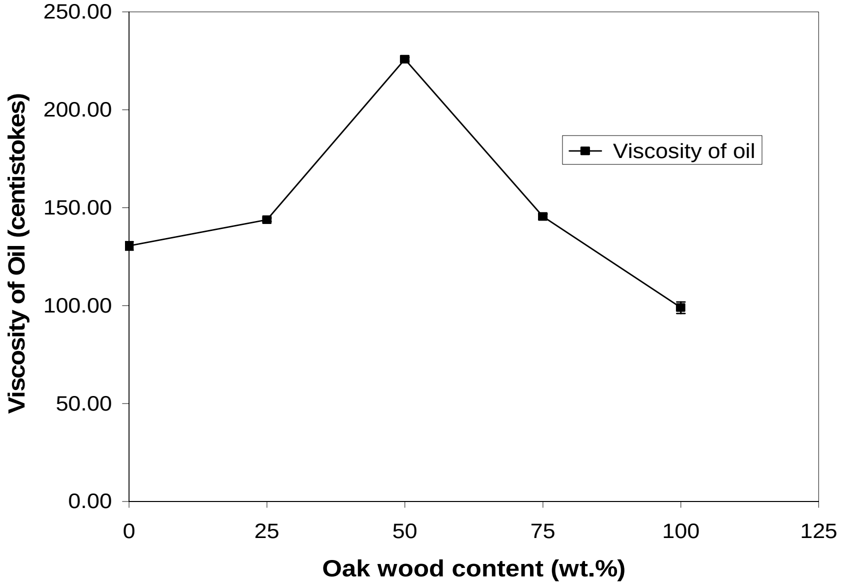

Figure 4.12 Kinematic viscosities of ESP oils of manure, oak wood and their mixtures

4.2.2.2. *FT-IR Analysis*

The FT-IR spectra of the oils are shown in Figure 4.12(a-d) and their band assignment and relative intensities are summarized in Table 4.10. The absorption band at 1510cm^{-1} which was attributed to aromatic skeletal vibration mode was relatively stable and as a result all other bands were semi-quantitatively analyzed by dividing their peak intensities by that at 1510cm^{-1}. The interpretations of the FTIR spectra were based on data presented by Silverstein and Webster, (1998); Bellamy, (1956); Smith, (1998); and Coates, (2000). The relative intensities of all the peaks at 1702-1710 cm^{-1} (Carbonyl C=O stretching), 1208-1234 cm^{-1} (Phenolic C-O-H deformation), 1112-1112 cm^{-1} (secondary alcohol C-O stretch) and 1034 cm^{-1} (C-O stretch of primary alcohol) increased as the oak wood content increased. However a decrease in the relative intensities of peaks at 2926 cm^{-1} (C-H stretches of methylene (CH_2) group) and 1409 cm^{-1} (C-N stretch of primary amides) occurred when the oak content in the mixture increased. The peak at

1656 cm^{-1} (amide carbonyl C=O stretching) also decreased in intensity with 50% oak increase, but disappeared when the 75% was added. The FT-IR analysis of the oils showed that the manure oil was rich in aliphatic hydrocarbons, primary and secondary amide compounds among other nitrogenous compounds from the decomposition of proteins in manure. Their intensities however decreased when the oak wood content increased (see figure 4.12d). The oak wood oil on the other hand was rich in primary and secondary aliphatic alcohols, phenols and aliphatic carbonyl/carboxyl groups due to carbohydrate and lignin decomposition. As a result, an increase in wood content in the manure/wood mixture increased their relative intensities compared to the pure manure. The hydrocarbons, nitrogen and oxygen functionalities of the oils were highly dependent on the composition of the manure/wood mixture. The intensities of the functional group intensities were probably more due to the dilution effect of the oak wood on the manure than chemical reactions between the decomposition products of manure and oak wood. This was confirmed by comparing the experimental values of the pH of the oils with those calculated from additivity rule. It was found that there was no difference between the experiment pH and the calculated pH of oils. The lack of intense chemical change seen in the oak as compared to pine may be attributed to difference between their chemical structure and composition.

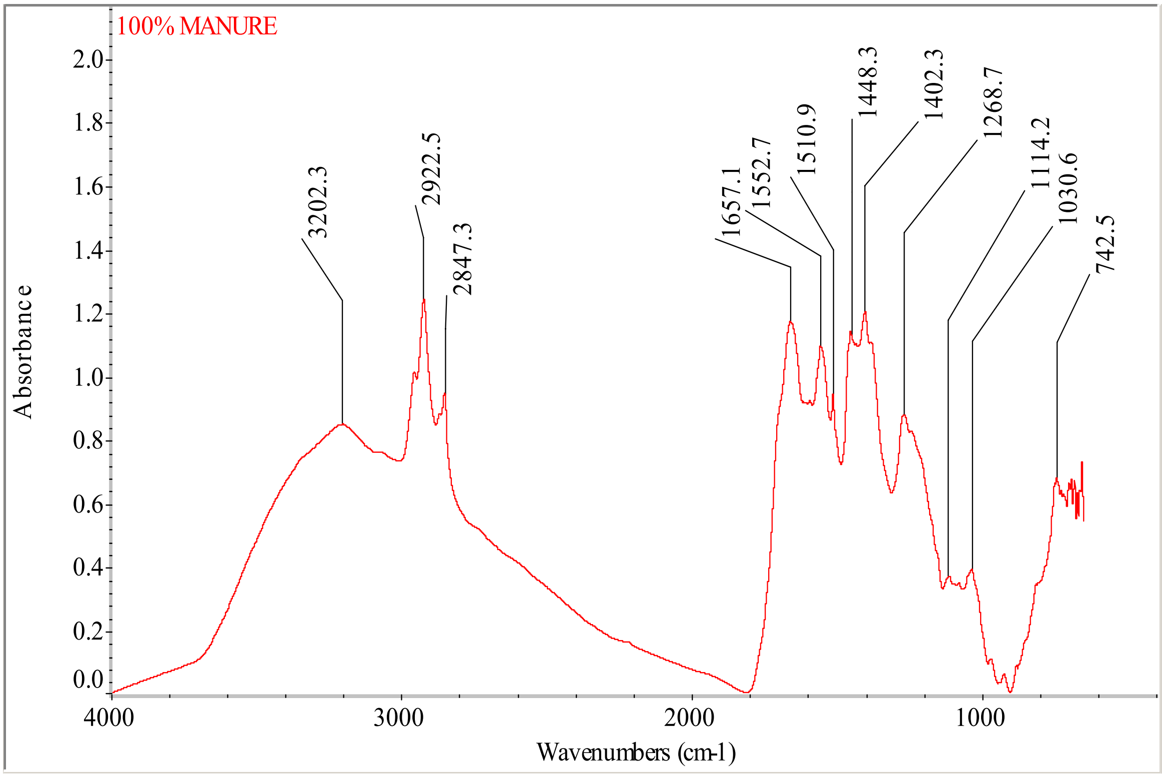

Figure 4.12a FT-IR spectrum of manure oil

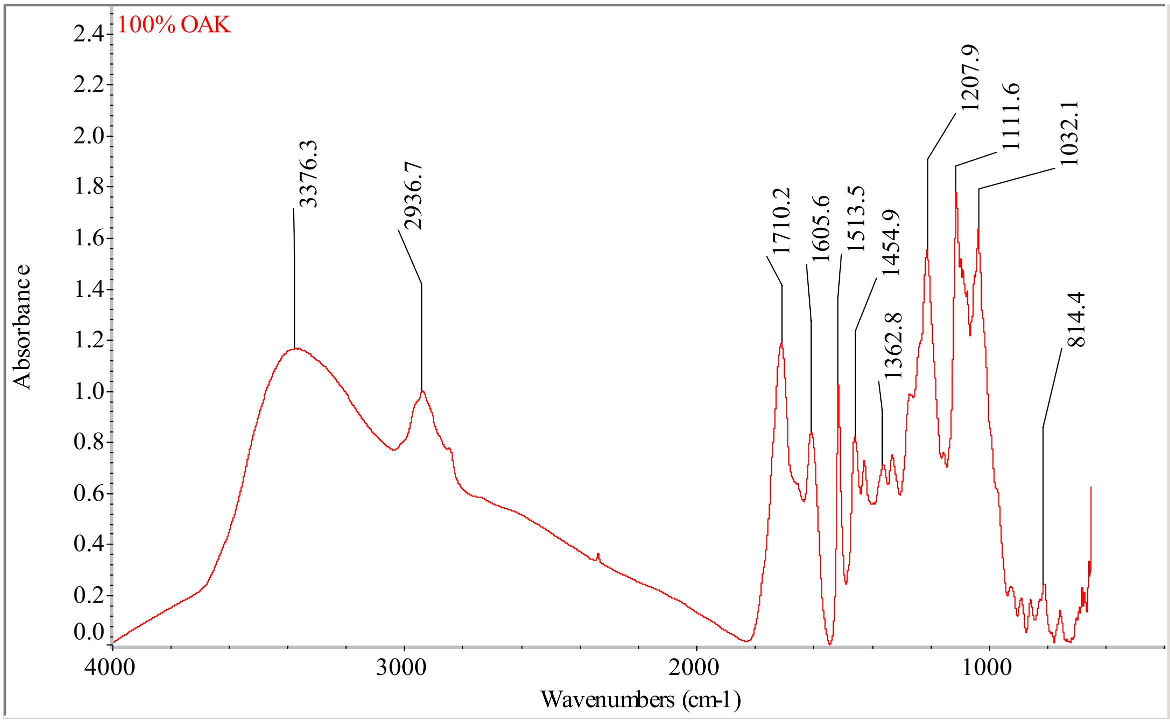

Figure 4.12b FT-IR spectrum of pure oak wood oil

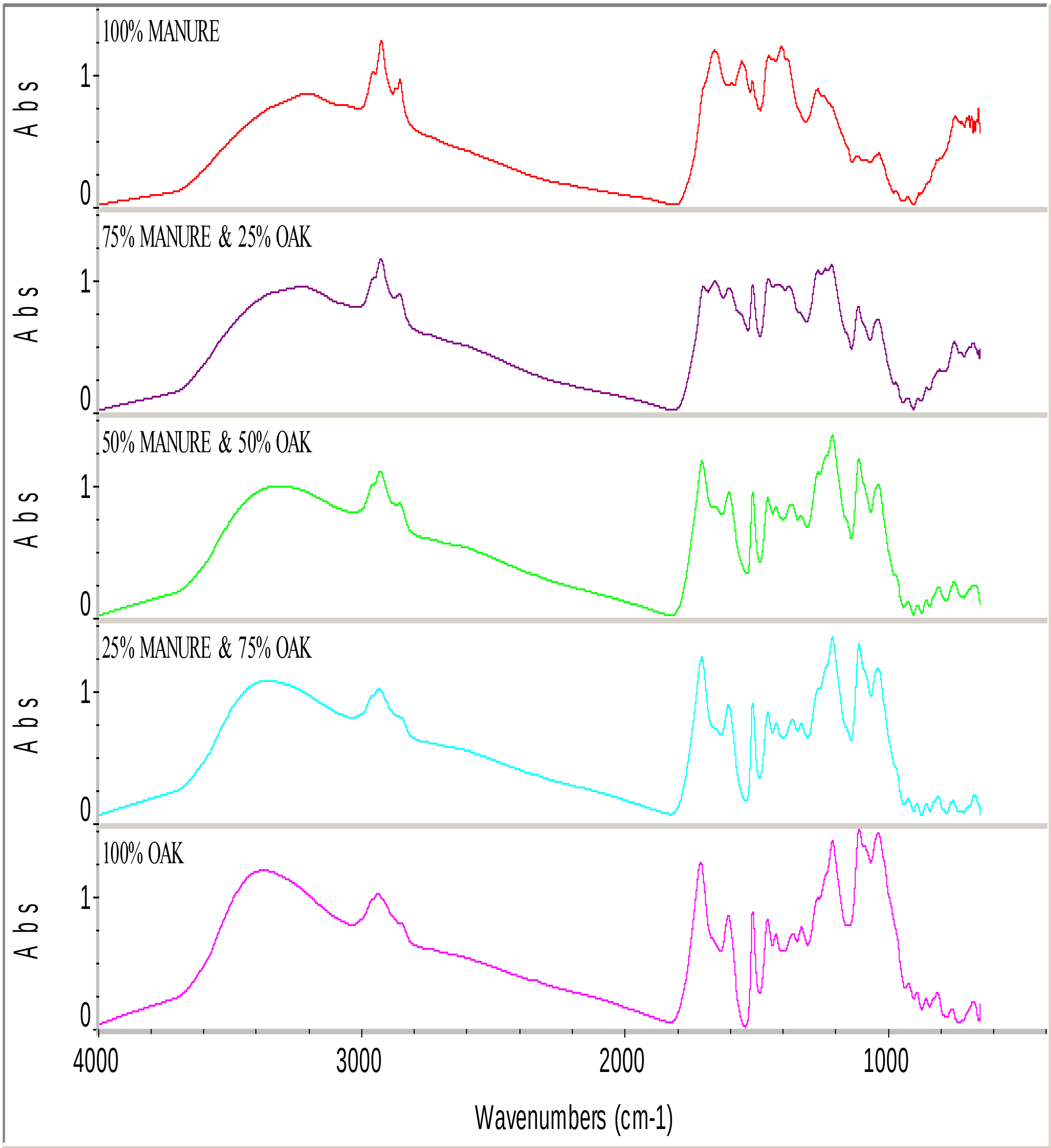

Figure 4.12c FT-IR spectra of oils from manure, oak wood and their mixtures.

Table 4.10

Summary of FT-IR assignment and their relative intensities oils manure and oak mixtures

Functional Group	**Wave number (cm^{-1})**	**Relative Intensity**				
		100% Manure	**M:O (75/25)**	**M:O (50/50)**	**M:O (25/75**	**100% Oak**
O-H stretch, N-H stretch	3363-3241	0.89	0.99	0.96	1.08	1.21
Methylene CH_2 asymmetric stretch	2929-2936	1.31	1.21	1.07	1.02	1.03
Methylene CH_2 symmetric stretch	2854	1.00	0.94	0.83	-	-
Carbonyl C=O stretching: unconjugated ketone and carboxyl group	1702-1710	-	1.00	1.15	1.26	1.27
Amide Carbonyl C=O	1658	1.24	1.03	0.81	-	-
Aromatic skeletal vibration with C=O stretching	1600	0.97	0.98	0.91	0.90	0.86
Amide II, N-H bending vibrations	1556	1.16	-	-	-	-
C-H deformation (asymmetric)	1451	1.2	1.05	0.87	0.83	0.85
C-N stretch of primary amides	1427-1408	1.27	1.01	0.81	0.77	0.74
C-H deformation (symmetric)	1378-1362	1.17	1.00	0.82	0.79	0.73
N-heterocyclic, aromatic amides Aromatic ether C-O-C	1267	0.93	1.12	1.06	1.02	1.00
Phenolic OH-deformations	1234-1208	1.27	1.01	0.81	0.77	0.74
Secondary aliphatic alcohol C-O stretch	1112-1112	0.39	0.83	1.19	1.38	1.56
Primary aliphatic alcohol C-O stretch	1032-1034	0.41	0.73	0.99	1.19	1.54
	925	0.06	0.10	0.11	0.17	0.33
Para substituted ring mode out-of-plane bending C-H	884	0.09	0.09	0.08	0.15	0.23
NH2 out-of-plane bend	752-742	0.72	0.55	0.27	0.17	0.16

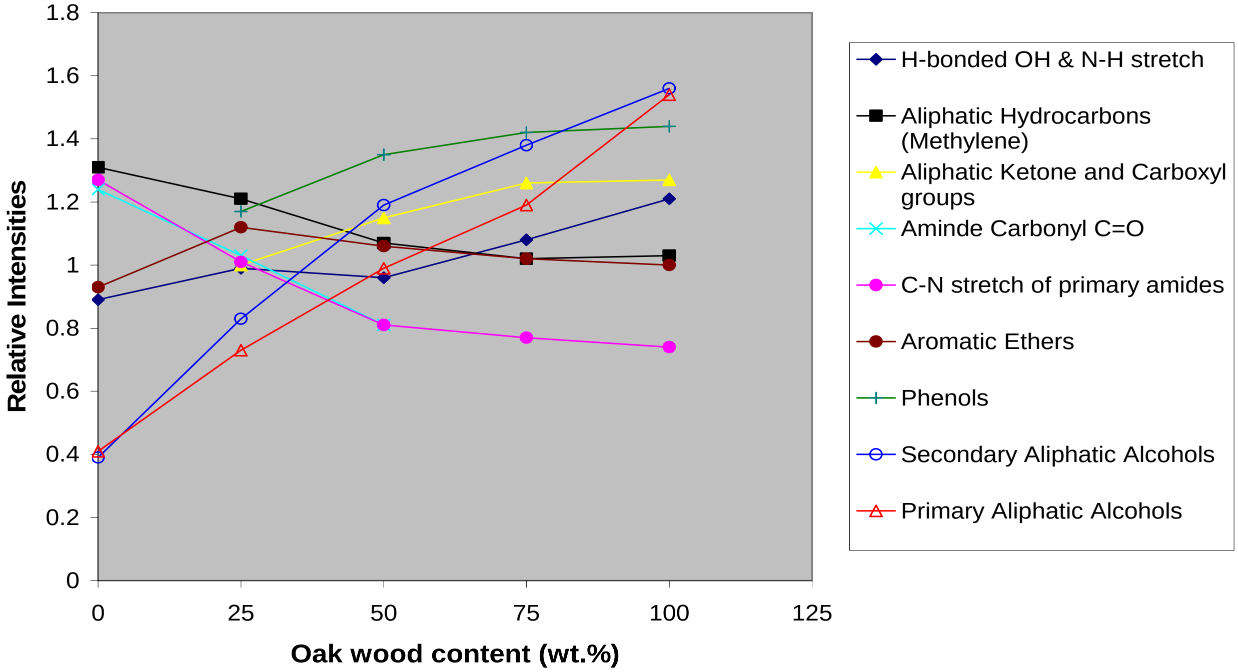

Figure 4.12d Relative intensities of absorption bands of oils from manure, oak wood and their mixture

4.2.2.3 ^{13}*C -NMR Analysis*

Figure 4.13a shows the ^{13}CNMR spectra of oils from manure, oak wood and their mixtures. The Table in 4.11 shows the relative intensity of some of the signals identified in the ^{13}CNMR spectra. A semi-quantitative analysis was conducted by integrating specific regions and signals with reference to TMS signal at 0 ppm and with an integration value of 10. As can be seen from the spectra in figure 4.13, an increase in oak content in the mixture consequently increased the intensity of methoxyl group (56ppm), C in levoglucosan (65, 72, 74, 77 and 108ppm) and the carbons in the aromatic compounds (105-160ppm). This was mainly due to the increase in decomposition products of carbohydrates and lignin in wood. Conversely, the carbons showing methylene in protein (30ppm) and saturated n-alkyl groups (5-35ppm) decreased as the oak wood content increased. This was also attributed to the decrease in protein decomposition products as the manure content in the mixture decreases. The signal at 174.8ppm which was assigned to an amide carbonyl decreased as 25% of oak was added and consequentially resulted in an increase in the carboxylic signal at 173ppm which was attributed to acetic acid. It is worth noting that the addition of 25% oak wood which caused a decrease in the amide carbonyl did not yield in the same measure an increase in the acetic signal (see Table 4.11). The general increase in decomposition product signals for both carbohydrate and lignin and the gradual decrease in signals from protein decomposition products as oak content increased showed that dilution effect may be influencing the product composition of the oils just as chemical reactions between the decomposition products of protein, carbohydrate and lignin affect the oil composition.

Table 4.11

^{13}CNMR spectra relative intensity of the oils from manure, oak wood and their mixtures

Type of Carbon	Chemical Shift, δ (ppm)	Relative Intensity				
		100% Manure	M:O (75/25)	M:O (50/50)	M:O (25/75)	100% Oak
Acetyl (CH_3)	21.5-22	5.1	13.1	12.5	14.2	12.4
Methylene(CH_2) in Proteins	30	24.1	23.39	16.68	12.38	6.74
Methylene carbons of saturated n-alkyl groups	5-35	144	144.0	115.9	116.0	88.8
Methoxyl (-OCH_3) in lignin	55-56	5.6	14.20	20.25	28.46	30.51
(levoglucosan C) in carbohydrates	65, 72, 74 77, 103	6.2	14.10	20.28	29.35	34.9
Aromatic C, C in N-heterocyclic & C in heteroaroamtic	105-160	154.0	156.4	188.0	198.0	200
Acetic Acid (C=O)	173.2-172.9	1.2	2.27	5.24	5.28	5.06
Amide (C=O)	174.8-175	4.77	0.28	0.82	0.73	0.95
C=O groups (carboxylic acids and derivatives)	160-180	21.5	13.6	15.6	15.1	18.7

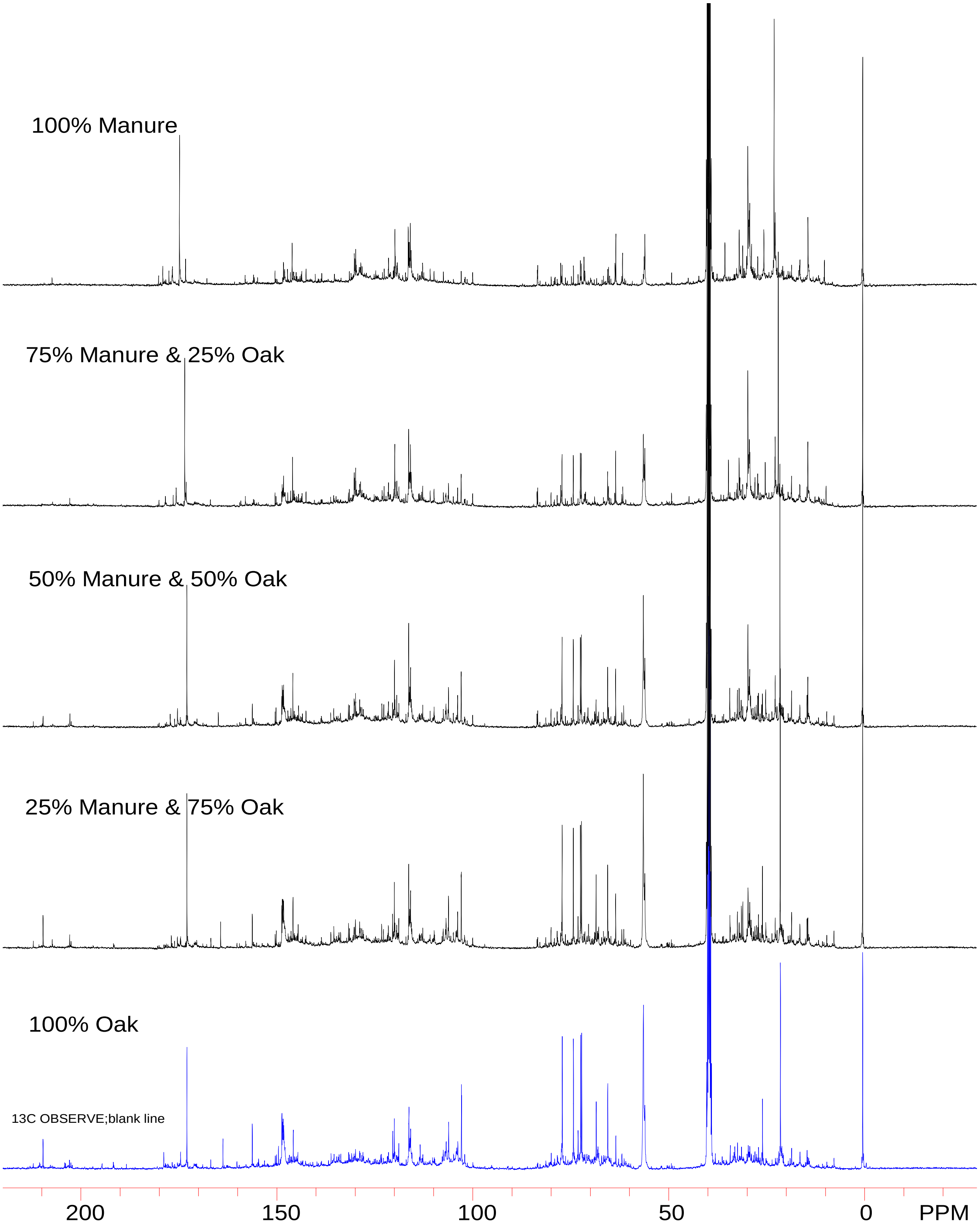

Figure 4.13a 13CNMR of oils from manure, oak wood and their mixtures

4.2.2.4 ^{1}*H -NMR Analysis*

The ^{1}HNMR spectra of the bio oils from manure and oak mixtures are shown in figure 4.13b. A semi-quantitative analysis was conducted by integrating specific regions and signals in the ^{1}HNMR spectra with reference to TMS signal at 0 ppm with integration value set to 10. The amide proton signal at 5.8 ppm (Silverstein et al., 2005) decreased in intensity form 35.3 to 11.1 (see Table 4.12) with 25% wood addition. The reduction in the amide signal at 5.8 ppm may be due to a chemical reaction. The 75% manure and 25% oak wood oil spectrum in figure 4.13b shows a shift in the signal from 5.8ppm to 6.1ppm. The chemical shift region between 6 and 8.5ppm most show aromatic protons in benzenoid structures and in N-heterocyclic (Silverstein et al., 2005). This could mean that, the addition of 25% oak wood lead to the formation of aromatic amides and possible N-heterocyclic compounds which resulted in the highest intensity for aromatic protons as seen in Table 4.12. This may also explain why a decrease in the amide carbonyl signal shown in the ^{13}CNMR spectra did not yield the same measure of increase in the acetic signal and hence the small change in pH of the oil from 5.93 to 5.31 with 25% oak. Generally, it was found that an increase in oak wood continually decreased the protons in the amide region of 5.7-6.1 ppm and also increased the methoxyl and hydroxyl protons in 3.3-5.5 ppm (Schnitzer et al., 2007). Additionally the aromatic protons increase and the protons of saturated n-alkyl groups decreased as oak wood content in the mixture increased.

Table 4.12

^{1}HNMR spectra relative intensity of the oils from manure, oak wood and their mixtures

Type of Hydrogen	Chemical Shift, δ (ppm)	Relative Intensity				
		100% Manure	M:O (75/25)	M:O (50/50)	M:O (25/75)	100% Oak
Aliphatic protons in CH_3, CH_2, & CH (further from an aromatic ring)	0.5-1.6	42.3	36.8	25.4	23.2	16.4
Aliphatic protons in CH_3, CH_2, & CH (Attached to an aromatic ring)	1.6-3.3	48.6	45.3	40.0	50.3	53.2
Methoxyl and Hydroxyl	3.3-5.5	24.6	29.9	32.5	62.0	94.2
Amide, NH_2 groups	5.7-6.1	35.3	11.1	2.9	6.5	3.7
Aromatic	6.1-8.5	29.3	46.7	34.5	39.7	39.9

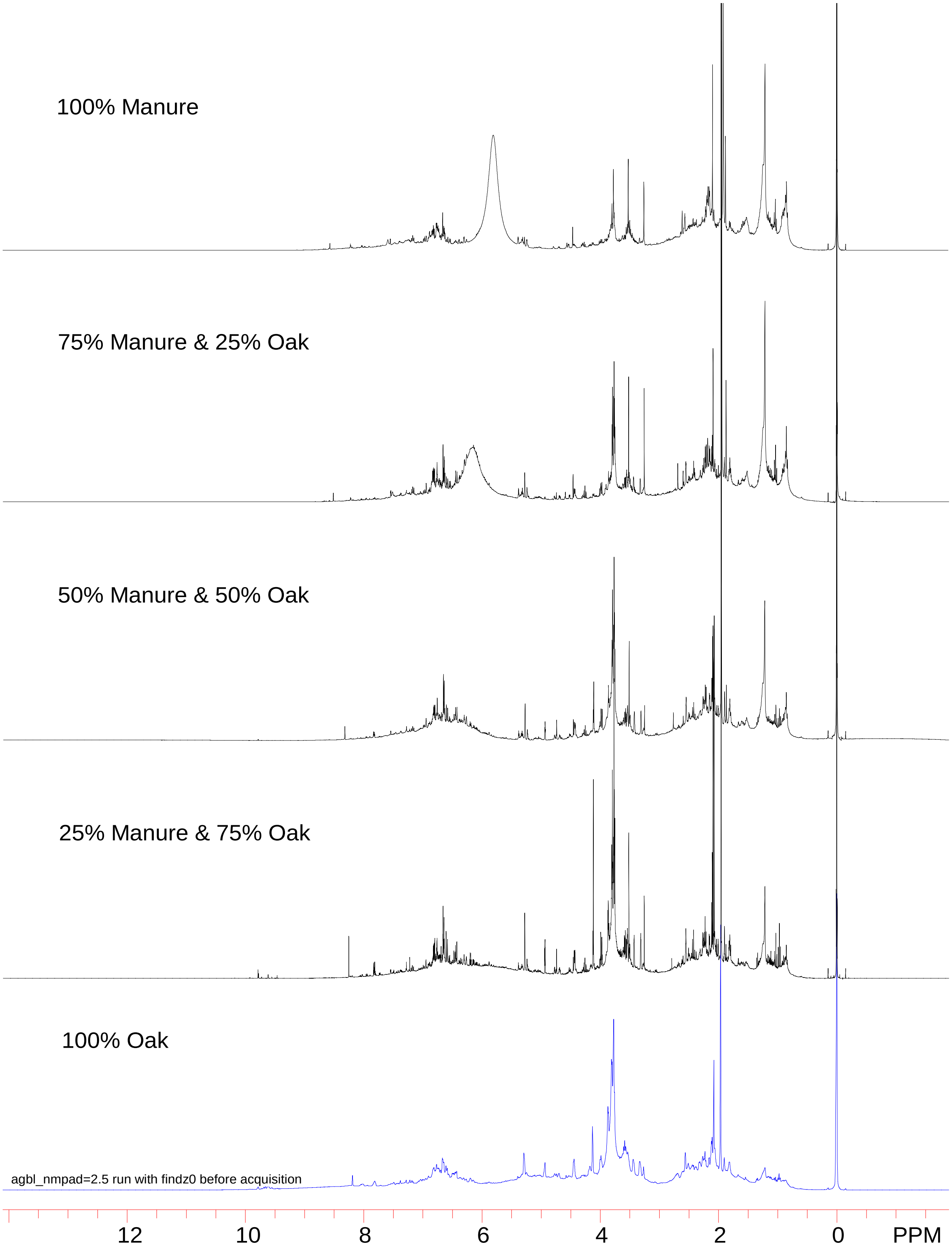

Figure 4.13b ^{1}HNMR of oils from manure, oak wood and their mixtures

4.2.2.5 *TG/DTG Analysis*

Figure 4.14 shows TG and DTG curves of oils manure, oak and their mixtures of 75:25 and 50:50 w/w. The TG curves showed the decomposition of the bio-oils with no distinct steps. The DTG curves of all the oils exhibited peaks below 150°C and a maximum rate of decomposition that occurred between 200^{o}C and 240^{o}C. The manure oil had in addition a well defined peak occurring at 392. When 25% of oak wood was added, the peak with the rate of decomposition at 392°C decreased, but when 50% of oak wood was added the peak at 392°C disappeared. This influence of oak wood addition to manure may be a result of dilution effect since there was no shift in the decomposition temperature at 392°C with 25% of oak wood. Decomposition peaks between 290-315°C were only evident in the oak oil and the mixtures. The peaks below 150 ^{o}C in all the oils were attributed to the evaporation of water and the decomposition of light compounds which were less thermally stable. The major peaks between 200 ^{o}C and 250 °C corresponds to the degradation of carbohydrates (Ba et al., 2004). The peaks at 392 ^{o}C in the manure and the 75:25 mixtures were attributed to decomposition of heavy non-polar compounds (Ba et al., 2004; Garcia-Perez et al., 2007) and compounds of larger molecular weights. The effect of oak wood addition to manure was evident in the decrease and disappearance of the decomposition peak at 392 ^{o}C as well as the appearance of peaks between 290-315^{o}C when the wood content increased to 50wt.%. The DTG curves showed that the oak bio-oil consisted of two main groups of compounds compared to three main groups observed in the manure and the mixtures of 75:25 w/w.

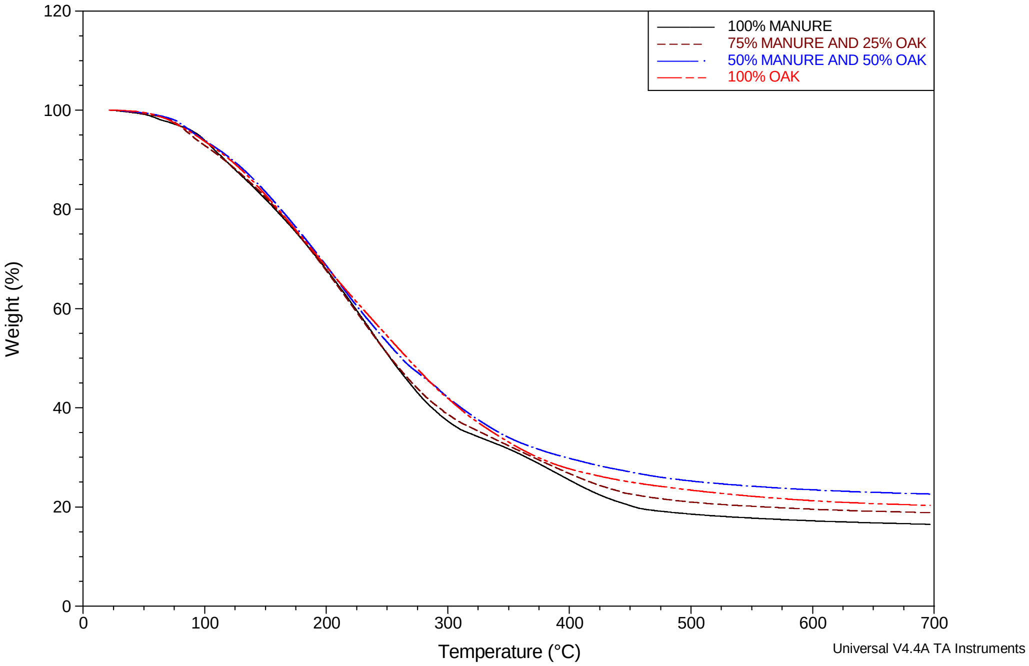

Figure 4.14a TG curves of manure and oak wood oils

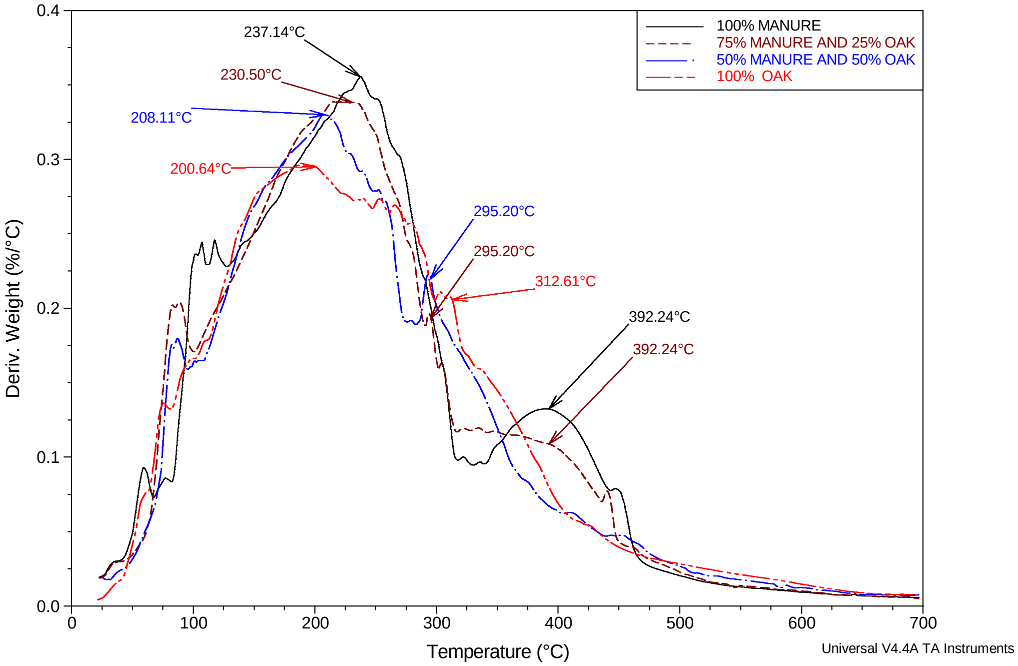

Figure 4.14b DTG curves of manure and oak wood oils

4.2.3 Effect of Pine wood compared with oak wood on the pyrolysis of layer manure

There are structural differences between hardwood and softwood polymers (hemicellulose and lignin) (Pandey, 1999). Also the lignin and extractives content are higher in softwoods than in hardwoods (Hon and Shiraishi, 1990). The elemental analysis of the oak and pine woods showed that the oak wood was higher in Carbon (C), Hydrogen (H), and Oxygen (O) compared to the pine wood (see Table 4.1). The ash content of pine wood (1.95%) was almost twice that of oak wood (1.11%). The effects of pine wood and oak wood on the pyrolysis of layer manure were different in some properties but similar in most of them. The pyrolysis product distribution showed that oak wood yielded relatively more bio oil, less char and more gas compared with that of pine/manure mixtures (see figure 4.15). This may be attributed to the fact that the oak has less in ash and lignin. Ultimate analysis of the oils obtained from the manure with 50% wood (oak and pine) did not show much difference in their C, H, N, O, and S contents (Table 4.13). However the chlorine content was high in the oak mixture (0.030%) compared to the pine mixture (149 ppm). The average chemical composition of the 50:50 mixtures ESP oils were $CH_{1.4}N_{0.04}O_{0.35}$ and $CH_{1.44}N_{0.03}O_{0.36}$, respectively for pine and oak. The manure/wood mixtures, 75:25 of pine and oak differed in pH, density and viscosity. The 75:25 mixtures from oak had a pH of 5.31, a density of 1.16 g/cm^3 and a viscosity of 144 cSt compared to a pH of 4.47, density of 1.19, and viscosity of 224 cSt for the pine mixture (see figures 4.16- 4.18). The major difference between pine and oak was paramount in the 75% manure and 25% wood mixture oils. The HHV of the oils derived from the mixtures were higher for pine than oak. A major difference in HHV between pine and oak was seen in the 75:25. The oil from pine mixture had a value of 28.9MJ/kg compared with 26.82 MJ/kg from the oak mixture. The FTIR spectra of manure and the 75:25 mixtures for both pine and oak presented in figure 4.19 distinctively shows the effect of 25% wood in the mixture for both pine and oak. It can be seen clearly that the addition of 25% oak to the manure leads to the reduction of both primary amides (1409cm^{-1}) and secondary amides (1556cm^{-1}) from protein decomposition. However an increase in the peaks at 3253, 1267 and 747, 1600, and 1510 cm^{-1} suggests the possible formation of aromatic compounds like amines and N-heterocyclic compounds. This agrees with the high relative intensity seen in the aromatic protons of ^{1}HNMR spectra (see Table 4.12). It can also be seen that there was no increase in the carboxylic group at 1705cm^{-1} and hence the small change in pH from 5.89 to 5.3 when 25% of oak was added. Conversely, the addition of 25% pine immensely reduced the amide groups at 1660, 1556 and 1409 cm^{-1} and lead to an increase in carboxylic groups at 1705cm^{-1} and a decrease in aliphatic hydrocarbons and aromatic compounds. The effect of the increased carboxylic groups was confirmed by the drop in pH from 5.89 to 4.47 when 25% pine was added. The FTIR result supports the findings by both ^{13}CNMR and ^{1}HNMR and further explains the difference seen in the physico-chemical properties (pH, viscosity, HHV and density) of the oils derived from the 75:25 mixture for pine and oak. The difference in the effect of pine and oak on the oil derived from 75% manure and 25% wood were attributed to the chemical structural differences between hardwoods and softwoods. Softwoods are prone to be more reactive because of the unsubstituted positions ortho to the phenol hydroxyl that exist in softwood lignin (Pandey, 1999) and the presence of dimethoxyphenols in oak wood shavings has the tendency to affect chemical interaction with the products from manure decomposition. The difference in the extractive content of pine and oak could have also contributed to the distinction in their chemical effect as seen in the difference in physico-chemical and chemical properties of the oils especially from 75% manure and 25% wood. Finally the DTG curves (figure 4.20) of the 50% manure and 50% wood oils also showed that the influence of pine and wood on the manure were different. The effect of wood addition on the peak at 395°C in the pure manure which was attributed to heavy non-polar compounds (Ba et al., 2004; Garcia-Perez et al., 2007) was different for pine and oak. The addition of 50% pine wood shifted the peak from 395°C to 349°C with no apparent change in the rate of decomposition. However the addition of 50% oak caused a disappearance of the peak at 395°C. This may be attributed to the fact that oak wood oil is high alcoholic groups and for that matter dissolve some of the possible structural component of the oil that shows up at 395°C. Additionally, the well defined peak between 200°C and 250°C which was attributed to degradation of carbohydrates (Ba et al., 2004) had a higher rate of decomposition for pine (0.338%/°C) compared to oak (0.315%/°C). The influence of wood on the manure may be a combination of chemical reactions and dilution effect. However the significant difference in their effect when 50% of wood is added could be due to the difference in their chemical composition and structure.

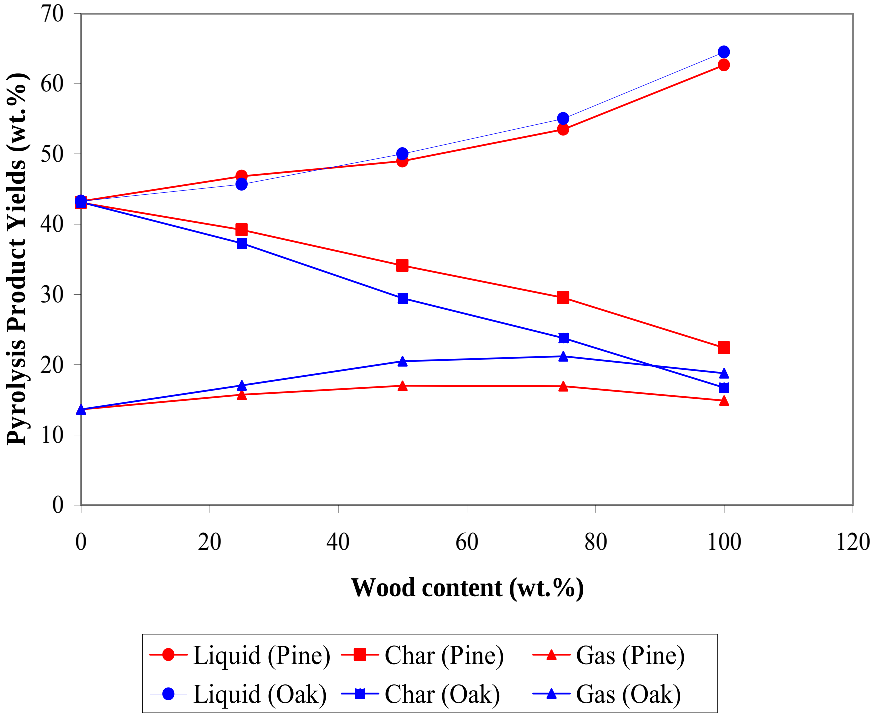

Figure 4.15 Yields of pyrolysis products of manure and wood (pine and oak) mixtures

Table 4.11

Elemental composition and HHV of 50% Manure & 50% wood pyrolysis oil (ESP)

Ultimate Analysis (wt.%)	50% Manure & 50% wood pyrolysis oil(ESP)	
	Pine	Oak
Moisture content	4.13	5.56
C	61.08	60.78
H	7.11	7.28
N	2.90	2.44
O	28.75	29.30
S	0.15	0.14
Cl	149ppm	0.030
H/C molar ratio	1.40	1.44
O/C molar ratio	0.35	0.36
N/C molar ratio	0.04	0.03
Ash	<0.06	<0.1
HHV (MJ/kg)	27.7	26.8

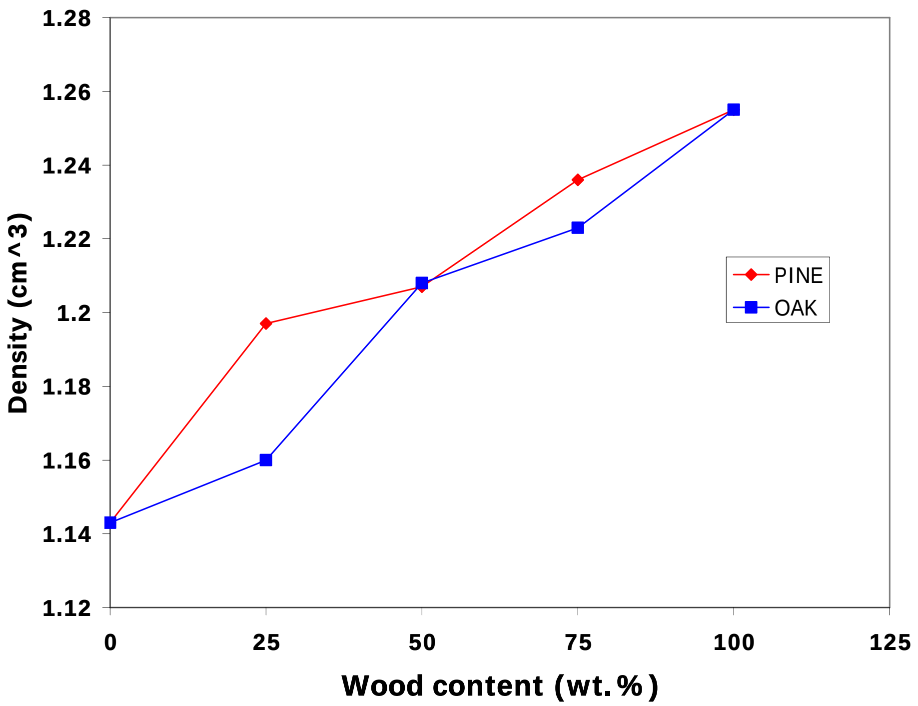

Figure 4.16 Density of ESP oils from manure and wood (pine and oak) mixtures

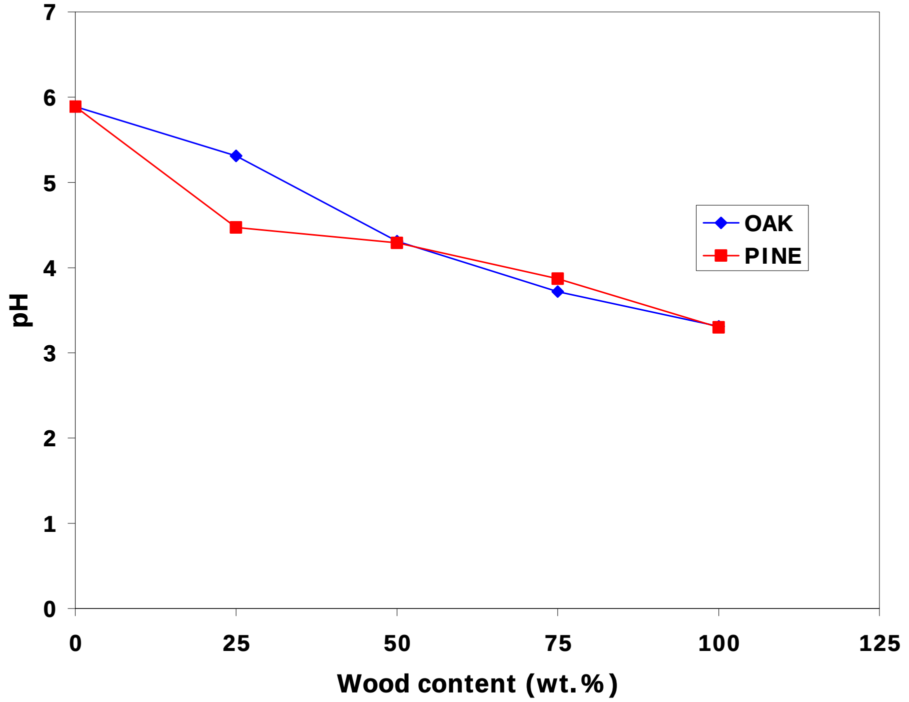

Figure 4.17 pH of ESP oils from manure and wood (pine and oak) mixtures

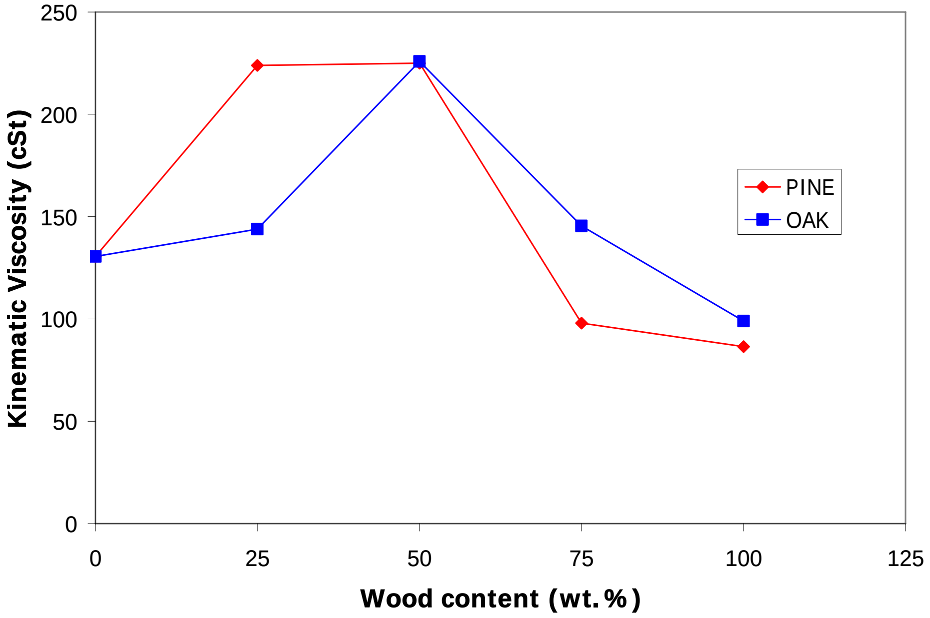

Figure 4.18 Kinematic viscosities of ESP oils from manure and wood (pine and oak)

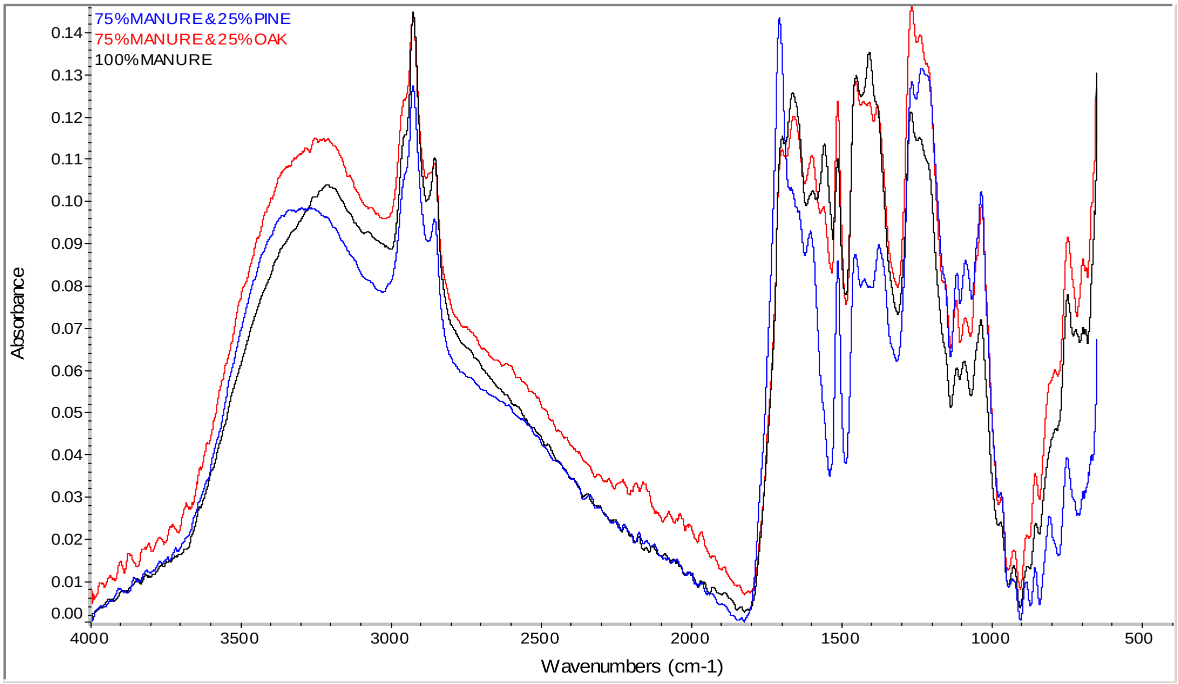

Figure 4.19 FT-IR spectra of 100% manure and 75/25 mixtures with pine and oak

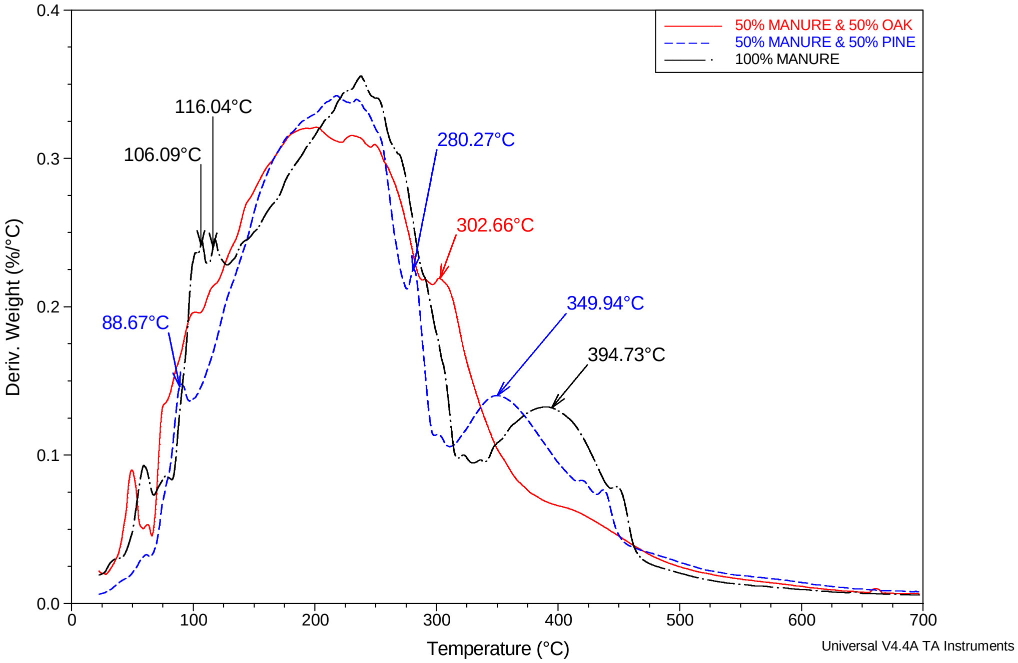

Figure 20. DTG curves of oils from manure and 50/50 mixture with pine and oak

4.3 Conclusion

The influence of wood addition on the pyrolysis of layer manure was significant in the distribution of pyrolysis products, the physical properties and the chemical composition of the bio oils. An increase in wood content in the manure/wood mixture increases the bio oil yield and lowers the char yield. The highest bio oil yield and the lowest char yield were achieved with oak wood. The physical properties and the chemical composition of the mixture of 75% manure and 25% wood differed greatly between pine and oak. The manure oil had the highest nitrogen, hydrogen, sulfur, and chlorine content and HHV but decreased as the wood content increased. FT-IR, ^{13}CNMR, and ^{1}HNMR analysis showed that pure manure oil was rich in aliphatic hydrocarbon and amide groups. The addition of wood to the manure essentially changed the chemical structure of the pyrolytic oils and caused an increase in compounds with oxygen functionalities and a decrease in aliphatic hydrocarbons and nitrogenous compounds. Some of the functional groups identified include, primary and secondary aliphatic alcohols, phenols, aromatic ethers, and carbonyl/carboxylic groups. TG/DTG analysis also showed that the thermal degradation of the oils from pure manure falls into two major groups of compounds compared with one major group in wood. It can be concluded that the amount and the type of wood in the pyrolysis of poultry litter will affect the yields and the physico-chemical properties of the derived oils.

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CHAPTER FIVE

PARAMETRIC STUDIES

ABSTRACT

In this work, pyrolysis of a mixture of 50wt% layer manure and 50wt% pine wood shavings in a bubbling fluidized bed was studied parametrically using a Box-Behnken experimental design to investigate the effect of temperature, gas flow rate and feed rate on the distribution of pyrolytic products and the physico-chemical properties of the oil. The operational variables were as follows: temperature (400-550°C), nitrogen gas flow rate (12-24 L/min), and feed rate (160-480 g/h). The bio oil, char and gas yields were examined in addition to the pH, viscosity, density and water content of the bio oils. Temperature, gas flow rate and feed rate had significant effects on the bio oil yields. Maximum bio oil yields (51.1wt.%) were achieved at 400 - 500 ^{o}C with a feed rate of 480g/h and N_2 flow rate of 12-18L/min. The highest char yield (36.31wt.%) and the lowest gas yield (14.7wt.%) were both achieved at 447 ± 20^{o}C with a feed rate of 320g/h and N_2 flow rate of 18 L/min. The lowest char yield (22.6wt.0%) was at 569 ± 29^{o}C, 320g/h and 12L/min. The highest gas yield (35.6%) occurred at 535 ± 38^{o}C, 480g/h feed rate and 24L/min N_2 flow rate. FT-IR spectroscopy showed significant influence of temperature on the carbonyl/carboxylic (C=O) and the primary aliphatic alcohol(C-O) groups in the oil.

Keywords: Layer manure; pine wood; fast pyrolysis, fluidized bed reactor; bio oil; Box-Behnken experimental design

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5.0 Introduction

The potential of using poultry litter as a renewable energy source to produce bio oil and char (fertilizer) is an attractive opportunity. In chapter four, fast pyrolysis was used to convert various mixtures of manure and wood shavings into bio oil, char and gas. The studies showed that the yield and composition of pyrolysis products were dependent on the composition of the feedstock. Among many factors and features that influence fast pyrolysis process, the choice of operating conditions affects the formation of the products mentioned above. The effect of operating conditions and reactor configurations on pyrolysis has been studied and reported in literature (Horne and Williams, 1996; José M. Encinar, 1997; Sensöz et al., 2000; Pütün et al., 2001; Yorgun et al., 2001; Beis et al., 2002; Pütün et al., 2002; Sensöz, 2003; Onay and Mete Kockar, 2004; Lee et al., 2005; Zhang et al., 2005; Kang et al., 2006; Nurgül Ozbay et al., 2006; Fonts et al., 2008; Garcia-Perez et al., 2008). Research on woody biomass pyrolysis has shown that for a high liquid yield, low temperature, high heating rate, and short gas residence time are required and for high yield of char, low temperature and low heating rate are necessary. To maximize the yield of gas product, high temperature, low heating rate and long gas residence time are preferred (Bridgwater and Cottam, 1992; Maschio et al., 1992; Klass, 1998; Meier and Faix, 1999). Woody biomass is composed of structural constituents (hemicellulose, cellulose, and lignin) and minor amounts of other organics that degrade at different rates, mechanisms and pathways (Bridgwater, 1999). The chemical composition of woody biomass is different from that of poultry litter due to the presence of manure in the poultry litter, thus its thermal degradation will also follow a different mechanism and pathway. Kim and Agblevor, (2006) studied the kinetic parameters during the pyrolysis of wood chips, broiler and flock litters. Among their findings, they establish that, the DTG curves of the broiler and flock litters had in addition to peaks common in wood chip, a peak at about 500°C which they attributed to the manure content of the litters. When wood is completely pyrolyzed, the hemicellulose component breaks down first, between of 200 to 260°C, and cellulose follows at 240 to 350°C, with lignin being the last component to decompose over a wider temperature range of 280 to 500°C (Soltes and Elder, 1981; Hon and Shiraishi, 1990; Mohan et al., 2006). The rate and extent of degradation of each of the components depends on the pyrolysis process parameters (Bridgwater, 1999). As a result of the differences in the decomposition of cellulose, hemicellulose, lignin and protein (manure), the yield and chemical composition of pyrolytic products from a mixture of 50% manure and 50% wood will be consequently affected by temperature. Additionally, temperature affects the degree of cracking (time-temperature relationship) which lowers the molecular weight distribution in the resulting oils and produces more gas (Mohan et al., 2006). Although a lot of research has been carried out on the influence of various operating conditions on fast pyrolysis, most of the work has focused on woody biomass pyrolysis. The purpose of this study was to investigate the influence of temperature, gas flow rate, and feed rate on the product distributions and the physicochemical properties of the bio oils obtained from fast pyrolysis of 50% manure and 50% wood in a fluidized bed reactor.

5.1 Materials and Methods

5.1.1 Materials

A prepared 50:50 w/w mixture of layer manure and pine wood shavings obtained from poultry growers in Shenandoah Valley, Virginia was used. The samples with moisture content of 8% to 10wt.% were ground in a Wiley mill to pass a 1mm mesh screen.

5.1.2 Method

5.1.2.1 Box-Behnken Experimental Design

The traditional approach to studying the effect of a variable or to optimize a multivariable system is to change one variable at a time. By this method it is difficult to develop an optimized formulation, as the method reveals nothing about the interactions among the variables. Design of Experiments (DOE) is a statistical technique that can be used for studying and optimizing such multivariable systems and hence a Box-Behnken statistical design was chosen for this study. The choice of range on the operating variables used in this parametric studies were based on previous studies conducted by Agblevor et al., (2007) on the pyrolysis of poultry litter. They performed their experiment at 460^{o}C, 18L/min and 320g/h. For this study, a 3-factor (temperature, feed rate and gas flow rate), 3 levels Box-Behnken experimental design on the responses (product yields, pH, viscosity, density and water content) with 3 replicates per treatment was used. A total of 27 experimental runs were generated and analyzed using JMP software. The experimental results for each response variable were analyzed statistically using analysis of variance (ANOVA), using software JMP version 7.0. The ANOVA analysis of the Box-Behnken design helps to quantify statistically significance effects of the principal factors and the interactions between them on the response variables. The confidence level chosen for the response variable was 95%.

Table 5.1

Variables and their levels in Box-Behnken design

Independent Variable	**Levels**		
	Low	Medium	High
Temperature (^oC)	400	475	550
Feed rate (g/hr)	160	320	460
Gas flow rate (L/min)	12	18	24

Table 5.2 Box-Behnken Experimental design

Design Pattern	Temperature (^oC)	Feed Rate (g/h)	N_2 Flow rate (L/min)
--0	400	160	18
-0-	400	320	12
-0+	400	320	24
-+0	400	480	18
0--	475	160	12
0-+	475	160	24
000	475	320	18
0+-	475	480	12
0++	475	480	24
+-0	550	160	18
+0-	550	320	12
+0+	550	320	24
++0	550	480	18

5.1.2.2 Fluidized bed Pyrolysis of feedstock

The parametric studies on the fast pyrolysis of 50% layer manure and 50% pine wood shavings were carried out in a bench-scale fluidized bed reactor unit located at the BSE Bioresource Eng. Lab, Virginia Tech, U.S.A (Figure 4.1). A detailed description of the fluidized bed reactor has been done in chapter four. 400g of feedstock were pyrolyzed at 400^{o}C, 475^{o}C, and 550^{o}C. They were fed at a rate of 160, 320, and 480g/h from a feed hopper using a twin-screw feeder to convey it into an entrainment zone. The total flow rate of nitrogen used to both entrain the feed through a jacketed air-cooled feeder tube and to fluidize the 100g bed of silica sand were 12, 18, 24L/min. The combinations of these parameters for each run are shown in Table 5.2. The pyrolysis vapors and aerosols exiting the reactor were passed through a hot gas filter to separate the char and any entrained lost sand from the pyrolysis vapors. The separated vapors and aerosols were condensed in two condensers connected in series, an electrostatic precipitator and a glass packed column.

5.1.2.3 Pyrolysis Products.

The mass of char was determined gravimetrically by weighing the hot gas filter and the reactor before and after each pyrolysis experiment. The total mass of bio oil was also determined gravimetrically by weighing the condensers, electrostatic precipitator and the glass packed column before and after each experiment. The total mass of the producer gas was calculated by difference. The yields were expressed in percentage on a moisture free basis.

5.1.2.4 Acidity

The pH was measured using a Corning pH Meter 440 equipped with F-55500-10 Accumet pH probe (Cole-Parmer Instrument Company, Vernon Hills, IL, USA). The reported values were obtained after 10 min stabilization of the mechanically stirred oil. The pH values were reported to two decimal places. The meter was frequently calibrated using standard pH solutions (Micro Essential Lab Inc., N.Y., U.S.A.).

5.1.2.5 Viscosity

The dynamic viscosities of the freshly produced oils were measured with a Brookfield DV-II+ Pro viscometer (Brookfield Engineering laboratories, Inc. MA, USA.) and a programmable temperature controller thermosel. The measurement was conducted at 60°C with Spindle SC4-18 and speed ranging from 1-30 rpm depending on the viscosity of the oil. Sample volume of 7ml was used and the reading of the instrument stabilized within 5-15min. The dynamic viscosities were also converted into kinematic viscosities.

4.1.2.6 Water content

A Metrohm 701KF Titrino (Brinkmann Instruments, Inc, N.Y, U.S.A) and a 703 titration stand setup were used for the Volumetric Karl Fischer titration. Hydranal® Composite 5 reagent was used. A solvent mixture of 40 mL of methanol + 20mL of toluene were placed in the titration vessel and conditioned. About 1g of oil sample was loaded into a hypodermic plastic syringe and weighed. The sample was injected into the titration solvent and syringe weighed again. The mass of sample used was determined by difference. The mixture was stirred to dissolve the oil. The water content was titrated volumetrically and the resulting mass was recorded. The water content was expressed as a percentage of the amount of sample used (1g).

5.1.2.7 Density

The densities were determined at 23 °C using a Mettler Toledo DA-110M density meter (Greifensee, Switzerland) according to ASTM D4052. Calibrations were done prior to measurements with distilled water free from bubbles. The oil sample was introduced into an oscillating sample tube and the density was calculated from measured resonance frequency. The values were reported to 3 decimal places in g/cm^3.

5.1.2.8 FT-IR Spectrometry

20mg of each sample was subjected to a Fourier-transform infrared (FTIR) analysis. The spectra were obtained over a range of 4000-650cm^{-1} using an IR spectrometer (Nicolet Avatar, 370 DTGS) equipped with a DTGS-KBR detector in multi-bounce horizontal attenuated total reflectance (HATR) mode. 64 scans at a 4 cm^{-1} resolution and a background gain of 4.0 were used. Data analysis was performed using the OMNIC 7.3 (Thermo Electron Corporation) software package.

5.2 Results and Discussion

5.2.1 *Effect of temperature, nitrogen gas flow rate and feed rate*

Table 5.3 shows a summary of the effect of temperature, feed rate and gas flow rate on the pyrolysis product distribution of the mixture of 50% manure and 50% of pine wood shavings. The reactor temperature is the mean value of the temperatures at the bottom, middle and top sections of the reactor. The statistical analysis of the experimental data helps to quantify the influence of the temperature, nitrogen flow rate and feed rate on the product yields. The analysis of the effect of temperature and its interaction effect with feed rate and nitrogen gas flow rate was done using JMP software. The significant effect of the factors and their interaction effects were tested at 95% confidence interval. The yields of the pyrolysis products were dependent on the various levels of operating conditions used in the study. The maximum bio oil yields (51.1wt.%) were achieved at 400 - 500 °C with a feed rate of 480g/h and N_2 flow rate of 12L/min. Low oil yields (38 - 43wt.%) occurred at temperatures greater than 500°C with a feed rates less than 480g/h and N_2 flow rate greater than18L/min. However there were some high oil yields that occurred at higher temperatures (>500 °C). The highest char yield (36.31wt.%) and the lowest gas yield (14.7wt.%) were both achieved at 447 ± 20°C with a feed rate of 320g/h and N_2 flow rate of 18 L/min. The lowest char yield (22.6wt.0%) was at 569 ± 29°C, 320g/h and 12L/min. The highest gas yield (35.6%) occurred at 535 ± 38°C, 480g/h feed rate and 24L/min N_2 flow rate.

Table 5.3

Results of pyrolysis product yields

Mean Reactor Temperature (^{o}C)	Feed Rate (g/h)	N_2 flow rate (L/min)	Liquid (wt.%)	Char (wt.%)	Gas (wt.%)
391 ± 38	320	24	46.74	29.89	23.37
411 ± 49	320	24	48.91	30.43	20.65
419 ± 54	320	24	47.21	30.38	22.42
421 ± 34	160	18	42.93	30.43	26.63
423 ± 45	480	18	48.39	32.26	19.35
437 ± 28	480	12	49.46	33.15	17.39
438 ± 42	160	18	41.69	29.62	28.68
446 ± 30	480	12	51.09	30.43	18.48
446 ± 39	320	12	45.11	32.07	22.83
449 ± 10	320	18	49.43	35.83	14.74
450 ± 48	480	12	51.10	27.47	21.43
451 ± 20	320	18	49.02	36.31	14.68
462 ± 16	160	18	47.79	33.22	19.00
466 ± 10	320	18	48.60	34.70	16.70
469 ± 35	320	18	48.89	29.14	21.98
477 ± 22	480	24	47.83	25.54	26.63
480 ± 20	160	12	45.80	26.90	27.30
488 ± 19	320	18	50.00	27.17	22.83
501 ± 27	320	18	49.45	29.12	21.43
505 ± 38	160	24	38.60	30.40	31.00
506 ± 28	160	12	45.00	26.36	28.64
514 ± 18	320	18	49.46	23.91	26.63
518 ± 38	160	24	38.00	31.80	30.20
521 ± 27	320	18	45.83	28.33	25.83
535 ± 38	480	24	39.05	25.38	35.56
549 ± 54	480	18	48.30	28.00	23.70
550 ± 28	320	24	41.90	28.65	29.45
550 ± 28	160	18	43.33	27.20	29.49
569 ± 29	320	12	45.87	22.61	31.52
572 ± 41	480	18	41.55	28.74	29.71
583 ± 34	320	18	40.99	24.69	34.32
594 ± 60	480	18	42.50	23.00	34.50

5.2.2 Effect of Temperature

As can be seen in Table 5.3, an increase in temperature generally increased the yield of the gaseous product and continuously decreased the char yield, but the bio oil yield increased through a maximum and then dropped with a further increase in temperature. The decrease in char yield at higher temperature was consistent with the increase in the gaseous product. The principal effect of temperature was significant on the liquid yield ($P=0.0022$), char yield ($P<0.0001$) and gas yield ($P<0.0001$). It is well understood in biomass pyrolysis that higher temperatures (> 500^{o}C) and longer vapor residence times cause secondary cracking of primary products reducing the char and oil yields (Boroson et al., 1989; Bridgwater, 1999; Di Blasi et al., 1999). Nevertheless, the study showed that the oil yield increased to a maximum value and decreased as the reactor temperature rose. The reason is that, the increase in the reactor temperature promoted the devolatilization of the organic matter thereby increasing the liquid yield in the lower temperature range from 400 to 500 ^{o}C. However there is the possible destruction of secondary tars for temperatures ranging from 500 to 600 °C which consequently increased the gas yield and decreased the char yield It is also worth mentioning that the maximum oil yields at the optimum temperatures were dependent on the nitrogen flow rate and the feed rate. There was an interaction between temperature and feed rate on both the liquid yield and the gas yield. From the interaction plot shown in figure 5.4 for liquid yield, it can be seen that the effect of temperature was stronger at a higher feed rate (480g/h). The interaction plot on the gas yield shown in figure 5.11 also shows that at a higher feed rate (480g/h), an increase in temperature affects the gas yield more than at a feed rate of 160g/h. However the influence of the interaction on the liquid and gas yield were insignificant. There was also an interaction between temperature and the gas flow rate on the liquid yield and the char yield, but the influence was only significant on the char yield (P=0.0464). Figure 5.7 showed that the decrease in char yield as the reactor temperature increased was stronger in the case of the lower gas rate (12L/min) compared to the higher gas rate (24L/min). It can also be observed in figure 5.4 that the effect of temperature on the liquid yield was stronger at a higher gas rate (24L/min).

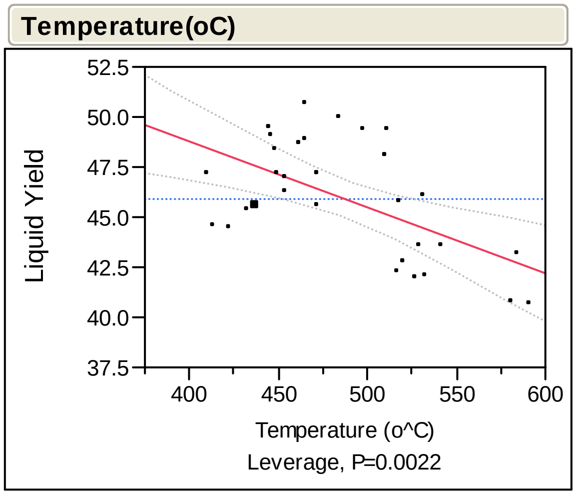

Figure 5.1 Effect of temperature on liquid yield

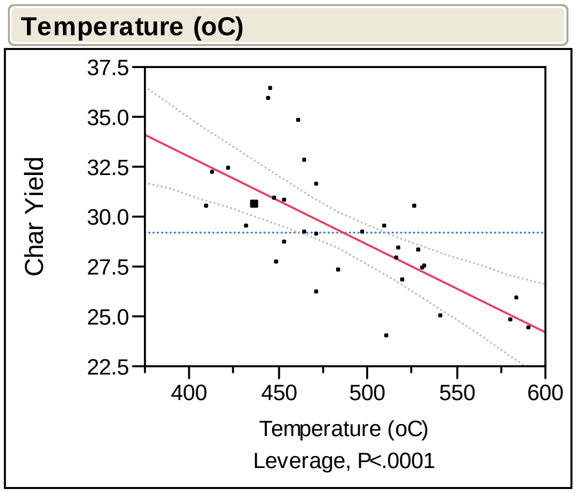

Figure 5.2 Effect of temperature on char yield

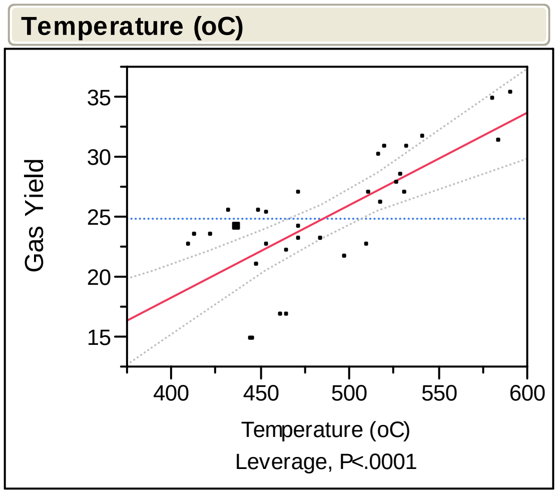

Figure 5.3 Effect of temperature on gas yield

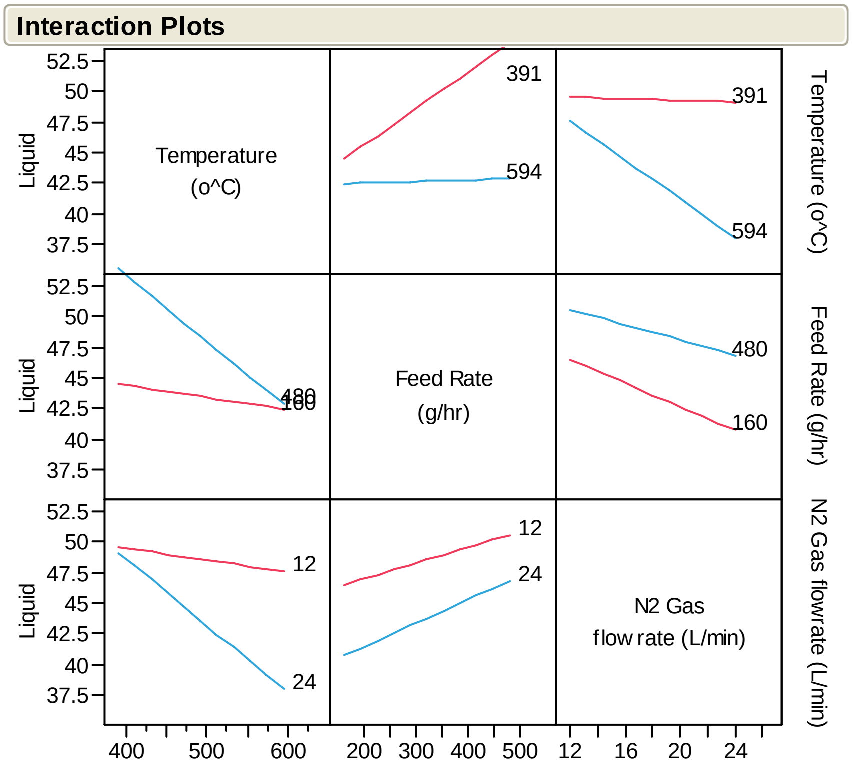

Figure 5.4 Interaction plots on liquid yield

5.2.3 *Effect of N_2 flow rate*

The rate of flow of the N_2 through the reactor bed influences the residence time of the vapor phase and consequently affects the pyrolysis product yield by preventing secondary cracking reactions in the vapor phase. However the extent of thermal cracking is a function of both temperature and time (Boroson et al., 1989). In determining the effect of N_2 flow rate, factor levels of 12L/min, 18L/min and 24L/min were used. From this experiment, it became evident that an increase in nitrogen flow rate decreases the liquid yield and gradually increased the gas yield. The char yield was not affected. Statistical analysis showed that the principal effect of the nitrogen flow rate on liquid yield was significant (P=0.0052). Research has shown that when the gas flow rate increases, the heat transfer improves, the vapors generated have shorter residence and secondary reactions such as thermal cracking, repolymerization and recondensation are minimized to maximize liquid yield (Boroson et al., 1989; Maschio et al., 1992; Bridgwater et al., 1999; Encinar et al., 2000; Pütün et al., 2001; Yorgun et al., 2001; Demirbas and Arin, 2002; Sharypov et al., 2002; Gonzalez et al., 2005; Kersten et al., 2005). But in this study, the lower gas flow rate (12L/min) gave higher liquid yield. It was also interesting that the char yield did not increase at a higher gas flow rate (24L/min). These observations were attributed to several possible reasons. Firstly, it could probably be that when the nitrogen flow increased, the volume of inert gas increases, and therefore the partial pressures of some of the vapors would not be able to reach their vapor pressures and therefore they would not condense and lead to lower liquid yield and higher gas yield. The second explanation could be that, at higher gas flow rates, the terminal velocities of some of the solid particles can be reached, and might leave the reactor without reacting and as a result decrease the liquid yield. However, if that was the case, an increase in char yield would be expected but at higher gas flow rates, the char yield was not significantly affected. Lastly, it could be that the suitable flow rate required to enhance the oil yield was 12L/min or less. The interaction effect between nitrogen gas flow rate and temperature was statistically significant for the char yield (P=0.0464). The interaction plot presented in figure 5.8 shows that at an increase in gas flow rate would decrease char yield at a lower temperature and increase char yield at a higher temperature. This could be due to the temperature difference between the reactor temperature (400-600 ^{o}C) and the hot gas filter (425^{o}C). Therefore for any pyrolysis at 400 ^{o}C or less, an increase in the gas flow rate would cause more char to leave the reactor to the hot filter (425 ^{o}C) and as a result the higher temperature effect would decrease the char yield depending on the duration of the run. But for a higher reactor temperature (> 425 ^{o}C), with a higher gas flow rate, the unreacted solids and char will leave a hotter zone (reactor) to a less hot zone (hot filter) and as a result increase the char yield.

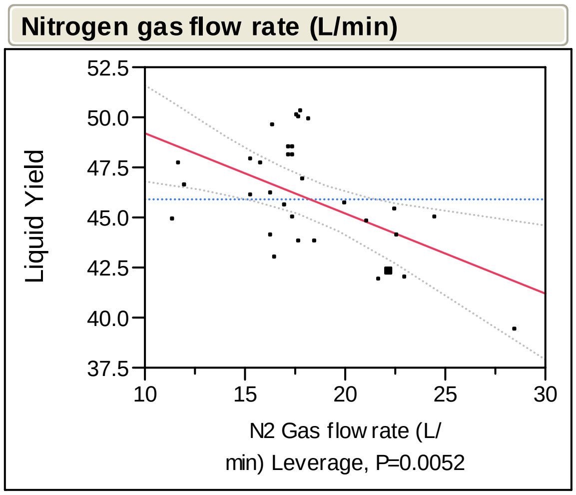

Figure 5.5 Effect of gas flow rate on liquid yield

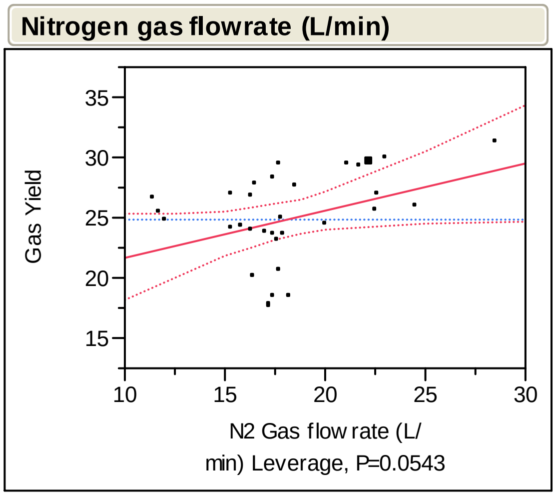

Figure 5.6 Effect of gas flow rate on gas yield

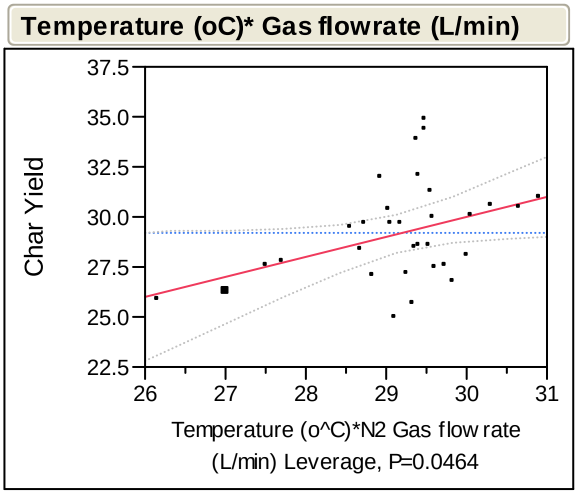

Figure 5.7 Temperature and gas flow rate effect on char yield

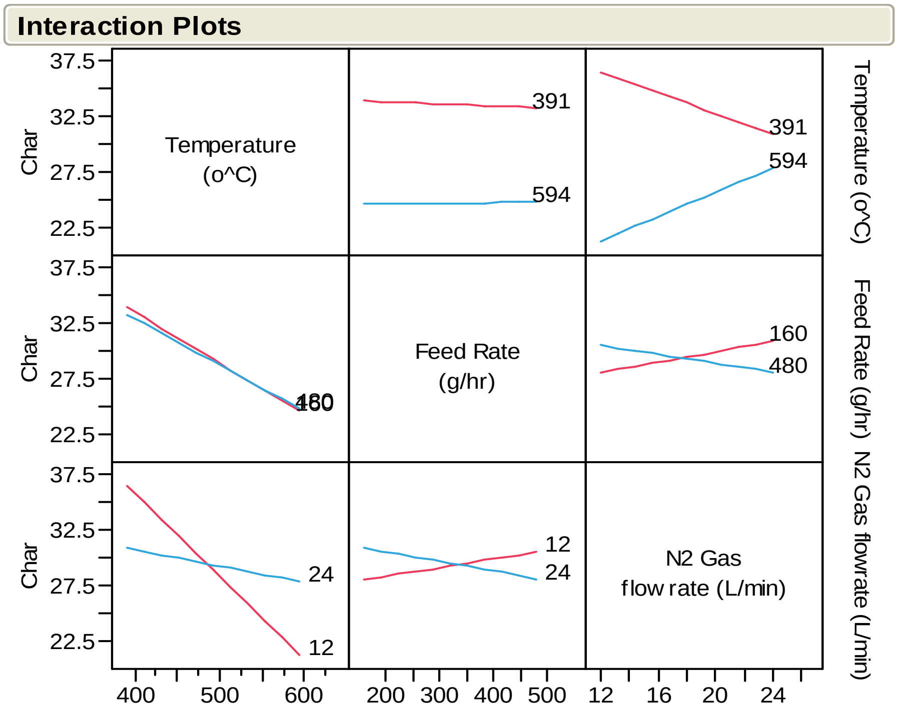

Figure 5.8 Interaction plots on char yield

5.2.4 *Effect of feed rate*

Feed rate affects the solid residence time in the reactor. In figures 5.9 and 5.10, an increase in the feed rate increased the liquid yield and decreased the gas yield. This observation was attributed to the fact that, the heat transfer decreases at higher feed rates and produces higher molecular weight products to maximize liquid yield and consequently decreasing gas yield. The statistical analysis showed that the principal effect of feed rate was significant on the liquid yield (P=0.0033) and the gas yield (P=0.0445). However the effect of the feed rate on the char yield was insignificant. There was an interaction between feed rate and temperature on the liquid and gas yields, but the effect was insignificant. The interaction plots in figure 5.4 suggest that at lower temperature (400°C), an increase in feed rate increases the liquid yield but barely affects the liquid yield at higher temperature (550 °C).

This might be due to the fact that an increase in feed rate causes the vapors generated to suffer less thermal cracking reactions and therefore their conversion into noncondensable gases is not favored at lower temperatures (400 °C) compared with higher temperatures (550) where there is a higher possibility of thermal cracking.

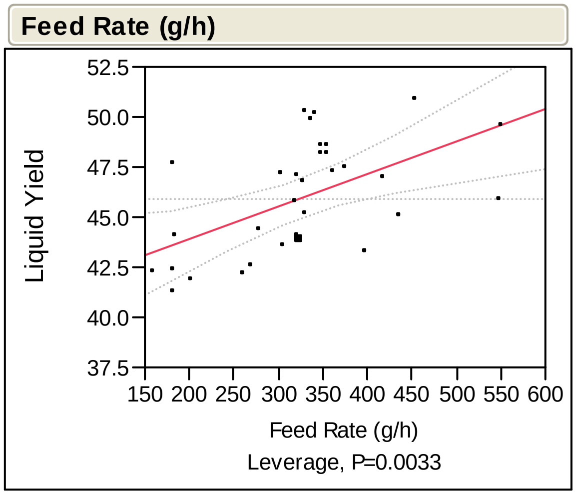

Figure 5.9 Effect of feed rate on liquid yield

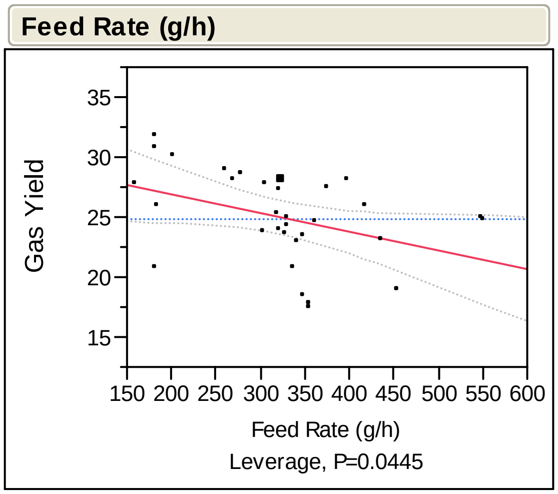

Figure 5.10 Effect of feed rate on gas yield

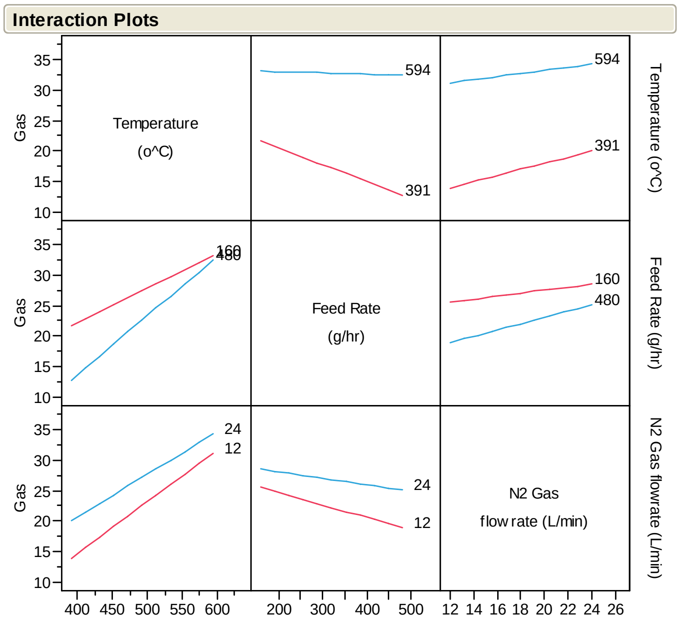

Figure 5.11 Interaction plots on gas yield

5.2.5 *Effect on physical properties*

The principal effect of temperature, feed rate, gas flow rate and their interaction effects have been shown to influence the pyrolysis product of 50% wood and 50% manure. Since the feedstock contains cellulose, hemicellulose, lignin and proteins which degrade at different temperatures and with different kinetic pathway, one would expect that these operating conditions of pyrolysis would not just influence the quantity but in addition affect the quality of the products. To examine the effect of temperature, feed rate and nitrogen flow rate, the oils were analyzed for their pH, density, water content and viscosity. Figure 5.12 shows the trend line for the regression of the viscosities measured in relation to the pyrolysis temperature. Increase in pyrolysis temperature caused increase in the viscosities of the oils. Viscosity varied widely depending on the water content of the oil (Soltes and Milne, 1988) and also the molecular weight of the various compounds present in the oil. Statistical analysis showed that the effect of temperature was significant (P=0.0054). The combined effect of temperature and feed rate was also significant (P=0.0001). However the feed rate and nitrogen flow rate did not show any significant effect. The interaction plot in figure 5.14 shows the effect of temperature and feed rate on the viscosity of the oil. It suggest that an increase in pyrolysis temperature slightly decreases the viscosity when the feed rate is low (160g/h) and increases the viscosity when the feed rate is high (480g/h). Alternatively an increase in feed rate at a lower temperature decreases the viscosity and increases in viscosity at a higher temperature. Figure 5.15 shows relationship of oil pH with an increase in temperature. The pH of the oil was low at lower temperature and increased as temperature increased. The observation was probably because the pyrolysis products at lower temperatures contain more of the decomposition products of wood that contributes to the acidity of the oil. However, the organic vapors of the wood decomposition products are cracked at a higher temperature into non condensable gases thereby reducing its content in the oil and results in a higher pH values. Also at a higher temperature, one would expect the oil to contain more manure decomposition products since the protein in the manure degrades at a higher temperature. This could cause neutralization of the acidic wood degradation components. Statistical analysis however showed that the effect of temperature was not significant (P=0.0680) at 95% confidence level. There was also no significant effect of feed rate and nitrogen gas flow rate on the pH of the oils. There was no significant effect of temperature, feed rate and gas flow rate on the density and the water content of the oils.

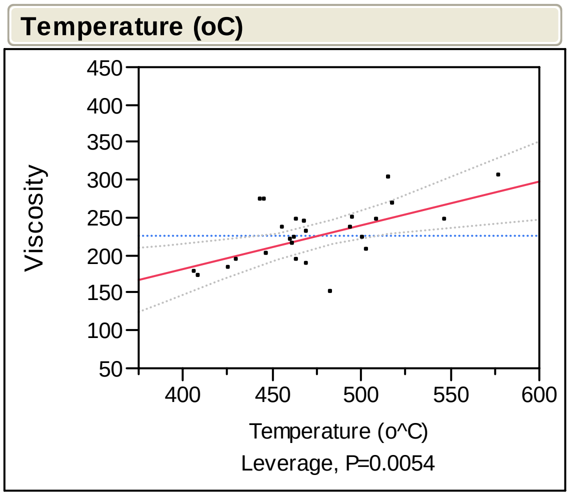

Figure 5.12 Effect of temperature on oil viscosity

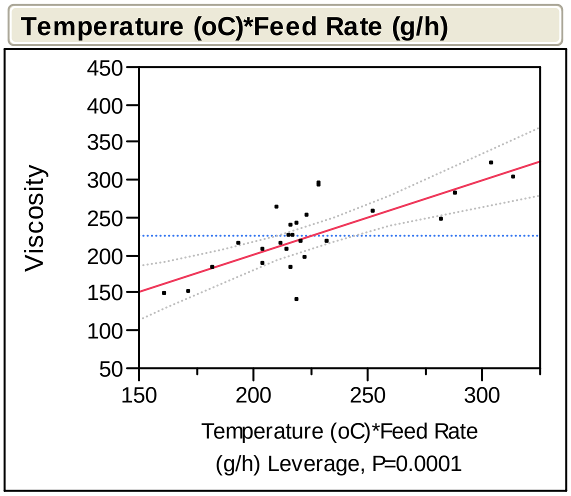

Figure 5.13 Interaction effect of temperature and feed rate on oil viscosity

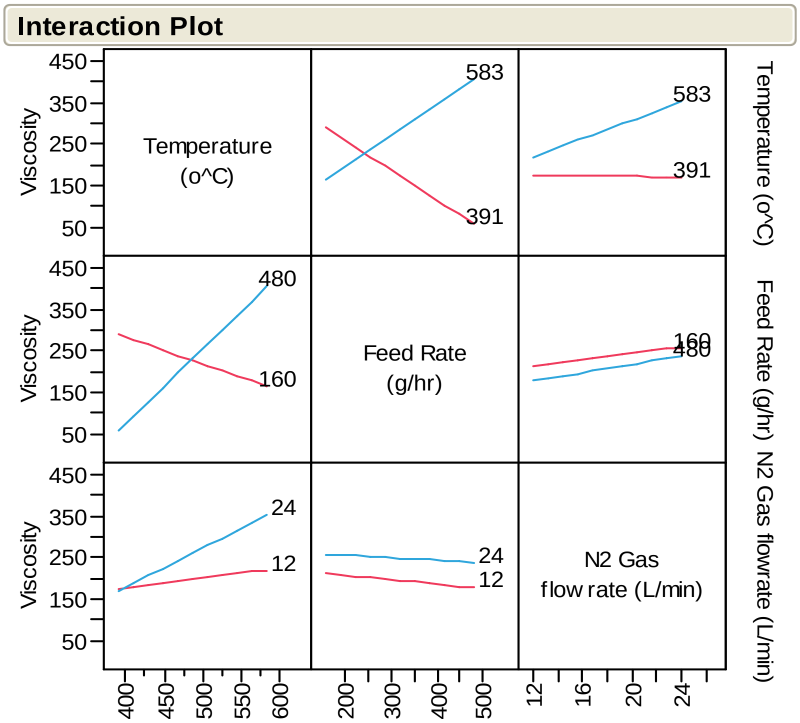

Figure 5.14 Interaction plot on oil viscosity

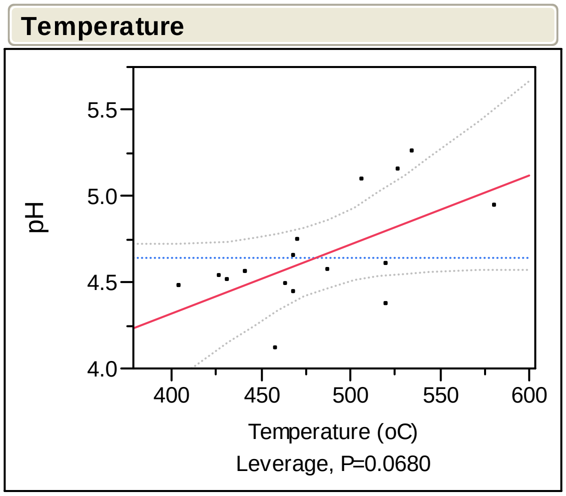

Figure 5.15 Effect of temperature on pH of oils

5.2.6 *Effect on functional groups*

In addition to the effect of operating conditions on the pyrolysis yields of 50% wood and 50% manure products and the physical properties, there was also a substantial change in the functional groups in the oil. The individual and combined effects of temperature, feed rate, and nitrogen gas flow rate on the relative intensities of the identified functional groups were also analyzed statistically to test their significance. The absorption band at 925 cm^{-1} which was assigned to C-H out-of plane bend, was relatively stable and as a result all other bands were semi-quantitatively analyzed by dividing their peak intensities by that at 925 cm^{-1}. Table 5.4 is a summary of the relative intensities of some of the functional groups identified. The analysis mainly showed that an increase in temperature generally decreased the relative intensities in aliphatic hydrocarbons, carbonyl (ketone and carboxylic acid), amide carbonyl, aromatic skeletal vibration, aromatic ethers, phenols and aliphatic primary alcohol. The feed rate did not have any effect and the nitrogen gas flow rate showed a slight increase in the intensities of the above mention functional groups. The temperature had a significant effect on the carbonyl/carboxylic group (P=0.0024) and the aliphatic primary alcohol (P=0.0463). However the effects of the feed rate and gas flow rate was not statistically significant. The interaction effect of temperature and feed rate on the carbonyl/carboxylic groups was significant (P=0.0374). The decrease in the carbonyl/carboxylic group with temperature increase complements the increase in pH values of the oils.

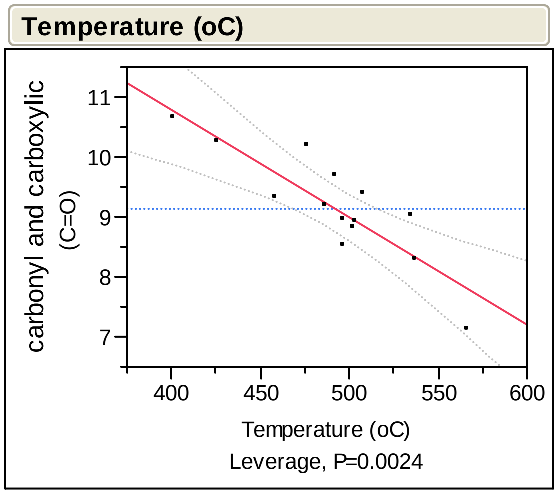

Figure 5.16 Effect of Temperature on carbonyl/carboxylic groups in the oil

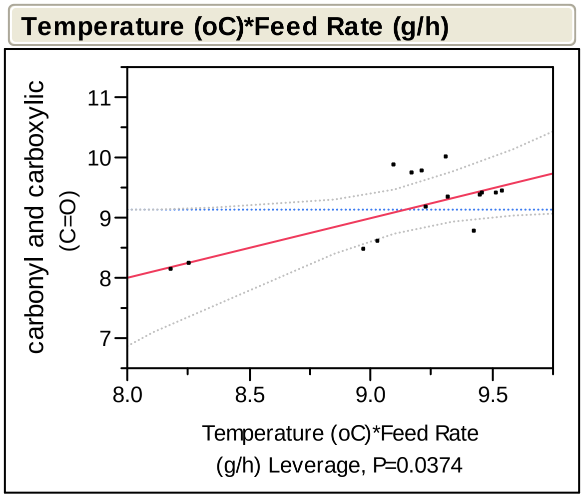

Figure 5.17 Interaction effect of temperature and feed rate on the C=O group in the oil

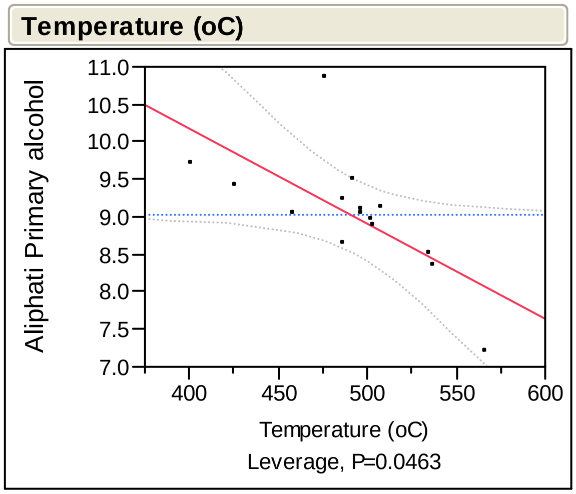

Figure 5.18 Effect of temperature on the primary alcohol in the oil

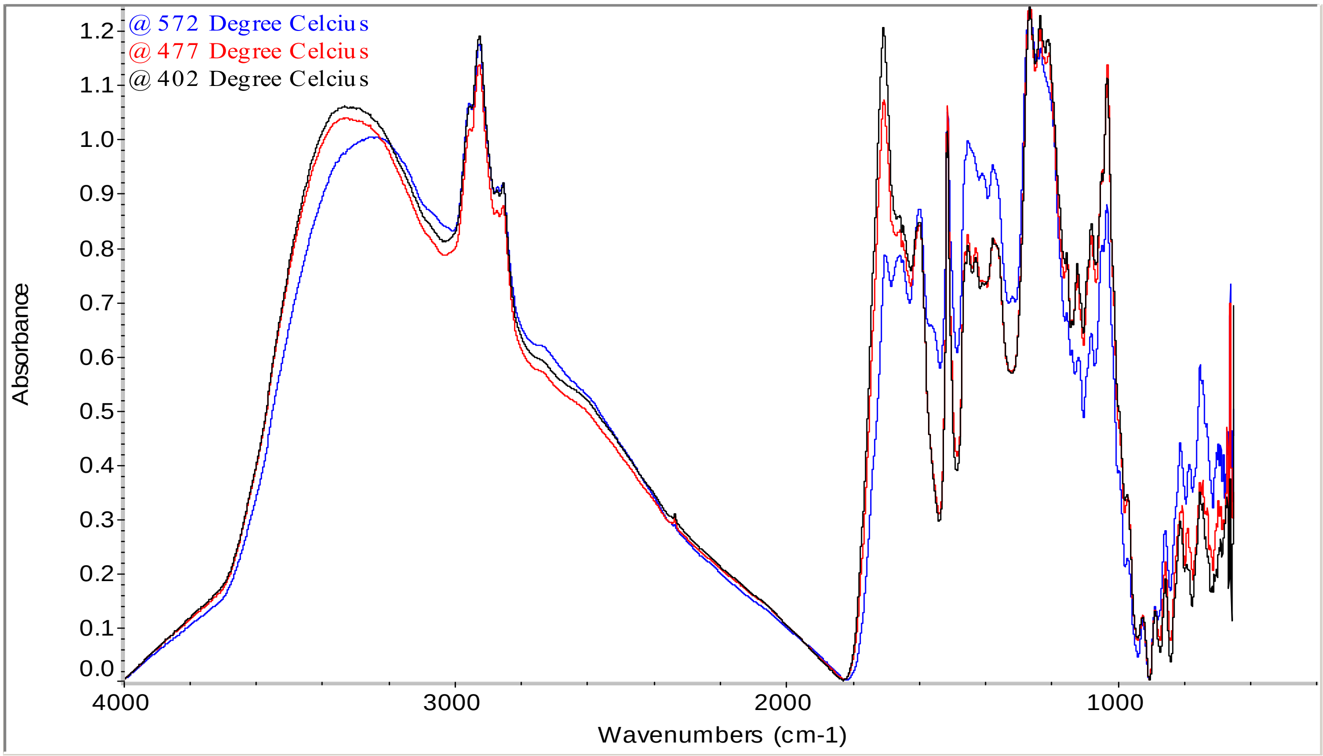

Figure 5.19 Effect of temperature on the functional groups in the oil

Table 5.4

Summary of the effect of temperature on the relative intensities

Design Factors			Relative Intensities						
Temperature (°C)	Feed Rate (g/h)	N_2 Flow Rate (L/min)	Aliphatic Hydro-carbon	C=O (1700)	Amide carbonyl	Aromatic Ring (1510)	Phenol (1208)	C-O Primary Alcohol (1036)
413	160	18	10.09	9.08	7.14	9.22	9.84	9.20
390	320	24	10.08	10.23	7.14	8.60	10.02	9.43
506	160	12	11.16	7.51	7.53	9.73	10.77	7.81
535	480	24	10.37	7.64	7.09	9.07	10.50	8.05
572	480	18	10.43	6.97	6.96	9.33	10.36	7.79
477	480	12	9.42	8.89	6.90	8.80	9.60	9.44
531	320	18	12.00	9.34	8.49	10.61	12.21	9.06
506	160	24	11.58	10.9	8.79	11.42	13.03	10.61
466	480	12	11.24	10.13	8.24	10.16	11.53	9.86
402	480	18	12.03	11.23	8.84	9.95	11.83	9.66
560	320	18	10.00	9.06	7.37	7.84	9.90	8.46
469	320	18	9.56	9.14	7.11	8.78	9.78	8.96
450	480	12	11.33	9.78	8.34	9.63	11.59	9.02
495	320	18	10.99	10.06	7.85	10.44	11.09	10.78
582	320	18	9.69	7.22	7.06	7.60	9.57	7.19

5.3 *Conclusion*

The results from the parametric studies of pyrolysis of a mixture of 50% manure and 50% pine wood in a fluidized bed reactor showed that the pyrolysis product yields, physical properties and the chemical composition of the oil were influenced. Temperature was the most influential factor for the intervals of the operational variables studied. The effect of temperature on the liquid, char and gas yields were significant. There was an interaction between temperature and gas flow rate on the char yield and its effect was significant. It is also worth noting that the maximum oil yield can be achieved between 400-500 ^{o}C depending on the gas flow rate and the feed rate. Gas flow rate on the other hand affected both the liquid and gas yield but was only significant on the liquid yield. Also the interaction effect between the gas flow rate and temperature on the char yield was significant. The feed rate had a significant effect on the liquid and the gas yields but the interaction effect between feed rate and temperature on the gas yield was insignificant. The physical properties of the oils were influenced however the effect of temperature, feed rate and gas flow rate were insignificant on pH, density and water content. Nevertheless an increase in temperature significantly increased the viscosity of the oils and the interaction between temperature and the feed rate on the oil viscosity was also significant. FTIR analysis showed that there were some changes in functional groups when the operating conditions were varied. The chemical composition of the oils were affected by temperature, gas flow rate and feed rate, however temperature was the only factor that affected significantly some of the functional groups in the oil. An increase in temperature decreased significantly the carbonyl/carboxylic group and the primary aliphatic alcohol groups. In conclusion, the studies showed that the choice of operating condition will depend on the pyrolysis product of interest.

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CHAPTER SIX

EEFFECT OF WOOD ON STABILITY OF POULTRY MANURE BIO OILS

ABSTRACT

The effect of wood and the addition of solvent on stability of the ESP fraction of the pyrolysis oils from manure, wood (pine and oak), and mixtures of manure and wood in proportions (75:25 50:50, and 25:75 w/w %) were investigated under ambient conditions in sealed glass vials for a storage period of 8 months and their stability was monitored by measuring the changes in viscosity with time. The manure oil was relatively more stable and the oil from the 50/50 mixture for both pine and oak was the least stable. It was found that the stability of the oils from the manure and wood mixtures were dependent on the amount and the type of wood (pine or oak) added to manure. The main difference observed between the effect of pine and oak was that the viscosities of the stored oils from oak mixtures were lower than those from pine for the same storage period. The addition of 10% methanol and 10% ethanol to the oil from 50% manure and 50% pine reduced the initial viscosity of the oil and was also beneficial in slowing down the increase in viscosity during storage. FTIR analysis showed that some of the functional groups in the oils change in intensity when stored. Chemical reactions that appeared to be causing an in increase in the viscosity of the oils when stored include esterification, olefinic polymerization and oxidation reactions.

Keywords: Manure; Pine wood; Oak wood; Stability; Viscosity; Methanol; Ethanol

6.0 Introduction

The increasing concerns about shortage of crude oil, reducing greenhouse gas emissions and increasing energy security, bio oils obtained from the pyrolysis of biomass residues are considered to be a promising fuel (Czernik et al., 1994) that can be used as a substitute for fossil fuels to generate heat, power and/or chemicals (Diebold and Czernik, 1997; Oasmaa and Czernik, 1999; Czernik and Bridgwater, 2004). However there are some drawbacks in the properties that limit the applications of bio oils. The stability, viscosity, poor volatility and corrosiveness are among many that could be considered as the most challenging properties (Czernik and Bridgewater, 2004). These bio oil properties are functions of feedstock, pyrolysis operating conditions, reactor configuration, condensation system, and storage conditions (Diebold, 1999). Bio oils produced by pyrolysis are not a product of thermodynamic equilibrium and as a result their chemical composition changes toward thermodynamic equilibrium when stored and causes a change in the viscosity and molecular weight of its many oxygenated compounds (Diebold, 1999). The viscosity of pyrolysis oils are initially low when freshly produced, but increase when stored and gradually change to a glue-like thick material when exposed to air in an open vessel (Oasmaa and Peacocke, 2001). The unstable nature of bio oils as seen as viscosity increase is mostly due to reactions between the oligomers (Diebold, 1999). A reviewed of the chemical and physical mechanisms of the storage stability of fast pyrolysis bio oils was conducted by Diebold (1999). He reported that many reactions that were normally thought to require catalysis were in fact occurring without the addition of any catalyst during a long storage period. Diebold suggested that the main reactions responsible for bio-oil aging were (1) reaction between aldehydes, ketones, and water to form hydrates; (2) dehydration; (3) esterification of organic acids; (4) acetal formation of aldehydes and alcohols; (5) resin formation from aldehydes and phenols; (6) aldehydes and proteins that form heavy compounds; and (7) air oxidation of alcohols and aldehydes to form acids. Aging is therefore described as the increase in viscosity with time as a result of the interaction between the reactive organic compounds present in the oil. The effect of pyrolysis oil composition, storage conditions and the addition of solvents on the aging and thermal stability of pyrolysis oils have been reviewed in literature (Czernik et al., 1994; Agblevor and Besler, 1996; Diebold and Czernik, 1997; Agblevor et al., 1998; Diebold, 1999; Boucher et al., 2000; Boucher et al., 2000; Ba et al., 2004; Ba et al., 2004; Chaala et al., 2004; Garcia-Perez et al., 2006). Czernik et al. (1994) investigated the effect of storage conditions on the physical and chemical properties of biomass pyrolysis oils exposed to elevated temperatures over extended periods of time. They reported that the molecular weight and viscosity of the bio-oil increased significantly with time and temperature. Agblevor et al. (1998) investigated the effect of char on the destabilization of biocrude oils. They reported that char and inorganic contents of bio-oils are important to aging characteristics, as they appear to catalyze polymerization reactions during storage, leading to viscosity increase. Roy and co-workers (Ba et al., 2004; Ba et al., 2004; Chaala et al., 2004) vacuum pyrolyzed softwood bark and reported that the increase in viscosity and the non-Newtonian behavior of the oil was due to the presence of microstructures (waxy materials, char particles and aqueous droplets) in the bio-oil and the polymerization of compounds present in the oil. Oasmaa et al. (1997) investigated the effect of solvent on hardwood bio oil by adding 2 wt %, 5%, 10%, and 20% ethanol. They found that the addition of 20% ethanol at 50^{o}C decreased the initial viscosity of the bio-oil from 50 cSt to 10 cSt and also decreased the rate of viscosity change from 0.12 cSt/day to 0.01 cSt/day during the aging studies. Diebold and Czernik (1997) also investigated stabilizing a hardwood bio-oil by adding 10 wt % methanol, ethanol, acetone, ethyl acetate, a 1/1 mixture of acetone and methanol, or a 1/1mixture of methanol and methyl iso-butyl ketone. They reported that the solvents had a dramatic impact on slowing the aging rate and viscosity increase of the bio oil and concluded that methanol was the cheapest and the most effective organic solvent on a weight basis to reduce the rate of viscosity increase and the aging rate. Boucher et al. (2000) also studied the effect of methanol and pyrolytic aqueous phase on the stability and aging of bio oils at 40, 50, and 80^{o}C. They found that the addition of methanol to the bio-oil improved its properties and increased its stability and the addition of an aqueous phase pyrolysate to the bio-oil also lowered its thermal stability significantly. However rapid phase separation occurred at 80 °C, therefore the researchers concluded that the total aqueous phase concentration in this oil should be limited to 15%. The stability and aging studies reported in the literature however have been on wood derived bio oils but none has been reported on poultry litter oils. Bio oils derived from poultry litter are higher in nitrogen and inorganic compounds than woody biomass and as a consequence their physical and the chemical nature would vary. Studies by Agblevor et al.,(2007) on the thermochemical conversion of broiler chicken litter; turkey litter and bedding material into bio-oils in a fast pyrolysis fluidized bed reactor showed that the viscosities of the oils depend on the feedstock composition (manure and wood). The bio oils derived from poultry litter had very high viscosities compared to the bedding material (wood). Thus the investigation of the stability of the oils during storage is discussed in this chapter.

6.1 Materials and Methods

6.1.1 Materials

The oils used for the studies were generated in previous work by fast pyrolysis of 400g of each feedstock; manure, wood (pine and oak), and mixtures of manure and wood in proportions (75:25 50:50, and 25:75 w/w %) at 450°C with 18L/min of N_2 and a feed rate of 320g/h. A hot gas filter was used to separate the char from the vapors before condensing them in the water cooled condensers and the electrostatic precipitator (ESP). The bio oils were collected into two fractions; fraction I from the water cooled condensers and fraction II from the ESP. In this studies, only the oil fractions form the ESP were used for the stability studies. The properties of the Fraction II oils have been detailed in chapter 4.

6.1.2 Methods

6.1.2.1 *Aging and stability test*

The stability characteristics of the oils were conducted with about 30g of sample in a 50mL glass vials tightly closed with a plastic cap. In the first test, the pure bio oil samples from all the mixtures of manure and wood shavings (pine and oak) were stored on a closed cabinet in the lab at ambient conditions for 8 months. Another set of test were conducted just on the bio oil from the mixture of 50% manure and 50% pine. In the test, 10wt.% each of methanol and ethanol was added to the bio oil and the samples were aged for 8 month at room temperature to assess its role in the stability of the oil. The viscosity measurements of all the samples were taken every week for the first month and then randomly for the rest of the aging period. The viscosity of the freshly produced oils and the aged oils were measured with a Brookfield DV-II+ Pro viscometer (Brookfield Engineering laboratories, Inc. MA, USA.). The measurements were performed at

60°C with Spindle SC4-18 and speed ranging from 1-30 rpm depending on the viscosity of the oil. The temperature was automatically maintained at the desired value with a Brookfield thermosel unit. The viscosity cup was however not vapor tight as it had a loosely fitting cap with a slotted hole in it for the spindle to pass through. Sample volume of 7ml was used and the viscosity readings of the instrument were allowed to stabilize within 5-15min before the value was recorded.

6.1.2.3 *FT-IR Spectrometry*

20mg of each sample was analyzed using Fourier-transform infrared (FTIR). The spectra were obtained over a range of 4000-650cm^{-1} using an IR spectrometer (Nicolet Avatar, 370 DTGS) equipped with a DTGS-KBR detector in multi-bounce horizontal attenuated total reflectance (HATR) mode. 64 scans at a 4 cm^{-1} resolution and a background gain of 4.0 were used. Data analysis was performed using the OMNIC 7.3 (Thermo Electron Corporation) software package.

6.1.2.4 *Carbon-13 nuclear magnetic resonance spectrometry (^{13}C-NMR)*

The oil was weighed to 2.0g and was dissolved in 2.5ml of DMSO in a 10mm sample tube. The ^{13}CNMR spectra were recorded on a Varian Unity 400 MHz NMR spectrometer. The observing frequency for the ^{13}C nucleus was 100.58MHz. The pulse width was 8.5µs, the acquisition time was 1.31s, and the recycle delay was 1s. The spectra were obtained with 1000 scans and a sweep width of 25.0 `MHz. Spectra were internally referenced to the solvent resonance.

6.1.2.5 *TG/DTG*

TGA was conducted on the oil using a TA Instruments Q600 SDT. 20mg of sample was placed in an alumina crucible and was subjected to thermogravimetric analysis with 20ml/min of N_2 as a carrier gas. The heating rate was at 5^oC/min from 25^oC to 700^oC. All the tests were repeated three times to ensure good reproducibility of the results.

6.2 Results and discussion

6.2.1 *Effect of pine wood shavings on bio oil viscosities during storage*

The viscosity changes of bio oils from manure, pine wood and the various mixtures are shown in Fig 6.1. The fresh bio oil from manure, wood and the mixture of 25% manure and 75% pine wood had relatively low viscosities compared to the mixtures of 50/50 and 75/25 wt.% of manure and wood. The manure oil was relatively more stable and the oil from the 50/50 mixture was the least stable. It is evident that the amount of wood in the mixture affected the oil viscosity when stored. Therefore the stability in the viscosity of the oils when stored is highly feedstock dependent. The manure oil which was relatively stable was found to be rich in nitrogenous compounds and aliphatic hydrocarbons but less in oxygenated compounds. FTIR and ^{1}HNMR analysis clearly indicated the presence of amide groups and methylene groups from the decomposition of protein and fatty acids in the manure (see chapter 4). Amide compounds exhibit strong hydrogen bonding and also the presence of lone pair of electrons on the nitrogen which interacts with the carbonyl π-bond makes it more stable than other carbonyl functional groups. In the presence of strong acids or bases amides hydrolyze to carboxylic acids or their salts respectively. Since the manure bio oils appear to have larger fractions of nitrogenous compounds and aliphatic hydrocarbons, these oils will be expected to be more stable than woody bio oils. The addition of wood to the manure introduces major decomposition products like hydroxyaldehydes, hydroxyketones, sugars, carboxylic acids and phenolic compounds. Some of these compounds are known to undergo several reactions including polymerization, esterification, condensation and etherification. Some of these reactions could potentially occur during storage. The FT-IR data in Table 6.1 showed that the relative intensities of some of the functional groups between the freshly produced and stored oils differed. In the fresh manure oil, the peak at 1705cm^{-1} due to carboxylic acid reduced in the stored oil (Fig 6.2). There were also reductions in peak intensities for amides, primary and secondary aliphatic alcohols, aromatic ethers and phenols. However, the methylene (CH_2) peak intensity increased during storage. Another FTIR spectra of a 50% manure and 50% pine oil showed a reduction in intensity for carboxylic C=O and primary alcohol group after 3 months of storage (Fig 6.3). The reduction in the alcohols and carboxylic peaks was probably due to esterification reaction. The increase in methylene peak intensities of some of the stored oils can be attributed to olefinic condensation (Diebold, 1999). Generally, the relative intensities of peaks associated with alcohols and amides decreased in all the oils. The phenolic O-H deformation peak at 1209cm^{-1} also decreased in all the oils except the mixture of 25/75 with no apparent change. The increase in intensity for the C=O stretch peak after 8 months of storage for the 50/50 and 25/75 mixtures oils may be products of oxidation reactions or possibly from the hydrolysis of acetals (Diebold, 1999). The CH_2 groups in the wood oil did not show any change in the relative intensity. It can therefore be inferred that the chemical reaction mechanism that lead to an increase in viscosity is feedstock dependent.

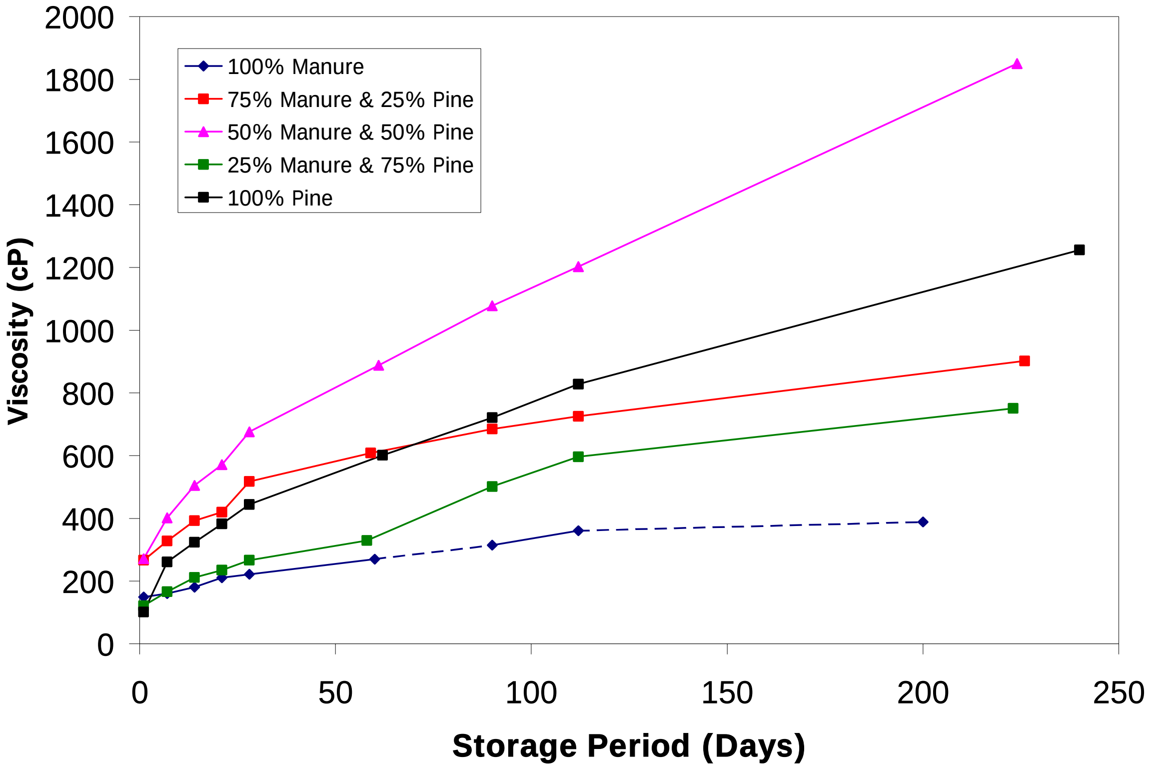

Figure 6.1 Effect of pine wood on aging rate of bio oil

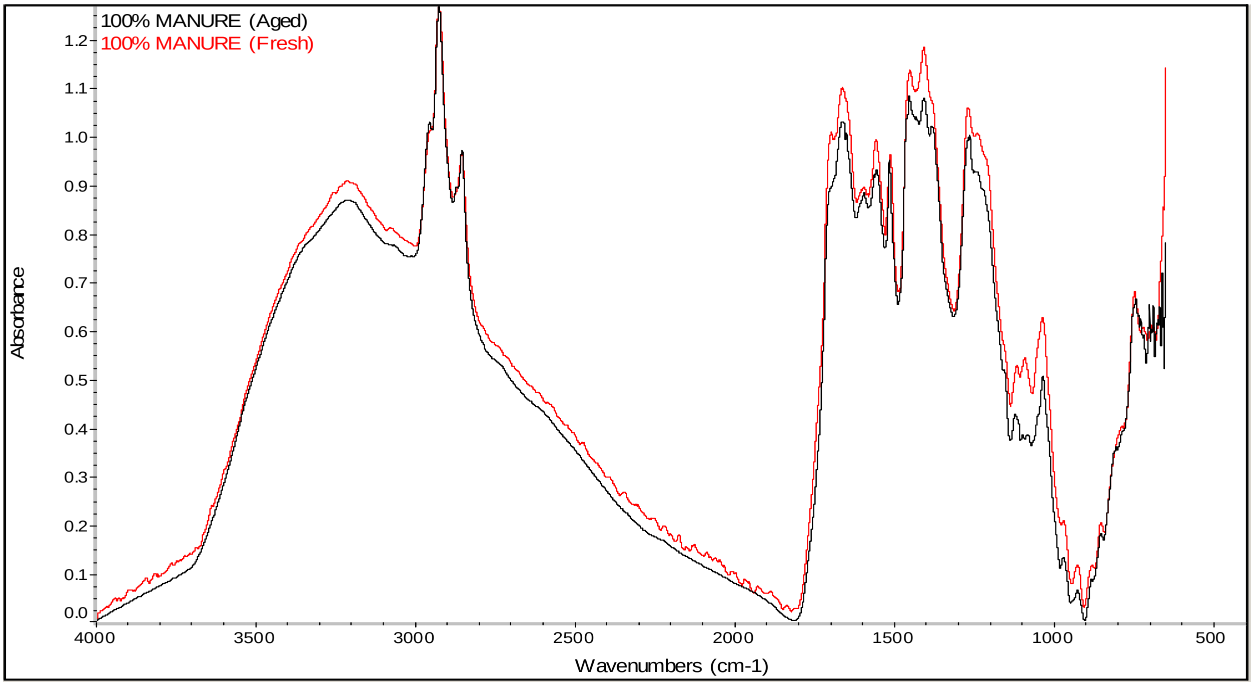

Figure 6.2 FTIR spectra of fresh and 8 months stored oil from 100% manure

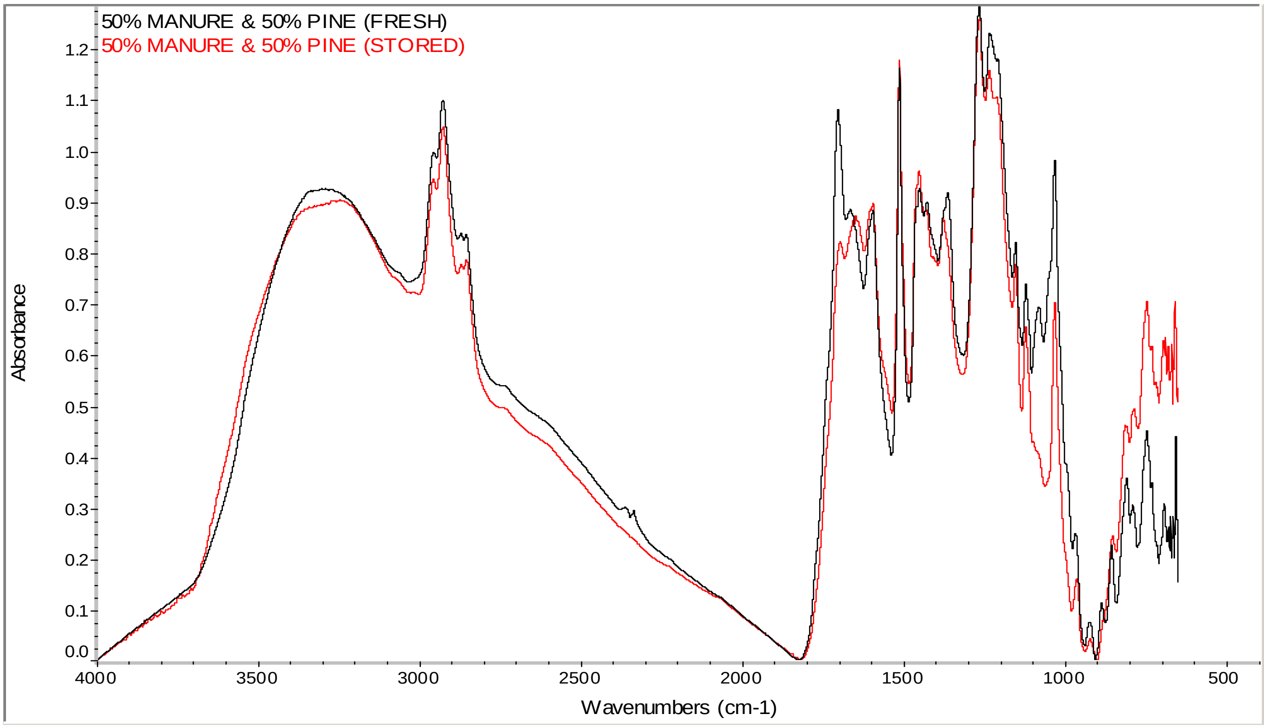

Figure 6.4 FTIR spectra of fresh and 3 months stored oil from 50% manure and 50% pine

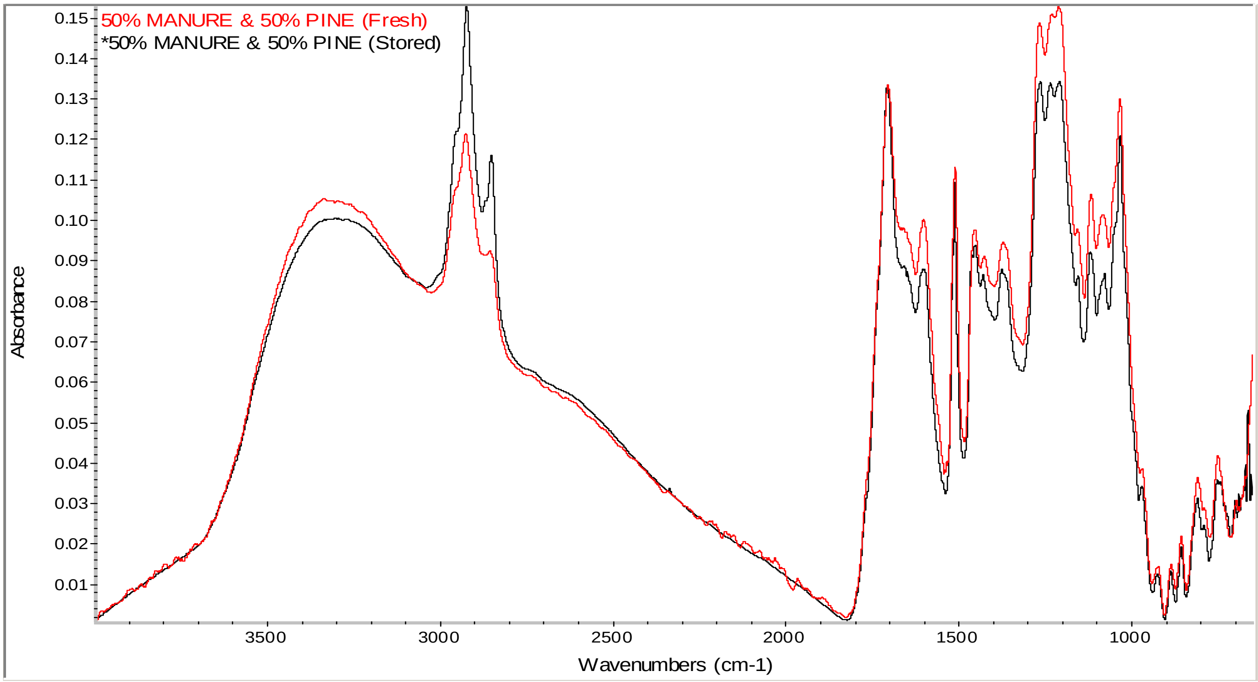

Figure 6.4 FTIR spectra of fresh and 8 months stored oil from 50% manure and 50% pine

Table 6.1

FTIR peak relative intensity of fresh and stored oils from manure, pine and their mixtures

Peak (cm^{-1})	Relative Intensity									
	100% Manure		75% Manure & 25% Pine		50% Manure & 50% Pine		25% Manure & 75% Pine		100% Pine	
	Fresh	Stored	Fresh	Stored	Fresh	Aged	Fresh	Aged	Fresh	Aged
1035	0.65	0.53	0.95	0.87	1.29	1.11	1.59	1.30	1.94	1.78
1117	0.55	0.45	0.77	0.68	1.03	0.84	1.22	0.94	1.4	1.19
1269	1.1	1.05	1.3	1.16	1.31	1.23	1.3	1.23	1.34	1.18
1556	1.03	0.98	0.95	0.88	-	-	-	-	-	-
1662	1.15	1.08	1.02	1.01	0.87	0.8	-	-	-	-
1705	1.05	-	1.13	1.06	1.16	1.22	1.12	1.20	1.22	1.18
2924	1.32	1.33	1.16	1.23	1.15	1.40	0.97	1.08	1.09	1.08
3209	0.95	0.91	0.89	0.99	1.05	0.92	1.03	1.05	1.25	1.22

6.2.2 *Effect of oak wood shavings on bio oil viscosities during storage*

The graph in figure 6.5 shows the viscosities of the oils from 100% manure, 100% oak wood and their various mixtures. It can be seen that, the oil from the mixture of 75% manure and 25% oak had relatively slow increase in viscosity. The oils from 100% oak and its mixture with 25% manure had similar increase in viscosity. The 50/50 mixture was the least stable with rapid increase in viscosity similar to the 50/50 manure/pine mixture oil. It is worth noting that in the oak mixture oils except for the 50/50 mixture had their initial viscosity below 180cP before storage. The viscosities of the stored oils from oak mixtures were lower than those from pine for the same storage period. This confirms that the storage and stability of the bio oils from the mixtures of manure and wood were not just dependent on the amount of wood but also on the type of wood. The difference between pine and oak on the aging of the oils were attributed to the chemical structural differences between hardwoods and softwoods. Firstly the weight-average molecular weight (*M*w) of softwood pyrolytic lignin is larger than that of hardwood samples and secondly softwood pyrolytic lignins have a larger tendency to polymerize, because unsubstituted positions ortho to the phenol hydroxyl exist in softwood lignins (Pandey, 1999). A study conducted by Scholze et al. (2001) on the characterization of the water-insoluble fraction from fast pyrolysis liquids showed that the molar mass of water-insoluble fractions of softwood-derived oils was larger than that of hardwood-derived oils. This phenomenon was attributed to the free C5 position for softwood lignins, which underwent polymerization reactions. Hence the presence of dimethoxyphenols in oak wood shavings can be a factor leading to the relatively low viscosity of the aged oils compared to pine. The presence of more extractives in pine than oak could also have affected the reactivity of the oils.

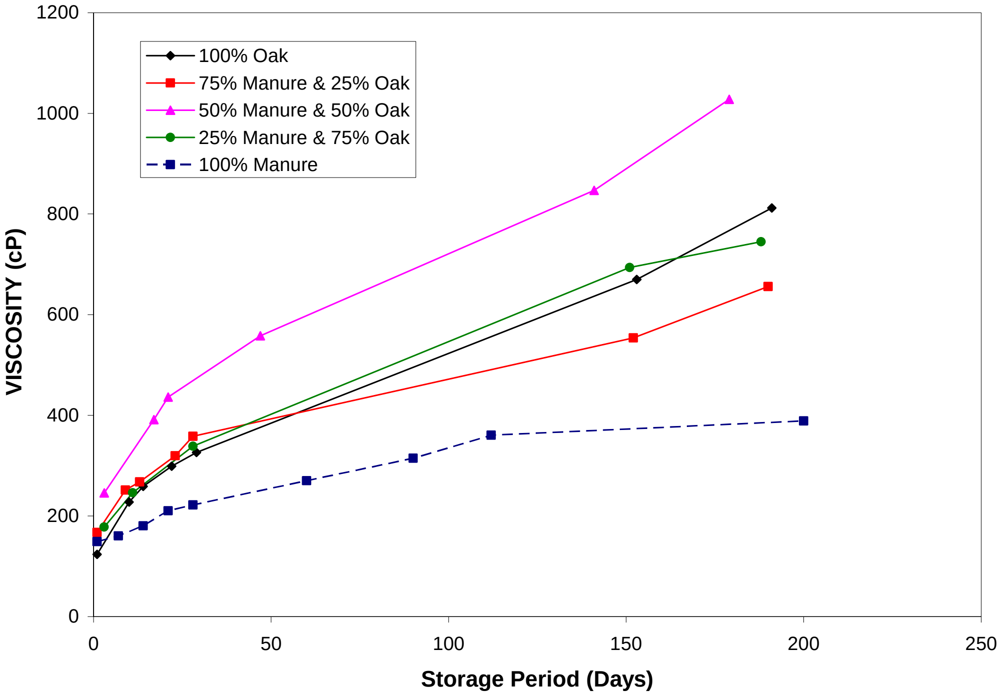

Figure 6.5 Effect of oak wood on aging rate of bio oil

6.2.3 *Effect of solvent addition on bio oil.*

The effect of 10% methanol and ethanol on the storage of the pyrolysis oil derived from the mixture of 50% manure and 50% pine wood is shown in figure 6.6 and 6.7. The two solvents were all added at the same weight percentage of 10%. After the addition of 10% methanol, the viscosity of the oil reduced by a factor of 6.4 and the 10% ethanol reduced it by a factor of 5.12. Both solvents were effective in slowing the aging rate of the bio oil, for roughly a period of 8 months storage, the raw bio aged at 2.38cP/day compared to 0.53cP/day and 0.66cP/day for the oils which had 10% ethanol and methanol respectively. The effectiveness of the solvent and the timing of their addition were also examined. The effect of methanol addition to the oil, both before and after storage at room temperature, was tested with oil that had relatively low initial viscosity (148cP). The bio oil was stored for approximately 8 months. As expected, the addition of 10% methanol reduced the viscosity from 148cP to 28cP before storage. At the end of the storage period, the viscosity of the bio oil with 10% methanol was 78.9cP. The oil that was stored without methanol, but had 10% methanol added after storage had a viscosity of 116 cP. The presence of methanol in the pyrolysis oil during storage results in an oil with a significantly lower viscosity than the addition of the same amount of methanol after storage. It is therefore advantageous to add the solvent before storage. The solvent addition can impact the bio oil viscosity in three ways; (1) physical dilution without affecting the chemical reaction rates of aging; (2) the lowering of the rate of reaction by the molecular dilution of the reactants in accordance with kinetic theory or by possibly changing the oil microstructure; or (3) the components in the pyrolysis oil could be reacting with the additives to become chain terminated either reversibly or irreversibly (Diebold and Czernik, 1997). As can be seen in figures 6.3 and 6.4, the addition of the solvent immediately reduced the viscosity by a factor of 5-6 indicating that there is a physical dilution effect. However the differences in the viscosities seen for the addition of methanol before and after storage also imply that chemical reactions that occur in the raw bio oil are slowed by the presence of methanol. The initial viscosity of the oil when freshly produced also affect the rate of reaction even with solvent present. It was observed that the lower the initial viscosity of the oil, the higher the effect of methanol addition. This was true for this study, the oil with initial viscosity of 148cP at room temperature aged at rate of 0.2cP/day with 10% methanol compared with the oil with initial viscosity of 315cP which aged at 0.66cP/day. Chemical reactions leading to viscosity increase obviously occur when the oils are stored. However specific reactions were not easily identified considering the complexity of the mixture of compounds present in the oil from the decomposition of wood and manure.

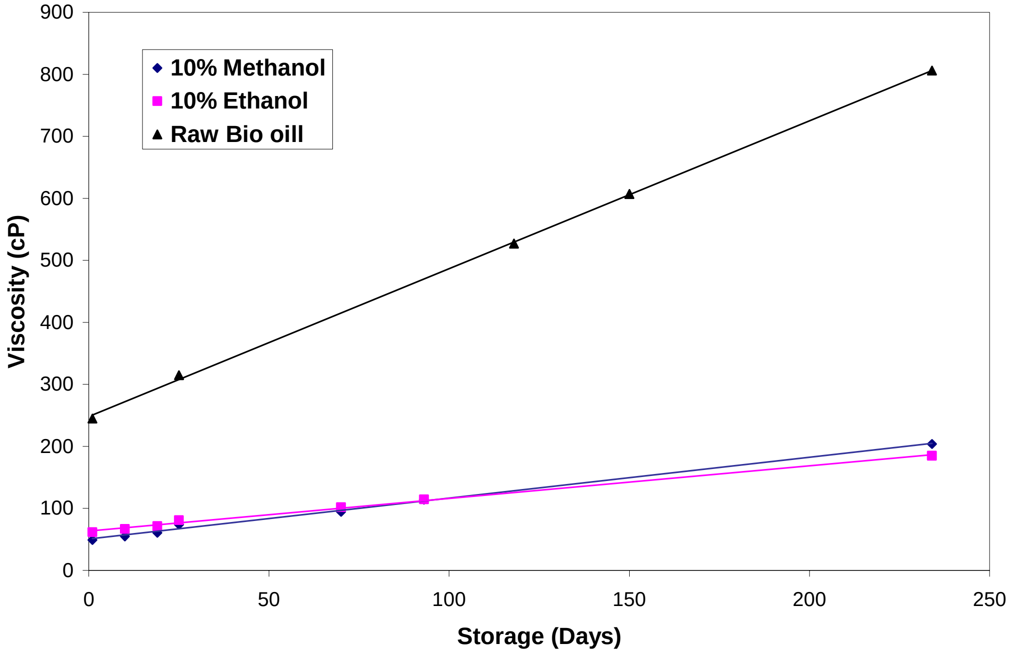

Figure 6.6 Effect of solvent addition before storage of 50% manure & 50% pine

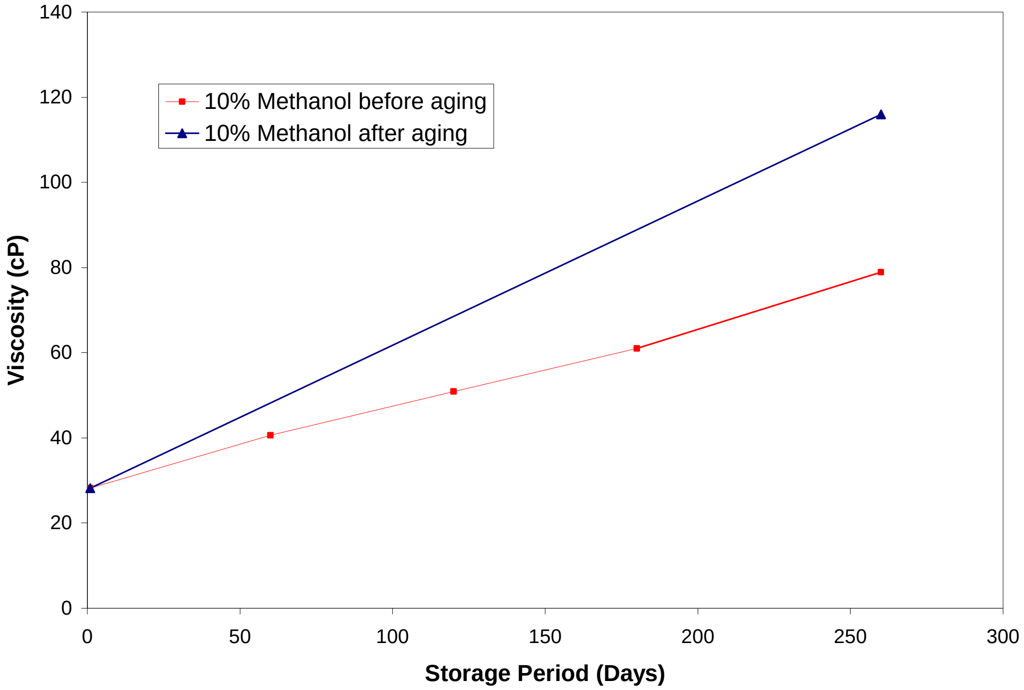

Figure 6.7 Effect of timing of methanol addition to pine/manure (50/50) bio oil.

6.2.3.1 *Spectroscopic analysis*

FTIR analysis of the functional groups showed some variations in the relative intensity of the amide, carboxylic/carbonyl, aliphatic hydrocarbon and the primary alcohols peaks for the stored raw bio oil and bio oils stored with both 10% methanol and 10% ethanol (fig 6.7). The amide peak at 1660cm^{-1} decreased during storage in all the oils. This suggests that amides are involved in reactions leading to viscosity increase and the addition of 10% of either methanol or ethanol did not have any effect on that. The carbonyl CO stretch at 1705cm^{-1} due to carboxylic acids and ketones however increased in the stored raw bio oil and decreased for the oils aged with methanol and ethanol. The increase in the carbonyl group in the raw aged oil may have been products of oxidation or possibly from hydrolysis of acetals (Diebold, 1999). The decrease in the carboxylic/carbonyl group for the oils stored with alcohols could possibly be due to esterification reaction. The relative intensity of the methylene peak at 2927cm^{-1} increased measurable when the oil was stored with no solvent but there was no apparent change in the oils aged with the solvents. Perhaps, the increase in methylene in the aged raw oil could be a product of reactions involving reactive unsaturated compounds or polymerization reaction. A semi-quantitative analysis of ^{13}CNMR spectra of the stored oils for both raw and solvent added oils (see fig 6.9) confirmed that the signal at δ 172.8 ppm and δ 21.9 ppm due to acetic acid decreased for oils stored with methanol and ethanol but there was no measurable changed in the raw bio oil. This further confirms the possibility of esterification reactions occurring in oils stored with methanol and ethanol. The carbonyl region from 190-210ppm showed an increase for the oils stored with the solvents. Diebold and Czernik (1997) also reported that a GC/MS analysis of pyrolysis oil stored with methanol had an apparent decrease in acetic acid and an increase in methyl acetate. The role of solvent in slowing aging by preventing the formation of larger molecules during storage in reacting with active groups like acids and aldehydes is not known. However, Diebold and Czernik (1997) found that the addition of solvent slows the polymerization of aromatics by dilution and making fewer reactive sites available for polymerization reactions at any one time. The figures 6.10 and 6.11 show DTG curves of before and after storage of the raw bio oil and oils with 10% methanol and ethanol. It can be seen that the addition of 10% of methanol and ethanol before storage clearly reduced the decomposition rate of the well defined peaks at 200 and 350^{o}C. The effect was attributed to the fact that, methanol and ethanol are good bio oil solvents and their addition to the oil dissolved some of the structured high molecular weight component resulting in a diluted system with low viscosity and hence the reduction in the decomposition peaks at 220, 350^{o}C and the disappearance of peaks at 89, 281 and 437 ^{o}C. However, after storage the raw bio and the oil with 10% methanol showed some similarities. The stored raw bio oil had a reduction in the rate of decomposition of the peak at 350^{o}C to about the same rate for both oils stored with solvents. It is therefore evident that during aging, chemical components in the raw oil corresponding to peak at 350°C under goes some chemical reactions that consequently increases the viscosity during storage. Additionally, the oil with 10% methanol showed the appearance of new peak at 303°C whiles the raw aged oil had the peak at 280°C shifted to 302°C. The oils stored with 10% ethanol did not show any drastic change except for the appearance of the peak at 280°C which was originally in the raw oil before the addition of solvent. The oil with 10% methanol had almost the same decomposition rate for the peaks at 220 and 457 °C as in the aged raw bio oil. It can be inferred that since the raw aged oil and the oil with 10% exhibited similarities in some of the peaks but with different decomposition rates, it effect on aging only slows down the formation of compounds leading to viscosity increase. The result shows that despite both solvent reduced the rate of aging, their chemical effect was different.

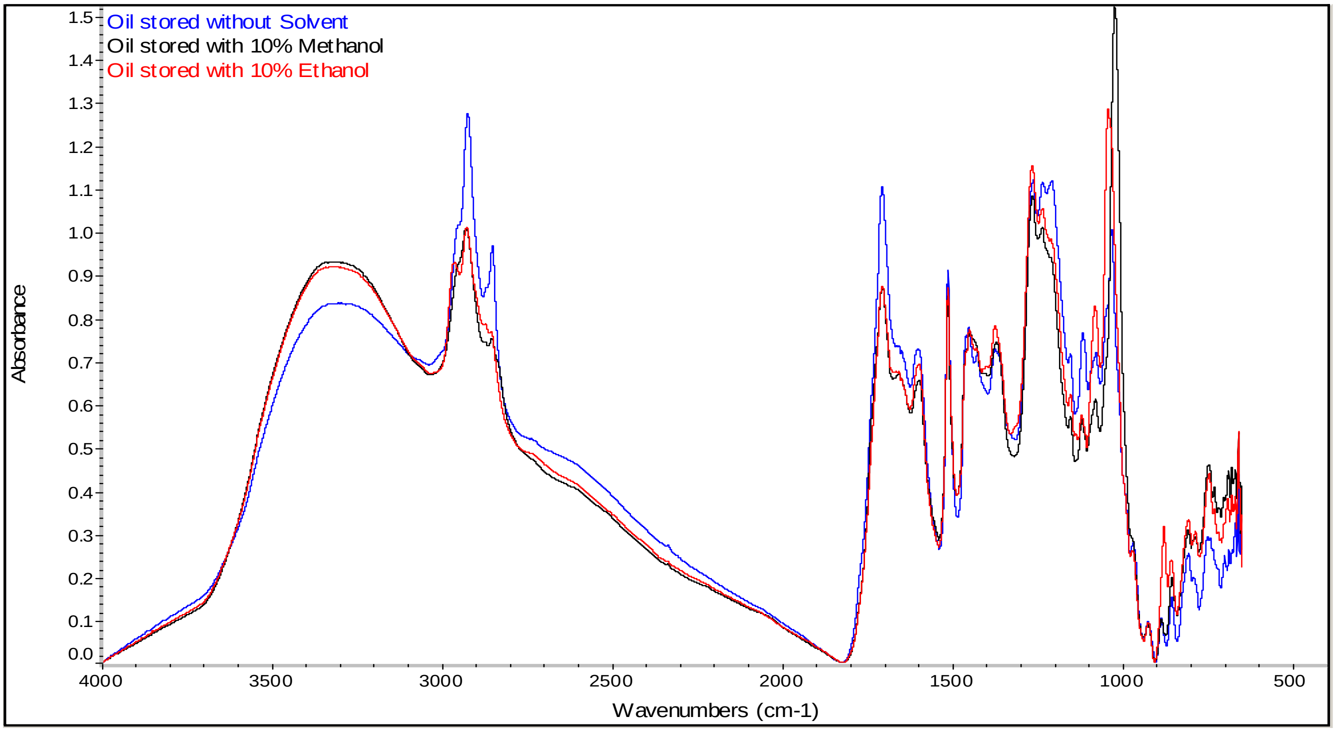

Figure 6.8 FTIR spectra of oil stored without solvent and oil stored with solvent

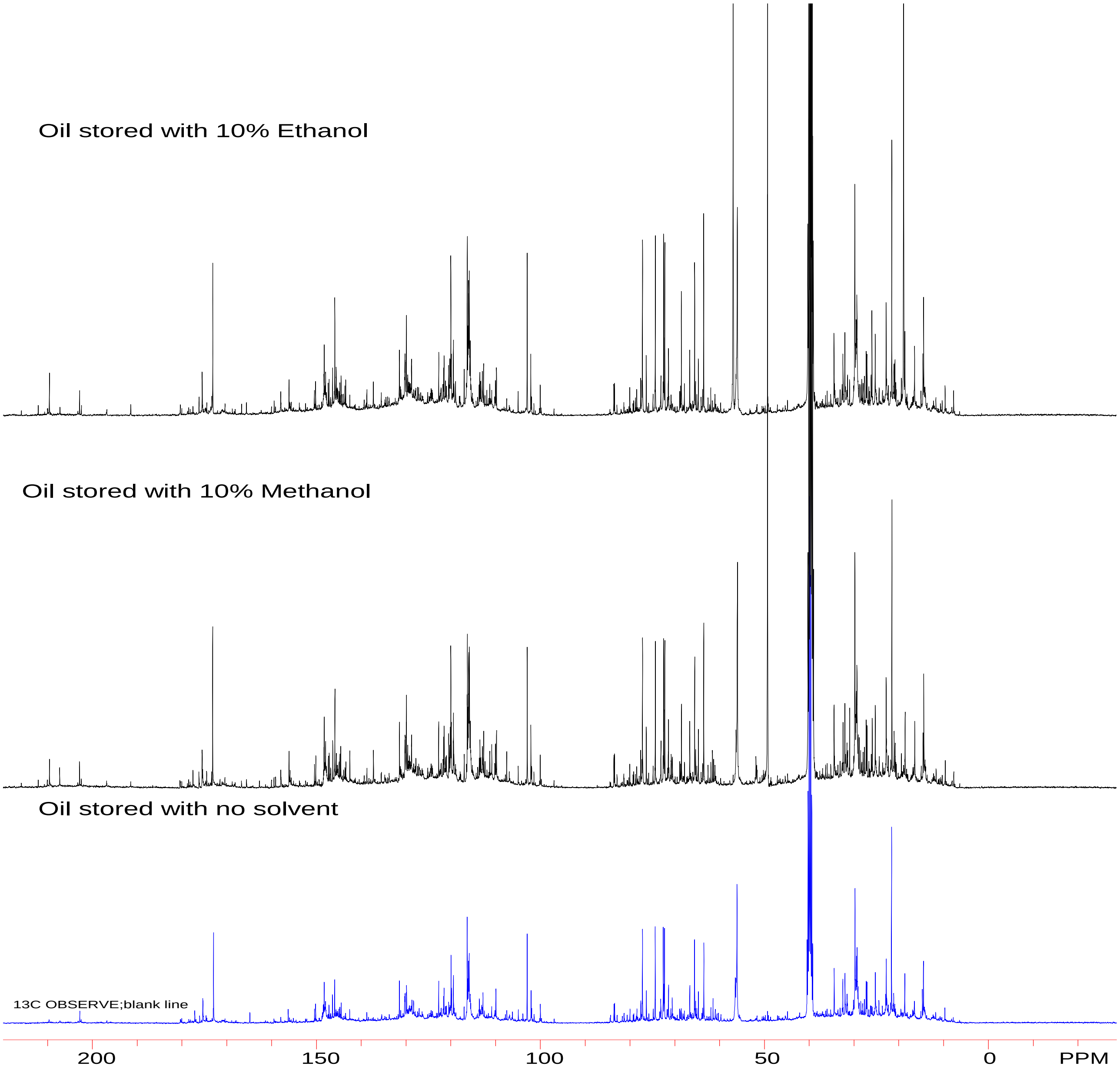

Figure 6.9 ^{13}CNMR spectra of 50% manure and 50% pine oil stored with 10% solvent

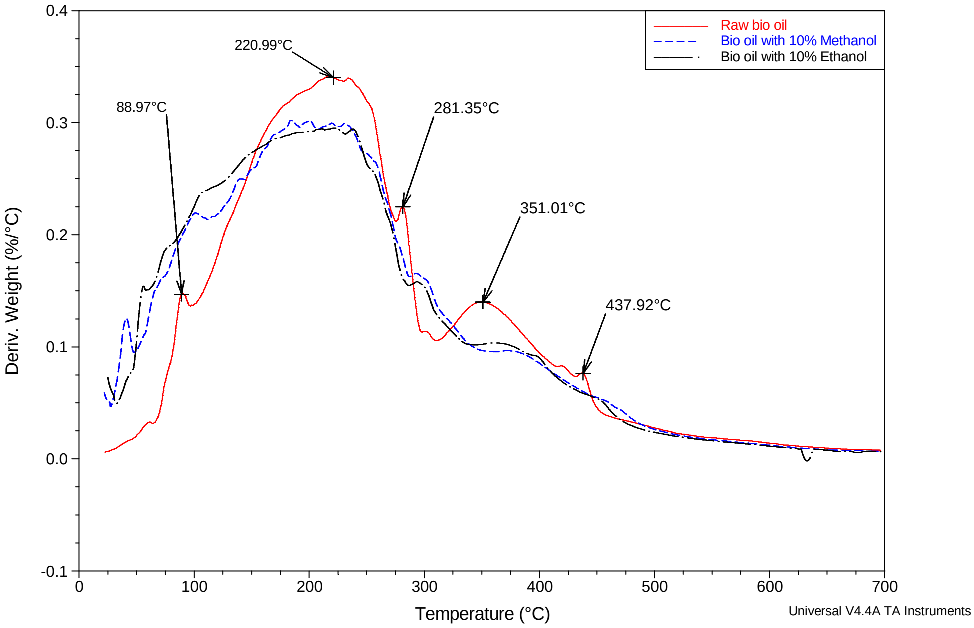

Figure 6.9 Effect of solvent addition before aging

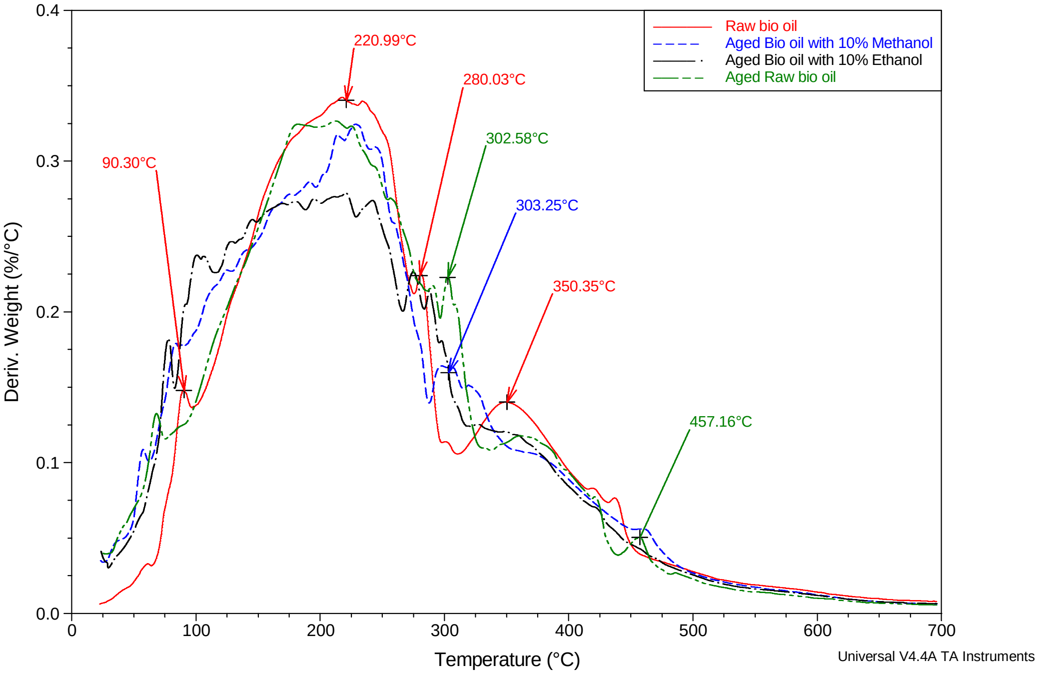

Figure 6.10 Effect of solvent addition after aging

6.3 Conclusion

Bio oils from manure which were rich in nitrogenous compounds and hydrocarbons were most were most stable than the mixtures. The introduction of oxygenated compounds from the addition of wood made the oils relatively unstable. The stability of the oils from the manure and wood mixtures were dependent on the amount and the type of wood (pine or oak) added to manure. Adding reactive solvents like methanol and ethanol effectively slowed the increase in viscosities. The addition of solvent to decrease the rate of aging appears to involve molecular dilution to slow the chemical reactions and the formation of intermediate products by the reaction of solvent with the pyrolysis oil. It was also shown that it is beneficial to add the solvent before aging, rather than after aging had taken place. In conclusion, the elimination of specific oxygenated groups of bio-oils derived from the mixture of manure and wood is necessary for improving their stability. These are mainly unsaturated groups like alkene, carbonyl and carboxylic functions, as well as guaiacyl groups.

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