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ASSESSING A HYDROTHERMAL LIQUEFACTION PROCESS USING BIOMASS FEEDSTOCKS

A Thesis

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
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in

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by
Jason S. Midgett
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The pages that follow this passage are the culmination of two and a half years of work in which at times I thought there was no end. To some these pages contain facts and nothing more. To me, however, it is a victory that I can share with everyone who provided me with the spirit to continue day in and day out. I would not have finished this thesis if I was not constantly lifted by the people surrounding me. I would like to thank my committee members, Dr. Chandra Theegala (major professor), Dr. Mailander, Dr. Thomas, and Dr. Spivey for their guidance and support of my work. I would like to thank all faculty and staff in the LSU Biological and Agricultural Engineering Department for their help during both my undergraduate and graduate years. I would like to extend a special thank you to all the personal at LSU Callegari Environmental Center for all their hard work conducting analyses for me. I am grateful for my parents, Lindsay and Sharon Midgett, and my brother Zachary for their moral support throughout all my life. I also want to thank my friends and roommates who provided me with relief from the study settings. I would like to thank my many undergraduate assistants for helping with the project. I would also like to thank Cigi Judd for her encouragement day in and day out to keep moving forward. To everyone thank you again for all that you have done I am grateful to have known and to have worked with you.

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ABSTRACT

The need to reduce the United States dependence on foreign oil has never been greater. In the past decade emphasis has been placed on developing new and/or improved means to procure clean renewable energy. Liquefaction, which was developed for coal conversion over a century ago is one of these areas. Liquefaction used for biomass conversions to bio-oils is grouped under the thermochemical conversion (TCC) area of energy conversion methods along with gasification and pyrolysis. This thesis discusses liquefaction experiments conducted using varieties of Louisiana biomass feedstocks. Dairy manure collected from the Louisiana State University Dairy Farm in Baton Rouge, was the main feedstock studied using various temperatures (250-350)°C and catalysts (Na_2CO_3, NaOH, and K_2CO_3) to determine optimum operating conditions for these two parameters. A bench scale 300 ml pressure vessel was used to conduct hydrothermal liquefaction (HTL) experiments. The HTL process yielded oil products (hydrocarbons) for all experiments. Temperature was found to have a significant influence ($P < 0.05$) on bio-oil energy content. One gram of sodium carbonate coupled with a processing temperature of 350°C is recommended as the optimum processing conditions for dairy manure in this study. However, the catalyst amount and type had had no significant effect ($P > 0.05$) on bio-oil when compared to no catalyst. Minimal differences were found when statistically comparing the types and quantities of catalysts with one another. Temperatures of at least 350°C are recommended for conversion of dairy manure to oil; although higher temperature trials were not conducted due to pressure vessel limitations. All additional feedstocks tested (tallowseed, switchgrass, pine sawdust, and poultry litter) yielded heating values that were comparable or higher than the 34.7MJ kg^{-1} reported as the maximum heating value for dairy manure oils. Oil yields are reported in the range of 20-33% on an organic basis.

CHAPTER 1: GLOBAL INTRODUCTION, LITERATURE REVIEW, AND METHODOLOGY

1.1 Global Introduction

Biomass is the world's fourth largest energy source worldwide, following coal, oil and natural gas. Theoretically, biomass has the capacity to provide 100 percent of the world's energy requirement; however, current production approaches and use of biomass for energy are not sustainable (Biomass Energy Facts). The general consensus among scientists is that biomass fuels used in a sustainable manner will result in no net increase in atmospheric carbon dioxide (CO_2). Biomass based fuels, if substituted for fossil fuels, have the capability to reduce global warming caused by increased atmospheric concentrations of CO_2. Additionally, many biomass sources are discarded improperly and cause increased pollution locally. The use of biomass feedstocks for alternative energy production would generate additional revenue for farmers instead of waste disposal problems, especially for animal production facilities.

The United States Department of Energy (DOE) reported 278 quadrillion BTU of bio-energy capacity available worldwide in 2004. However, only 2.7 quadrillion BTU were available for use in the United States, most from the pulp and paper industry using combined heat and power systems (Agency, 2004). Biomass conversion technologies are steadily improving and biomass energy production is increasing throughout the U.S. and world. Ethanol fuels derived primarily from agricultural crops are increasing dramatically. As of January 2006, the United States (U.S.) had 95 ethanol plants in operation, 14 more than the previous year, 8 being expanded, 31 more under construction, and many more proposed (Association, 2006). In 2005 the U.S. produced a record 3.9 billion gallons of ethanol; in August 2005 the national Energy Bill was put into effect, mandating production of 7.5 billion gallons per year by 2012 (Congress, 2005).

In 2004, the U.S. consumed approximately 140 billion gallons of gasoline, this number continues to rise with consumption exceeding 145 billion gallons in 2006 (Administration, 2006). The 7.5 billion gallons of ethanol mandated to be produced in 2012 only represents 2% of the current gasoline usage in the United States. Ethanol has 70% of the energy content compared to gasoline per unit volume and cannot solely reduce U.S. dependence on foreign oil; however, coupled with additional methods of procuring energy and fuels, from biomass, the U.S. can begin to reduce its dependency.

Diesel production from agricultural sources is on the rise as well. The biologically derived diesel fuel substitute is created by chemically reacting used cooking oils, vegetable oils, or animal fats with alcohol. In the United States most of the biodiesel is derived from soybean oil or recycled restaurant greases. In 2005, approximately 75 million gallons of biodiesel were produced, tripling the 25 million gallons produced in 2004 (Administration, 2006). Unfortunately, 75 million gallons of biodiesel only represents a small fraction of the roughly 40 billion gallons of diesel used each year for on-road transportation. This cleaner burning biodiesel fuel is currently available from 35 plants across the nation and at 450 retail pumps available to the public. It is reported that currently 65 new plants are under construction and 13 of the existing 35 are in an expansion phase. The potential production capacity of these plants is expected to be 1.4 billion gallons per year, or 3.5% of current diesel consumption (Board, 2006).

1.1.1 Thermochemical Conversion

Thermochemical conversion (TCC) technologies have been studied as early as the seventeenth century with the first patent issued in 1788 by Robert Gardner for his work in the gasification area. However, during the span from 1800-1970 the TCC technologies were “forgotten” due to an abundance of oil. When the TCC research continued, it began to focus on sources outside of wood and coal. In the late 70's and early 80's the Lawrence Berkeley Laboratory conducted research on biomass liquefaction. Initial experiments confirmed the processes ability to convert various biomass sources to oil products (Figueroa et al, 1982). However, once again the low cost of fossil fuels in the 1980's curbed major technological and commercial advances in this area.

TCC technologies include, but are not limited to, gasification, liquefaction, pyrolysis, direct combustion, and supercritical fluid extraction. Gasification and liquefaction continue to be heavily researched and used commercially throughout the world. Researchers are focusing efforts to attempt to understand the complex reaction mechanisms that occur during these processes.

1.1.2 Hydrothermal Liquefaction

Hydrothermal liquefaction (HTL) or direct liquefaction is a promising technology to treat waste streams from various sources and produce valuable bi-products such as bio-oils. A major problem with commercializing HTL processes for biomass conversion today is that it remains uneconomical when compared to the costs of diesel or gasoline production. High transportation costs of large quantities of biomass increase production costs, and poor conversion efficiency coupled with a lack of understanding complex reaction mechanisms inhibits growth of the process commercially.

Louisiana, in particular, has an abundance of waste streams and biomass producing areas in its large agricultural and industrial sectors. Specifically, manures generated and collected from Louisiana’s major animal farms have a potential to provide 50,000 homes with power if converted using a HTL process. This is a small percentage of the state’s energy requirements; however, if coupled with additional agricultural biomass sources, a significant reduction of coal, oil, and natural gas would be possible. Louisiana has enough land available to grow dedicated energy crops such as switchgrass and energy cane, which can provide additional sources of biomass. Energy crops are also beneficial because they will not compete with food sources. The research for this thesis was done in order to assess an HTL process using feedstocks available in Louisiana. This work begins to explore the effect that various operating parameters have on the production of oil-like products produced during the process.

1.2 Research Objectives

The overall goal of this research will be to assess the potential of a hydrothermal liquefaction process using biomass feedstocks available in Louisiana. This goal will be accomplished by meeting the following objectives:

1. Determining optimum operating conditions (process temperature and catalyst type/quantity) for the conversion of biomass to bio-oil products.
2. To characterize bio-oils produced during the process quantitatively and by heating value.
3. To determine the waste reducing potential of the process by chemical oxygen demand (COD)
4. To explore the feasibility of using various Louisiana based feedstocks in the process.

1.3 Literature Review

1.3.1 Thermochemcial Conversion Technologies

Biomass consists of a variety of materials with distinctive physical and chemical characteristics. Typically it is categorized into either woody, herbaceous, or crop residues. It may be converted to energy by many different processes, depending on the raw characteristics of the material and the type of energy desired. Biomass conversion processes are broken down into six main categories as shown below in Figure 1.1. Thermochemical conversion processes include three sub-categories: pyrolysis, gasification, and direct liquefaction. Pyrolysis is the thermal decomposition of organic matter occurring in the absence of oxygen. This process was studied as early as the 1920's (Hurd, 1929; Linnell, 1933). The products of pyrolysis can be gaseous, liquid, and/or solid. Flash pyrolysis describes the rapid, moderate temperature (400-600ºC) pyrolysis that produces liquids. Biomass is heated at rates of 100-10,000ºC/sec and the vapor residence time is normally less than 2 seconds. The oil products are maximized at the expense of char and gas. Pyrolysis processes typically use dry biomass sources.

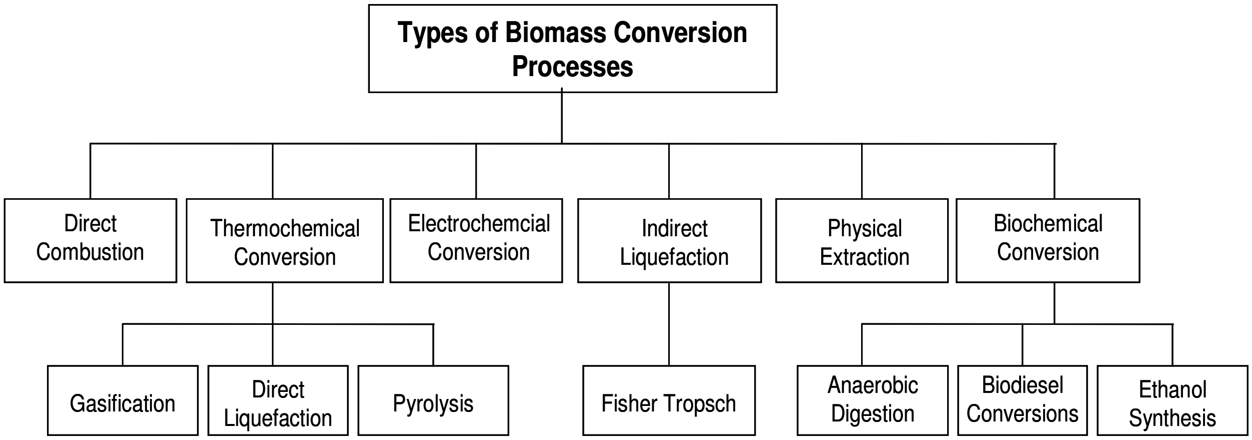


Figure 1.1: Classification of biomass conversion processes, note thermochemical conversion (TCC) and its three subcategories.

Gasification describes the process in which oxygen-deficient thermal decomposition of organic matter primarily produces synthesis gas. Gasification is a combination of pyrolysis and combustion. Gasification has more potential for near-term commercial application than other thermochemical processes (Brown, 1994). Benefits of gasification over combustion include: more flexibility in terms of energy applications, more economical and thermodynamic efficiency at smaller scales, and potentially lower environmental impact when combined with gas cleaning and refining technologies. An efficient gasifier will decompose high-molecular-weight organic compounds released during pyrolysis into low-molecular-weight, non condensable compounds in a process referred to as tar cracking. Undesirable char that is produced during gasification will participate in a series of endothermic reactions at temperatures above 800ºC which converts carbon into a gaseous fuel. Typically gaseous products include: CO, H_2, and CH_4. Fisher tropsch processes may be used to upgrade gaseous products to liquid fuels through the use of catalysts. Gasification requires feedstocks that contain less than 10% moisture.

Hydrothermal liquefaction was historically linked to hydrogenation and other high-pressure thermal decomposition processes that employed reactive hydrogen or carbon monoxide carrier gases to produce a liquid fuel from organic matter at moderate temperatures (300-400ºC). Liquefaction was first used to convert coal into liquid fuels; however, recently it has been used to describe any thermochemical process that yields a liquid or oil as its primary product. Liquefaction consists of direct or indirect processes. Indirect processes are not typically defined as a thermochemical process but as chemical upgrading, such as Fisher tropsch processes. Direct liquefaction involves rapid pyrolysis to produce bio-oils and/or condensable organic vapors. Carbonaceous materials are converted to liquefied products through a complex sequence of physical and chemical changes. Numerous reactions are responsible for the conversion to oil products these include: solvolysis, depolymerization, decarboxylation, hydrogenolysis, and hydrogenation. Solvolysis is a type of nucleophilic substitution where the nucleophile is a solvent molecule. This reaction results in micellar-like substructures of the feedstock. De-polymerization reactions lead to smaller molecules. Decarboxylation and dehydration leads to new molecules and the formation of carbon dioxide through splitting off of carboxyl groups (Demirbas 2000). When hydrogen is present, hydrogenolysis and hydrogenation of functional groups, such as carboxyl, keto, and hydroxyl groups also occur (Chornet and Overend, 1985). All of these reactions help to achieve the main purpose of liquefaction; to increase the H:C ratio of the oil product relative to that present in the feedstock. A decrease of the O:C ratio is also necessary to achieve hydrocarbon products. In biomass materials oxygen removal occurs via internal dehydration and decarboxylation reactions, which occur during the initial pyrolytic stages. Liquefaction reactions use uniform feedstock slurries in a liquid carrier, i.e., an aqueous system or specific solvent.

1.3.2 Hydrothermal (Direct) Liquefaction of Biomass

Research on direct liquefaction has been widely studied in the past, especially in the late 70's and early 80's for the purpose of alternative energy production. The feedstocks mainly consisted of wood and municipal solid wastes (MSW). Since then, many aspects of the process are still being studied: the type and condition of various feedstocks, the operating carrier media, and reducing reagents. More specifically researchers are focusing on various operating conditions, such as pH, processing gas, temperature, pressure, catalyst, retention time, solid content, gas to volatile solid ratio, and solvents for extraction or processing. In addition to studying these conditions researchers are still focusing efforts to understand the complex reactions that occur during the process. Biomass is complex by nature and varies by location. Developing a process that will handle many biomass sources, and one that is flexible to handle variations of biomass, is desired to increase the potential impact the process may have. Economics currently limit large scale biomass liquefaction treatment facilities and on-site treatment remains difficult and expensive. However, researchers continue to move forward with their studies and many alternative organic feedstocks have been processed through this technology as a means of waste management as well as renewable energy production.

One of the first HTL studies was conducted by Kranich (1984) using MSW as a source to produce oil. Three different types of materials from a MSW plant were used: primary sewage sludge, settled digester sludge, and digester effluent. Using a magnetically stirred batch autoclave with a hydrogen-feed system, slurry feed device, a pressure and temperature recorder, and a wet-test meter for measuring gas product, Kranich processed the waste sources. The feedstock was first dried then powdered. The wastes were also separated into different oil and water slurries and processed separately. Temperatures ranged from 295-450ºC with pressures up to 14MPa. Retention times also varied between 20-90 minutes. Hydrogen was used as the reducing gas with initial pressures up to 8.3MPa. Three types of catalyst were studied: sodium carbonate (Na_2CO_3), nickel carbonate ($NiCO_3$), and sodium molybdate (Na_2MnO_4). The slurry feedstock was injected into the reactor through a pressurized injector and the oil product was extracted by pentane and toluene. Results showed that organic conversion rates varied from 45% to 99% and oil production rates were reported from 35-63.3%. Gas products were found to contain H_2, CO_2, and C_1-C_4 hydrocarbons. The experimental results showed no significant differences between the applications of the three different catalysts. Kranich recommended that the water slurry system was not feasible for scale-up and considerations of a commercial scale process were confined to only the oil slurry system. It was also concluded that no further development work on hydroliquefaction of sewage sludge to oil was necessary.

Kranich's recommendation did not hold, mainly due to increases in crude oil prices and the need to find new technologies for energy procurement, and thus many studies on liquefaction of sewage sludge have since been conducted. Research has indicated that liquefaction is a feasible method for the treatment of sewage sludge wastes and has a high oil producing potential (Molten, 1985; Suzuki, 1986; Itoh, 1994; Inoue, 1997; and Furness, 2000). Today HTL research is still being conducted with sewage sludge; however, focus has shifted to include many varieties of biomass materials. Countless numbers of studies have been conducted on conversion of biomass to oil, including, a wide range of processing residues, agricultural crop residues, various manures, and dedicated energy crops.

Cellulose is an attractive feedstock due to its enormous abundance throughout the world; in fact, cellulose is the most abundant material in the world. Minowa et al. (1997 & 1998) conducted experiments using cellulose and glucose with and without catalyst. Using a conventional autoclave, slurry solutions of cellulose and glucose were heated in a nitrogen atmosphere to various temperatures between 200-350ºC. Results indicate that decomposition of cellulose started at 200ºC and increased with reaction temperature. Temperatures of 240ºC and below lead to formation of water soluble products. Temperatures above 240ºC allowed for formation of oil, char, and gas. At temperatures above 260ºC non-recoverable char began to form decreasing the carbon balance. The maximum oil yield was obtained at 280ºC; increasing temperatures lead to increasing char and gas formation but lower oil yields, indicating a secondary decomposition of oil to char and gas. The results suggest that water-soluble products and oil are intermediates for char formation. Minowa and coworkers concluded that the use of catalyst's, specifically, sodium carbonate caused the suppression of the secondary decomposition of the oil phase. The use of a nickel catalyst could catalyze the steam reforming reaction of aqueous products as intermediates and the methanation reaction. However, nickel or metal based catalysts tend to promote gas production instead of oil production. Figure 1.2 depicts a proposed reaction model of the role catalysts may play in the conversion of cellulose to oil. It is important to note that hydrolysis plays an important role in the decomposition of cellulose to sugar; Minowa states that hydrolysis is the first reaction that occurs during the liquefaction of cellulose as well.

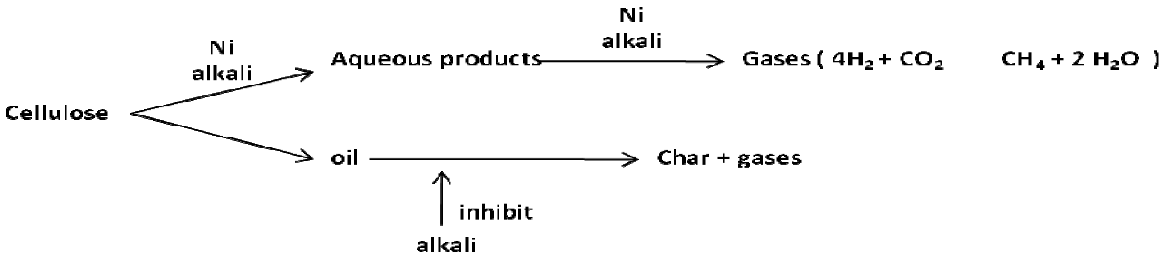


Figure 1.2: Proposed reaction for metal and base catalysts roles during an HTL operation. (Minowa, 1997)

The liquefaction of Indonesian biomass residues was the topic of another study conducted by Minowa and his colleagues (Minowa, 1998b). In this study 18 different kinds of biomass found in Indonesia were liquefied to heavy oil in hot-compressed water with sodium carbonate as the catalyst at 300ºC and 10Mpa. All residues tested were converted successfully to oil or gas products. Oil yields were reported in the range of 21-36% on a carbon basis with calorific values of 25MJ kg^{-1} calculated by elemental analysis using Dulong's formula. The highest yields of oil products were from the shells of coconuts and oil-palms. The shell of the coconut also yielded the highest calorific value at 27.4MJ kg^{-1}. Coconuts and oil-palms contain a higher percentage of natural oil, which may explain the higher yields. In a recent study Veski (2005) and colleagues used three variations of liquefaction to convert reed to an oil product. Semicoking at temperatures up to 520ºC (Fisher retort), water conversion, and catalytic hydrogenation at 380ºC were tested. The processes differ from traditional liquefaction mainly because of the higher operating temperatures. The highest yield of liquid product was obtained using the Fisher retort (25.7%). The water conversion method (15.4%) and the hydrogenation method (8.3%) both produced oil fractions, however, most of the material ended up in the coke fraction.

1.3.2.1 Catalyst Usage

Catalyst use during the liquefaction of biomass has been the focus of many studies. The aim is to improve the yield and heating values of oils produced during the process. Alkali catalyst used in the process is proposed to limit the amount of secondary reactions of the oil phase to char during processing. Other catalysts may be used to promote fisher tropsch reactions, which favor production of the gas phase. These catalyst types promote the return of gas produced during the process back to the liquid fraction. Ultimately the characteristics of the biomass used in the process dictate the types of catalyst that will be effective.

Ogi et al (1985) studied the effect of various salts and bases ($CaCO_3$, $Ca(OH)_2$, NaOH, HCOONa, NaCl, K_2CO_3, KOH, and HCOOK) at temperatures of 300-350ºC and discovered that up to 50% heavy oil-like products were obtained in the presence of base catalysts. Nickel catalyst, was used by Fang et al (2004), nickel promoted conversion to gas (74%) instead of oil; while Na_2CO_3 yielded an oil fraction of 43% on an organic basis. RbOH and CsOH were used for the catalytic hydrothermal treatment of pine wood (Karagoz, 2005). Again both base catalysts hindered the formation of char and favored the formation of oil products. The catalytic process produced mainly phenol compounds and benzenediol derivatives. In another study conducted by Karagoz (2006) the effects of K_2CO_3 and the biomass/water ratio were tested using sawdust. Biomass converted in the absence of water lead to much higher gas formation. Little difference is noted for all results (oil yield and heating value) between a sample of 5g biomass to 30ml water and a sample of 10g biomass to 30ml water. Potassium carbonate had effects similar to that of other base catalysts. A solution of 0.94 M K_2CO_3 yielded 96% conversion of organic compounds versus a .235 M K_2CO_3 solution yielding only 64% at the same operating conditions.

1.3.3.2 Mechanisms of Catalyzed Biomass Liquefaction

A study on the mechanisms of biomass liquefaction and pyrolysis reactions was reported by Demirbas (2000). Mechanisms have been poorly studied in the past due to difficulties in sampling the slurry during the process. The reaction mechanism for a sodium carbonate-catalyzed liquefaction of carbohydrate in the presence of carbon monoxide is described below. First the reaction of sodium carbonate and water with carbon monoxide to yield sodium formate.

$Na_2CO_3 + 2CO + H_2O \rightarrow 2HCOONa + CO_2$

Dehydration of vicinal hydroxyl groups in a carbohydrate to an enol, followed by isomerization to ketone.

$-CH(OH)-CH(OH)- \rightarrow -CH=C(OH)- \rightarrow -CH_2-CO-$

The reduction of newly formed carbonyl group to the corresponding alcohol with formate ion and water.

$HCOO^- + -CH_2-CO- \rightarrow -CH_2-CH(O^-)- + CO_2$

$-CH_2-CH(O^-)- + H_2O \rightarrow -CH_2-CH(OH)- + OH^-$

The hydroxyl ion reacts with additional carbon monoxide to regenerate the formate ion

$OH^- + CO \rightarrow HCOO^-$

According to the mechanism described above, deoxygenation occurs through decarboxylation from ester formed by the hydroxyl group and formate ion derived from the carbonate.

Demibras also describes the reactions that alkali salts catalyzed. Sodium carbonate and potassium carbonate can act as catalysts for hydrolysis of macromolecules, such as cellulose and hemicelluloses, into smaller fragments. The fragments are then broken down further to smaller compounds by dehydration, dehydrogenation, deoxygenation and decarboxylation. The compounds then rearrange through condensation, cyclization and polymerization leading to new compounds. Some of these new compounds are aromatic hydrocarbons.

These proposed reactions are general and the type of biomass will dictate the type of processes or reactions required to breakdown and rearrange molecules. The more complex the raw biomass is chemically, the more complex the reaction mechanisms required, and thus the increased difficulty in determining them.

1.3.2.3 Swine Study

A research group at the University of Illinois at Champaign conducted one of the more complete liquefaction studies of manures available today (He et al, 1998, 2000a, 2000b, 2001a, 2001b). Using solely swine manure as their feedstock they have studied the majority of the parameters associated with liquefaction processing. These include temperature, retention time, types of process gas and initial pressure, feedstock pH, total solid content, agitation, gas to solid ratio, and included waste reducing characteristics.

The group used a 1.8 liter batch reactor with extreme operating conditions of 375ºC and 34.5MPa. The reactor was equipped with systems for: agitation, temperature, pressure and safety control; pressure and temperature monitoring, and process gas introduction. The feedstock was collected from the partial slotted floor of a swine finishing room. The total solid content of the fresh manure was 27.4% by weight and had a natural pH of 6.06. The feedstock was prepared individually for each test by adjusting the total solids content with tap water.

Many conclusions were made from testing the various parameters through the 100 plus experiments conducted by the group. The feedstock pH was tested in a range from 4-10 by adjusting raw the pH. High pH values favored oil production; however, the benzene solubles of the oil product was 10% lower than those at pH 4 and pH 7. Benzene soluble was used to determine how “oil-like” the products were. The effect of the amount of initial process gas was also studied. The carbon monoxide to volatile solid ratio (CO/VS) varied from 0.07-0.25 in the experiments. The oil production efficiency increased from 55-70% as the CO/VS ratio increased from 0.07 to 0.25, respectively. However, the total COD reduction of the process decreased by

50%, while the CO/VS ratio increased to 0.25. The group recommended a CO/VS ratio not higher than 0.1. The total solid content of the manure was tested and found that the higher the solid content, the higher the oil production and COD reduction efficiencies. Unfortunately, the handling of the feedstock slurries becomes difficult at solid contents higher than 20% for swine. Solid content of 20% was recommended for the processing and handling of the swine slurries.

Alternative process gases were also studied to determine effects on oil production and waste reduction. By replacing costly reducing process gases, such as CO, with inert gases, such as compressed air, a vast improvement in the overall economics of the process will occur. Five separate gases (CO, H_2, CO_2, N_2, and compressed air) were tested. It was concluded from the study that the addition of a process gas, inert or reducing, was necessary for the process to yield an oil product. High operating pressures created by water vapor only (without the use of a process gas) did not lead to oil formation. Nitrogen and carbon dioxide affected the biomass conversion process and had an effect on oil production efficiency similar to CO. The oil quality using inert gases nitrogen (N_2) and carbon dioxide (CO_2) was lower than reducing gases of carbon monoxide (CO) and hydrogen (H_2). The process yielded an oil product using compressed air as a process gas, but the quality of the oil was poor. The COD reduction efficiencies were virtually the same among all gases tested; CO and N_2 yielded the best results for the process.

The operating temperature and retention time are two key parameters affecting the oil production. He and associates tested operating conditions from 275-350ºC and 5-120 minutes. Temperatures of at least 285ºC were needed for the formation of oil products and temperatures of 335ºC and higher lead to higher solid char formation. The suggested operating temperature and retention time for the process are 295-305ºC and 15-30 minutes.

The research group used ultimate elemental analysis (CHN), to estimate heating values. Dulong's formula was used for calculation of the values. The average heating value of the oil products was 34.76MJ kg^{-1}. The group did not test catalyst effects on the process because they stated enough minerals and elements existed in the raw manure. The highest reported COD reduction rate was 72%. The highest oil yield was 63% of the initial volatile solids in the raw slurry. The benzene solubility of the oil product was reported as high as 90%. The overall consensus from this research is that the liquefaction of swine manure to reduce waste and produce an oil product is feasible if scaled up to a continuous process.

1.3.3 Methods of Biomass Treatment

Biomass wastes are continuing to create increasing pollution problems across the U.S. Liquid and solid animal wastes, sewage sludge, and municipal solid wastes generate considerable gas and odor, harbor disease, and contribute to environmental problems. Additional sources from processing facilities, such as wood wastes accumulate in landfills and cause storage problems locally. Animal confinement facilities and urban areas are growing in size; these effects are becoming more concentrated, resulting in millions of dollars being spent annually on transportation, storage, and treatment of the waste with no benefits other than decreasing pollution in the urban areas. Many traditional treatment options exist and are currently employed throughout various treatment facilities across the United States. Hydrothermal liquefaction uses high-liquid content wastes as an energy source and provides a significant waste reduction potential and could be a solution to pollution control for biomass wastes. (Appleford).

1.3.3.1 Typical Use and Problems Associated with Dairy Manure

Dairy manure that is collected from dairy farms is typically disposed of via field application as a fertilizer. Sometimes field application is in excess of the nutrient assimilation capacity of the soil, leading to problems associated with nitrogen and phosphorus runoff (Ribaudo, 2003). Dairy manure is collected in both solid and liquid form. In operations using tiestall barns, manure is collected in gutters behind the cows and removed by a barn cleaner. In operations using freestall barns, manure is either scraped to the end of the barn for temporary storage or (in barns equipped with an alley way) flushed and deposited in a storage pit or lagoon. Milking parlor wastes are dilute (up to 50% of the waste volume but only 15% of total solids) and contain little manure, but contain residual milk and may include quantities of cleaning products. Some collection pits permit separation of solids from the liquid portion of the manure (EPA, 2001). Liquid storage systems are more common in the southern U.S. (66% of operations in 2000) relative to the northern U.S (29% of operations) (Ribaudo et al, 2003).

The problem of excessive application of manure for fertilizer is particularly important for large dairy operations that store manure wastes as liquids, due to the large volumes of manure produced and the frequency of manure collection. The USDA identified 68 counties where manure nitrogen levels exceed the soil nutrient assimilative capacity of all the county's crop and pasture land (primarily in North Carolina, northern Georgia, Alabama, central Mississippi, western Arkansas, and California) and 152 counties where the manure phosphorus levels exceed the county assimilative capacity (concentrated in eastern North Carolina, northern Georgia, northern Alabama, western Arkansas, central California, and western Washington). Additionally, 155 and 337 counties were identified where manure nitrogen and phosphorus levels, respectively, exceed half of the county soil nutrient assimilative capacity (Gollehon, 2001; Ribaudo, 2003; Ribaudo, 2006). These counties are most in need of alternative waste management methods.

1.3.3.2 Manure Treatment

There are physical and chemical treatment options available depending on the manure type and quantity available for treatment. The physical treatment of manure in conducted through liquid-solid separation by gravity sedimentation or various mechanical methods such as screening, filtering, and centrifugation. Concentrating to reduce waste volume and solids for further treatment or re-use is achieved through evaporation. Concentrated sludge can be pelleted and dried for easier transportation and utilized as a fertilizer for greenhouses or gardens. Chemical treatments are usually conducted to disinfect, control odor, and adjust pH. Normally, chemical precipitation, flocculation, incineration, and pyrolysis are used as treatments; however, physical and chemical processes are typically used together. Flocculation and coagulation processes help to control manure effectively in terms of solid and liquid separation, but does nothing for odor and runoff issues. Biological treatments are needed to break down organic matter.

Biological treatment processes include aerobic and anaerobic lagoons or digesters, oxidation ponds, compost piles, and various filtration methods. The most common treatment process for manures in North America is the combination of lagoons and digesters coupled with composting. Digesters convert raw manures into a less harmful sludge material, but more importantly produces a valuable energy by-product, biogas. Biogas is a mixture composed of 40% CO_2 and 60% methane. Large scale farms are typically more economical for digester treatment, however, technological improvements are beginning to allow relatively small animal operations to benefit from digester treatment.

Aerobic digestion (not lagoon treatment) is another waste treatment process and its advantages include reduced odor emissions, BOD removal, and the elimination of many pathogens. Large surface areas are needed to treat manures aerobically because of the dissolved oxygen requirement in the liquid manure, which is only achieved at the air-liquid interface (Boyd, 1998). Aerobic treatment processes for manure is still under investigation and new technology is on the horizon.

Composting is a biological treatment process for whole manure. It can be applied as an aerobic or anaerobic process. Typically the anaerobic process is avoided if possible because of odor. The operating factors affecting the composting process include moisture and oxygen content, organic composition, the ratio of carbon to nitrogen, the degree of mixing, and retention time. The main products of aerobic composting are CO_2, water, and heat. The high temperatures drive off pathogens, most weeds, and insects, making the compost suitable for land application. Composting is a state-of-the-art technology used in solid waste treatment, especially in MSW treatment. The composting of manures has been studied by many researchers and proven to be an effective treatment (Choi, 1999; Lopez and Baptista, 1996; and Lau et al. 1992).

1.3.3.3 Additional Waste Treatments

Crop residues in Louisiana continue to be burned off fields after harvesting with the exceptions of farmlands close to large cities where EPA or DEQ restrictions prevent it. Burning is the cheapest way to rid cropland of decomposing residues, and also acts as a fertilizer providing vital nutrients for next year's crops. However, this burning poses several environmental problems; air quality issues and harmful run-off into water sources. Crop residues must be removed from top soils or they will hinder the growth of the next season's crops through de-nitrification of the soil by the decomposing biomass. Currently research is being conducted to produce chemicals that will aid in quick decomposition instead of field burning. Tons of biomass is wastefully burned across the state because of high costs in transportation and collection. The addition of these new chemicals may also increase run-off pollutants. One possible solution is to collect this biomass and use it in a thermochemical conversion process.

1.3.3.4 Liquefaction Treatment Potential

Liquefaction research has not only been conducted as a means of alternative energy production but also as an organic waste management process. The early study by Kranich (1984) concluded that using MSW as a feedstock for conversion to oils on a commercial scale was not feasible. Two years later Suzuki et al. (1986) studied the direct thermochemical liquefaction of sewage sludge in an attempt to develop a new method for waste disposal. Experiments were carried out using a 300-ml autoclave and oil yields increased with reaction temperature. Heavy oils contained ~70% carbon, 7-9% hydrogen and 21-25% oxygen. Corresponding heating values of the oil products were 31-33MJ kg^{-1}. The process was determined to net energy at temperatures of 275ºC or higher. The group concluded that operating at 300ºC was most efficient because the oil production efficiency was maximized. They also concluded that the treatment of sewage sludge by direct thermochemical liquefaction could be a profitable alternative means of sludge disposal.

Itoh et al. (1994) reached a similar conclusion by using a scaled-up process for production of oil from sewage sludge by direct thermochemical liquefaction. They stated that liquefaction is an economical solution to sludge disposal. A demonstration plant with a capacity of processing up to 5 tons/day of dewatered sludge was operated at temperatures up to 300ºC and 10MPa. Conversion of organics in the sludge to oils was ~50% heavy oils of which one quarter was separated by high-pressure distillation. Heating values of 37-39MJ kg^{-1} were achieved. Estimations based on a practical scale concluded that 1.5 tons/day of separated heavy oil could be produced as surplus energy through the treatment of 60 tons/day dewatered sludge. Inoue et al

(1997) also conducted experiments on sewage sludge to determine the effects a liquefaction process has on nitrogen. Partition of nitrogen to oil occurred at temperatures greater than 150ºC. As reaction temperatures increased solubilization and decomposition of nitrogen increased lowering the percent of nitrogen in oil phases. Organic nitrogen decomposed to NH_4-N with increasing reaction temperatures. Nitrogen is a problem not only with ground and water pollution but excess nitrogen in the oil products produce nitrous oxides when burned which negatively affect air quality. It is also expensive to remove the nitrogen after or during processing because of the additional equipment needed.

Liquefaction research on garbage was conducted by Minowa et al. (1995). Garbage consisted of cabbage, boiled rice, boiled and dried sardines, butter, and the shell of short-necked clam. This mixture yielded a water content of 90%wt and was heated under pressurized nitrogen at 250, 300, or 340ºC for 0.1, 0.5, or 2 hours, with or without sodium carbonate as a catalyst (0-4% on a dry solid basis). Oil production efficiency and its properties strongly depended on the catalyst addition and reaction temperature, while holding time showed no significant effect. The highest oil yield (27.6%) on an organic basis was obtained at 4% wt catalyst, 340 ºC, 18MPa pressure, and 0.5 hours holding time. The elemental compositions of carbon, hydrogen, nitrogen and oxygen were 73.6%, 9.1%, 4.6%, and 12.7%, respectively. The calculated heating value of the oil product was 36.0MJ kg^{-1}.

Agricultural wastes have also been the studied by liquefaction treatment, such as sugar cane bagasse. Lancas et al. (1999a, 1999b) presented the results of direct catalytic liquefaction of sugar cane bagasse, in aqueous medium and ethanol. The experiments were conducted with and without catalysts. No catalyst use showed that the conversion of sugar cane bagasse into liquefied products was not influenced by the pH of the reaction mixture. The use of different catalysts such as 10% palladium on activated carbon permitted increases in the yields of liquefied products up to 92.4%. The researchers conducted experiments on 12 different types of catalysts systematically. All catalysts converted bagasse into liquefied products; the highest conversion yield was observed when a nickel catalyst on SiO_2-Al_2O_3 was used.

Olive oil food processing wastes, specifically the olive oil, solid wastes, and mill wastewater, were treated to reduce the organic waste content and by recovering it as energy. The research group reports that applying a thermochemical conversion process to olive wastes would yield a 96% reduction in the energy costs for a typical olive oil milling industry unit. They also report that up to an 85% reduction in the organic discharge load is possible (Taralas, 2005).

Chemical manufacturing plants may also benefit from using liquefaction as a wastewater treatment method. A continuous feed system with consistent operating conditions of 350ºC and 21MPa with processing rates between 4 and 15 L/h were used by Elliott et al. (1999) to treat chemical wastewaters. Results showed aqueous effluents with low residual COD (as low as 100 ppm) and a product gas of medium-to high BTU quality have been produced continuously from organic chemically contaminated sources. Results also show that careful monitoring and control of feedstock trace components (e.g., calcium, sulfate, and chloride) are critical for maintaining long-term catalyst activity.

1.4 Impact Potential of HTL Process in Louisiana

The LSU AgCenter (2006) reports a potential of 6,620 million kWh or an energy equivalent for powering 367,799 homes from various biomass sources throughout the state of Louisiana. Some of this energy is already installed, for example, Agrilectric a 13 megawatt plant in Lake Charles, uses rice hulls in a gasifier to produce electricity. They produce enough electricity to power 6,000 homes from 300 tons of rice hulls per day. Other examples include landfill gas projects, bagasse burning at sugar mills, and cogeneration of wood waste at paper mills. The AgCenter also reports a potential of 395 million kWh of power potential from dairy manure, which is enough electricity to supply 21,963 homes. The power is reported only considering that the manure is put through anaerobic digestion for production of methane. A calculation of the potential power output from a liquefaction process using three major sources of manure from Louisiana animal production facilities was conducted. Exact numbers on amounts of manure generated across the state are unknown. The assumptions on animal size reported later in this section were derived from several sources and typically the lowest average was used for a conservative estimate. Only dairy, swine, and poultry manures were used for these calculations.

The dairy industry in Louisiana is a major concern due to the fact that the number of farms is down from 3000 just over a decade ago to less than 300 today. Dairies are closing and moving north where climates are cooler and restrictions on waste treatment are less expensive for farmers to manage. In 2005 the LSU AgCenter reported 32,237 cows on 268 farms. Assuming an average cow size of 1,200 lbs and that one cow produces 4.31 kg of volatile solids per day, approximately 50 million kg of manure is produced from dairy cows per year. However, most cattle at Louisiana dairies are allowed to pasture graze and are only brought to holding stalls for specific feedings and for milking. The amount of swine manure generated in Louisiana is even more difficult to determine. Pigs vary in size drastically from full grown boars weighing over 200lbs to small feeder pigs and litters weighing as little as 25lbs. The size of the pig directly affects the amount of manure produced. Table 1.1 shows ratios of size to manure production. Pigs are also sold quickly and sows give birth to various litter sizes. To ease calculations the total amount of pigs sold in the state of Louisiana in 2005 (43,748) was used as a head count. Estimates below assume that the average size of these pigs was 100 lbs corresponding to about 6 lbs of manure production per pig/day of which 77% is organic. This results in 2.1kg of volatiles produced per pig/day, yielding approximately 33.5 million kg of volatiles from swine manure per year. The AgCenter also reports that 944,150 wet tons of poultry manure was generated in 2006 with an energy potential of 251 kWh or 14,502 homes. Poultry manure consists of the litter or bedding material which is used to absorb manure on housing floors. Using the 944,150 wet tons and a 25% solid composition with 70% of those solids being volatile, approximately, 150 million kgs of volatile poultry litter was produced in 2006.

Table 1.1: Ratio of pig size to manure produced daily.

Pig Weight (lbs)	Manure Produced (lbs/day)
25	2.3
65	4.2
150	9.8
200	13.0

A total of 233.5 million kg of volatile solids were produced from all three sources of manure in one year. If conversion efficiency of organic solids in a liquefaction process was 100%, then 233.5 million kg of oil products would be produced with slightly varying heating values between the three oils. Of course, efficiency of the liquefaction process is not 100% and other issues, such as the ability to efficiently collect and transport all of the manure exist.

The Louisiana State University dairy farm, in Baton Rouge, was used as the model for this study. Most dairies across the state do not follow operating practices similar to LSU and allow cows to graze except when being milked. If the dairies across the state farmed using the same practices, then cows would be exposed to concrete feeding and milking platforms approximately 16 hours of the day where manure could be easily collected. No study has been conducted on what percent recovery of manures may be collected from concrete pads, so an estimate of 75% was used. Another issue is conversion efficiency of biomass to oil products.

Research suggests that up to 70% of organics in slurry mixture can be converted in a liquefaction process. In this research a maximum of only 30% was achieved. An estimate of 50% conversion was used for all calculation purposes. Applying corrections for collection issues for dairy manure, approximately 25 million kg of volatiles are available for conversion. The conversion of this manure to oil products would result in 12.7 million kg of oil/year or 419MJ of energy. Using an average of 18,000 kW-hour/year per household this would yield enough power for 3,234 homes. Converting this to a petroleum oil equivalent 1,606 gallons of high grade diesel equivalent could be produced. Table 1.2 reports the results of the calculations for all three sources with the maximum conversion listed first and then recalculated for collection and conversion issues.

Table 1.2: Total amounts of oil production from various sources of manure. DM (dairy manure), SM (swine manure), PM (poultry manure) and TF (total fixed). Max is the total theoretical maximum and fixed is adjusted for collection and conversion issues.

Source	VS Mkg/yr	Oil HV(MJ kg^{1})	% to Oil	MJ M/yr	BTU in M/yr	Million kWh/yr	# of homes	Oil (gal)
DM	50	33	100	1650	1563833	458	25463	12644
DF	12	33	50	209.5	198607	58	3234	1606
SM	33	36	100	1206	1143020	335	18611	9241
SF	30	36	50	542.7	541359	151	8375	4159
PM	150	35	100	5250	4975832	1458	81019	40230
PF	135	35	50	2362	2239124	656	36458	18103
TF	177			3114	2952090	905	48067	23868

Swine manure unlike dairy manure should be easier to collect because pigs are kept in holding pins all day. Applying the correction and assuming a 10% loss from transporting and collection, 33.5 million kg of organic solids are available, yielding enough electricity production for 8,375 homes per year or 4,159 gallons of petroleum grade diesel. Swine manure is a more attractive feedstock for the process because it is easier to collect than dairy manure. Also the heating value of the oil products is reported to be slightly higher than dairy. Swine manure oils are reported at a maximum value of 36.0MJ kg^{-1} and dairy only at a maximum of 33.0MJ kg^{-1}.

The 944,150 wet tons of poultry manure that the AgCenter reported could result in an energy potential of 251 kWh or 14,502 homes. However, they do not discuss what method is used to procure this energy. Using the same assumptions for swine manure to conversion of oil, and the assumptions for solid content mentioned above, poultry manure yields the highest of the three sources with potential of 36,468 homes, or 18,003 gallons of oil equivalent.

Totaling all energy potential from dairy, swine, and poultry manure approximately 905 million kWh could be generated which translates into 48,067 homes or 23,868 gallons of petroleum equivalent oil. However, this is not taking the energy required to produce the oil products. Comparing results to the LSU AgCenter study, where it is reported that 36,465 homes could be powered from poultry and dairy wastes in Louisiana, the process is attractive because the same amount of energy could be produced from poultry litter alone in a liquefaction process. Swine and dairy energy production in the process is lower due to lower solid content in the original feedstock, which also leads to smaller amounts of organic solids available for conversion to oils. Poultry litter is also available in larger quantities in the state than swine or dairy manures.

There are many issues associated with the efficiency of biomass thermochemcial conversion processes, some of which have already been noted prior. Most important is that liquefaction equipment is far too expensive to have on-site conversion units at every farm. A centralized facility or facilities would be needed and waste would have to be transported to those locations (similar to trash collection). Second, feedstocks vary significantly; therefore, either a process would have to be developed to handle all types of wastes to prevent separate processing of different sources. Finally, results for liquefaction numbers were obtained from batch scale processing. A continuous process is more appealing and should improve overall efficiency.

Liquefaction of animal manures is a process that can be used to produce energy and substantially reduce wastes. The results of this study show that a significant amount of power could be generated from animal wastes if processing efficiency were maximized. Additionally if the liquefaction process were run in a continuous mode, it is expected that economical issues will improve. It is difficult to develop an economic analysis for a biomass energy process because of technological uncertainties, demand issues, and fluctuating costs of petroleum. As oil prices continue to rise, liquefaction could become economical. Along with a little help from federal and state governments through subsidies it could become a solution to all agricultural and municipal wastes problems everywhere in North America.

1.5 Methodology and Materials

This methodology section describes procedures used throughout this work for this thesis. Appendix A includes step-by-step procedures for replicating some of the analytical work and vessel operation.

1.5.1 Feedstock Collection and Processing

Dairy manure was the primary feedstock used in assessing the HTL process due to its availability. Additional feedstocks, included tallow seed, poultry manure, pine sawdust, and switchgrass. All feedstocks are readily available in Louisiana. All feedstocks were dried in an oven at 105°C for 24 hours prior to use in the process. The solid content of the feedstocks were measured by ASTM E1756-01 (Standard Test Method for Determination of Total Solids in Biomass). Volatile solids were measured according to ASTM E1755-01 (Standard Method for the Determination of Ash in Biomass). CHN analysis was conducted on all pre-processed feedstocks to compare to post-processed oils obtained in the HTL process. Appendix C.2 shows pictures of the 6 different pre-processed raw feedstocks.

1.5.1.1 Dairy Manure

Dairy manure was collected from the Louisiana State University dairy farm and characterized prior to processing. The manure was flushed from concrete feeding pads and separated by an inclined gravity screen to remove excess water before collection. Manure was collected only once for all experimentation. After collection and prior to drying, the manure was rinsed to remove excess sand and debris. The manure was then dried at 105ºC for one day to remove all moisture and then ground using an industrial blender to ensure a homogeneous sample. Rocks, trash material, and any large un-ground portions of the sample were removed prior to storage. The separated manure resembled dirty sawdust. The total and volatile solid content of the manure was measured immediately after drying. In addition to CHN analysis, ICP was conducted by the LSU AgCenter's Callegari Environmental Center to determine nutrient content and heating value of the raw manure for comparisons to post-processed oils. These results are reported in Appendix C Figures. The dried raw manure was stored in a refrigerator at 4ºC until needed.

1.5.1.2 Tallow Seed

Tallow seeds contain readily available oil that may be extracted without liquefaction. The seeds were tested to determine if the HTL process could improve heating values and/or quantities of oils obtained from seeds. Mature tallow seeds were collected from a Chinese tallow tree located on the LSU campus. The seeds were collected in the spring from trees after they bloomed, but before new growth occurred. Two separate sets of seeds were processed during experimentation. One set was processed as is. The second was crushed to expose a higher surface area of the seed before processing.

1.5.1.3 Switchgrass

Switchgrass was obtained from the LSU AgCenter's Hill Farm location. Entire plants (stalk and leaves) were processed. The plant was ground and dried similarly to that of dairy manure to produce a homogenous sample.

1.5.1.4 Pine Dust (Sawdust)

Pine dust (sawdust) was collected from the Department of Biological Engineering's wood shop. Other then drying no additional processing was done.

1.5.1.5 Poultry Litter

Poultry Litter was obtained from the LSU AgCenter's poultry farm. The litter was used for 4 rotations of birds. Unfortunately, this is not a close representation to that of industry where dozens of rotations of birds may be allowed access to the litter before it is disposed. The poultry litter, like dairy manure, was dried and ground to obtain uniform samples.

1.5.1.6 Additional Trials

Additional trials were conducted to help understand various components of the HTL process, to determine extraction efficiency, and to see if readily available oils were converted to gas and char. Two additional materials were tested, pure vegetable oil and peanuts. Store bought vegetable oil was used to test extraction efficiency as well as to detemine if heating value could be improved. Peanuts, like tallow seeds, have high oil contents and were tested to confirm assumptions made by Minowa (1998b) that sources containing readily extractable oil would yield higher oil fractions from the process.

1.5.2 HTL Processor

A bench top 300ml stainless steel, bolted closure pressure vessel from Autoclave Engineers ® was used to conduct HTL experiments. The vessel could operate up to 350ºC and 38MPa. Agitation was achieved using a magnetic drive coupled to a motor and controller with one propeller for liquid to gas mixing. This mixing was achieved via a hollowed out propeller shaft, in which allowed gas to flow from high pressure to lower pressure areas (upper gas portion to lower liquid portion). Agitation speed of the propeller was maintained at a constant rate, 200 revolutions per minute (200RPM) throughout all experiments. Process gas (CO) was introduced to the vessel through a high pressure inlet valve and tubing. A ceramic heater was installed around the vessel to provide the heat source. A temperature controller provided by Autoclave Engineers was used to control operating temperatures. The controller was equipped with a Proportional-Integral-Differential (PID) control and safety functions to prevent overheating and to control heating rates. Temperatures were maintained within 5ºC of set conditions. A rupture disc was used to prevent damage to the vessel if operation exceeded the maximum rated conditions. A stainless steel liner provided by Autoclave Engineers ® was used to facilitate easy transfer of pre and post-processed slurries since the vessel was not equipped with a drain port. DASYlab 9.0 software was used to log temperature and pressure during operation through the use of a k-type thermocouple and a pressure transducer connected to a USB based hardware system (Measurement Computing Corp, DASYlab). A manually controlled water loop was installed for rapid cooling upon completion of the heating cycle. The HTL processor and its various components are illustrated in Figure 1.3. Appendix A.7 discusses the procedure for operation of the process vessel in more detail. A photograph of the actual vessel and its components is available as Figure 1.4.

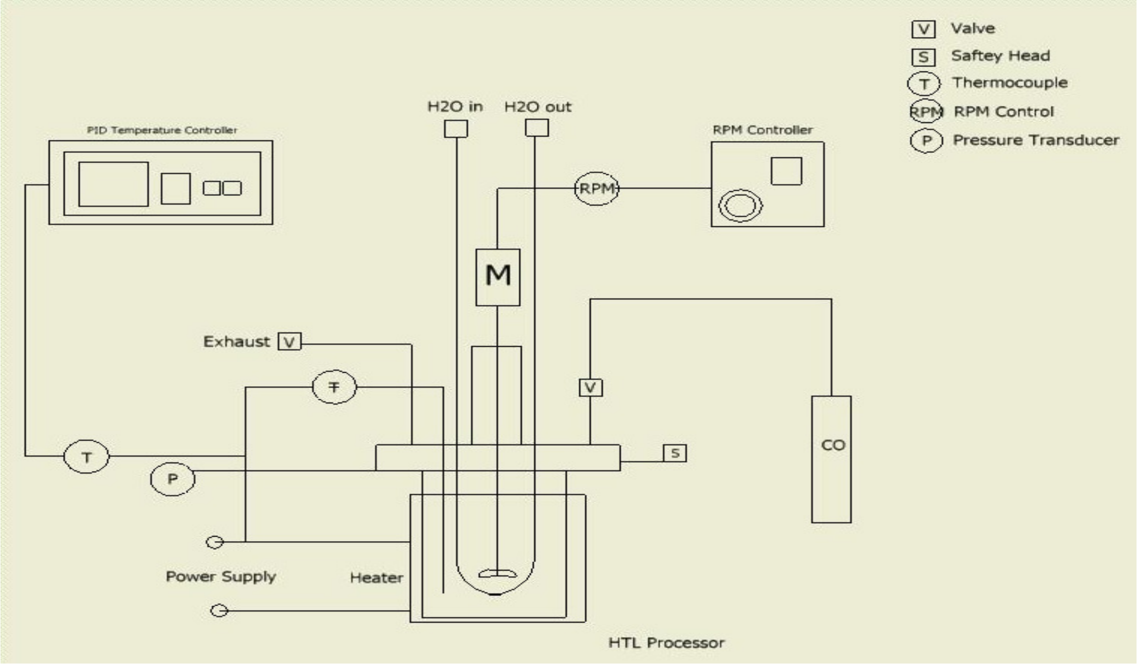


Figure 1.3: Diagram of vessel components including M (agitation device), RPM controller, cooling loop, PID temperature controller, valves, lines, and the safety head or rupture disc.

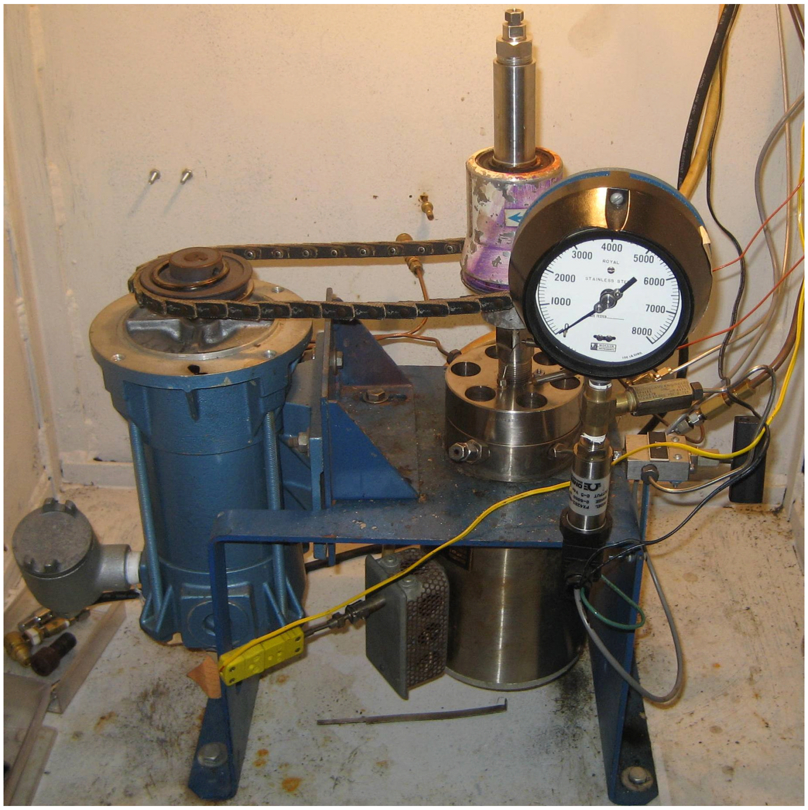


Figure 1.4: Picture of the 300ml HTL Processor at LSU.

1.5.3 Extraction and Oil Analysis

Upon completion of an experiment, the gases produced during the process were quantified, but not characterized, by volume measurement using gas collection bags. The gaseous product was separated from the post-processed slurry through a gas relief valve immediately after the vessel returned to the initial operating temperature and the final pressure and temperature were recorded. Once the gas was collected the vessel was safe to open and the liner containing the post-processed water (solids and liquid) was removed from the vessel. The solid residue remaining after the reaction was composed of char and non-volatile solids (dirt and sand) from the raw feedstock. The liquid included the post-processed water and water soluble hydrocarbons. Figure 1.5 shows the process used to collect and quantify the oils produced.

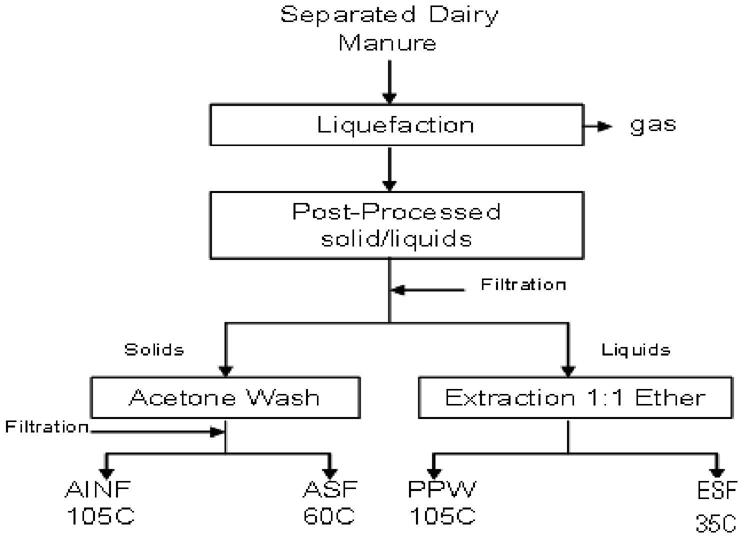


Figure 1.5: Procedure for the separation of oil products. AINF (Acetone Insoluble Fraction dried at 105ºC), ASF (Acetone Soluble Fraction dried at 60ºC), PPW (Post-Processed Water dried at 105ºC), ESF (Ether Soluble Fraction dried at 35ºC).

A 7 micron glass fiber filter (Fisher Scientific, Pittsburgh, PA) was used to separate any solids from the post-processed water. The separated water was combined with ACS grade ethyl ether anhydrous ($(CH_3CH_2)_2O$) in a 1:1 ratio. Using a gravimetric funnel the mixture was thoroughly shaken for 2 minutes to allow for extraction of light oils. The bottom layer contained water, which was drained and labeled PPW (post-processed water). The remaining top layer contained light oils and ether and was drained and labeled ESF (ether soluble fraction). Moisture was evaporated from the PPW at 105ºC and ether from the ESF at 35ºC (slightly above boiling point of ether). The remaining solids on the filter paper, liner, and cooling loop coils were washed with ACS grade acetone (C_2H_6O) to extract oil-like compounds. The acetone mixture was again filtered and labeled ASF (acetone soluble fraction). The remaining solids from the filter paper were named AINF (acetone insoluble fraction). The ASF and AINF fractions were dried at 60ºC and 105ºC, respectively, to evaporate any remaining acetone or moisture. All fractions were allowed to dry for 24 hours and then any remaining solids or oils were quantified. The AINF fraction was further tested for volatile solids by firing at 550ºC. carbon, nitrogen and hydrogen (CHN) analysis was performed on all four fractions to determine heating values.

1.5.4 Carbon Hydrogen and Nitrogen (CHN) Elemental Analysis

Carbon, Hydrogen and Nitrogen (CHN) elemental analyses were conducted on the ASF, AINF, PPW, and ESF fractions. Using a Vario El elemental analyzer (Elementar), LSU Callegari Environmental Center conducted all CHN analyses; using procedures developed by Elementar which follows guidelines from ASTM procedure number D5291-02. Dulong's formula (1) was used to calculate heating values based on the percent of carbon (C), hydrogen (H), and nitrogen (N) and assuming the remainder percent to be oxygen (O). The weight percentage of nitrogen is not used as a factor in Dulong's formula, it is only used to determine the oxygen content more accurately. CHN was conducted in triplicate for each fraction and runs that yielded a relative standard deviation higher than 10% between the three trials were conducted again.

$$\text{Heating value (MJ kg}^{-1}\text{)} = \frac{33.5\times wt\%C}{100} + \frac{142.3\times wt\%H}{100} - \frac{15.4\times wt\%O}{100} \quad \text{......................(1)}$$

This formula is a mathematical model used to approximate heating values based on elemental (ultimate) analysis of coal or biomass. This particular version of Dulong's formula was recommended for use by Demirbas (2006). The formula considers oxidation heats of C and H and the reduction heat of O, assuming that the effect of the O content of a biomass fuel on its higher heating value (HHV) is negative. CHN and heating value estimation is discussed further in Appendix A.4.1 and A.6.1, respectively.

1.5.5 Bomb Calorimeter

A 1341 Parr Oxygen Bomb Calorimeter assembly was used to conduct a calorimetric study on the ASF fraction for comparison to the theoretical values obtained by CHN analysis. The calorimeter was operated according to Parr manuals No.204 and 205, which includes procedures for proper calibration. The procedure is outlined in Appendix A.6.2.

1.5.6 Chemical Oxygen Demand

COD studies were conducted by Standard Methods 5220. Initial COD values were determined in order to report the waste reducing potential of the process. COD testing was conducted from two separate samples from the main batch of manure, and the averaged value for 20g in 80ml of de-ionized water (same concentration used in the HTL process) was determined to be 74,914 mg/L. Only the PPW and AINF fractions of the post processed slurry were measured for COD because they should be the only discharged portions from the process. Only dairy manure was tested for COD because it is the only feedstock that is typically treated via lagoons which leads to greater water pollution issues (runoff, odor and seepage). COD procedures and a calibration curve are available in Appendix A.3.

1.5.7 Gas Chromatography by Mass Spectroscopy (GC/MS)

The Department of Chemical Engineering at LSU conducted a scan on the ASF fraction to find possible oil-like compounds. No verification of these compounds in the ASF fraction was obtained. The results reported in Chapter 2 and are only based upon a library used to compare various sizes that compounds may break into during testing. The GC/MS procedure is discussed in Appendix A.5

1.6 Statistical Methods

Statistics conducted for data analysis were done using SAS/STAT® (statistical analysis software). Most of the tests conducted were two tail t-tests comparing two arrays of data using the hypothesis that there is a significant difference if the following is true (Pr .05> |t|). A 95% confidence or an alpha of 0.5 was assumed for all t-tests. Appendix D contains SAS output data from a regression analysis conducted for data represented and discussed in throughout Chapter 2.

1.7 Chapter Summary

In summary, biomass conversion processes have a potential to lessen the demand for foreign oil and to reduce green house gas emissions to the atmosphere. The use of these processes across the United States and world is becoming more widespread and more economical due to advances in technology and the increased costs of exploration, retrieval, and production of fossil fuels. The advantages of these biomass conversion processes are obvious; they use readily available waste feedstocks, which are produced from renewable resources. However, even with rising oil costs large scale biomass conversion processes continue to be overlooked, mainly because of initial start up costs. It is also due to a lack of infrastructure to transport large quantities of biomass efficiently, and poor subsidies on a state and national level which would provide additional benefits for producers of alternative fuels. The latter is beginning to change as many states are beginning to develop renewable energy portfolios, which require certain amounts of energy to come from “green sources” throughout the state and provide producers tax incentives. Advances in biomass conversion technologies are evident through commercialization, one company known as Changing World Technologies® (CWT), operates a version of a hydrothermal liquefaction process with cooperation from ConAgra Foods®. This company uses leftover turkey waste as a feedstock to produce a bio-oil like product (Changing World Technologies).

The hydrothermal liquefaction process used as a thermochemical conversion process was adapted from coal liquefaction and is proven technology. Its key advantage over gasification is generally stated that no drying of feedstocks is needed. Samples for this thesis were dried only to ensure a homogenous sample. The liquefaction process may not require drying but it requires much more energy input during conversion than gasification to keep the process running. However, liquefaction and gasification are both valuable processes and both of them along with many additional sources of procuring alternative or renewable energy processes will be needed to reduce dependence on fossil fuels. As more studies are conducted a better understanding of the reactions will occur and further progress will be made to commercialize the process

CHAPTER 2: HYDROTHERMAL LIQUEFACTION OF SEPERATED DAIRY MANURE FOR PRODUCTION OF BIO-OILS WITH SIMULTANEOUS WASTE TREATMENT

2.1 Introduction

Increasing demands, rising costs, and supply issues coupled with treatment and disposal problems for large waste sources are creating needs for new and/or improved biomass energy conversion processes. Biomass feedstocks with high contents of lingo-cellulosic compounds are ideal for the depolymerization and reforming reactions that occur in a heated oxygen free environment. Several thermochemical conversion (TCC) processes exist; gasification, pyrolysis, and liquefaction are the primary studied processes. Products of a TCC process depend solely on the raw biomass source and the type of energy desired.

Biomass refers to living and recently dead biological material that can be used as fuel or for industrial production. Biomass also presents many waste problems for agricultural farmers, especially those who raise animals. The USDA estimates that in 1997, 27 million tons (dry matter) of manure were generated by dairy operations, of which 21.3 million tons were on operations where the cattle were confined (USDA-ERS, 2001). The EPA estimates that as of 2005, approximately 2,623 dairy farms were good candidates for biogas collection and bioenergy production. Nearly 38% of these farms were located in California, and 80% of the candidate farms were located in the top 10 dairy production states.

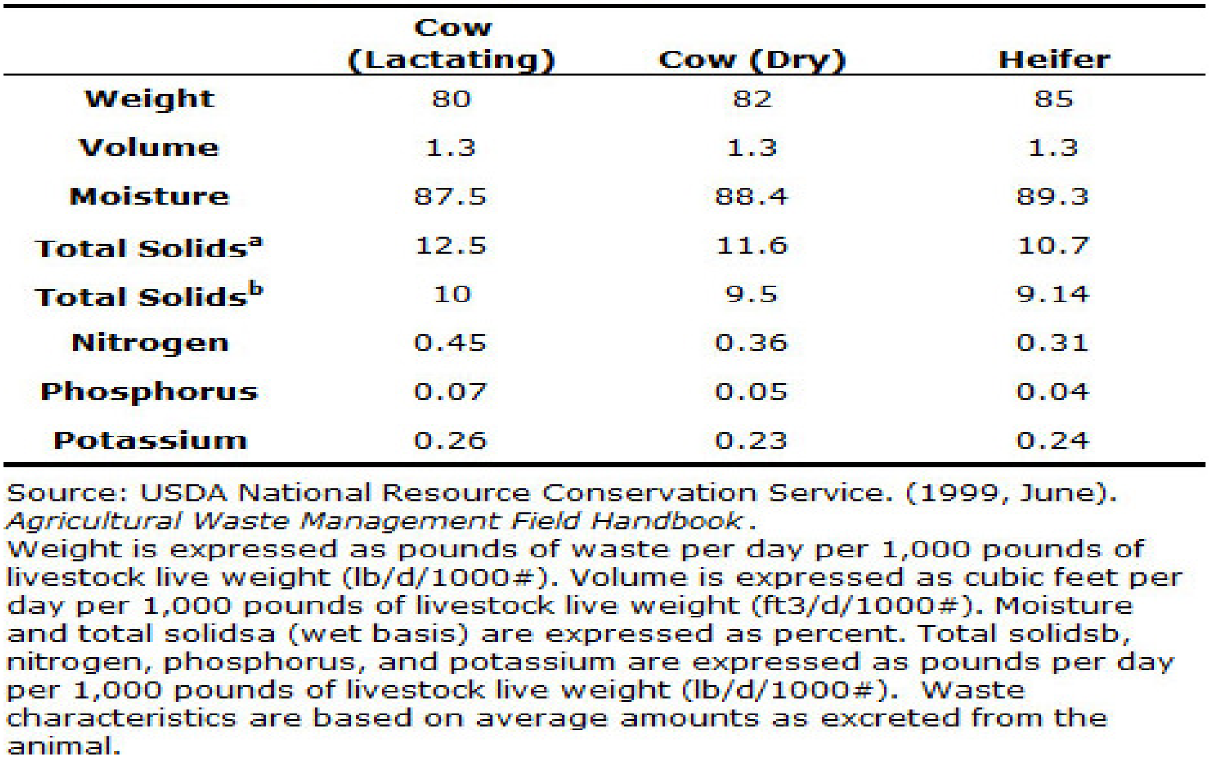
Louisiana has lost a countless number of dairies in the last decade, mainly due to climate issues. However, the waste treatment regulations imposed by the EPA and DEQ in the state concerning confined animal practices has drastically changed in the last decade as well. Stricter environmental policy may also be responsible for the decrease in operations. A new way of treating manures is being sought after by farmers. TCC processes have been studied by many researchers as a method for waste treatment as well as energy procurement. More specifically, hydrothermal liquefaction (HTL) has been reported as an effective treatment method for biomass sources containing high moisture contents (He et al, 2000b; Inoue et al, 1997; Kranich, 1984; and Molten et al, 1985).

An initial HTL study was conducted using dairy manure as a feedstock. The focus of the study was to determine the efficiency of the process to reduce organic loading into lagoons and to maximize the production of valuable energy products or bio-oils. Two important operating parameters were studied; temperature and effect of catalyst. Alkali catalysts are an important role in the process as they may reduce the amount of volatile solids that are converted to char, thus increasing the oil fractions. Temperature has been stated to be the most important operating parameters, as it is directly responsible for driving the various depolymerization and reforming reactions that occur.

2.2 Dairy Manure to Oil

The physical and chemical properties of dairy manure slurries are complex and vary widely with the animal species, diet, and management practices. Also manures may vary if the cow is lactating or not. It is nearly impossible to predict an exact composition of dairy manure for several reasons. Table 2.1 contains average values reported by the USDA for three various conditions for dairy cows. Lactating cows produce slightly more solids (dryer manures) then dry or non-lactating cows. It is also interesting to note the nitrogen increase in lactating cows. Fortunately, for conversion to oil, specifically using a liquefaction process, the differences in the composition of dairy manures will have only minor effects on the products produced and the reactions needed to obtain those products.

Table 2.1. Characteristics of dairy manure by animal type and condition. See table caption below for units (USDA).

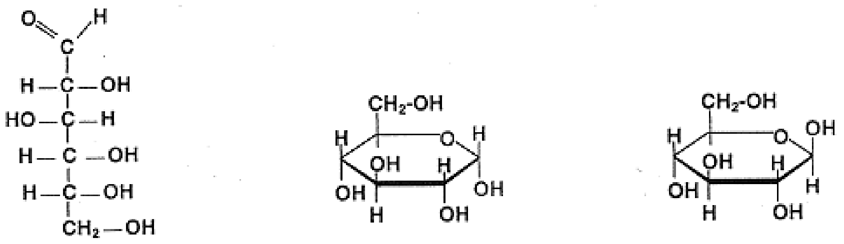


	Cow (Lactating)	Cow (Dry)	Heifer
Weight	80	82	85
Volume	1.3	1.3	1.3
Moisture	87.5	88.4	89.3
Total Solids[a]	12.5	11.6	10.7
Total Solids[b]	10	9.5	9.14
Nitrogen	0.45	0.36	0.31
Phosphorus	0.07	0.05	0.04
Potassium	0.26	0.23	0.24

Source: USDA National Resource Conservation Service. (1999, June). *Agricultural Waste Management Field Handbook*.
Weight is expressed as pounds of waste per day per 1,000 pounds of livestock live weight (lb/d/1000#). Volume is expressed as cubic feet per day per 1,000 pounds of livestock live weight (ft3/d/1000#). Moisture and total solidsa (wet basis) are expressed as percent. Total solidsb, nitrogen, phosphorus, and potassium are expressed as pounds per day per 1,000 pounds of livestock live weight (lb/d/1000#). Waste characteristics are based on average amounts as excreted from the animal.

2.2.1 Carbohydrates

Carbohydrates are a major part of the composition of dairy manure. Glucose ($C_6H_{12}O_6$), one of the simplest carbohydrates may be used to help describe the formation of oil products. The open-chain form of glucose contains an active aldehyde functional group at one end. The carbon immediately next to the aldehyde group is named the α-carbon, the second is the β-carbon, the third is the γ-carbon, and the fourth is the δ-carbon. When a dehydration reaction occurs, intra-molecularly between the aldehyde group and the hydroxyl group at the δ-carbon, a ring structure forms. The ring-form is the predominant form of glucose. D-Glucose has two ring steroisomers. Ring form (a) of D-glucose is also called α-D-glucopyranose, and form (b) is called β-D-glucopyranose. Figure 2.1 shows the structures of D-glucose. The difference between the two ring structures is the position of the hydroxyl group that bonds to the α-carbon.



Open-chain form Ring form (a) Ring form (b)

Figure 2.1. Structures of D-glucose (He et al, 2001a).

In nature, glucose is usually formed from the biological decomposition of cellulose, which is the unit structure of cellulose in biomass or dairy manure. Cellulose is a polysaccharide, an unbranched polymer of glucose units joined by β-1,4 glycosidic linkage. The cellulose could contain as many as 10,000 glucose units. The structure is stabilized by hydrogen bonds between adjacent glucose units in the same strand. In a natural process, cellulose is decomposed biologically by the function of cellulase, an enzyme that catalyzes the hydrolysis decomposition process of cellulose. Cows' complex stomachs contain some cellulase enzymes that other animals including humans do not. They are capable of reducing cellulose into sugar for nutrition. However, cows generally do not digest all the cellulose they eat and it remains the major leftover product in their manure. Besides cellulase, cellulose is also readily degradable to glucose through acid hydrolysis processes at temperatures of 80-180°C and retention time of 30-240 minutes. Therefore, cellulose can be decomposed easily through thermochemical conversion processes. When dry cellulose is heated slowly to 120°C in the presence of air, water, vacuum, or in various liquids, it begins to depolymerize and change in many aspects such as viscosity, strength, and solubility (Garner, 1973). An aqueous distillate begins to form at 200°C, tar and gases begin to form at 230°C. The reaction becomes exothermic at 270°C and extensive decomposition results in the formation of gases and liquid products. Between 270°C and 350°C the rate of gas production peaks and remains constant above 350°C.

Cellulose is one of the major components of biomass, however, in a natural state it is rarely in a pure form. Ligin and hemicelluloses are typically the natural forms. Hemicellulose is chemically related to cellulose and has a lower polymerization than cellulose, usually with only 100-200 sugar units. Depending on the source, hemicelluloses contents of biomass vary greatly and can be as high as 85%. The chemical structure of lignin is more complex than cellulose and hemicelluloses. It mainly consists of benzene ring-containing compounds. Lignin contains more than 60% carbon and about 30% oxygen, while cellulose and hemicelluloses contain less than 50% carbon and 50% oxygen. Lignin usually represents about half of the available combustible energy in naturally occurring sources of cellulose. Thermal decomposition of lignin needs a high temperature 280°C or higher. Hardwood lignin needs 350°C to decompose (Chronet, 1985).

2.2.2 Amino Acids and Lipids

Besides carbohydrates, amino acids are a considerable portion of the dairy manure composition. Manures used for this thesis were separated; consisting mainly of the cellulose fraction. Realistically, it would be difficult to recover whole "fresh" manure that would contain much more amino acids.

Amino acids are the basic structural units of proteins. An α-amino acid consists of an amino group ($-NH_2$), a carboxyl group (-COOH), a hydrogen atom, and a distinctive R group bonded to a carbon atom (the one adjacent to the carboxyl group). The different R groups differentiate the types of amino acids. Amino acids are the major source of nitrogen present in dairy manure and are also responsible for the majority of organic sulfur. Lipids and proteins are the basic structural units of biological membranes, linked together by carbohydrates. Three major classes of membrane lipids are phospholipids, glycolipids, and cholesterol. Phospholipids are the most abundant class and they are derived from either glycerol or sphingosine. The lipids derived from glycerol are called phospoglycerides. They consist of a glycerol backbone, two fatty acid chains, and a phosphorylated alcohol.

Fatty acids are a class of compounds containing a long hydrocarbon chain and a terminal carboxyl group. Fatty acids are not only the structural units of lipids, but also the “fuel molecules”. They are stored as triacylglycerols. All of these compounds affect some portion of the conversion of dairy manure to oil products. It is the complex structure of biomass that inhibits researchers the ability to fully understand all the reaction mechanisms involved in the thermochemical conversion of biomass.

The carbon content of dairy manure, more specifically the organic carbon is the most important compound in biomass. Organic carbon is the compound that has the potential of being converted in to liquid fuels through thermochemical processes. The ratio of H:C is also very important in oil conversion. Hydrocarbons such as gasoline, kerosene, and diesel have the general molecular formula H_nC_{2n+2}. It is very different with the carbohydrates, amino acids, and lipids present in biomass. It is difficult to determine the H:C ratio of biomass because of the high oxygen content. Hydrogen atoms are not directly bonded to carbon chains, instead they bond to oxygen atoms in the form of hydroxyl groups, carboxyl groups, or amino acids. For glucose and cellulose the oxygen content is as high as 53% by weight, which negatively effects the conversion of organic matter to oil products. The low H:C ratios directs the reactions to form char instead of oil.

2.2.3 Possible Reactions in the TCC Process of Dairy Manure

Reactions involved in the thermochemical conversion of dairy manure are complex due the complex chemical composition of manure. It is difficult to determine exactly what types of reactions occur during liquefaction processes. Liquefaction of carbonaceous materials takes place through a sequence of structural and chemical changes which involve at least the following steps (Chronet, 1985; and Demirbas, 2000).

1. Cracking and reduction of polymers such as lignin and lipids;
2. Hydrolysis of cellulose and hemicelluloses to glucose;
3. Hydrogenolysis in the presence of hydrogen;
4. Reduction of amino acids;
5. New molecular rearrangements through dehydration and decarboxylation;
6. Hydrogenation of functional groups.

The reaction mechanisms may not follow the exact order described above, and the reactions in biomass depolymerization process are much more complex. Many researchers have tried to investigate and propose reaction mechanisms but no definitive study has been conducted. A summary of some the proposed mechanisms are described below.

After "cracking" reactions a hydrolyzing of the polymers and monomers, such as glucose, are then further reduced with the presence of reductive compounds. The oxygen element is eliminated and high hydrogen and carbon containing compounds are yielded. To increase the conversion rate of organic matter to oil, high hydrogen content in the feedstock is desirable. The use of hydrogen gas was studied by Datta and McAuliffe (1993) and Kranich (1984). No difference in yields between CO and H used as a process gas were noted. Apell et al. (1980) concluded that the use of CO was more than efficient for conversion to oil products. Apell also states that the water-gas shift reaction under high temperatures would be responsible for the increase in the conversion rate from organic matter to oil. Figure 2.2 depicts the water-gas shift reaction. He et al, (2001a), determined that any process gas could produce bio-oil and that the initial gas prevented complete vaporization of the slurry during processing.

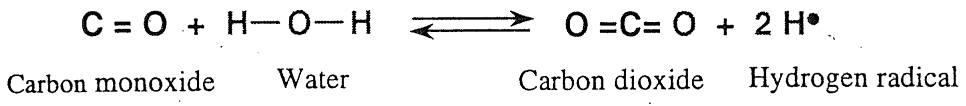


Figure 2.2. Water gas shift reaction proposed to be responsible for increase in the conversion rates of organic matter to oil (Apell et al, 1980).

The hydrogen radicals then react with other oxygen containing functional groups to eliminate oxygen elements and yield hydrocarbon like compounds. Carbon monoxide, as a highly reductive compound, participates in the redox reactions directly. It combines with oxygen in the hydroxyl and carboxyl groups to form CO_2. The hydrogen radical that is released is then ready to combine with carbon. Carbon dioxide forms through numerous routes and can form through decarboxylation reactions as well.

2.2.4 Properties of Water During the HTL Process

Water is the solvent used for most HTL processes and was used for the conversion of dairy manure to oil. Most substrates are not soluble in water under normal conditions, but salvation can occur between the hydroxyl groups and water under high temperatures and pressures. Water is a medium for intermediate hydrolysis of cellulose and other high-molecular-weight carbohydrates to water-soluble sugars. The primary reactions in the conversion to oil likely involve the formation of low-molecular weight, water soluble compounds such as glucose. Alkaline catalysts are water soluble as well, facilitating their dispersion throughout the process vessel in a readily available form. Water is also used to mix reactants and to diminish condensations to chars by diluting the reaction intermediates.

Water is a reactant at high temperatures. Hydrogen may be added to the substrate through the water-gas shift reactions, which consumes carbon monoxide from carbon dioxide and hydrogen. This is also advantageous to raw dairy manure where large quantities of water exist and dewatering is expensive and time consuming. Taking advantage of water in raw manure will greatly enhance the value of the conversion process and reduce the pollution potential of wastewater from farms.

2.3 Materials and Methodology

Appendix A and section 1.5 contain detailed procedures and methodologies for this thesis. Section 2.3 is similar to section 1.5; however, additional information is included.

2.3.1 Feedstock Preparation and Characterization

Dairy manure was collected from the Louisiana State University Dairy in Baton Rouge and characterized by solids testing, inductively coupled plasma (ICP), and carbon-hydrogen-nitrogen (CHN) analysis. The solid content of the feedstock was measured by ASTM E1756-01 (Standard Test Method for Determination of Total Solids in Biomass). Volatile solids were measured according to ASTM E1755-01 (Standard Method for the Determination of Ash in Biomass). The manure used for processing was not raw manure. It consisted mainly of the herbaceous materials that remained after a gravimetric screening process. To minimize the variability in feedstock, manure was collected one time and stored in freezer bags at 4ºC after drying and homogenization by grinding to a powder. The dry manure was adjusted to 20% total solids by addition of de-ionized water before addition into the HTL processor. The manure had an average volatile solid content of 83.2% on a dry weight basis. The heating value of the raw manure was calculated to be 11.9MJ kg^{-1}. Table 2.2 contains the results of elemental analysis and other testing performed on the raw manure. Appendix C includes results for the ICP testing.

2.3.2 HTL Processor

The basic requirements for a HTL reactor in this study includes the ability to work under high temperatures and pressures, easy to control, the ability to record temperature and pressure, and to operate safely. Based on the criteria, a bench top 300ml stainless steel reaction pressure vessel from Autoclave Engineers was chosen to conduct HTL experiments. The vessel could operate at extreme conditions of 350ºC and 38MPa. Chapter 1.5.2 contains more specifics on the operating components of the HTL processor. For safety reasons, the entire system was enclosed in a steel chamber to prevent exposure to rapidly escaping gases or liquids due to failure of any seals or valves. A sketch and a photograph of the vessel can be found in Figures 1.3 and 1.4, respectively.

Table 2.2. Raw dairy manure characteristics for a powdered homogeneous mixed sample.

Separated Properties	Values	Elemental Composition (CHN)	Weight %
Moisture content (wt %)	84.3	C	38.84
Volatile solids (wt %)	83.2	H	5.14
Heating value[b] (MJ kg^{-1})	11.9	O[c]	54.72
		N	1.3

[a] Organic content on a dry basis
[b] On a dry basis
[c] Calculated by difference

2.3.3 Experimental Setup

In order to ensure no leaks or contamination during the process, all equipment was thoroughly washed before each new trial. The raw manure, water, and catalyst (if needed) were first added to the stainless steel liner and mixed thoroughly. The pH was then recorded and the liner containing the slurry mixture was placed into the vessel. The vessel cover was installed containing the cooling loop, agitation drive, propeller, and thermowells. Six bolts were then used to bolt the top to the vessel and create a leak free seal. Using a star pattern the bolts were torqued to no more than 46.08 cm-kg (40in-lb) increasing only 11.52 cm-kg (10in-lb) per rotation. Once closed the vessel was then purged with process gas (CO) and checked for leaks. After five complete purge cycles the vessel was charged to the desired initial pressure 2.06Mpa (300psi). Next the thermocouples, pressure transducer, and rpm of the propeller were set and tested. The rpm of the motor was monitored and set by the use of a hand held laser tachometer. The rpm controller displayed only percent power therefore the tachometer was used to confirm the 200 rpm required. The heater and data acquisition units were started and the process was allowed to continue until completion of the 15 minute retention time. Upon completion the heater was turned off and the cooling valve was turned on. This was done manually; the water was allowed to cool the vessel to room temperature. Typically five minutes after turning on the cooling loop the vessel cooled to temperatures below 150°C terminating any reactions. Once cooled the final pressure was noted and the gas was collected in a gas bag. At this time the vessel was safe to open and the contents were removed for further processing.

2.3.3.1 Temperature and Pressure Control

Temperature is the most important operating parameter during the process. It directly affects thermal depolymerization reactions. The control of the operating pressure was indirectly achieved through temperature control because the water vapor-liquid system was in equilibrium when the operation reached its steady state. A pressure transducer was used to set initial pressures and provide electronic signal to the data acquisition system. The control of operating temperature led to the control of operating pressure. Therefore, the operating pressure was measured and monitored, but not controlled in this thesis work.

The vessel was then heated to the desired temperature for the preset amount of time and then rapidly cooled. A temperature controller from Autoclave Engineers was used. The controller featured a proportional-integral-differential (PID) control, a high temperature limit indication/cutoff, and a thermocouple malfunction protection control. Three type k thermocouples were used as temperature sensors, two placed in the thermowell of the reactor, and one serving as a heater temperature recorder for high temperature cutoff. One of the thermowell thermocouples was used with the temperature controller to provide internal vessel temperature. The other used for the same reason but connected to the data acquisition equipment to provide temperature monitoring. The controller was set to only provide 50% of the output power to the heater. This helped to control the rate of heating and with help from the PID controller; a maximum heating rate of 10°C/min was maintained during operation.

2.3.4 Process Parameters

The parameters studied for this paper were operating temperature, catalyst quantity, and its effects on oil quality and quantity. Temperature is the most important parameter in the thermochemical process since it directly affects the conversion reactions involved in the process (He et al, 1998). The operating range for this study was 250-350ºC with corresponding pressures of 5.5-17.9MPa. The catalyst used was anhydrous sodium carbonate (Na_2CO_3). Amounts of 0, 1, 2, 3 and 4 grams of catalyst were tested with each operational temperature of 250, 275, 300, 325, and 350ºC, yielding a total of 25 experiments.

The powdered manure had 20% total solids (TS) of which approximately 85% was organic. The 20% total solids were recommended by (He et al, 2000), higher solid content impaired mixing by the agitation system. The amount of volatile solids is directly correlated to the quantity of oil and gas produced from the system. The retention time (RT, time material remained at set operating temperature) for all experiments was 15 minutes. The pH level of all experiments was monitored but not controlled. The pH of raw manure in slurry (no catalyst) was approximately 6.5 and increased to 10.5 with the addition of 4 grams of Na_2CO_3 to the slurry. The pH of the slurry was directly related to the amount of catalyst present. The pH of the manure is important to the depolymerization reaction rates of carbohydrates and other cellulose compounds; however, typically a more acidic environment aids these reactions. Carbon monoxide (CO) was used as the process gas with initial pressure of 2.1MPa (300 psi) for all experiments. Once the 15 min RT was complete the cooling loop was initiated to cool the vessel back to pre-run conditions.

2.3.5 Product Analysis

Gases produced during the process, which contributed to the pressure increase, were quantified but not characterized. Up to three liters of gas were produced from the process. Increased operating temperature directly corresponded to increased production of gas. At low temperatures (250°C), no gas production was detected. The maximum gas production occurred during the 350°C trials. The gaseous product was separated from the post-processed slurry through a gas relief valve immediately after the vessel returned to the initial operating temperature and the final pressure and temperature were recorded. The gas fraction even though discarded for this study contains a portion of the mass from the processed feedstock. Light hydrocarbons C_2-C_4 are predicted to be present in the gas fraction (He et al, 2000).

The solid residue remaining after processing was composed of char and non-volatile solids (dirt and sand) from the raw manure. The liquid included the post-processed water and water soluble hydrocarbons. Chapter 1.5.3 and Figure 1.5 discuss and depict the process used to separate and quantify oil and char produced in the process. Two hundred and fifty milliliters of ACS grade acetone was used for extraction of the heavy oil fraction. The vessel parts and char (AINF fraction) were soaked and rinsed with acetone. Ethyl ether was used in a 1:1 ratio with the filtered slurry portion, typically 60-70 ml.

A separate characterization study included one test, in triplicate, on the optimum conditions. This study was conducted to determine waste reducing characteristics (using COD test), to confirm the presence of oil-like compounds (using GCMS), and to verify heating values calculated from CHN analysis (using a bomb calorimeter). It is also used as a quality control check to ensure a consistent process.

2.4 Results and Discussion

2.4.1 Overall Process

Temperature and pressure for the process was recorded for all experiments. Figure 2.3 is an example of data recorded from one of the trials. Note the increase of pressure in the figure (initial vs. final), this confirms that the process produced a gaseous product. This was consistently the case throughout all trials conducted above 250°C. Dulong's formula (1) was used to calculate heating values based on the percent of carbon (C), hydrogen (H), and nitrogen determined by CHN analysis and assuming the remainder percent to be oxygen (O). The weight percent of nitrogen is not used as a factor in Dulong's formula; it is only used to determine oxygen content. Table 2.3 shows CHN values and calculated heating values by dulong’s formula for several experiments. A trend of increasing temperature with increasing heating value can be observed.

All fractions were tested for CHN to determine their heating value. The ESF fraction consistently yielded a very low quantity of oil-like products, less than 0.2 grams. Occasionally the extraction did not obtain a large enough sample for CHN testing. Throughout all the trials the ESF fraction yielded a heating value slightly less than the ASF fraction. The ASF fraction was used as the main fraction for further testing and reporting throughout the remainder of this thesis. Recommendations are made in Chapter 4 about improving the extraction procedure.

Heating values obtained for the PPW and AINF fractions varied significantly throughout all the trials. The highest heating value obtained for the AINF fraction was 14.0MJ kg^{-1}. Twelve of the 28 trials reported in this chapter yielded slightly negative heating values for the AINF fraction. Dulong's formula does not automatically adjust the heating values to 0 and it is not correct to assume that there was no heating value (no carbon) in these fractions. The oxygen percent that is assumed to be the remainder represents too large a value in these particular trials. The calculated heating values for the AINF fraction are error prone due to low carbon and

Table 2.3. CHN values for 2g sodium carbonate catalyst runs and their calculated heating values for the ASF fraction.

Temp°C	Catalyst(g)	%C	%H	%N	%O	HV (MJ kg^{-1})
350	2	75.1	8.2	2.7	14.1	34.7
325	2	72.1	7.1	2.5	18.3	31.4
300	2	68.4	7	2.4	22.3	29.4
275	2	69.3	6.8	2.5	21.4	29.7
250	2	62.6	6.4	2.6	28.4	25.8

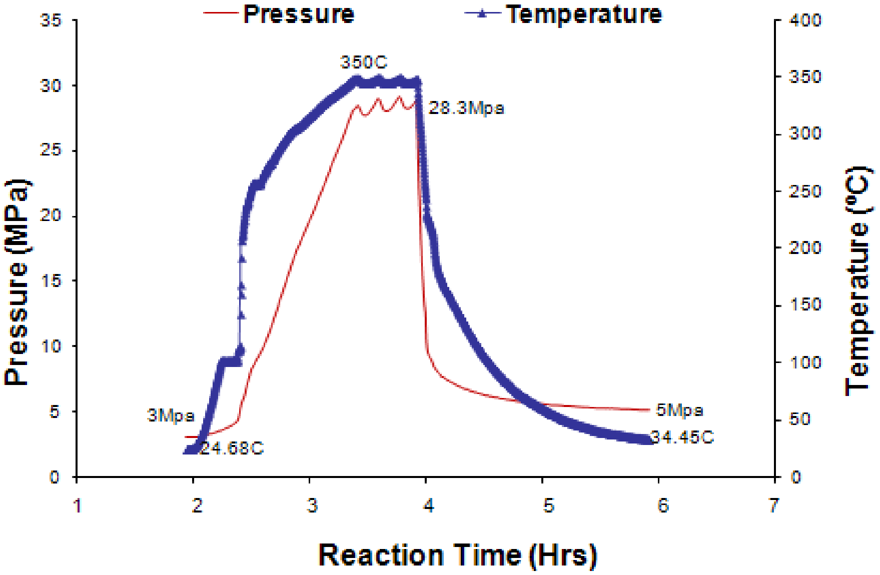


Figure 2.3. Temperature and pressure response for 350°C and 2 grams of sodium carbonate catalyst. The initial, maximum, and final temperatures and pressures are shown (24, 350, 34) °C and (3, 28, 5) MPa, respectively.

hydrogen presence. Volatile testing was conducted to report the percentage of carbon remaining. At low temperatures (250°C and 275°C) up to 32% carbon remained at the end of processing. As the temperature increased above 300°C the carbon remaining dropped below 10% confirming that temperature directly influences carbon conversion. The PPW fractions heating value was relatively constant throughout all trials with an average of 10.0MJ kg^{-1} and a range of 5-15MJ kg^{-1}. This shows that further processing or improved efficiency is needed to recover more of the carbon into either the oil phase or as a secondary product.

2.4.2 Temperature Effects

Operating temperature is the primary control parameter of the liquefaction process. Temperature indirectly controls pressure of the closed system by properties of thermodynamics corresponding to saturated water vapor. Figure 2.4 depicts the effect of operating temperature on heating value and oil product yield of the ASF fraction. Each temperature data point is the average of 5 trials at that temperature (note: sodium carbonate catalyst amounts in the trials varied from 0-4 grams). Heating values steadily increased with an increase in processing temperature. Average yields of the ASF fraction were constant except for the 350ºC trials where a 4% increase in conversion of volatile solids is observed. The ESF fraction also followed the same increasing trend; however ESF yields were constant and just above 1% conversion of the original volatile solids. Further research is needed to conclude whether 350ºC is the overall optimum temperature for dairy manure conversion or whether temperatures that approach supercritical conditions yield higher quantities and heating values. Tests above 350ºC were not conducted because of safety reasons. The liquefaction vessel was rated for a maximum temperature of 344°C at 38Mpa (5500psi). Testing beyond 350°C would have been unsafe due to the rapidly increasing pressures. Increased rupture disc ratings and new seals would allow for operation beyond 350°C. However, the severe reaction conditions of supercritical water (374°C) result in subsequent decomposition of hydrolysis intermediates to form primarily gaseous products. Therefore it is speculated that temperatures approaching supercritical conditions will yield higher gaseous products, and either the same or lower oil yields compared to trials conducted at 350°C

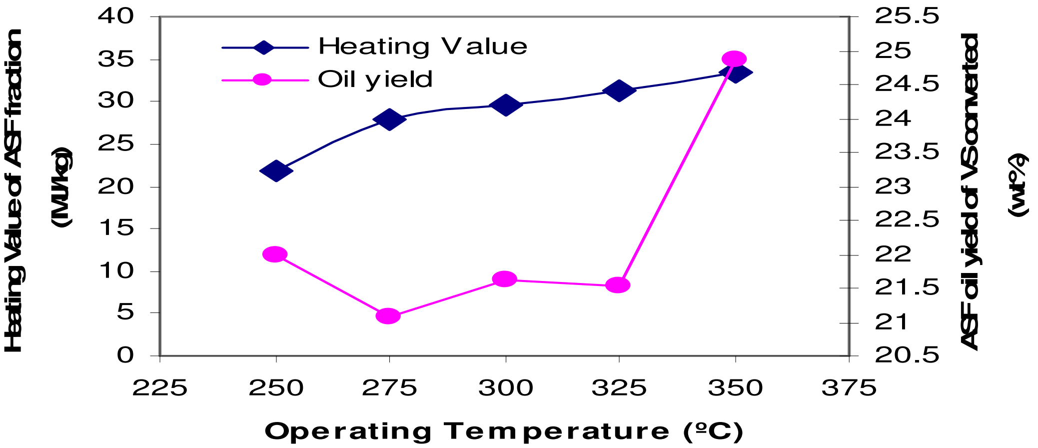


Figure 2.4. Temperature effect on the oil product yield (% of VS converted) of the ASF fraction and its calculated heating value. The operating conditions were initial CO pressure of 2.1MPa, TS=20%, RT=15min and feedstock pH of 6-10.5. The corresponding pressures were 5~18MPa.

2.4.3 Catalyst Effects

The effect of catalyst loading on the ASF and ESF, heating value or quantity, was determined to be minimal if any at all tested temperatures. Figure 2.5 depicts quantities of Acetone Soluble Fraction (ASF), Ether Soluble Fraction ESF, Post Process Water PPW, and Acetone Insoluble Fraction (AINF), for trials conducted at 350ºC with varying catalyst amounts. The added catalyst ended up in the PPW fraction, which was evident by the increasing PPW amounts with increasing catalysts amounts. The heating value of the ASF fraction for all 5 experiments conducted was in the range of 32.4-34.6MJ kg^{-1}. The ESF fraction also varied slightly with a range of 24.2-25.3MJ kg^{-1}. The ASF quantities were similar for all 5 experiments; 4.3g was collected with 4 grams catalyst and 3.8g with no catalyst. Throughout all 25 trials a similar trend was noticed. An increase in yields of the ASF fraction was noticed between 0 and 1 gram usage of sodium carbonate for all trails conducted at 300ºC or above. Slight increases in quantities and sometimes only decreases of the ASF fraction were seen with 2-4 grams use. Table 2.4 shows catalyst use and respective heating values and quantities for the ASF fraction for all trials conducted.

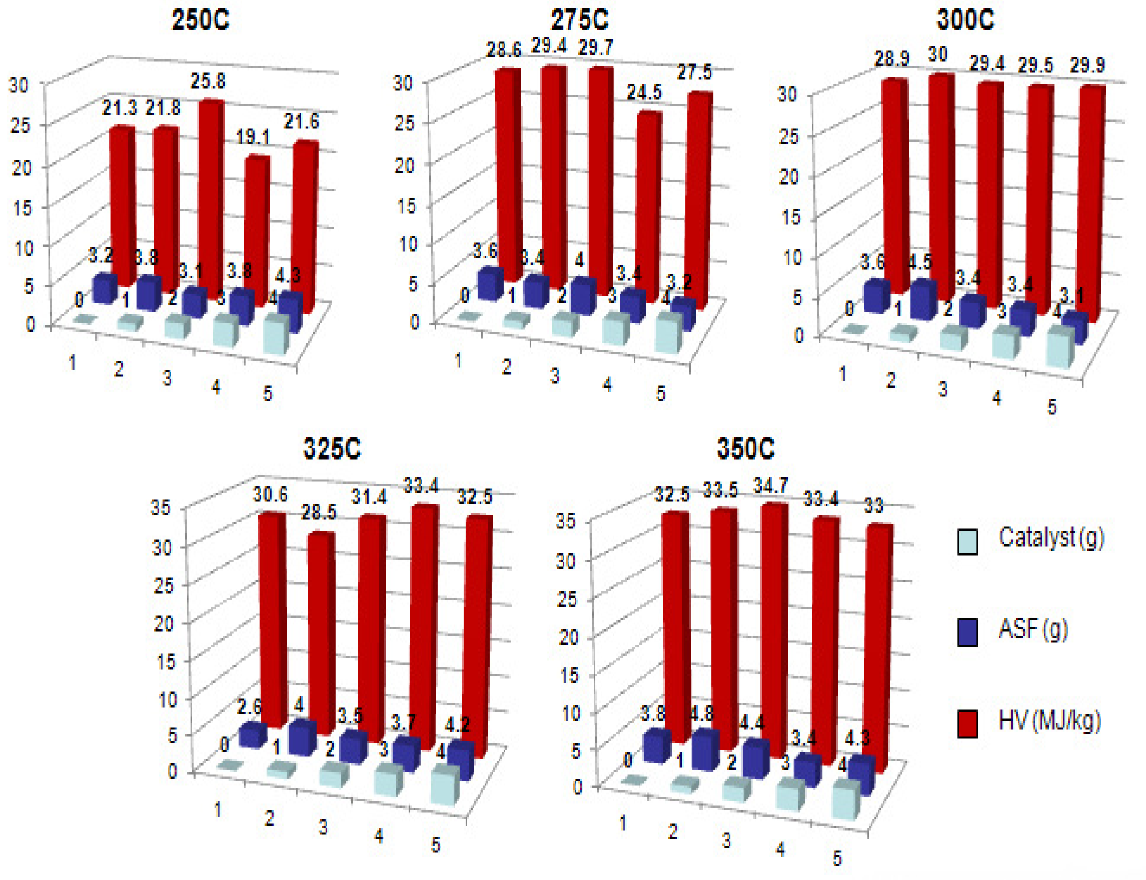


Figure 2.5. Effect on ASF fraction for all trials conducted at various temperatures with increasing sodium carbonate catalyst amounts.

The alkali catalyst did not inhibit the formation of chars. The AINF fraction was only influenced by temperature. At 350°C the average char fraction was 5 grams and at 250°C the average was 10 grams. This is due to a higher conversion rate of volatile solids in the feedstock. There was only a slight trend noticed in the results. In Table 2.5 the AINF with 0g catalyst is

6.67 and all the remaining AINF fractions are at least 1 gram lower. Unfortunately, this is the only trend noticed in the results for all the different temperatures.

Table 2.4. Quantities of ESF, PPW, AINF, and ASF fractions collected from experiments conducted at 350ºC and 0,1,2,3 and 4 grams of sodium carbonate. Note the increase in PPW with catalyst amounts verifying where the catalyst ends up at the end of the experiment.

Catalyst (g)	ESF (g)	PPW(g)	AINF(g)	ASF(g)
0	0.33	1.38	6.67	3.77
1	0.29	2.21	4.72	4.76
2	0.17	3.48	5.00	4.40
3	0.11	3.93	5.00	3.42
4	0.14	5.87	5.47	4.34

A regression analysis coupled with an analysis of variance (ANOVA) was conducted to determine whether catalyst and/or temperature have an effect on the energy content (MJ) of the ASF fraction. Several assumptions are made: a linear relationship exists and all other operating parameters are assumed to be constants including heating rates and temperature profiles even though different temperatures were tested. Only temperature and catalyst were tested with (MJ) for trials conducted above 300°C. See Appendix D for the SAS output and Table D.1 for the input data. From the results of this testing there is no significant dependence using (Pr .05> |t|) of catalyst on the energy content in the ASF fraction. There is a noticeable difference, however, for temperature.

2.4.4 Characterization Study

A three trial characterization study was conducted to confirm the reproducibility of the process and to provide sufficient samples to conduct Bomb Calorimetric work, a Gas Chromatography by Mass Spectroscopy library scan, and COD analysis of the AINF and PPW fractions to determine the discharge COD of the process. Table 2.5 shows results from those 3 experiments and the original 350°C no catalyst run. Good reproducibility was achieved. Little variance exists throughout the reported data, only the PPW and ESF fractions were high and their results are insignificant for discussion purposes.

Table 2.5. Results of the characterization experiment conducted at 350ºC with no catalyst.

Trial #	AINF (g)	ASF (g)	PPW (g)	ESF(g)	Heating Value ASF (MJ kg^{-1})	Heating Value ESF (MJ kg^{-1})
1	7.26	3.25	1.04	0.3	32.0	25.1
2	7.12	3.44	0.68	0.2	32.0	24.8
3	6.80	3.67	0.96	0.29	32.4	25.1
Trial 25	6.67	3.77	1.38	0.33	32.5	25.5
Mean	6.96	3.53	1.02	0.28	32.25	25.09
SD	0.27	0.23	0.29	0.06	0.25	0.29
CV	3.9%	6.6%	28.4%	20.0%	0.8%	1.2%

2.4.5 Bomb Calorimeter

A 1341 Parr Oxygen Bomb Calorimeter assembly was used to conduct a calorimetric study on the ASF fraction for comparison to the theoretical values obtained by CHN analysis. The calorimeter was operated according to Parr manuals No.204 and 205, which includes procedures for proper calibration. All three fractions were tested in triplicate and Table 2.6 reports all values obtained and the theoretical calculated values.

Table 2.6. Bomb calorimeter values obtained from characterization study of ASF fractions compared to heating values obtained by calculating theoretical values calculated using Dulong's formula (1). All values are shown in units of MJ kg^{-1}.

Trial #	ASF Bomb Run 1	ASF Bomb Run 2	ASF Bomb Run 3	Calculated Value[b]
1	52.62[a]	31.7	30.8	32.0
2	32.8	34.0	31.8	32.0
3	32.0	33.3	33.0	32.4
Mean	32.4	33.0	31.9	32.2
SD	0.55	0.47	0.82	0.27
CV	2%	1%	3%	1%

[a] this run was not included for calculating mean or standard deviation (SD).
[b] Calculated from Dulong's formula.

The bomb study confirmed the theoretical values obtained by using Dulong's formula (1) with the CHN values obtained by elemental analysis. Trial 1 had one outlier with a value of 52.62. The rest of the bomb trials showed heating values similar to that of the calculated value heating value and confirms that the formula is a good estimator of heating values using elemental analysis.

2.4.6 GC/MS Scan

The Department of Chemical Engineering at LSU conducted a library scan on the ASF fraction to find possible oil-like compounds. There was a minimum of 175 peaks for all samples only 10% had quality matches of 90% or higher. Table 2.7 reports only 10 possible compounds with quality matches of 90% or higher. Most compounds are aromatic hydrocarbons confirming that the ASF fraction contained oil-like compounds.

Table 2.7. Compounds reported by GC/MS library search that may be present in the ASF fraction.

Compound	Ref #	Cas #	Quality
2-Cyclopenten-1one,3-methyl	2768	002758-18	95
Phenol	2538	000108-95-2	95
Phenol, 2-methyl	5244	000095-48-7	95
Phenol, 4-ethlyl	9605	000123-07-9	94
1-Pentadecene	63047	013360-61-7	95
1H-Indole, 2,5-dimethyl	20371	001196-79-8	94
1-Tridecene	44129	002437-56-1	94
Hexadecanoic acid,methyl ester	100709	000112-39-0	96
Octadecanoic acid, methyl ester	116666	000112-61-8	95

2.4.7 Waste Reduction

COD studies were conducted by Standard Method 5220. Initial COD values were determined in order to report the waste reducing potential of the process. COD testing was conducted from two separate samples from the main batch of manure and the averaged value for

20g in 80ml of de-ionized water (same concentration use in HTL process) was determined to be 78,866 mg/L. Only the PPW and AINF fractions of the post processed slurry were measured for COD because they should be the only discharged portions. COD reduction varied from 54-75% with an average value of 62%.

Improved extraction procedures and/or higher conversion of organics would lead to an increase in the COD reduction percentages thus improving the waste treatment potential of the process on an organic base. The process also kills all pathogens and bacteria due to the extreme operating temperatures and corresponding pressures.

2.4.8 Mass and Energy Balances

Mass and energy balances for the process are difficult to determine. Several reasons exist why mass balances are not reported. The gas fraction was not analyzed and portions of the organics in the feedstock were converted to a gaseous product. The extraction procedure left an undeterminable amount of char and residue (up to 3 g predicted) on glassware and vessel parts. Most trials had over 5 grams unaccounted for. Energy balances are not reported for similar reasons. Again the extraction procedure and gaseous product difficulties exist. However, a watt meter was used to record the amount of energy the processor consumed (mainly from heating) during processing. For a 250°C trial approximately 0.5 kWh of power was consumed compared to 1.25 kWh for a 350°C trial. Current coal powered electricity costs are approximately $0.078 per kWh. Therefore, costs were less than 10 cents per trial to run the vessel during at 350°C. Using Table 2.5 it was determined that 4.8 grams of ASF oil with a heating value of 33.5MJ kg^{-1} was the maximum ASF oil yield. This converts to 0.161MJ of energy or 0.045kWh. This shows that the operation of the process was not efficient in terms of netting any energy production. However, the gas fraction was not included nor was the process optimized.

2.5 Conclusions

A preliminary study of the thermochemical conversion of dairy manure has been conducted. The HTL process was successful in converting raw dairy manure into oil-like compounds. Temperatures of 350ºC or greater are recommended. Modifications to the vessel which will allow for higher temperature trials must be done. Results from process temperatures greater than 350ºC are needed in order to determine an optimum temperature for conversion of separated dairy manure to bio-oils. It was determined from this study that sodium carbonate may have an effect on production quantities of oils yet had no effect on preventing the formation of char. Initial testing showed that the process is capable of reducing lagoon loading by reducing the waste strength. COD reduction was as high as 74%. GC/MS library scans and bomb calorimetric studies on the ASF fractions confirmed production of hydrocarbons and heating values. However, further upgrading of compounds is needed to increase heating values by reducing oxygen contents in the oil fraction. Conversion efficiency of 34% on an organic base was achieved and with a calculated heating value of 34.5MJ kg^{-1}. Energy and mass balance computations remain to be determined because post-process gas composition is unknown. The HTL processor and the extraction methods need to be refined to help increase oil production from the process. HTL is a promising alternative energy technology with a positive waste reducing effect.

CHAPTER 3: THE EFFECTS OF USING VARIOUS CATALYST AND LOUISIANA BASED FEEDSTOCKS IN THE HTL PROCESS

3.1 Introduction

The effects of using various catalysts and Louisiana based feedstocks in the HTL process of biomass was investigated to determine additional information on catalyst use and to verify the processes ability to convert many different feedstocks to oil products. The alkali catalyst, sodium carbonate (Na_2CO_3), was investigated in Chapter 2 prior to this study and was found to minimally affect the production of oils in the process. Additionally, it was determined that the catalyst showed no signs of inhibiting char production. The ability of an HTL process to convert many different sources of biomass to oil products is important in order to improve overall efficiency and thus the economics of the process. Louisiana is home to a wide variety of feedstocks that may be used as a biomass source. The paper industry alone produces over 8.5 million wet tons of waste annually. Other sources include rice hulls, soybean straw, corn stalk, cotton gin trash, wheat straw, sweet potato vine, animal wastes (poultry, swine, and dairy), and bagasse. It is reported that up to an additional 6 million wet tons of waste is produced each year from these sources (LSU Agcenter, 2006). Many of these feedstocks are already being used as an energy source by facilities or specific producers across the state. Other potential feedstocks exist that were not reported by the LSU Agcenter during their study. Switchgrass may be potentially grown in the state, specifically for conversion to energy. Tallow seeds from the Chinese tallow tree, which is otherwise considered a nuisance, may contain valuable oil. This chapter discusses the use of dairy and poultry manures, tallow seeds, pine sawdust and switchgrass as an alternative feedstock. It also includes information concerning oil upgrading by comparing conversion of feedstocks containing readily available oil (extractable oils) to oils produced from the HTL process. These include peanuts, tallow seed, and raw vegetable oil.

Two additional catalysts were also studied, potassium carbonate (K_2CO_3) and sodium hydroxide (NaOH). The catalysts were compared directly to the sodium carbonate study with dairy manure in reported in chapter 2. The study was conducted to confirm the results in the prior study and to determine whether different alkali catalyst may benefit the process further. Dairy manure was the sole feedstock used in the catalyst trials.

3.2 Materials and Methodology

3.2.1 Feedstock Preparation

The feedstocks used for this study were tested for total and volatile solid content and elemental analysis (CHN) to determine raw heating values. All feedstocks except raw vegetable oil were dried in an oven at 105°C. All but one feedstock was ground and homogenized using a blender prior to being processed. Two different trials using tallow seeds were conducted: one trial contained whole seeds processed directly off the tree; the other trial was homogenized, both were dried in an oven at 105°C prior to testing. Appendix C.3 shows the pre-processed feedstocks. All feedstocks except switchgrass and pine saw dust were combined with de-ionized water to yield a 20% total solid solution to be used as the pre-processed slurry by combining 20g solids to 80 ml de-ionized water. Switchgrass and pine saw dust were difficult to mix using the same ratio as other feedstocks; therefore, 10g solids to 80 ml de-ionized water was used to yield an 11% solid slurry. The raw vegetable oil was processed as is with 20ml to 80ml de-ionized water. Feedstocks were tested mainly to determine if the feedstock was worthy of further exploration in the HTL process.

3.2.2 Catalysts

Two additional catalysts were used to study the effects of the HTL process on the production of oil products; quantity and quality by heating value. Sodium hydroxide (NaOH, ACS grade anhydrous), and potassium carbonate (K_2CO_3, ACS grade anhydrous) were used in the processing of dairy manure. The 8 trials conducted using 1, 2, 3 and 4 grams of each catalyst were compared directly to the study using sodium carbonate discussed in section 2.4.3. The objective of this study was to confirm the results of the prior study that alkali catalyst did little to influence the production of oils and inhibit char formation in the HTL processing of dairy manure. It was also conducted to compare the two carbonates to the hydroxide to see if the different base structure led to any differences in results.

3.2.3 Experimental Setup

All experiments discussed in this chapter were conducted using the 300ml batch HTL processor described in section 1.5.2. The operating temperature was 350°C, and carbon monoxide (CO) was used as the process gas. One gram of sodium carbonate was used as the catalyst in the feedstock study. The vessel was operated as describe in section 2.3.3. Statistical analysis conducted for Chapter 3 were consisted only of two tail t-tests comparing two arrays of data to determine if there was a difference using the hypothesis (Pr .05> |t|) for significance.

3.2.4 Analytical Procedures

The extraction procedures as well as the CHN procedures for both the catalyst and feedstock study were the same as described in section 1.5.3 for all trials. No further testing (bomb calorimeter, COD, or GC/MS) was conducted on any portion of the post-processed slurry for this study.

3.3 Results and Discussion

3.3.1 Catalyst Comparisons

Catalysts are compared below to the first set of data collected and reported in section 2.4.3, by type (carbonate vs. hydroxide), and between both carbonates. Dairy manure was the only feedstock used in the study and was obtained from the same batch of material processed for the trials in chapter 2. The ASF fraction remained the most important fraction in these studies; ESF continued to yield very low quantities (<0.5 g). All trials were conducted at 350°C, with 15 minute retention time, 200 rpm, CO as the process gas with 300 psi initial pressure, and 20% total solid slurry of dairy manure. The 0 catalyst trial was conducted only once and reported as the same trial throughout the three Tables (3.1, 3.2, and 3.3).

Table 3.1. Increasing catalysts amounts (g) and Acetone Soluble Fraction (ASF) quantities for the 3 different catalysts tested.

Catalyst (g)	Na_2CO_3 (g)	K_2CO_3 (g)	NaOH (g)
0	3.77	3.77	3.77
1	4.76	3.6	4.11
2	4.4	2.94	4.87
3	3.42	2.84	2.54
4	4.34	2.8	3.6
Mean[a]	4.23	3.05	3.78
SD[a]	0.57	0.37	0.98
CV	13%	12%	26%

[a] Does not include control (0g catalyst)

It is difficult to determine which catalyst if any is beneficial in the process from the results obtained and because only one trial was conducted for each set of conditions. The control experiment was not used for the comparison between feedstocks. No difference was detected in for the comparison of sodium hydroxide to sodium carbonate or for potassium carbonate to sodium hydroxide with an alpha of 0.05. T-testing was also done between the control and each of the 1-4g trials conducted. No difference was found. The highest ASF fraction (4.87g) was obtained using 2g of sodium hydroxide (NaOH) (Table 3.1). Potassium carbonate (K_2CO_3) did not yield a higher ASF fraction when used as a catalyst in the process. Using more than 2g, or a 10% ratio of catalyst to solid, is not recommended as ASF fractions obtained from processing with greater catalysts amounts did not improve quantities. The catalysts again continued to end up in the post processed water fraction (PPW) at the end of the extraction as discussed in section 2.4.3.

The highest heating value (34.7MJ kg^{-1}) (Table 3.2) for the ASF fraction was obtained using 2g sodium carbonate (Na_2CO_3). Sodium carbonate consistently yielded the highest heating value except when using 4g catalyst where NaOH yielded a higher value 34.6MJ kg^{-1} compared to 32.5MJ kg^{-1} in the sodium carbonate ASF fraction. Potassium carbonate yielded similar values to sodium hydroxide which again were lower than sodium carbonate. The overall highest ASF fraction (quantity (4.76g) and heating value (33.4MJ kg^{-1})) occurred when using 1g sodium carbonate. Significance testing was conducted on the using the same tests for the heating value data (Table 3.2) as it was for the quantity data in Table 3.1. A difference exists between sodium carbonate and sodium hydroxide only.

Table 3.2. Increasing catalyst amounts (g) and corresponding Acetone Soluble Fraction (ASF) heating values for the three different catalysts types tested.

Catalyst (g)	Na_2CO_3 (MJ kg^{-1})	K_2CO_3 (MJ kg^{-1})	NaOH (MJ kg^{-1})
0	33.0	33.0	33.0
1	33.4	31.9	32.2
2	34.7	31.0	30.6
3	33.5	31.1	28.0
4	32.5	25.5	34.6
Mean[a]	33.50	29.86	31.35
SD[a]	0.90	2.97	2.76
CV	3%	10%	9%

[a] Does not include control (0g catalyst)

Alkali or basic catalysts have been reported to hinder char formation when used in HTL processes. In the 2g trials using potassium carbonate and sodium hydroxide, significant reduction in char formation (AINF) was found (Table 3.3); however, trials using 3g and 4g of catalysts did not confirm these results. Table 3.3 also shows slight decrease in char formation in most of the trials when comparing them to the no catalyst trial. Again sodium carbonate had the largest decrease in char formation from 0-1g catalyst use 6.67g to 4.72g, respectively, than the other two catalysts. The only difference determined was for sodium carbonate where a slight significant reduction of AINF fraction occurs from 0 to 1-4g usage.

From all the results, 1g of sodium carbonate used at the tested conditions is recommended over the other catalysts tested in this study. The 1g catalyst corresponds to 5% of the 20g in processing slurry. However, the general result from all t-tests was that no difference existed between catalysts types and amounts. Additionally from Chapter 2 it is reported that sodium carbonate had no effect on MJ production. Additional testing is needed in order to confirm this conclusion because not enough trials were conducted to have conclusive results.

Table 3.3. Acetone Insoluble Fraction (AINF) compared to various catalyst amounts used for the three different catalysts types tested. .

Catalyst (g)	Na_2CO_3 (g)	K_2CO_3 (g)	NaOH (g)
0	6.67	6.67	6.67
1	4.72	5.78	5.54
2	5	1.69	1
3	5	6.05	4.78
4	5.47	7.14	6.7
Mean[a]	5.05	5.17	4.51
SD[a]	0.31	2.39	2.47
CV	6%	46%	55%

[a] Does not include control (0g catalyst)

3.3.2 Feedstock Results and Comparisons

The discussions of the results for the feedstocks are broken down by individual feedstocks. Table 3.4 is used to report the results at the end of this section and is the only table that is referred to throughout section 3.3.2. The testing conditions for this study were the optimum conditions reported for dairy manure in chapter 2. These include a processing temperature of 350°C, 15 minutes retention time, 200rpms, CO as the process gas, 1g sodium carbonate, and 20% total solids if possible. A comparison of the raw energy content of each feedstock to the total MJ (ASF +ESF) obtained during processing was conducted and reported in Table 3.4. The process did not increase the energy content of the oil products compared to the raw energy content for any of the feedstocks. Water to solid ratio (W/S) testing of feedstocks during liquefaction was not explored in this work. A higher W/S ratio may play an important role in the conversion efficiency of the process because of the excess water available to aid in the reactions.

3.3.2.1 Tallow Seeds (Whole and Processed)

Tallow seeds were converted whole (as is off the tree) and processed (ground and homogenized). Tallow trees have the potential of producing up to 60 pounds of seed per tree or up to 10,000 pounds per acre. Oil content is reported as high as 27.5% by weight. The seeds were processed whole to determine whether or not homogenizing and grinding is necessary for seed-like feedstocks. The raw heating value of the tallow seeds was calculated as 26.9MJ kg^{-1} with an organic content of 97.5% by weight. The ASF quantities were 8.90g and 5.57g for whole tallow and ground tallow respectively. The heating values for the ASF fraction were similar at 34.4MJ kg^{-1} and 33.7MJ kg^{-1}. The 8.9g or 46.5% conversion on an organic basis is the highest yield of the ASF fraction for all experiments conducted for this thesis. Aside from the large quantity difference in the ASF fraction the rest of the results were essentially the same. This quantity difference resulted in the overall energy content differences between the two separate trials (0.31MJ whole and 0.19 ground). Due to the fact the trials were not conducted in triplicate the significance cannot be tested. The processing provided increases to the raw oil heating value vs. the ASF heating value and produced similar quantities of oil compared to pre-existing raw oil present in the tallow seeds.

Table 3.4. Feedstock study results, all trials conducted at 350°C, with 15 minute retention time, CO as process gas, 200 rpms, and 1g sodium carbonate. HV (heating value) reported in MJ kg^{-1}, ASF (acetone soluble fraction), ESF (ether soluble fraction), AINF (acetone insoluble fraction), PPW (post processed water), Raw (unprocessed feedstock).

	Dairy	Poultry	Saw Dust[a]	Tallow Whole	Tallow Ground	Switch[a]	Peanuts	Veg Oil
(g) or (ml) RAW	20g	20g	10g	20g	20g	10g	20g	20ml
RAW % VS	83.2	83.3	99.9	97.5	97.5	95.3	97	99.3
VS (g)	16.6	16.7	10.0	19.5	19.5	9.5	19.4	19.9
RAW HV	11.9	11.7	16.0	26.9	26.9	16.4	24.1	40.1
ASF (g)	4.8	3.3	6.2	8.9	5.6	5.1	7.4	6.5
ESF (g)	0.3	0.2	0.4	0.2	0.1	0.6	0.2	8.2
AINF (g)	4.7	4.2	4.4	3.2	4.2	1.4	0.8	0.3
PPW (g)	2.2	3.6	1.0	2.3	3.1	7.0	4.4	0.3
ASF HV	33.5	32.5	31.1	34.4	33.7	33.6	35.4	33.6
ESF HV	25.3	23.8	25.8	24.6	26.6	31.0	28.7	37.4
RAW (MJ)[b]	0.20	0.19	0.16	0.52	0.52	0.16	0.47	0.80
ASF + ESF (MJ)[b]	0.17	0.11	0.10	0.31	0.19	0.10	0.27	0.53

[a] Quantities (g) for (ASF, ESF, AINF, and PPW) were doubled in order to compare to other feedstocks.
[b] MJ determined by multiplication of (g) for reported fraction times HV (MJ g^{-1}) (not kg^{-1})

3.3.2.2 Peanuts

Peanuts also contain readily extractable oil. The raw heating value is 24.1MJkg^{-1} with a volatile solid content of 97%. Peanuts yielded 38% conversion on an organic basis with 7.39g produced in the ASF fraction with a heating value of 35.4MJ kg^{-1}. The remaining AINF fraction contained only 0.76g of char with 2.39% being volatile.

3.3.2.3 Pine Sawdust

The wood and paper industries in Louisiana produce the largest volumes of biomass. Liquefaction is ideal for using this almost pure (99.85%) organic waste source for the production of renewable energy. Pine sawdust from the Biological Engineering wood shop was used as an example of this type of feedstock. The raw heating value of the sawdust was calculated to be 16.0MJ kg^{-1}. The ASF fraction yielded a low quantity 3.33g compared to peanuts or tallow seeds, with a heating value of 32.5MJ kg^{-1}. The process was unable to mix a 20% total solid mixture using the 20g samples as in other trials. Therefore, only 10g (11.1%) of solids were processed with 80ml of de-ionized water. The ASF quantity obtained must be adjusted for comparison purposes because only half the amount of sawdust was used (10g). Doubling the quantity of the ASF will properly adjust the data to a 6.66g ASF value.

3.3.2.4 Switchgrass

Switchgrass is a fast growing plant that could be easily grown commercially as a biomass source solely for the purpose of energy procurement. Switchgrass grown at LSU's Hill Farm in Homer, Louisiana was used. The raw heating value was calculated to be 16.4MJ kg^{-1} with an organic content of 95.25%. The ASF fraction yielded 2.62g of 33.6MJ kg^{-1} bio-oil. The process setup like the pine sawdust study was also unable to mix 20g of feedstock, therefore, only 10g was used. Adjusting the ASF fraction quantity by doubling it due to only half the original feedstock being used compared to other feedstocks tested would yield a 5.24g ASF fraction. This is comparable to the dairy and sawdust studies.

3.3.2.5 Poultry Litter

Poultry farming is the largest confined animal production system currently being used in the state of Louisiana. Poultry manure consists of the manure and urine, and also the bedding material used to line the housing barn floors. Therefore, the feedstock is termed poultry litter. Compared to dairy manures raw heating value of 11.9MJ kg^{-}1, poultry manures raw heating value of 11.7MJ kg^{-1} are basically the same. This is due to the same organic content of 83.2% by weight. The heating values of the ASF fractions were also similar with a value of 33.5MJ kg^{-1} for dairy and 32.5MJ kg^{-1}. The ASF quantities, however, are different 4.76g for dairy and 3.33g for poultry. The volume of poultry litter in the state versus dairy manure makes poultry litter more attractive as a feedstock in the HTL process even with the lower conversion yields.

3.4 Existing Oil Upgrading

A trial to determine whether the process is capable of upgrading (heating values) pre-existing oils was conducted.

3.4.1 Vegetable Oil

Store bought vegetable oil was used to determine whether the reactions that occur in the HTL process are capable of further up-grading the oil contents heating value. 20 ml of oil was added to 80 ml of de-ionized water. Raw vegetable oil used in this trial had a calculated heating value of 40.1MJ kg^{-1}. The ASF fraction yielded only 6.47g with a heating value of 33.6MJ kg^{-1}. This trial was the only one throughout all trials conducted and reported for this thesis that had a yielded an ESF fraction larger than 1g. The ESF fraction collected was 8.15g with a heating value of 37.4MJ kg^{-1}. In total, 14.26g of oil with an average heating value of 35.8MJ kg^{-1} was recovered from the extraction process. Comparing this to the original 20ml of oil the process did not upgrade the raw oil.

3.5 Conclusions

The catalysts study did not yield definitive results. It is not conclusive whether catalysts (sodium carbonate, potassium carbonate, and sodium hydroxide) benefit the conversion of dairy manure to oil products even with the statistical testing. Without replicate trials it is difficult to have confidence in the statistical results. The optimum catalyst (type and amount) is 1g of sodium carbonate; this combination yielded the highest heating value (MJ) of all trials conducted for sodium carbonate (Table D.1) and from the few differences noted throughout this chapter sodium carbonate could be concluded as the better type.However, there was no difference detected between the energy content and the cata Further studies are recommended to confirm these results with the use of a larger conversion vessel capable of handling larger sample sizes.

All the feedstocks tested were effectively converted to an oil product with a heating value of 32.0MJ kg^{-1} or higher. Poultry litter was the only feedstock that did not yield a higher quantity of ASF fraction then dairy manure. Switchgrass and sawdust ASF and ESF fraction energy contents were increased compared to the raw feedstocks energy content. All feedstocks should be studied further using the HTL process. Oil upgrading using pre-existing oil was determined not to occur using the current liquefaction processor setup.

CHAPTER 4: CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE HTL WORK

Liquefaction of biomass has been widely researched and is proven technology that is rarely used in commercial treatment of biomass waste feedstocks. Louisiana has an abundance of waste producing sources especially in the agricultural sector in which liquefaction could provide two benefits; waste treatment and energy production. Potentially 50,000 homes could be powered from dairy, swine, and poultry manures produced in the state alone using an HTL process. Currently in the United States only 2.7 quadrillion Btu's of installed biomass capacity is available. In order to reduce our dependence on foreign oil many different technologies will have to be employed together across the nation. Liquefaction has the potential to aid in this process to provide the nation with cleaner "alternative fuels and energy."

The objectives of this research have been met through a series of preliminary experiments designed to begin the HTL research of Louisiana biomass-based feedstocks. The 300ml bench scaled HTL processor was used effectively to convert various feedstocks to oil-like products. Temperature is the most important parameter in the HTL process. It is concluded that temperatures of 350°C or more are needed to optimize the conversion of dairy manure to oil and temperature directly affects the energy content of the oil products. The use of alkali catalyst may aid in producing higher quantities of oils and reducing char formation, yet statistically in this work catalysts use was determined to not affect the total energy content of the oils produced and no differences were noted when testing different catalysts quantities versus no catalyst use. Several alkali catalysts were explored and the addition of 5% by weight (1g to 20g solids) of sodium carbonate was determined to provide the best results for MJ production, but essentially no differences were detected between the catalysts types. Four additional Louisiana feedstocks (poultry litter, tallow seed, sawdust, and switchgrass) were studied and results indicated that all are capable of producing bio-oils. Further research is needed using these feedstocks and dairy manure to optimize the conversion to oil and to reduce wastes.

To complete the objectives for this research recommendations to improve the processing of these feedstocks are discussed below.

The HTL processor was sufficient for processing feedstocks during this initial study; however, improvements are needed in order to further explore the other operating parameters associated with the HTL process. The current vessel is only capable of processing up to 20g of solids in a trial. A larger vessel would allow for larger quantities of samples to be processed thus improving the results obtained by minimizing the effect of mass losses. It was difficult to decipher slight differences in the data collected from similar trials. It is unclear whether the agitation system is providing sufficient gas mixing. It is important in the process that the process gas (CO) be mixed thoroughly throughout the feedstock slurry to allow for the reducing reactions to occur. The agitation shaft is designed to create a draft which will move the gas from the high pressure air space to the lower pressure slurry through a hole in the shaft. This design was tested outside the reactor for gas mixing and it was unclear whether this was actually occurring. High rpm's are needed for this to occur, unfortunately, when attempting to increase rpm's above 200 the propeller spun off the shaft to prevent damage. The liner, which was added to aid in transfer of the pre- and post-processed slurries, created a smaller diameter in the vessel and is the predicted cause of this problem. An improved design or different agitation system is needed to test the gas mixing capabilities of the processor. A control system, which automatically implements the cooling cycle at the appropriate time, would improve the consistency of retention time by eliminating human error.

The extraction used for this process was adapted from several other researchers; however, the efficiency of the extraction process could be improved. A soxhlet system, or a vacuum drier would aid in improving extraction efficiency. Mass losses were as high as 9g per trial. This occurred because of material remaining on equipment after exposure to solvents and from unaccounted conversion to gaseous products.

Recommendations for future testing include equipping the vessel with the proper safety features to allow for testing above 350°C. Carbon monoxide was the sole gas used and other gas types may improve processing. Compressed air may be viable for processing, which would reduce processing costs significantly. Additional catalysts tests are needed as well, non-alkali catalysts such as nickel need further investigation. However, non alkali catalysts tend to promote gas production. The gas fraction needs to be analyzed to determine the energy potential so an energy balance can be performed. Finally, a complete experimental design should be developed prior to any new testing to prevent similar problems associated with not being able have confidence in the statistically tested results that were presented in this thesis work, in particular the lack of replicate trials.

The HTL processing of Louisiana based feedstocks is promising and may provide additional revenues to farms and valuable energy products. Larger scale processing facilities (city or regionally based), should improve production and conversion efficiencies.

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APPENDIX A: ANALYTICAL METHODS AND PROCEDURES

The analytical methods and procedures are adopted from several different resources; the standard Methods for the Examinations of Water and Wastewater (Standard Methods), the American Society for Testing Materials (ASTM), and instruction manuals or procedures from several equipment manufactures.

A.1 Solids

A.1.1 Total Solids (TS)

ASTM E1756-01 (Standard Test Method for Determination of Total Solids in Biomass)

Apparatus:

1. Porcelain crucible.
2. Drying oven, operating at 103-105ºC.
3. Desiccator, with desiccant containing a color indicator.
4. Muffle furnace, operating at 550ºC.
5. Analytical balance, capable of weighing to 1 mg.

Procedure:

1. Preparation of evaporation crucible. Ignite clean the crucible at 550ºC for 1 hour, store in desiccator until needed. Weigh immediately before use.
2. Sample analysis. Take a sample of well-mixed manure about 100ml, record the sample size. Transfer the sample to a pre-weighed crucible. Dry in oven at 103ºC for 12 hours. Cool the crucible in desiccators to room temperature (2 hours). Weigh the crucible and dried sample, record data.
3. $TS(mg/L)=(B-A)x10^6/\text{sample size (ml)}$

Where B=weight of dried residue + crucible, g, and A=weight of crucible, g.

A.1.2 Volatile Solids (VS)

ASTM E1755-01 (Standard Method for the Determination of Ash in Biomass)

Procedure:

1. Place the sample from TS measurement into muffle furnace at 550ºC for two hours. Take the crucible out and let most of the heat dissipate into the air. Transfer the crucible into the desiccators and let cool to room temperature (2 hours). Weigh the crucible plus dried sample with balance, record data.

2. VS (mg/L)= (C-A)x10^6/sample size (ml)

   Where: C=weight of burned residues+crucible, g, and A=weight of crucible, g.

A.2 pH Values

4500-H^+ B, Standard Methods

Apparatus:

1. pH meter, permit to read to 0.01 unit.
2. Glass electrode.
3. Thermometer, permit to read to 0.1ºC.
4. Beaker and magnetic stirrer.

Reagent:

1. Standard pH buffer solutions at pH 4, pH 7, and pH 10.

Procedure:

1. Instrument calibration. Estimate the sample pH range, and calibrate the pH meter using standard pH solutions. Calibrate the meter according to the procedure provided by the manufacturer. Repeat calibration several times until the pH readings are in the range of 0.02 units.

2. Rinse the probe with de-ionized water thoroughly, and get rid of the drops on the probe.

3. Moderately stir the sample in a beaker with a magnetic stirrer. Dip the pH probe and thermometer in the solution for measurement. Record the reading once it becomes stable for at least three seconds.

4. With dilute and poorly buffered solution, immerse the probe in three successive sample portions for equilibrating the electrode. Take a fresh sample to measure the pH.

A.3 Chemical Oxygen Demand (COD)

Standard Methods 5220

Apparatus:

1. COD reactor.
2. Spectrophotometer with cuvette.
3. COD vial and cap.
4. Pipet 0-1 ml.
5. Blender.

Reagent:

1. COD digestion reagent vial, High Range.
2. Potassium Acid Phthalate, ACS.

Calibration Curve:

Instrument Preparation:

1. Preheat the COD reactor to 150ºC.
2. Turn on the spectrophotometer to allow for it to warm to steady state.

Sample Preparation:

3. A 10,000 mg COD/L Potassium Acid Phthalate (KHP) solution is needed. Pre-dry the KHP at 120ºC for 12 hours. Dissolve 2.1250g of KHP in a clean beaker with 150ml of de-ionized water. After the chemical dissolves, transfer the solution into a 250ml volumetric bottle. Rinse the beaker twice with 25 ml of de-ionized water each time, and transfer the water into the bottle. Using de-ionized water fill the beaker to 250ml. Store the solution at room temperature until needed.

4. Repeat the above step for the preparation of 2500, 5000, 12500 and 15000mgCOD/L by dissolving .5312, 1.0625, 1.5937, 2.6562, and 3.2280g, respectively, in de-ionized water and bringing the total volume to 250ml. It is also acceptable to dilute a large solution of 15000mgCOD/L to the desired mg COD/L solutions.

5. Remove the cap of a COD Digestion Reagent (High Range), add 0.2ml of the prepared sample into the vial by holding it at a 45° angle. Replace the cap tightly. Rinse the vial with de-ionized water and wipe it with a chemwipe or paper towel.

6. Hold the vial by the cap and over a sink. Invert several times to mix the contents. Place the vial in the preheated reactor.

7. Prepare a blank by repeating steps 6 and 7, substituting the 0.2ml de-ionized water for the sample.

8. Heat the vials for 2 hours.

9. Turn off the reactor, wait 20 minutes for the vials to cool to 120ºC or less. Invert each vial several times while still warm and cool the vials to room temperature.

The Measurement:

10. Set the wavelength on the spectrophotometer to 600nm. Transfer the COD solution to a clean cuvette wiping clean before and after sample addition. Place the cuvette into the cell holder and Zero (blank) the instrument the display should read an absorbance of 0.

11. Repeat step5-10 using the remaining samples recording the sample concentration and absorbance.

Calibration Curve Construction:

12. Plot the COD concentration measured vs. the COD concentration prepared, and the calibration curve is constructed see Figure A-1.

A.3.1 Measurement Procedure

Instrument Preparation:

1. Preheat the COD reactor to 150ºC.

2. Turn on the spectrophotometer to allow for it to warm to steady state.

Sample Preparation:

3. Homogenize a 100ml sample for 2 minutes in a blender.

4. Dilute the homogenized sample with de-ionized water to a proper concentration (0 to 15,000mg/L). Repeat if necessary.

5. Remove cap of a COD digestion reagent (High Range Plus), add 0.2ml the prepared sample into the vial by holding it at 45° angle. Replace the cap and rinse the vial with de-ionized water and wipe with a chemwipe or paper towel.

6. Hold the vial by the cap and over a sink. Invert several times to mix the contents. Place the vial in the preheated reactor.

7. Prepare blank repeating steps 5 and 6, substituting the 0.2ml de-ionized water for the sample.

8. Heat the vials for 2 hours.

9. Turn the reactor off, wait 20 minutes for the vials to cool to 120ºC or less. Invert each vial several times while still warm and cool the vials to room temperature.

The Measurement:

10. Set the wavelength on the spectrophotometer to 600nm. Transfer the COD solution to a clean cuvette wiping clean before and after sample addition. Place the cuvette into the cell holder and Zero (blank) the instrument the display should read an absorbance of 0.

11. Repeat steps 5-10 using the remaining samples recording the sample concentration and absorbance.

Calculation of the sample COD:

12. The COD of the sample can be obtained by converting the readings from the spectrophotometer measurement based on the calibration curve (Figure A-1) to a concentration.

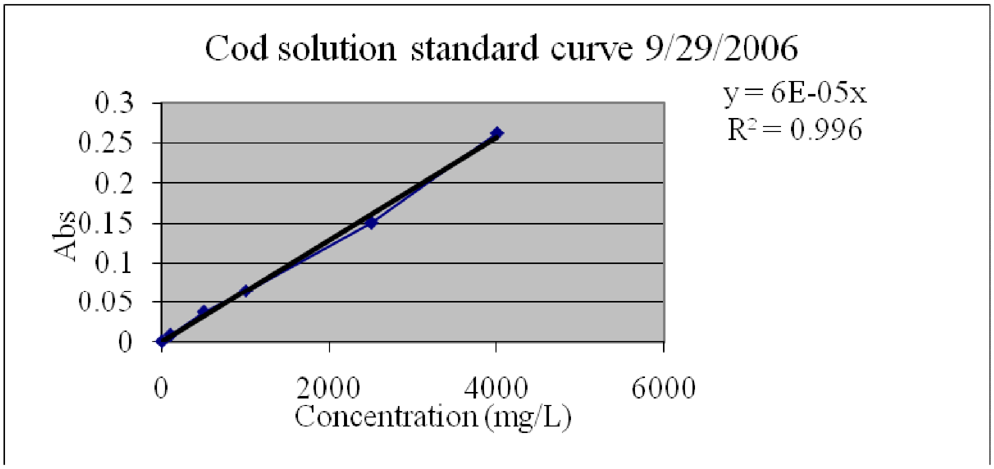


Figure A.1. COD measurement standard curve dried and homogenized dairy manure.

A.4 Elemental and Physical Analyses

The elemental analysis was done in LSU AgCenter's Callegari Environmental Research Lab. The elemental analysis includes carbon, hydrogen, and nitrogen (CHN) analysis, and metallic elements analysis. The analyses are performed by carbon-hydrogen-nitrogen analyzer, and Inductively Coupled Plasma (ICP).

A.4.1 Elemental Analysis

A.4.1.1CHN

CHN is an abbreviation for Carbon, Hydrogen, Nitrogen analyzer Model Vario El by Elementar. (Germany). This instrument can also detect oxygen and sulfur if needed, however, it is costly and time consuming. To detect CHN the sample needs to be broken down into its atomic components and then separated. To break the sample down it is combusted in an oxygen atmosphere at 980ºC. At this temperature all of the elements to be detected react with oxygen to form CO_2, H_2O, and N_xO_y. These gases are carried via a stream of helium gas to a detector. The detector reports a value to the computer that compares it to the known value of a standard. These values are calculated based on the weight of the sample.

The procedure for conducting CHN is tedious and time consuming. First an aliquot of a solid or liquid sample is taken and place in a tin capsule, weighed, then sealed. The capsule is then placed in an auto sampler which will drop the sample into the combustion furnace one at a time. From there the sample is transported through a series of valves and columns that separates the various compounds before reaching the detector.

In Appendix C Table C-1 three separate raw manure sample results from a CHN run are shown.

A.4.1.2ICP

ICP is an abbreviation for Inductively Coupled Plasma Model MPX-Vista by Varian (Palo Alto, CA, USA). The basic operating principle is based on intensity of emission from elements in an excited state. Digested samples are aspirated into the plasma where a portion of the sample is excited. The excited element emits light (UV/VIS) at characteristic wavelengths. A computer then compares the intensity of a sample to the intensity of a known standard to determine concentration and type of element. An inductively coupled plasma is a ultra-high temperature source that vaporizes, excites, vaporizes, and ionizes atoms. The sample is nebulized as a fine vapor into the torch with argon gas as its carrier. The argon keeps the torch from melting and is the fuel for the creation of the plasma.

A strong radiofrequency generator in the coils around the torch produces a magnetic field which generates the argon plasma. The temperature in the plasma approaches 10,000K in the quartz torch. Metal atoms in the plasma are excited to a higher energy level and as they return to a ground state they emit light. The light given off by the atoms is separated into separate wavelengths by a grating. A photomultiplier tube is normally the detector of choice. The amount of light given off is also proportional to the amount of that element in the sample, so the concentration of a given element in a sample can be accurately determined.

In appendix C Table C-2 shows results of and ICP scan for three separate raw dairy manure samples. The manure was pre-processed (dried and homogenized) prior to digestion.

A.5 Oil Compound Analysis

A.5.1 GC/MS.

Gas chromatography-mass spectroscopy (GC/MS) was performed by the Chemical Engineering Department at Louisiana State University. GC/MS is actually two techniques that are combined to form a single method of analyzing mixtures of chemicals. Gas chromatography separates the components of a mixture and mass spectroscopy characterizes each of the components individually. By combining the two techniques, both qualitatively and quantitatively evaluations of a solution containing a number of chemicals can be analyzed.

A.5.2 GC

Gas Chromatography is used to separate mixtures of chemicals into individual components. Once isolated, the components can be evaluated individually. Separation occurs when the sample mixture is introduced into a mobile phase, typically helium. The mobile phase carries the sample mixture through what is referred to as a stationary phase. The stationary phase is usually a chemical that can selectively attract components in a sample mixture. It is usually contained in a tube or column. The mixture of compounds in the mobile phase interacts with the stationary phase. Each compound in the mixture interacts at a different rate. The faster interacting compounds will elute from the column first and the slower compounds last. Changing the characteristics of the mobile or stationary phase allows different mixtures of chemicals to separate completely. Adjusting the temperature or pressure in the system will also help to further separate compounds that may elute too close together. The detector is capable of creating an electronic signal whenever the presence of a compound is detected. The higher the concentration the higher the electronic signal the detector sends to a computer for processing.

A.5.3 MS

As the individual compounds elute from the GC column, they enter the electron ionization (mass spec) detector. In this chamber compounds are bombarded with a stream of electrons which cause them to break apart into a large variety of fragments from the original molecules. The fragments are actually charged ions with a certain mass. The mass of the fragment divided by the charge is called the mass to charge ratio (M/Z). Most fragments have a charge of +1, the M/Z usually represents the molecular weight of the fragment. A group of four electromagnets, called a quadrapole, focuses each of the fragments through a slit and into the detector. The quadrapoles are programmed by a computer to direct only certain M/Z fragments through the slit. The rest bounce away. The computer has the quadrapoles cycle through different M/Z's one at a time until a range of M/Z's are covered. This occurs several times per second and each cycle of ranges is referred to as a scan.

When GC is combined with MS, a powerful analytical tool is created. A researcher can take an organic solution, inject it into the instrument, separate the individual components, and identify each of them. If a set of standards is used the researcher can determine the concentration of each of the components. For this thesis study only a scan of the ASF fraction was conducted and the reported results are not confirmed compounds.

A.6 Heating Value Determination

A.6.1 Estimation of Heating Value

Heating value or heat of combustion is a thermodynamic property of a substance. It indicates the energy content in the substance. Heating value is defined as the amount of heat evolved by the complete combustion of a unit amount of the substance. In the metric system, heating value is usually in the unit of kilojoules per mole (kJ/mol). The heating values for ethanol (C_2H_5OH) and propane (C_3H_8) are 1,366.8kJ/mol and 2,202.8kJ/mol, respectively. Converting the two values into per unit weight basis, they are 29,713kJ/kg and 49,955 kJ/kg, respectively. Obviously, propane contains more energy than ethanol, because the high H:C molar ratio in propane (H:C= 2.67:1) and the oxygen content (35%wt) in ethanol.

Heating value of a substance is usually measured experimentally with a standard calorimetric method using a bomb calorimeter. However, it is easier to estimate the heating value for cases where the multiple samples are required to for testing at different times because calorimeter methods are sensitive to atmospheric conditions and are labor intensive, and additonally the exact value is not crucial to the experiments. Estimation of heating value is even more useful when the material to be dealt with is a mixture of organic compounds. When the composition of the mixture changes from case to case, it is accepted to estimate the heating value based on an elemental analysis such as in coal evaluation. One of the most widely used is the Dulong's formula for estimating heating values based upon CHOS concentrations in a sample. The traditional Dulong's formula:

$$H_t(\text{ kJ/kg}) = 33{,}823C + 144{,}250\,(H\text{-}O/8) + 9{,}419S \ldots\ldots (C.1)$$

Where H_t is the heating value; C,H,S, and O are the fractions of the elements of carbon, hydrogen, sulfur, and oxygen in the substance, respectively. The error of the heating values calculated by Dulong's formula was within 1.5% to that measured by oxygen bomb calorimeter for different types of coal. For biomass derived oils, its elemental composition is usually uncertain from batch to batch and calorimetric measurement of heating value for each experimental sample is not necessary. An equation to estimate the heating value of our raw TCC oil, Equation (1) in chapter 1 was recommended by Demibras (2006) as an alternative Dulong's formula full formula. Oxygen was estimated from the difference of CHN and sulfur was not determined but expected to represent a negligible fraction on a weight basis. The CHN analyzer at Callegari Center was not equipped to determine S or O, therefore equation (1) was best suited for our calculations.

A.6.2 Bomb Calorimeter

A bomb calorimetric study was conducted to confirm the heating values that were calculated by equation (1). Using the ASF fraction from the three characterization trials calorimetric work was conducted in triplicate.

A calorimeter is a device used for measuring the heat of chemical reactions or physical changes as well as heat capacity. A Parr 1108 oxygen combustion bomb was used to conduct the study. Parr manuals 204M and 205M were used to calibrate and operate the bomb. Due to the nature of the sample some modifications of the Parr procedures were required. Due to the length and complexity of the procedure it is not describe here. The Parr procedures are available online at parrinst.com. The minor adjustments made to these procedures for the ASF fractions are

1. The combustion capsule was covered with tape prior to firing to aid in combustion. The heating value of the tape was determined and corrected for in the results.
2. The fuse wire was coiled around a wooden dowel to increase the surface area in contact with the sample.
3. A data acquisition system was used to record temperature data through the use of a thermocouple. A thermometer was used as a check occasionally throughout the experiments.
4. The bomb was calibrated using Parr procedures with benzoic acid tablets. Calibration was conducted on several occasions to ensure quality of the results.

A.7 Vessel Operation

Vessel operation consists of many different types of procedures to complete one trial. Data acquisition, rpm control, gas loading, vessel loading, sealing, and post process tasks exist. All parts of the vessel must be clean and free of any debris prior to any new trial run.

Vessel loading

A stainless steel liner was purchased to aid in the transportation of pre and post processed slurries. Before loading the liner into the vessel the slurry mixture must be added to the liner. The liner can then be placed into the vessel and the metal seal placed into position. The top (portion with cooling loop, and support for the magnetic stirring drive) of the vessel is placed into the proper position.

Vessel sealing

In order to properly seal the vessel all valves, bolts, washers and seals must be checked regularly for leaks and tightened if needed. Six bolts are required to close the main seal. These are to be torque in 2.27kg (5lb) increments using the proper star technique to close the vessel. The bolts should not be torqued to more than 15.88kg (35lbs).

Gas loading

Now that the vessel is sealed gas can be added. Gas is then purged through the vessel using 5 complete replacements and allowed to fill the vessel to the desired initial pressure.

Data acquisition and control

The magnetic drive uses a motor and a chain to spin. The RPM controller for our system is set up for percent power not RPM. A laser RPM sensor was purchased to help control and keep the RPM constant throughout the experiments. A pressure transducer and additional thermocouple were added so that temperature and pressure data could be recorded. Once logging begins it must be stopped manually by the user. The pressure transducer also aids in setting the initial pressure to a constant 2.06Mpa (300psi) for all studies. The PID controller provided with the system must be set to maintain a desired temperature within 5ºC. The heater controller is set to 100ºC above the desired temperature in order to overcome heat loss to the surroundings. The controller included safety a feature which would turn off the heater if temperature and heating rate limits occurred.

Post Process

Once the vessel reaches the desired temperature and the required retention time the heater is turned off and the cooling loop initiated. The cooling cycle last until the vessel returned to pre-run temperatures. The final pressure and temperature are noted and the data acquisition is stopped. The gas is then collected through the exhaust valve into a gas bag to prevent exposure to harmful process gases. For this research the gas was not analyzed but is expected to contain light hydrocarbons that could benefit the processes efficiency. Once all the gas is exhausted the vessel can be safely opened by removing the 6 closure bolts. The post-processed slurry is now ready to go through the extraction process.

A.8 Extraction Notes

The extraction procedures were developed from several research groups who have conducted similar experiments on biomass liquefaction. Four main products from the process exist; gas, heavy oil (ASF), light oil (ESF), and post processed water (PPW). Char (AINF) is also produced in the process but is not considered a desirable product, the post processed water contains some carbon and could be further refined. Section 1.5.3 describes the process used to extract the heavy and light oils from the post processed slurry.

APPENDIX B: COMPLETE TRIAL INFORMATION

The following pages in appendix B contain all the relevant data collected for every liquefaction experiment used in writing this thesis. There were a total of 43 liquefaction experiments conducted not including any pre-testing.

Legend:
Temp = Temperature
Reten = Retention
Int = Initial
TS = Total Solids
VS = Volatile Solids
COD = Chemical Oxygen Demand
Bomb = Bomb Calorimetric Results
ASF = Acetone Soluble Fraction
ESF = Ether Soluble Fraction
AINF = Acetone Insoluble Fraction

Trial #	Temp	Ret Time	Int Pressure	%TS	%VS	Catalyst	pH	Gas
1 Dairy	250C	15 Mins	300Psi	20	83	none	6.7	CO

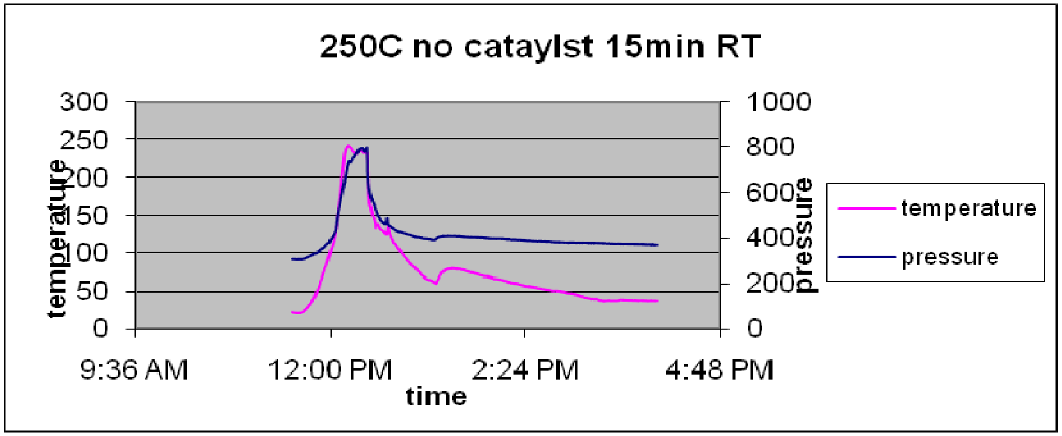
CHN Results	ASF	ESF	AINF	Post H20
%C	54.36	60.30	17.72	35.38
%H	6.14	6.78	2.00	5.37
%N	2.66	2.19	0.53	2.63
%O	36.84	30.73	79.76	56.62
HV (MJ kg^{-1})	21.27	25.12	-3.51	10.77

Oil quantity	
ESF (g)	0.183
ASF (g)	3.238
AISF (g)	10.066
post H20 (g)	1.325
(g) recovered	14.811
total (g) lost	5.189
total (g) VS	5.392
% total VS left	32.401

Power used	
KWH	0.47

COD (mg/L)	
Initial	71200
Final	N/A

BOMB	
Cal/g	N/A
Btu/lb	N/A


250C no cataylst 15min RT

Trial #	Temp	Reten Time	Int Pressure	%TS	%VS	Catalyst	pH	Gas
2 Dairy	250C	15 Mins	300Psi	20	83.20	1 g	8.4	CO

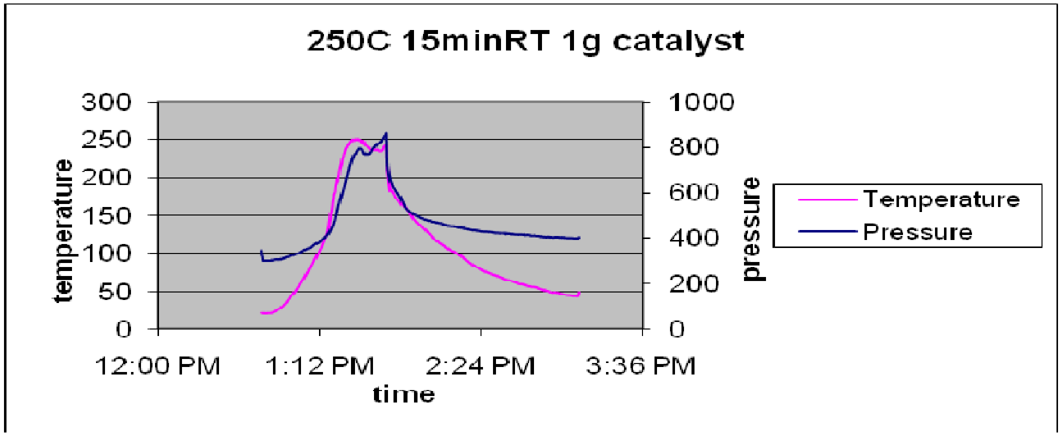
CHN Results	ASF	ESF	AINF	Post H20
%C	55.53	54.40	42.89	34.83
%H	6.15	6.22	5.24	5.70
%N	2.40	1.95	1.13	1.89
%O	35.92	37.43	50.73	57.58
HV (MJ kg^{1})	21.83	21.31	14.01	10.91

Oil quantity	
ESF (g)	0.176
ASF (g)	3.836
AISF (g)	8.911
post H20 (g)	2.117
total (g) collected	15.040
total (g) lost	4.960
total (g) VS remain	5.201
%of total VS remain	31.254

Power used	
KWH	0.48

COD (mg/L)	
Initial	71200
Final	N/A

BOMB Results	
Cal/g	N/A
Btu/lb	N/A



Trial #	**Temp**	**Reten Time**	**Int Pressure**	**%TS**	**%VS**	**Catalyst**	**pH**	**Gas**
3 Dairy	250C	15mins	300	20	83.20	2g	10	CO

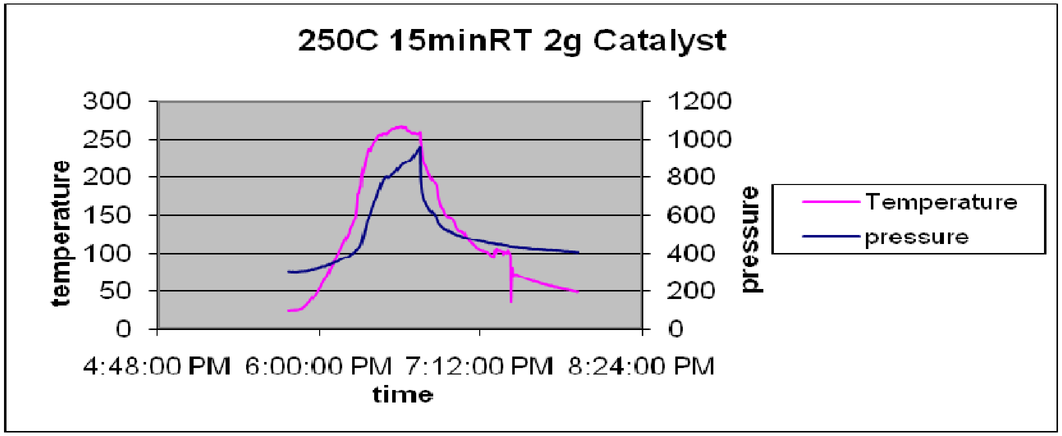
CHN Results	**ASF**	**ESF**	**AINF**	**Post H20**
%C	62.63	55.63	38.57	31.34
%H	6.44	6.66	4.76	5.76
%N	2.56	2.58	1.10	1.27
%O	28.37	35.12	55.57	61.64
HV (MJ kg^{-1})	25.78	22.71	11.14	9.20

Oil quantity	
ESF (g)	0.147
ASF (g)	3.138
AISF (g)	8.723
post H20 (g)	3.005
total (g) collected	15.013
total (g) lost	4.987
total (g) VS remain	4.890
%of total VS remain	29.383

COD (mg/L)	
Initial	71200
Final	N/A

BOMB Results	
Cal/g	N/A
Btu/lb	N/A

Power used	
KWH	0.48



Trial #	Temp	Reten time	Int Pressure	%TS	%VS	Catalyst	pH	Gas
4 Dairy	250C	15mins	300	20	83.2028	3g	10.36	CO

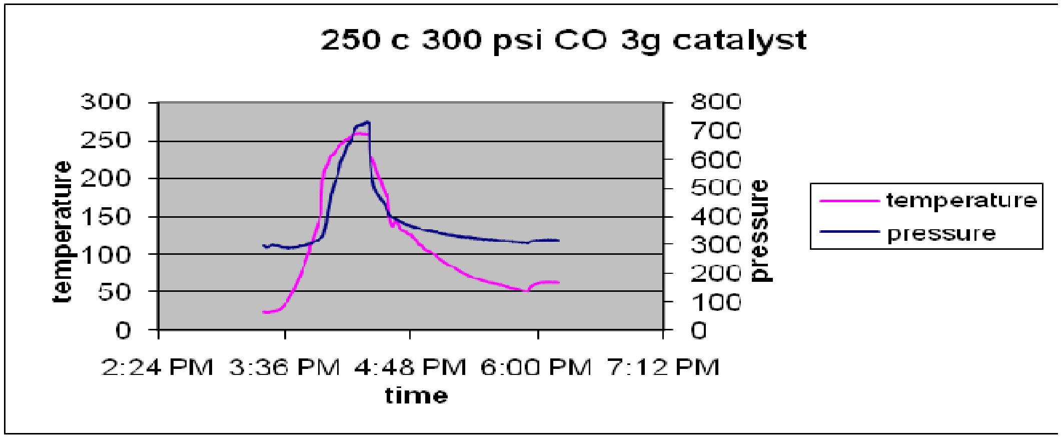
CHN Results	ASF	ESF	AINF	Post H20
%C	48.54	50.71	28.08	31.40
%H	6.62	6.17	3.98	5.28
%N	1.98	2.42	0.57	1.09
%O	42.86	40.69	67.37	62.22
HV (MJ kg^{-1})	19.07	19.50	4.70	8.45

Oil quantity	
ESF (g)	0.068
ASF (g)	3.776
AISF (g)	12.164
post H20 (g)	2.489
total (g)	18.497
total (g) lost	1.504
total (g) VS left	5.823
%of total VS left	34.990

Power used	
KWH	0.56

COD (mg/L)	
Initial	71200
Final	N/A

BOMB	
Cal/g	N/A
Btu/lb	N/A



Trial #	Temp	Reten Time	Int Pressure	%TS	%VS	Catalyst	pH	Gas
5 Dairy	250C	15mins	300	20	83.203	4g	10.36	CO

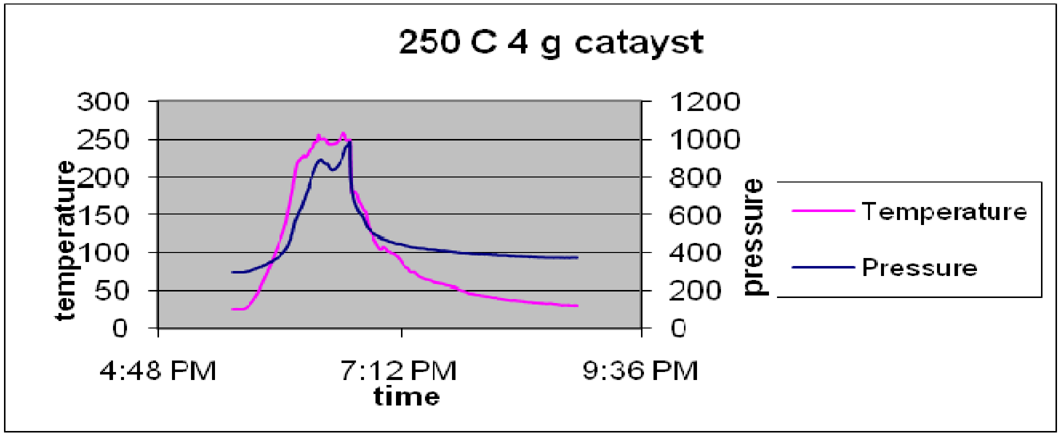
CHN Results	ASF	ESF	AINF	post H20
%C	54.51	52.27	24.86	26.63
%H	6.36	6.39	3.63	5.34
%N	1.97	2.12	0.47	0.71
%O	37.16	39.22	71.04	67.33
HV (MJ kg^{-1})	21.59	20.56	2.55	6.15

Oil quantity	
ESF (g)	0.084
ASF (g)	4.293
AISF (g)	10.452
post H20 (g)	4.306
total (g) collected	19.134
total (g) lost	0.866
total (g) VS left	5.848
%of total VS left	35.144

Power used	
KWH	0.56

COD (mg/L)	
Initial	71200
Final	N/A

BOMB	
Cal/g	N/A
Btu/lb	N/A



Trial #	Temp	Reten Time	Int Pressure	%TS	%VS	Catalyst	pH	Gas
16 Dairy	275	15mins	300	20	83.2028	4g	9.1	CO

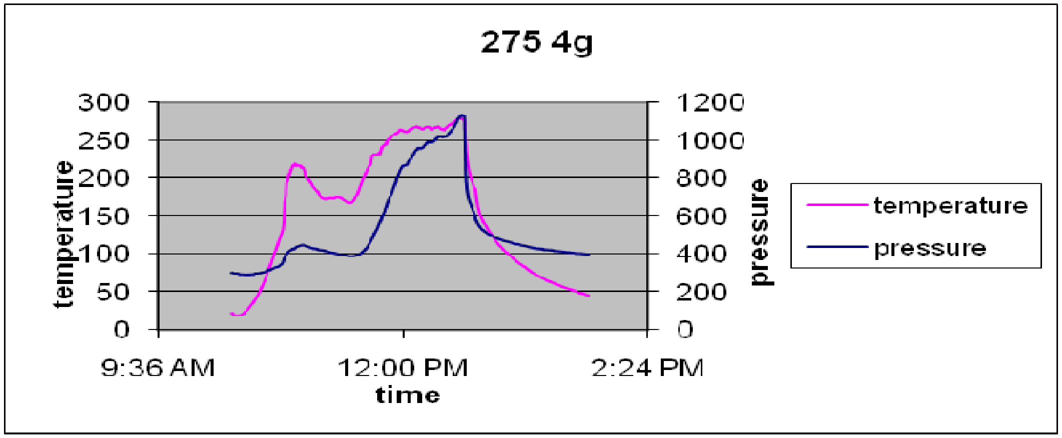
CHN Results	ASF	ESF	AINF	post H20
%C	65.64	74.90	25.03	33.02
%H	6.63	5.43	2.52	5.60
%N	2.51	2.50	0.98	0.83
%O	25.23	17.17	71.47	60.56
HV (MJ kg^{-1})	27.53	30.17	0.96	9.70

Oil quantity	
ESF (g)	0.091
ASF (g)	3.154
AISF (g)	8.183
post H20 (g)	6.255
total (g) collected	17.683
total (g) lost	2.317
total (g) VS remain	2.749
%of total VS remain	16.517

Power used	
KWH	0.81

COD (mg/L)	
Initial	71200
Final	N/A

Bomb	
Cal/g	N/A
Btu/lb	N/A



Trial #	Temp	Reten Time	Int Pressure	%TS	%VS	Catalyst	pH	Gas
17 Dairy	275	15mins	300	20	83.2028	3g	9.1	CO

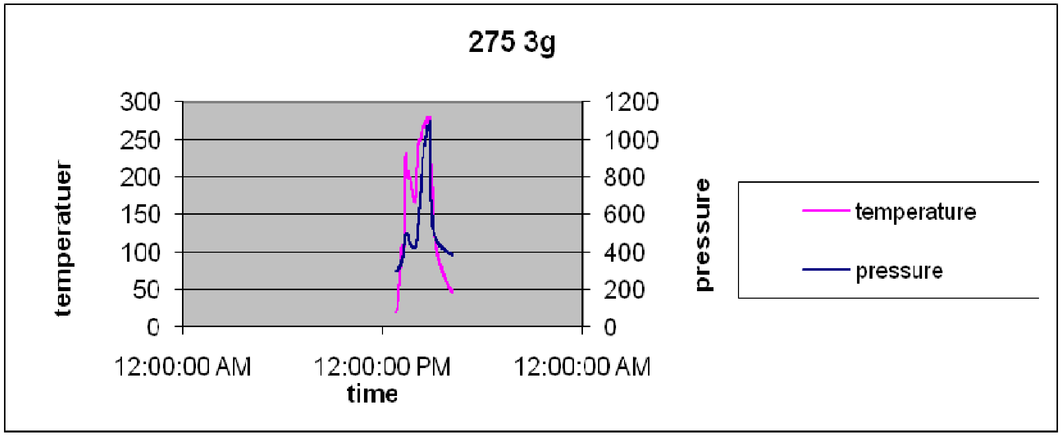
CHN Results	ASF	ESF	AINF	post H20
%C	59.64	52.74	27.48	32.68
%H	6.58	6.20	2.77	5.61
%N	2.27	1.89	1.10	0.89
%O	31.51	39.17	68.66	60.82
HV (MJ kg^{-1})	24.49	20.46	2.57	9.56

Oil quantity	
ESF (g)	0.177
ASF (g)	3.446
AISF (g)	8.653
post H20 (g)	5.238
total (g) collected	17.514
total (g) lost	2.486
total (g) VS left	3.499
%of total VS left	21.024

Power used	
KWH	0.79

COD (mg/L)	
Initial	71200
Final	N/A

BOMB Results	
Cal/g	N/A
Btu/lb	N/A



Trial #	Temp	Reten Time	Int Pressure	%TS	%VS	Catalyst	pH	Gas
18 Dairy	275	15mins	300	20	83.2028	2g	9.8	CO

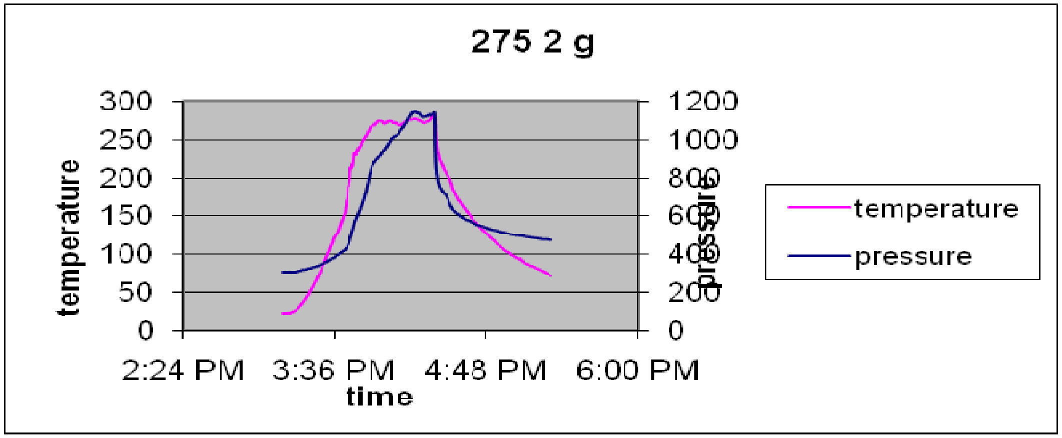
CHN Results	ASF	ESF	AINF	Post H20
%C	69.31	59.87	34.62	34.68
%H	6.83	6.48	4.67	5.19
%N	2.50	1.60	1.11	1.12
%O	21.36	32.04	59.60	59.01
HV (MJ kg^{-1})	29.65	24.34	9.07	9.92

Oil quantity	
ESF (g)	0.270
ASF (g)	3.992
AISF (g)	6.927
post H20 (g)	4.443
total (g) collected	15.631
total (g) lost	4.369
total (g) VS left	1.143
%of total VS left	6.866

Power used	
KWH	0.62

COD (mg/L)	
Initial	71200
Final	N/A

BOMB Results	
Cal/g	N/A
Btu/lb	N/A



Trial #	Temp	Reten Time	Int Pressure	%TS	%VS	Catalyst	pH	Gas
19 Dairy	275	15mins	300	20	83.2028	1g	7.1	CO

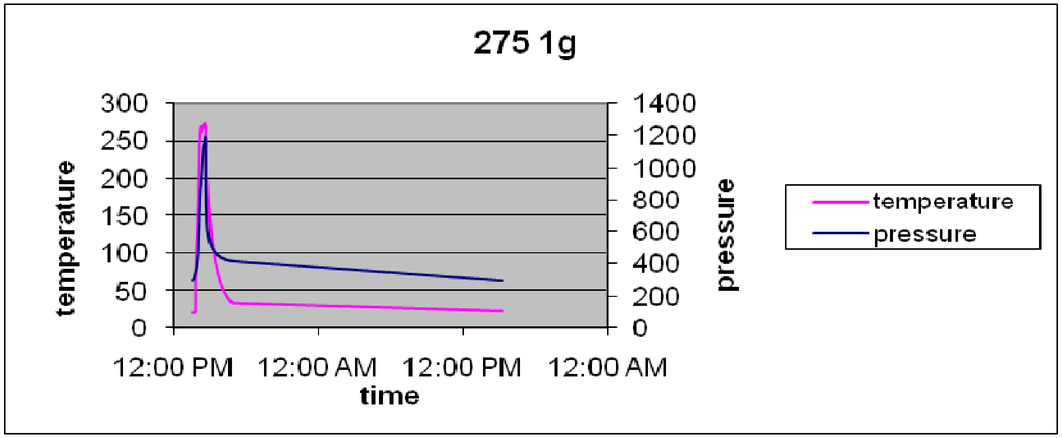
CHN Results	ASF	ESF	AINF	Post H20
%C	69.28	59.68	37.53	37.71
%H	6.72	6.35	4.98	5.61
%N	2.29	1.85	1.60	1.61
%O	21.71	32.11	55.89	55.07
HV (MJ kg^{-1})	29.43	24.09	11.06	12.13

Oil quantity	
ESF (g)	0.276
ASF (g)	3.365
AISF (g)	8.742
post H20 (g)	3.014
total (g) collected	15.398
total (g) lost	4.602
total (g) VS remain	2.136
%of total VS remain	12.837

Power used	
KWH	0.6

COD (mg/L)	
Initial	71200
Final	N/A

BOMB	
Cal/g	N/A
Btu/lb	N/A



Trial #	Temp	Reten Time	Int Pressure	%TS	%VS	Catalyst	pH	Gas
20 Dairy	275	15mins	300	20	83.2028	none	7.1	CO

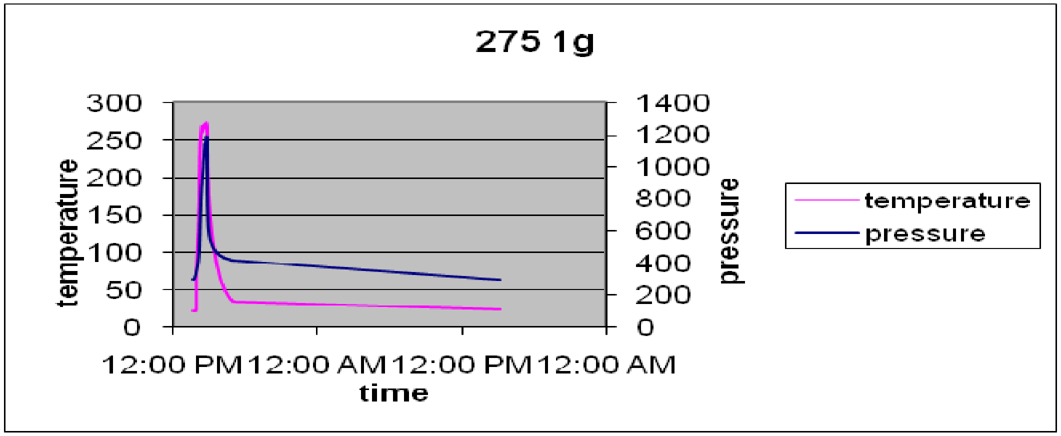
CHN Results	ASF	ESF	AINF	Post H20
%C	69.28	59.68	37.53	37.71
%H	6.72	6.35	4.98	5.61
%N	2.29	1.85	1.60	1.61
%O	21.71	32.11	55.89	55.07
HV (MJ kg^{-1})	29.43	24.09	11.06	12.13

Oil quantity	
ESF (g)	0.276
ASF (g)	3.365
AISF (g)	8.742
post H20 (g)	3.014
total (g) collected	15.398
total (g) lost	4.602
total (g) VS remain	2.136
%of total VS remain	12.837

Power used	
KWH	0.6

COD (mg/L)	
Initial	71200
Final	N/A

BOMB	
Cal/g	N/A
Btu/lb	N/A



Trial #	Temp	Reten Time	Int Pressure	%TS	%VS	Catalyst	pH	Gas
11 Dairy	300	15mins	300	20	83.2028	4g	9.9	CO

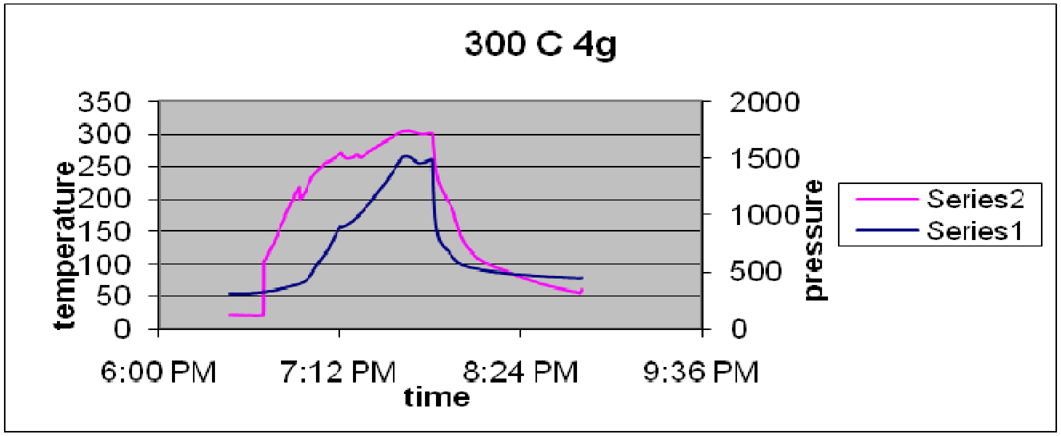
CHN Results	ASF	ESF	AINF	Post H20
%C	69.60	58.14	28.47	30.11
%H	6.92	6.05	2.82	4.17
%N	2.42	1.68	1.06	0.56
%O	21.06	34.14	67.64	65.16
HV (MJ kg^{-1})	29.92	22.82	3.14	5.98

Oil quantity	
ESF (g)	0.157
ASF (g)	3.136
AISF (g)	6.813
post H20 (g)	7.017
total (g) collected	17.123
total (g) lost	2.877
total (g) VS left	1.865
%of total VS left	11.208

Power used	
KWH	0.77

COD (mg/L)	
Initial	71200
Final	N/A

BOMB	
Cal/g	N/A
Btu/lb	N/A



Trial #	Temp	Reten Time	Int Pressure	%TS	%VS	Catalyst	pH	Gas
12 Dairy	300C	15mins	300	20	83.2028	3g	9.8	CO

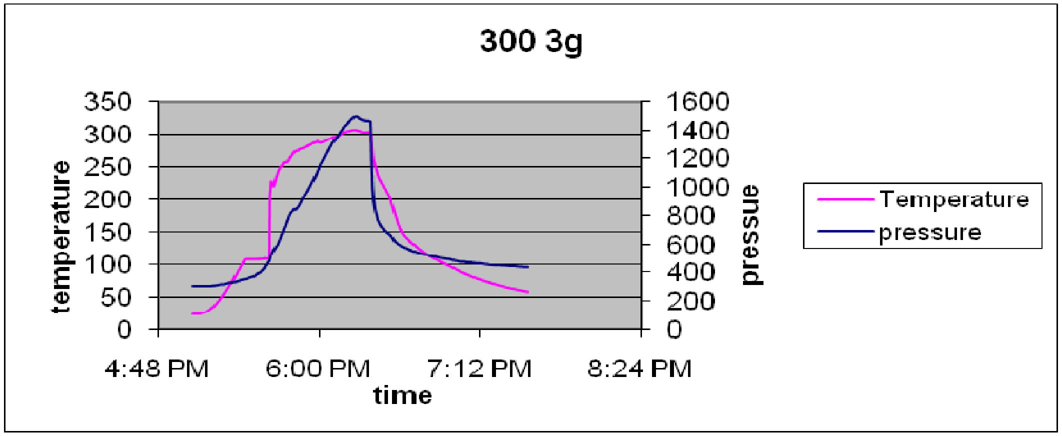
CHN Results	ASF	ESF	AINF	Post H20
%C	69.05	56.14	20.35	32.83
%H	6.81	5.92	2.01	4.24
%N	2.63	1.82	0.82	0.82
%O	21.52	36.13	76.81	62.11
HV (MJ kg^{-1})	29.51	21.67	-2.15	7.47

Oil quantity	
ESF (g)	0.187
ASF (g)	3.400
AISF (g)	7.248
post H20 (g)	5.238
total (g) collected	16.073
total (g) lost	3.927
total (g) VS remain	1.512
%of total VS remain	9.087

Power used	
KWH	0.75

COD (mg/L)	
Initial	71200
Final	N/A

BOMB	
Cal/g	N/A
Btu/lb	N/A



Trial #	Temp	Reten Time	Int Pressure	%TS	%VS	Catalyst	pH	Gas
13 Dairy	300C	15mins	300	20	83.2028	2g	10	CO

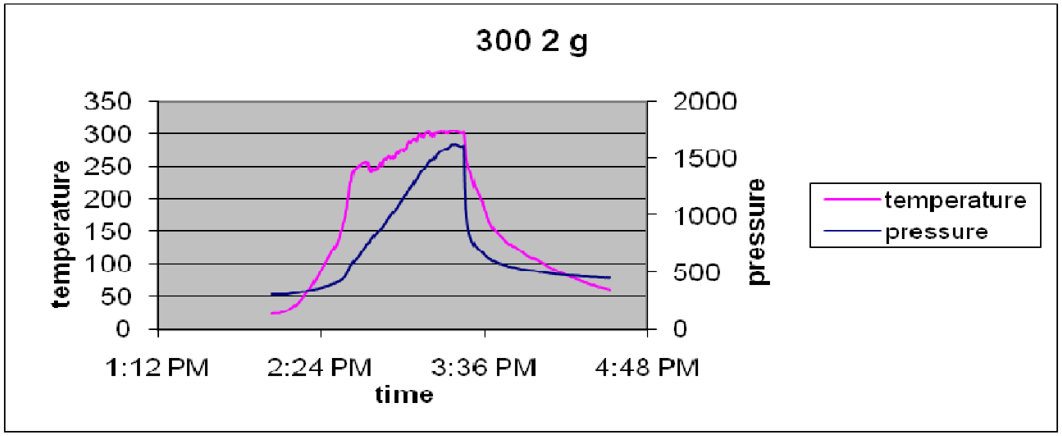
CHN Results	ASF	ESF	AINF	Post H20
%C	68.34	55.79	19.74	33.89
%H	6.95	6.31	1.89	4.62
%N	2.42	1.49	0.81	1.09
%O	22.28	36.41	77.57	60.40
HV (MJ kg^{-1})	29.36	22.06	-2.65	8.62

Oil quantity	
ESF (g)	0.256
ASF (g)	3.377
AISF (g)	7.599
post H20 (g)	3.814
total (g) collected	15.047
total (g) lost	4.953
total (g) VS remain	1.017
%of total VS remain	6.110

COD (mg/L)	
Initial	71200
Final	N/A

BOMB	
Cal/g	N/A
Btu/lb	N/A

Power used	
KWH	0.81

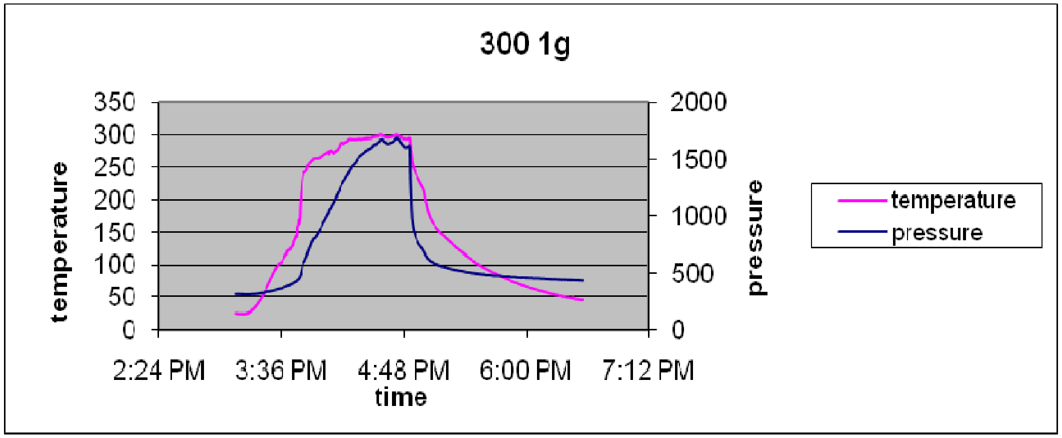


Trial #	**Temp**	**Reten time**	**Int Pressure**	**%TS**	**%VS**	**Catalyst**	**pH**	**Gas**
14 Dairy	300C	15mins	300	20	83.2028	2g	9.5	CO

CHN Results	**ASF**	**ESF**	**AINF**	**Post H20**
%C	69.59	59.58	15.56	36.63
%H	7.00	6.32	1.55	6.68
%N	2.33	1.32	0.72	1.68
%O	21.08	32.78	82.17	55.01
HV (MJ kg^{-1})	30.03	23.91	-5.23	13.30

Oil quantity	
ESF (g)	0.3691
ASF (g)	4.5202
AISF (g)	5.4884
post H20 (g)	2.8473
total (g) collected	13.225
total (g) lost	6.775
total (g) VS remain	1.0977
%of total VS remain	6.59653179
Power used	
KWH	0.86

COD (mg/L)	
Initial	71200
Final	N/A
BOMB	
Cal/g	N/A
Btu/lb	N/A



Trial #	Temp	Reten Time	Int Pressure	%TS	%VS	Catalyst	pH	Gas
15 Dairy	300C	15mins	300	20	83.20281283	0	6	CO

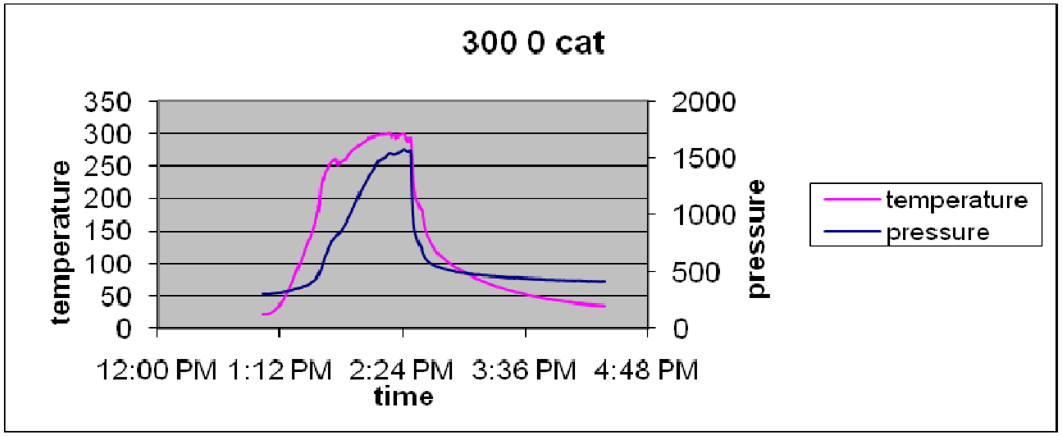
CHN Results	ASF	ESF	AINF	post H20
%C	68.67	59.86	0.54	42.53
%H	6.60	6.30	3.54	5.82
%N	2.27	1.28	130.47	2.77
%O	22.46	32.56	-34.54	48.88
HV (MJ kg^{-1})	28.94	24.01	10.53	15.00

Oil quantity	
ESF (g)	0.2107
ASF (g)	3.562
AISF (g)	5.8332
post H20 (g)	1.1403
total (g) collected	10.7462
total (g) lost	9.2538
total (g) VS remain	1.5257
%of total VS remain	9.16856022

COD (mg/L)	
Initial	71200
Final	N/A

Bomb	
Cal/g	N/A
Btu/lb	N/A

Power used	
KWH	0.86



Trial #	Temp	Reten Time	Int Pressure	%TS	%VS	Catalyst	pH	Gas
6 Dairy	325C	15mins	300	20	83.2028	4g	10.35	CO

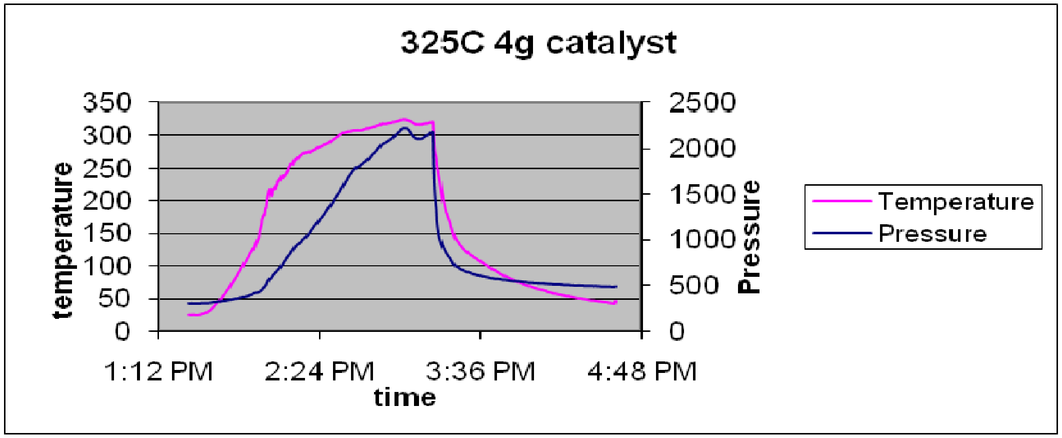
CHN Results	**ASF**	**ESF**	**AINF**	**post H20**
%C	72.35	58.61	17.42	27.95
%H	7.70	6.94	2.84	4.74
%N	2.56	2.07	0.56	0.46
%O	17.40	32.38	79.18	66.86
HV (MJ kg^{-1})	32.51	24.52	-2.32	5.81

Oil quantity	
ESF (g)	0.151
ASF (g)	4.155
AISF (g)	6.364
post H20 (g)	6.247
total (g) collected	16.917
total (g) lost	3.083
total (g) VS left	1.379
%of total VS left	8.287

Power used	
KWH	1.06

COD (mg/L)	
Initial	71200
Final	N/A

BOMB	
Cal/g	N/A
Btu/lb	N/A



Trial #	Temp	Reten Time	Int Pressure	%TS	%VS	Catalyst	pH	Gas
7 Dairy	325C	15mins	300	20	83.2028	3g	10	CO

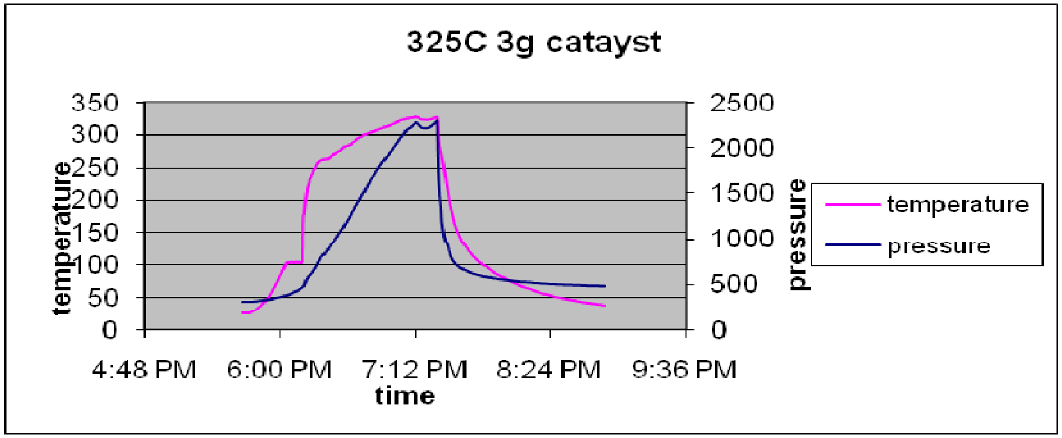
CHN Results	ASF	ESF	AINF	Post H20
%C	73.88	64.79	23.43	31.35
%H	7.77	6.93	2.94	5.70
%N	2.70	2.59	0.87	0.62
%O	15.65	25.68	72.76	62.33
HV (MJ kg^{-1})	33.40	27.62	0.82	9.02

Oil quantity	
ESF (g)	0.148
ASF (g)	3.702
AISF (g)	6.106
post H20 (g)	4.697
total (g) collected	14.653
total (g) lost	5.347
total (g) VS remain	1.782
%of total VS remain	10.706

COD (mg/L)	
Initial	71200
Final	N/A

BOMB	
Cal/g	N/A
Btu/lb	N/A

Power used	
KWH	1.05



Trial #	Temp	Reten Time	Int Pressure	%TS	%VS	Catalyst	pH	Gas
8 Dairy	325C	15mins	300	20	83.2028	2g	9.5	CO

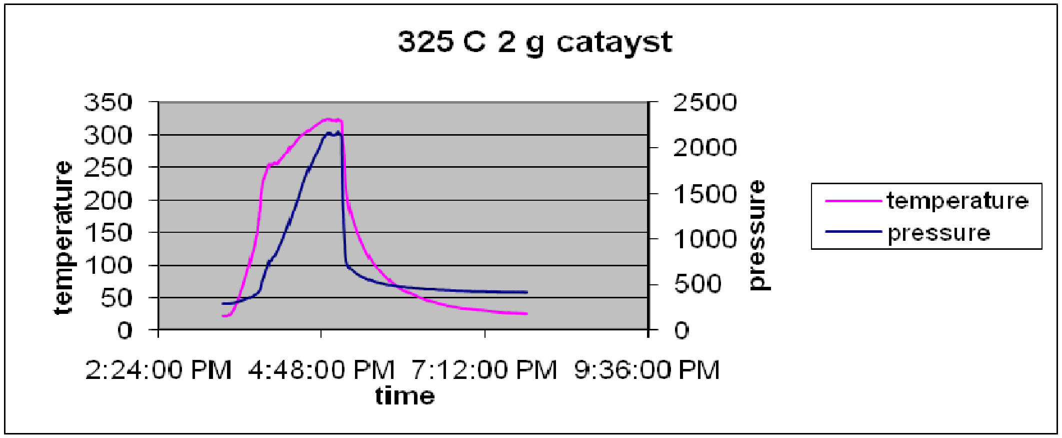
CHN Results	ASF	ESF	AINF	Post H20
%C	72.11	60.19	30.72	25.27
%H	7.10	5.87	2.77	5.39
%N	2.47	1.90	1.26	0.59
%O	18.31	32.05	65.24	68.74
HV (MJ kg^{-1})	31.45	23.57	4.19	5.55

Oil quantity	
ESF (g)	0.158
ASF (g)	3.497
AISF (g)	4.966
post H20 (g)	3.628
total (g) collected	12.250
total (g) lost	7.751
total (g) VS remain	1.211
%of total VS remain	7.277

Power used	
KWH	1.05

COD (mg/L)	
Initial	71200
Final	N/A

BOMB	
Cal/g	N/A
Btu/lb	N/A



Trial #	**Temp**	**Reten Time**	**Int Pressure**	**%TS**	**%VS**	**Catalyst**	**pH**	**Gas**
9 Dairy	325C	15mins	300	20	83.2028	1g	10	CO

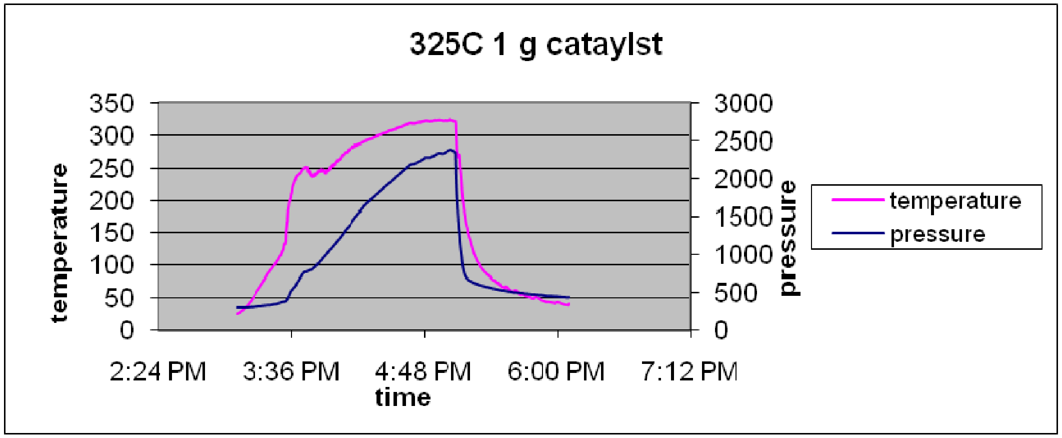
CHN Results	**ASF**	**ESF**	**AINF**	**Post H20**
%C	68.09	65.54	11.16	34.61
%H	6.50	3.90	1.09	4.64
%N	2.35	1.31	0.46	1.13
%O	23.06	29.25	87.29	59.62
HV (MJ kg^{-1})	28.50	23.00	-8.15	9.02

Oil quantity	
ESF (g)	0.1278
ASF (g)	3.9852
AISF (g)	5.0957
post H20 (g)	2.1481
total (g) collected	11.3568
total (g) lost	8.6432
total (g) VS remain	1.0647
%of total VS remain	6.39822119

Power used	
KWH	1.24

COD (mg/L)	
Initial	71200
Final	N/A

Bomb	
Cal/g	N/A
Btu/lb	N/A



Trial #	Temp	Reten Time	Int Pressure	%TS	%VS	Catalyst	pH	Gas
10 Dairy	325C	15mins	300	20	83.2028	none	6.3	CO

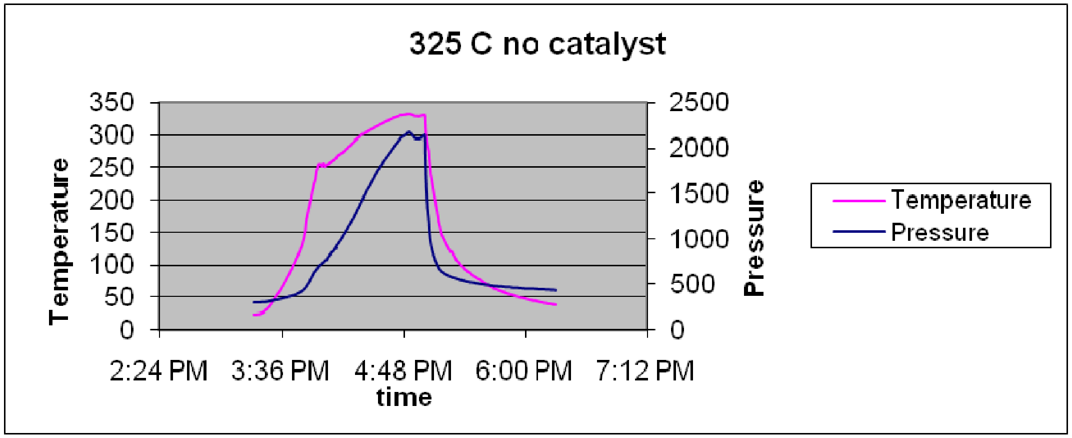
CHN Results	ASF	ESF	AINF	Post H2O
%C	71.34	61.25	19.37	40.49
%H	6.82	6.21	1.69	5.42
%N	2.36	1.24	0.81	2.85
%O	19.48	31.30	78.13	51.24
HV (MJ kg^{-1})	30.60	24.53	-3.13	13.39

Oil quantity	
ESF (g)	0.325
ASF (g)	2.582
AISF (g)	4.521
post H20 (g)	1.772
total (g) collected	9.200
total (g) lost	10.800
total (g) VS remain	1.068
%of total VS remain	6.420

Power used	
KWH	1.08

COD (mg/L)	
Initial	71200
Final	N/A

Bomb	
Cal/g	N/A
Btu/lb	N/A



Trial #	Temp	Reten Time	Int Pressure	%TS	%VS	Catalyst	pH	Gas
21 Dairy	350	15mins	300	20	83.2028	4g	10	CO

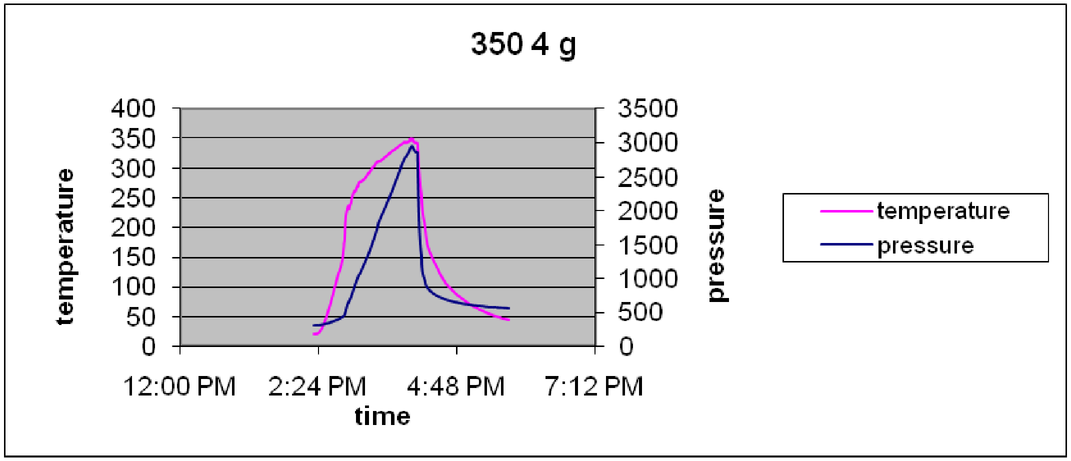
CHN Results	ASF	ESF	AINF	Post H2O
%C	72.10	31.80	28.10	44.06
%H	8.09	3.17	3.10	5.72
%N	2.49	3.90	0.67	2.62
%O	17.32	61.13	68.13	47.60
HV (MJ kg^{-1})	33.00	5.74	3.33	15.58

Oil quantity	
ESF (g)	0.144
ASF (g)	4.342
AISF (g)	5.473
post H20 (g)	5.866
total (g) collected	15.825
total (g) lost	4.175
total (g) VS remain	1.065
%of total VS remain	6.401

Power used	
KWH	1.16

COD (mg/L)	
Initial	71200
Final	N/A

Bomb	
Cal/g	N/A
Btu/lb	N/A



Trial #	Temp	Reten Time	Int Pressure	%TS	%VS	Catalyst	pH	Gas
22 Dairy	350	15mins	300	20	83.20	3g	9.3	CO

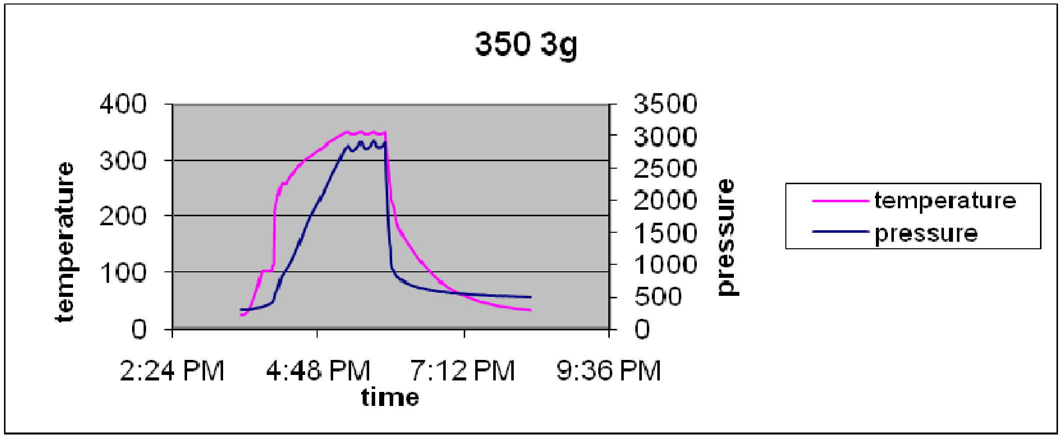
CHN Results	ASF	ESF	AINF	Post H2O
%C	74.17	29.49	13.20	28.97
%H	7.69	2.95	1.04	4.14
%N	2.37	3.14	0.46	0.42
%O	15.78	64.42	85.30	66.46
HV (MJ kg^{-1})	33.35	4.16	-7.24	5.37

Oil quantity	
ESF (g)	0.11
ASF (g)	3.42
AISF (g)	5.00
post H20 (g)	3.93
total (g) collected	12.47
total (g) lost	7.53
total (g) VS remain	1.56
%of total VS remain	9.39

Power used	
KWH	1.23

COD (mg/L)	
Initial	71200
Final	N/A

Bomb	
Cal/g	N/A
Btu/lb	N/A



Trial #	Temp	Reten Time	Int Pressure	%TS	%VS	Catalyst	pH	Gas
23 Dairy	350	15mins	300	20	83.2028	2g	9	CO

CHN Results	ASF	ESF	AINF	post H20
%C	75.10	59.61	18.81	32.61
%H	8.20	6.45	1.70	4.89
%N	2.65	1.88	0.64	0.67
%O	14.05	32.06	78.85	61.84
HV (MJ kg^{-1})	34.66	24.21	-3.42	8.36

Oil quantity	
ESF (g)	0.166
ASF (g)	4.401
AISF (g)	5.001
post H20 (g)	3.452
total (g) collected	13.020
total (g) lost	6.980
total (g) VS remain	1.274
%of total VS remain	7.654

Power used	
KWH	1.21

COD (mg/L)	
Initial	71200
Final	N/A

Bomb	
Cal/g	N/A
Btu/lb	N/A

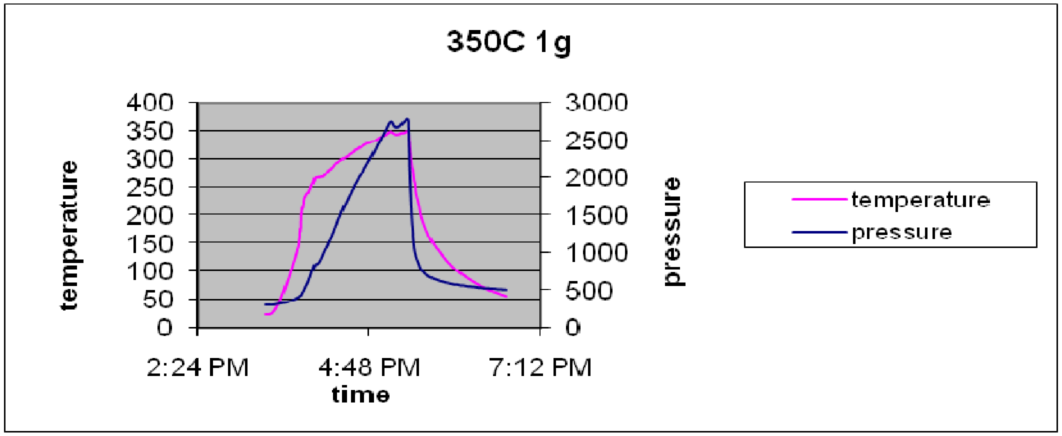
Graph N/A

Trial #	Temp	Reten Time	Int Pressure	%TS	%VS	Catalyst	pH	Gas
24 Dairy	350	15mins	300	20	83.2028	1g	8.3	CO

CHN Results	ASF	ESF	AINF	Post H20
%C	73.55	61.59	7.81	35.00
%H	7.99	6.55	0.85	5.38
%N	2.44	1.62	0.32	1.26
%O	16.02	30.24	91.02	58.37
HV (MJ kg^{-1})	33.54	25.30	-10.18	10.38

Oil quantity	
ESF (g)	0.27
ASF (g)	4.76
AISF (g)	4.72
post H20 (g)	2.21
total (g) collected	11.98
total (g) lost	8.03
total (g) VS remain	0.96
%of total VS remain	5.80
Power used	
KWH	1.23

COD (mg/L)	
Initial	71200
Final	N/A
Bomb	
Cal/g	N/A
Btu/lb	N/A



Trial #	Temp	Reten Time	Int Pressure	%TS	%VS	Catalyst	pH	Gas
25 Dairy	350	15mins	300	20	83.2028	none	6	CO

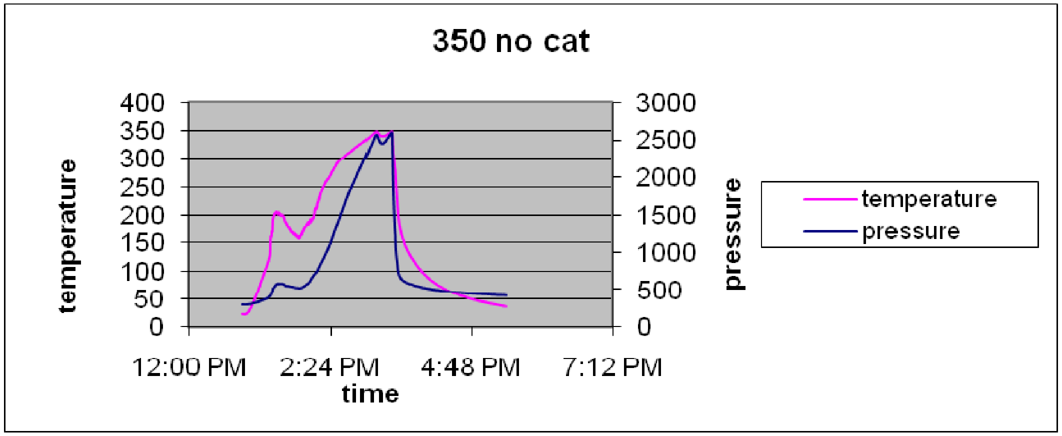
CHN Results	ASF	ESF	AINF	Post H2O
%C	72.71	62.24	17.33	39.66
%H	7.56	6.49	1.30	6.06
%N	2.42	1.37	0.61	2.97
%O	17.30	29.90	80.75	51.32
HV (MJ kg^{-1})	32.46	25.48	-4.77	14.00

Oil quantity	
ESF (g)	0.333
ASF (g)	3.772
AISF (g)	6.669
post H20 (g)	1.377
total (g) collected	12.151
total (g) lost	7.849
total (g) VS remain	1.089
%of total VS remain	6.542

Power used	
KWH	1.31

COD (mg/L)	
Initial	71200
Final	N/A

Bomb	
Cal/g	N/A
Btu/lb	N/A



Trial #	**Temp**	**Reten Time**	**Int Pressure**	**%TS**	**%VS**	**Catalyst**	**pH**	**Gas**
Characterization 1	350	15mins	300	20	83.2028	0	5.9	CO

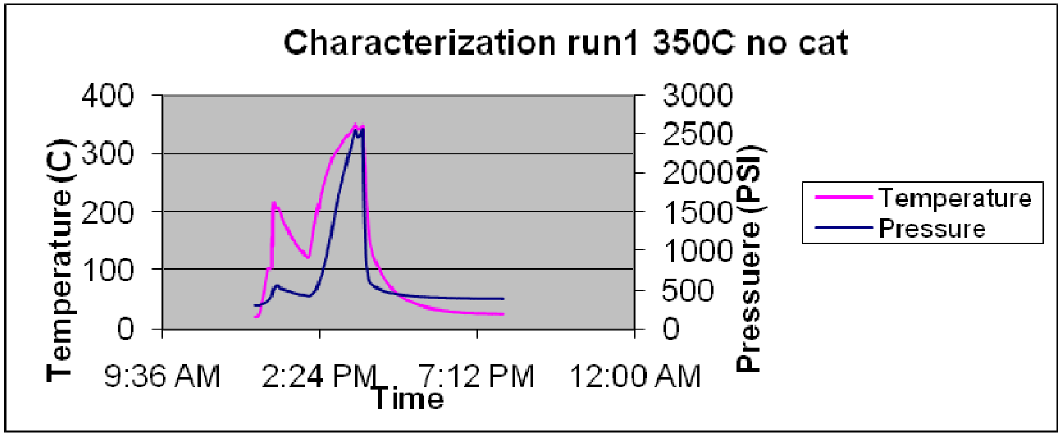
CHN Results	**ASF**	**ESF**	**AINF**	**Post H20**
%C	72.37	60.78	25.71	39.57
%H	7.40	6.68	2.13	5.91
%N	2.32	1.50	1.01	3.00
%O	17.91	31.05	71.15	51.51
HV (MJ kg^{-1})	32.02	25.08	0.69	13.74

Oil quantity	
ESF (g)	0.29
ASF (g)	3.25
AISF (g)	7.26
post H20 (g)	1.04
total (g) collected	11.85
total (g) lost	8.15
total (g) VS remain	0.98
%of total VS remain	5.86

Power used	
KWH	1.31

COD (mg/L)	
Initial	78660
Final	19515

Bomb	
Cal/g	7470.54
Btu/lb	13446.97
MJ kg^{-1}	31.27



Trial #	**Temp**	**Reten Time**	**Int Pressure**	**%TS**	**%VS**	**Catalyst**	**pH**	**Gas**
Characterization 2	350	15mins	300	20	83.2028	0	5.9	CO

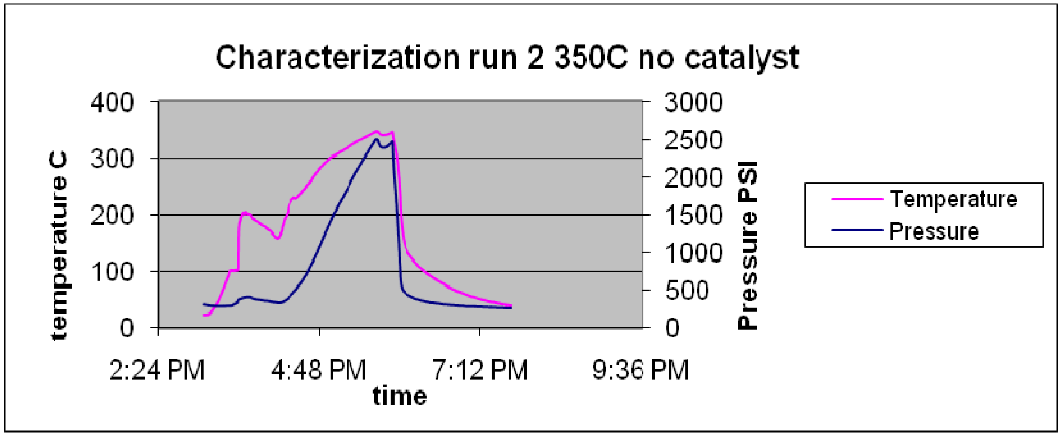
CHN Results	**ASF**	**ESF**	**AINF**	**Post H2O**
%C	72.71	60.20	44.05	40.08
%H	7.31	6.63	3.32	5.85
%N	2.27	1.65	1.58	3.15
%O	17.70	31.52	51.05	50.92
HV (MJ kg^{-1})	32.04	24.74	11.62	13.92

Oil quantity	
ESF (g)	0.202
ASF (g)	3.441
AISF (g)	7.122
post H20 (g)	0.684
total (g) collected	11.448
total (g) lost	8.552
total (g) VS remain	1.277
%of total VS remain	7.673

Power used	
KWH	N/A

COD (mg/L)	
Initial	78660
Final	35397

Bomb	
Cal/g	7852.088
Btu/lb	14133.759
MJ kg^{-1}	32.868



Trial #	Temp	Reten Time	Int Pressure	%TS	%VS	Catalyst	pH	Gas
Characterization 3	350	15mins	300	20	83.2028	0	5.9	CO

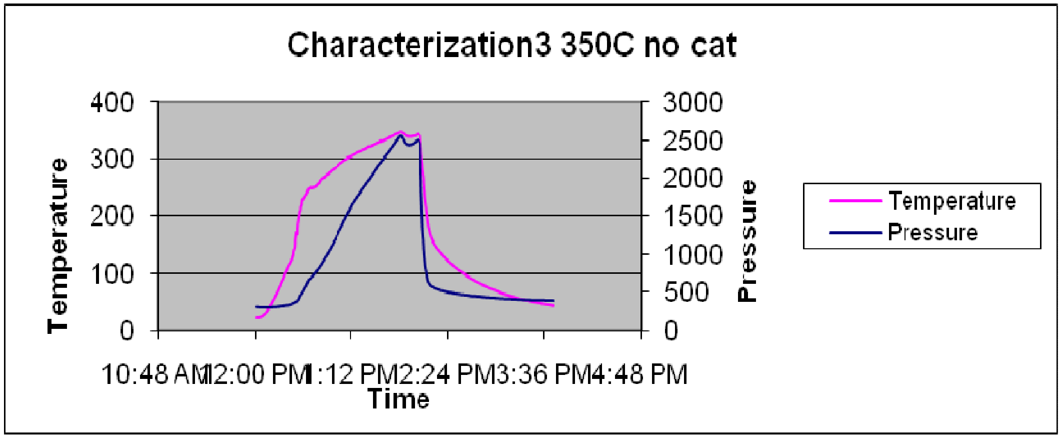
CHN Results	ASF	ESF	AINF	Post H2O
%C	72.96	60.63	24.20	40.63
%H	7.48	6.72	1.95	5.88
%N	2.25	1.42	0.97	3.28
%O	17.30	31.23	72.88	50.21
HV (MJ kg^{-1})	32.42	25.06	-0.34	14.24

Oil quantity	
ESF (g)	0.294
ASF (g)	3.671
AISF (g)	6.796
post H20 (g)	0.960
total (g) collected	11.721
total (g) lost	8.279
total (g) VS remain	1.982
%of total VS remain	11.911

Power used	
KWH	N/A

COD (mg/L)	
Initial	78660
Final	34610

Bomb	
Cal/g	7828.47
Btu/lb	14091.25
MJ kg^{-1}	32.77



Trial #	Temp	Reten Time	Int Pressure	%TS	%VS	Catalyst	pH	Gas
k2co3run1	350	15mins	300	20	83.20281283	1g	N/A	CO

dairy used

CHN Results	ASF	ESF	AINF	Post H2O
%C	72.75	61.46	22.89	24.15
%H	7.23	6.53	2.00	6.88
%N	2.44	1.65	0.94	0.58
%O	17.58	30.36	74.18	68.40
HV (MJ kg^{-1})	31.95	25.21	-0.91	7.34

Oil quantity	
ESF (g)	0.229
ASF (g)	3.595
AISF (g)	5.788
post H20 (g)	1.937
total (g) collected	11.549
total (g) lost	8.451
total (g) VS remain	1.312
%of total VS remain	7.883

Power used	
KWH	N/A

COD (mg/L)	
Initial	N/A
Final	N/A

BOMB Results	
Cal/g	N/A
Btu/lb	N/A
MJ kg^{-1}	N/A

Trial #	**Temp**	**Reten Time**	**Int Pressure**	**%TS**	**%VS**	**Catalyst**	**pH**	**Gas**
k2co3run2	350	15mins	300	20	83.2028	2g	N/A	CO

dairy used

CHN Results	**ASF**	**ESF**	**AINF**	**Post H2O**
%C	70.70	51.02	9.05	26.19
%H	7.23	5.86	1.01	6.73
%N	2.45	1.39	0.31	0.49
%O	19.63	41.73	89.64	66.59
HV (MJ kg^{-1})	30.95	19.01	-9.34	8.10

Oil quantity	
ESF (g)	0.1413
ASF (g)	2.9404
AISF (g)	1.6291
post H20 (g)	3.1375
total (g) collected	7.8483
total (g) lost	12.1517
total (g) VS remain	0.6207
%of total VS remain	3.73004216

Power used	
KWH	N/A

COD (mg/L)	
Initial	N/A
Final	N/A

Bomb	
Cal/g	N/A
Btu/lb	N/A
MJ kg^{-1}	N/A

Trial #	**Temp**	**Reten Time**	**Int Pressure**	**%TS**	**%VS**	**Catalyst**	**pH**	**Gas**
k2co3run3	350	15mins	300	20	83.2028	3g	N/A	CO

dairy used

CHN Results	**ASF**	**ESF**	**AINF**	**Post H2O**
%C	70.27	59.05	8.31	23.20
%H	7.44	6.61	1.10	7.69
%N	2.49	2.19	0.28	0.34
%O	19.81	32.15	90.31	68.78
HV (MJ kg^{-1})	31.08	24.23	-9.56	8.13

Oil quantity	
ESF (g)	0.0337
ASF (g)	2.8349
AISF (g)	6.0581
post H20 (g)	4.5241
total (g) collected	13.4508
total (g) lost	6.5492
total (g) VS remain	1.3871
%of total VS remain	8.33565569

COD (mg/L)	
Initial	N/A
Final	N/A

Bomb	
Cal/g	N/A
Btu/lb	N/A
MJ kg-1	N/A

Power used	
KWH	N/A

Trial #	Temp	Reten Time	Int Pressure	%TS	%VS	Catalyst	pH	Gas
k2co3run4	350	15mins	300	20	83.20281283	4g	N/A	CO

dairy used

CHN Results	ASF	ESF	AINF	Post H2O
%C	60.12	25.33	38.01	21.84
%H	7.09	5.47	3.57	4.95
%N	1.73	0.49	1.26	0.13
%O	31.06	68.71	57.17	73.08
HV (MJ kg^{-1})	25.45	5.69	9.00	3.11

Oil quantity	
ESF (g)	0.106
ASF (g)	2.797
AISF (g)	7.147
post H20 (g)	4.537
total (g) collected	14.587
total (g) lost	5.413
total (g) VS remain	1.387
%of total VS remain	8.336

Power used	
KWH	N/A

COD (mg/L)	
Initial	N/A
Final	N/A

Bomb	
Cal/g	N/A
Btu/lb	N/A
MJ kg^{-1}	N/A

Trial #	Temp	Reten Time	Int Pressure	%TS	%VS	Catalyst	pH	Gas
naohrun1	350	15mins	300	20	83.20281	1g	11	CO

dairy used

CHN Results	ASF	ESF	AINF	Post H2O
%C	71.98	46.05	7.49	32.78
%H	7.61	6.30	0.90	5.72
%N	2.25	1.33	0.26	0.92
%O	18.15	46.32	91.36	60.58
HV (MJ kg^{-1})	32.15	17.26	-10.28	9.79

Oil quantity	
ESF (g)	0.209
ASF (g)	4.107
AISF (g)	5.541
post H20 (g)	2.929
total (g) collected	12.787
total (g) lost	7.213
total (g) VS remain	1.071
%of total VS remain	6.437

Power used	
KWH	N/A

COD (mg/L)	
Initial	N/A
Final	N/A

Bomb	
Cal/g	N/A
Btu/lb	N/A
MJ kg^{-1}	N/A

Trial #	Temp	Reten Time	Int Pressure	%TS	%VS	Catalyst	pH	Gas
naohrun2	350	15mins	300	20	83.2028	2g	12	CO

dairy used

CHN Results	ASF	ESF	AINF	Post H2O
%C	69.79	38.57	9.58	29.30
%H	7.30	6.19	1.30	5.67
%N	2.40	1.03	0.26	0.39
%O	20.51	54.21	88.87	64.64
HV (MJ kg^{-1})	30.61	13.39	-8.63	7.93

Oil quantity	
ESF (g)	0.174
ASF (g)	4.873
AISF (g)	0.999
post H20 (g)	5.883
total (g) collected	11.929
total (g) lost	8.071
total (g) VS remain	9.876
%of total VS remain	59.348

Power used	
KWH	N/A

COD (mg/L)	
Initial	N/A
Final	N/A

Bomb	
Cal/g	N/A
Btu/lb	N/A
MJ kg^{-1}	N/A

Trial #	Temp	Reten Time	Int Pressure	%TS	%VS	Catalyst	pH	Gas
naohrun3	350	15mins	300	20	83.2028	3g	13	CO

dairy used

CHN Results	ASF	ESF	AINF	Post H2O
%C	0.60	48.94	12.92	27.18
%H	7.49	6.58	1.94	5.85
%N	203.37	1.53	0.31	0.26
%O	-111.46	42.95	84.83	66.71
HV (MJ kg^{-1})	28.03	19.15	-5.98	7.15

Oil quantity	
ESF (g)	0.143
ASF (g)	2.536
AISF (g)	4.781
post H20 (g)	5.738
total (g) collected	13.198
total (g) lost	6.802
total (g) VS remain	1.433
%of total VS remain	8.610

Power used	
KWH	N/A

COD (mg/L)	
Initial	N/A
Final	N/A

Bomb	
Cal/g	N/A
Btu/lb	N/A
MJ kg^{-1}	N/A

Trial #	Temp	Reten Time	Int Pressure	%TS	%VS	Catalyst	pH	Gas
naohrun4	350.00	15min	300	20	83.2028	4g	14	CO

dairy used

CHN Results	ASF	ESF	AINF	Post H2O
%C	76.25	25.23	3.69	23.20
%H	7.83	5.82	0.68	4.86
%N	2.35	0.52	0.06	0.12
%O	13.57	68.43	95.57	71.83
HV (MJ kg^{-1})	34.59	6.19	-12.51	3.62

Oil quantity	
ESF (g)	0.136
ASF (g)	3.601
AISF (g)	6.701
post H20 (g)	6.003
total (g) collected	16.440
total (g) lost	3.560
total (g) VS remain	0.749
%of total VS remain	4.499

COD (mg/L)	
Initial	N/A
Final	N/A

Bomb	
Cal/g	N/A
Btu/lb	N/A
MJ kg^{-1}	N/A

Power used	
KWH	N/A

Trial #	Temp	Reten Time	Int Pressure	%TS	%VS	Catalyst	pH	Gas
Peanutsapp	350	15mins	300	20	97.0069	1g	N/A	CO

CHN Results	ASF	ESF	AINF	Post H2O	Raw
%C	70.75	60.72	7.73	40.07	53.93
%H	9.96	8.68	5.73	6.27	7.87
%N	3.51	4.43	159.80	4.14	4.62
%O	15.78	26.17	-73.26	49.52	33.58
HV (MJ kg^{-1})	35.44	28.66	22.03	14.72	24.09

Oil quantity	
ESF (g)	0.229
ASF (g)	7.387
AISF (g)	0.757
post H20 (g)	4.428
total (g) collected	12.801
total (g) lost	7.199
total (g) VS remain	0.502
%of total VS remain	2.588

Power used	
KWH	N/A

COD (mg/L)	
Initial	N/A
Final	N/A

BOMB	
Cal/g	N/A
Btu/lb	N/A
MJ kg^{-1}	N/A

Trial #	**Temp**	**Reten Time**	**Int Pressure**	**%TS**	**%VS**	**Catalyst**	**pH**	**Gas**
Pinesawdust	350	15mins	300	9.09	99.845	1g	7.5	CO

used only 10g to begin

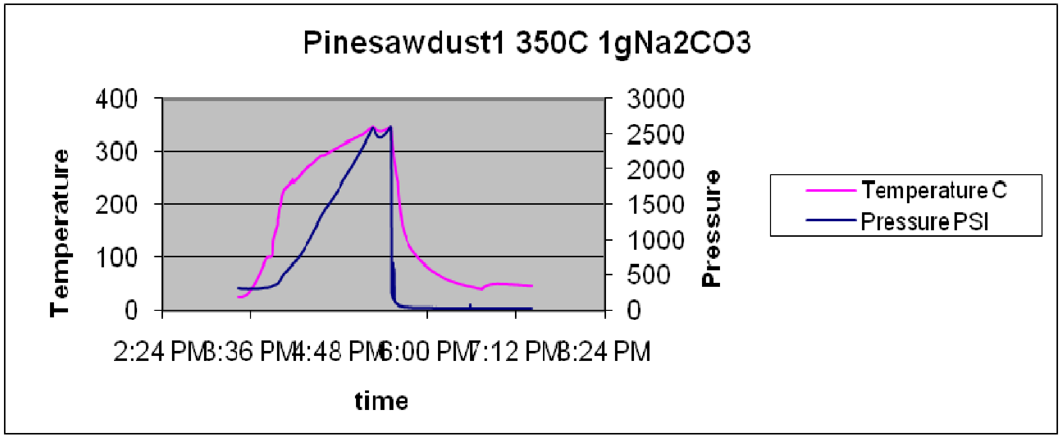
CHN Results	**ASF**	**ESF**	**AINF**	**Post H2O**	**Raw**
%C	73.79	63.37	69.36	29.27	45.09
%H	6.61	6.43	4.66	5.14	5.90
%N	0.12	0.05	0.20	0.05	0.07
%O	19.47	30.16	25.79	65.55	48.94
HV (MJ kg^{-1})	31.13	25.73	25.90	7.02	15.97

Oil quantity	
ESF (g)	0.398
ASF (g)	3.083
AISF (g)	0.486
post H20 (g)	2.156
total (g) collected	6.123
total (g) lost	3.877
total (g) VS remain	0.406
%of total VS remain	4.065

COD (mg/L)	
Initial	N/A
Final	N/A

BOMB	
Cal/g	N/A
Btu/lb	N/A

Power used	
KWH	N/A



Trial #	**Temp**	**Reten Time**	**Int Pressure**	**%TS**	**%VS**	**Catalyst**	**pH**	**Gas**
poultrylitter	350	15mins	300	20	83.2519	1g	N/A	CO

CHN Results	**ASF**	**ESF**	**AINF**	**Post H2O**	**Raw**
%C	71.05	56.82	29.03	23.43	36.48
%H	7.84	6.71	2.86	5.08	5.46
%N	4.94	5.46	1.98	1.68	4.38
%O	16.17	31.01	66.13	69.81	53.68
HV (MJ kg^{-1})	32.47	23.80	3.61	4.33	11.73

Oil quantity	
ESF (g)	0.215
ASF (g)	3.333
AISF (g)	4.179
post H20 (g)	3.642
total (g) collected	11.369
total (g) lost	8.631
total (g) VS remain	1.697
%of total VS remain	10.189

Power used	
KWH	1.31

COD (mg/L)	
Initial	N/A
Final	N/A

Bomb	
Cal/g	N/A
Btu/lb	N/A
MJ kg^{-1}	N/A

Trial #	Temp	Reten Time	Int Pressure	%TS	%VS	Catalyst	pH	Gas
swithgrass	350	15mins	300	9.09090	95.250	1g	N/A	CO

only 10g initial sample used

CHN Results	ASF	ESF	AINF	Post H2O	Raw
%C	68.11	61.98	5.19	24.97	45.05
%H	9.95	6.58	4.50	4.99	6.10
%N	0.08	0.48	145.13	0.15	0.82
%O	21.86	30.95	-54.82	69.89	48.04
HV (MJ kg^{-1})	33.61	25.37	0.00	4.71	16.37

Oil quantity	
ESF (g)	0.245
ASF (g)	2.620
AISF (g)	0.716
post H20 (g)	3.486
total (g) collected	7.066
total (g) lost	2.934
total (g) VS remain	0.465
%of total VS remain	4.882

Power used	
KWH	N/A

COD (mg/L)	
Initial	N/A
Final	N/A

Bomb	
Cal/g	N/A
Btu/lb	N/A
MJ kg^{-1}	N/A

Trial #	Temp	Reten Time	Int Pressure	%TS	%VS	Catalyst	pH	Gas
tallowground	350	15mins	300	20	97.505	1g	N/A	CO

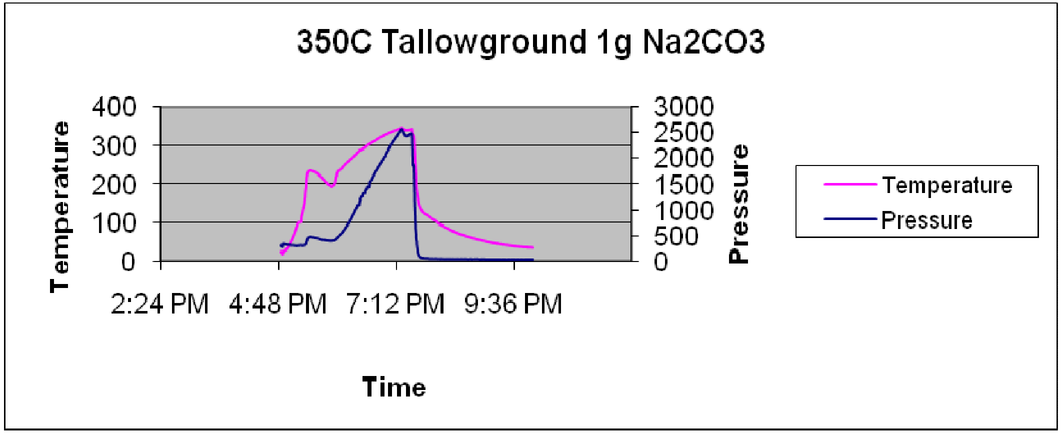
CHN Results	ASF	ESF	AINF	Post H2O	Raw
%C	71.38	62.28	8.65	38.99	59.10
%H	8.79	7.10	6.35	6.62	8.25
%N	2.07	2.04	171.23	1.40	2.28
%O	17.77	28.58	-86.23	52.98	30.37
HV (MJ kg^{-1})	33.68	26.57	25.22	14.32	26.86

Oil quantity	
ESF (g)	0.13
ASF (g)	5.57
AISF (g)	4.17
post H20 (g)	3.06
total (g) collected	12.93
total (g) lost	7.07
total (g) VS remain	2.75
%of total VS remain	14.09

Power used	
KWH	N/A

COD (mg/L)	
Initial	N/A
Final	N/A

Bomb	
Cal/g	N/A
Btu/lb	N/A
MJ kg^{-1}	N/A



Trial #	Temp	Reten Time	Int Pressure	%TS	%VS	Catalyst	pH	Gas
tallowwhole	350	15mins	300	20	97.5046	1g		CO

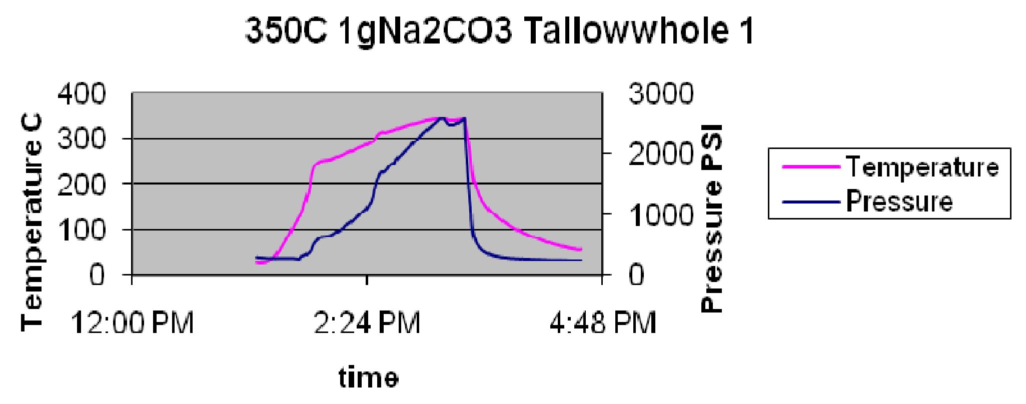
CHN Results	ASF	ESF	AINF	Post H2O	Raw
%C	71.32	59.88	7.73	31.65	59.10
%H	9.28	6.60	5.73	5.49	8.25
%N	1.54	1.81	159.80	1.12	2.28
%O	17.86	31.70	-73.26	61.74	30.37
HV (MJ kg^{-1})	34.35	24.57	0.00	8.90	26.86

Oil quantity	
ESF (g)	0.164
ASF (g)	8.899
AISF (g)	3.205
post H20 (g)	2.267
total (g) collected	14.535
total (g) lost	5.465
total (g) VS remain	2.166
%of total VS remain	11.107

Power used	
KWH	N/A

COD (mg/L)	
Initial	N/A
Final	N/A

Bomb	
Cal/g	N/A
Btu/lb	N/A
MJ kg^{-1}	N/A



Trial #	Temp	Reten Time	Int Pressure	%TS	%VS	Catalyst	pH	Gas
vegoil	350	15mins	300	20	100	0	N/A	CO

CHN Results	ASF	ESF	AINF	Post H2O	Raw
%C	68.1125	73.05333333	0	n/a	77.80166667
%H	9.949875	10.82	0		11.075
%N	0.08175	0.231	0		0.052
%O	21.855875	15.89566667	100		11.07133333
HV (MJ kg^{-1})	33.6105549	37.421794	-15.4	n/a	40.118298

Oil quantity	
ESF (g)	0.164
ASF (g)	8.899
AISF (g)	3.205
post H20 (g)	2.267
total (g) collected	14.535
total (g) lost	5.465
total (g) VS remain	2.166
%of total VS remain	11.107

Power used	
KWH	N/A

COD (mg/L)	
Initial	N/A
Final	N/A

Bomb	
Cal/g	N/A
Btu/lb	N/A
MJ kg^{-1}	N/A

APPENDIX C: ADDITIONAL INFORMATION

C.1 Raw Dairy Manure Statistics

Table C.1: CHN Ultimate Analysis Raw Dairy Manure

Raw Manure		**Total N**	**Organic C**	**Total H**
Identifier	**Replicate**	**N %**	**C %**	**H %**
Manure	1	1.259	38.67	5.129
	2	1.332	39.29	5.192
	3	1.306	38.57	5.099
	Average	1.299	38.84	5.14
	Std. Dev.	0.037	0.3903	0.0475
	%RSD	2.80%	1.00%	0.90%

Table C.2: ICP Analysis raw dairy manure

Matrix: Manure		**Lab ID:**	**1**	**2**	**3**	**Average**	**Std Dev**	**%RSD**
Element	**MDLs mg/L**	**Unit**						
Al	0.06	mg/kg	1127.5	1586.0	1264.4	1326.0	235.4	0.2
B	0.02	mg/kg	25.7	30.0	25.4	27.0	2.5	0.1
Ba	0.02	mg/kg	16.3	25.2	18.6	20.0	4.6	0.2
Ca	0.02	mg/kg	8351.4	11241.0	8899.6	9497.3	1534.7	0.2
Co	0.001	mg/kg	9.0	7.5	5.6	7.4	1.7	0.2
Cr	0.001	mg/kg	18.7	26.5	27.3	24.2	4.8	0.2
Cu	0.001	mg/kg	53.0	64.2	46.2	54.5	9.1	0.2
Fe	0.001	mg/kg	1031.7	1510.6	1170.0	1237.4	246.5	0.2
K	0.032	mg/kg	431.0	641.1	496.9	523.0	107.5	0.2
Mg	0.005	mg/kg	1606.6	2336.4	1770.4	1904.5	382.9	0.2
Mn	0.001	mg/kg	62.1	89.8	69.2	73.7	14.4	0.2
Mo	0.038	mg/kg	0.9	ND	0.8	0.8	0.1	0.1
Na	0.029	mg/kg	373.5	679.2	435.5	496.1	161.6	0.3
Ni	0.001	mg/kg	92.9	126.9	93.7	104.5	19.4	0.2
P	0.024	mg/kg	1348.7	1953.2	1486.7	1596.2	316.8	0.2
Pb	0.002	mg/kg	4.8	7.4	4.4	5.5	1.7	0.3
S	0.011	mg/kg	1168.0	1619.8	1253.2	1347.0	240.1	0.2
Sr	0.02	mg/kg	20.4	30.1	22.2	24.2	5.2	0.2
V	0.01	mg/kg	1.8	2.6	2.1	2.1	0.4	0.2
Zn		mg/kg	65.7	90.7	66.0	74.1	14.4	0.2

Table C.3: COD Results for raw manure

Initial COD 20g to 80ml H20 with 20 times dilution (mg/L)						
#	ABS1	ABS2	ABS3	AVGABS	CON	Corrected for dilution
1	0.248	0.243	0.232	0.24	4016.67	84350.00
2	0.241	0.206	0.209	0.22	3644.44	76533.33
3	0.207	0.21	0.205	0.21	3455.56	72566.67
4	0.221	0.189	0.178	0.20	3266.67	68600.00
5	0.211	0.203	0.201	0.21	3416.67	71750.00
					average	74760.00

Retested for verification						
#	ABS1	ABS2	ABS3	AVGABS	CON	Corrected
1	0.192	0.194	0.201	0.20	3261.11	68483.33
2	0.251	0.248	0.239	0.25	4100.00	86100.00
3	0.271	0.261	0.266	0.27	4433.33	93100.00
					average	82561.11

Total avg 78660.56

7866.06mg COD original slurry

C.2 Pictures of Pre-Processed Feedstocks

Dried Ground Tallowseed

Dried Swine Manure

Dried Ground Dairy Manure

Dried Peanuts

Switchgrass

Dried Sawdust (pine)

APPENDIX D: STATISTICAL INFORMATION

SAS Output Report

```
Randomize complete design (one-way anova)
Effect of Temperature and catalyst on energy production
List of Data

Obs   MJ     T  CA
  1   0.104  1   1
  2   0.135  1   2
  3   0.100  1   3
  4   0.100  1   4
  5   0.093  1   5
  6   0.080  2   1
  7   0.114  2   2
  8   0.110  2   3
  9   0.124  2   4
 10   0.137  2   5
 11   0.124  3   1
 12   0.161  3   2
 13   0.153  3   3
 14   0.114  3   4
 15   0.142  3   5
```

```
Randomize complete design (one-way anova)
Effect of Temperature and catalyst on energy production
List of Data
The REG Procedure
Model: MODEL1
Dependent Variable: MJ
Number of Observations Read         15
Number of Observations Used         15

Analysis of Variance
                                Sum of          Mean
Source               DF        Squares        Square    F Value    Pr > F
Model                 2        0.00273       0.00136       3.54    0.0618
Error                12        0.00462    0.00038522
Corrected Total      14        0.00735
Root MSE             0.01963    R-Square     0.3712
Dependent Mean       0.11940    Adj R-Sq     0.2664
Coeff Var           16.43809

Parameter Estimates
                      Parameter      Standard
Variable     DF        Estimate         Error    t Value    Pr > |t|     Type I SS     Type II SS
Intercept     1         0.08140       0.01719       4.74      0.0005       0.21385        0.00864
T             1         0.01620       0.00621       2.61      0.0228       0.00262        0.00262
CA            1         0.00187       0.00358       0.52      0.6119    0.00010453     0.00010453

Randomize complete design (one-way anova)
Effect of Temperature and catalyst on energy production
Multiple regression with PROC MIXED
```

```
The Mixed Procedure

Model Information
Data Set                    WORK.J
Dependent Variable          MJ
Covariance Structure        Diagonal
Estimation Method           REML
Residual Variance Method    Profile
Fixed Effects SE Method     Model-Based
Degrees of Freedom Method   Residual

Dimensions
Covariance Parameters  1
Columns in X  3
Columns in Z  0
Subjects   1
Max Obs Per Subject     15

Number of Observations
Number of Observations Read          15
Number of Observations Used          15
Number of Observations Not Used       0

Covariance Parameter
Estimates
Cov Parm     Estimate
Residual      0.000385

Fit Statistics
-2 Res Log Likelihood        -51.9
AIC (smaller is better)      -49.9
AICC (smaller is better)     -49.5
BIC (smaller is better)      -49.4
```

```
Solution for Fixed Effects
Standard
Effect       Estimate    Error      DF    t Value   Pr > |t|
Intercept    0.08140     0.01719    12    4.74      0.0005
T            0.01620     0.006207   12    2.61      0.0228
CA           0.001867    0.003583   12    0.52      0.6119

Type 1 Tests of Fixed Effects
          Num    Den
Effect    DF     DF    F Value   Pr > F
T          1     12    6.81      0.0228
CA         1     12    0.27      0.6119

Type 2 Tests of Fixed Effects

          Num    Den
Effect    DF     DF    F Value   Pr > F
T          1     12    6.81      0.0228
CA         1     12    0.27      0.6119

Type 3 Tests of Fixed Effects
          Num    Den
Effect    DF     DF    F Value   Pr > F
T          1     12    6.81      0.0228
CA         1     12    0.27      0.6119
```

Table D.1. Data used for SAS input (Temperature and catalysts treatment numbers follow for input to SAS (temperature:1 for 300, 2 for 325, 3 for 350; Catalyst quantities treated as 1 for 0, 2 for 1, 3 for 2, 4 for 3, and 5 for 4)). MJ data was inputted as is.

TEMP	Catalyst	ASF	HV		
		g	MJ kg^{-1}	MJ/g	MJ
300	0	3.6	28.9	0.0289	0.104
300	1	4.5	30.0	0.0300	0.135
300	2	3.4	29.4	0.0294	0.100
300	3	3.4	29.5	0.0295	0.100
300	4	3.1	29.9	0.0299	0.093
325	0	2.6	30.6	0.0306	0.080
325	1	4.0	28.5	0.0285	0.114
325	2	3.5	31.4	0.0314	0.110
325	3	3.7	33.4	0.0334	0.124
325	4	4.2	32.5	0.0325	0.137
350	0	3.8	32.5	0.0325	0.124
350	1	4.8	33.5	0.0335	0.161
350	2	4.4	34.7	0.0347	0.153
350	3	3.4	33.4	0.0334	0.114
350	4	4.3	33.0	0.0330	0.142

VITA

Jason Scott Midgett was born in 1982, in Lake Charles, Louisiana. He graduated from his high school Alfred M. Barbe, in May 2000. Following high school, he attended Louisiana State University, Baton Rouge, where he earned a Bachelor of Science in biological engineering in May 2005. Jason has been a full time graduate student at Louisiana State University in the Department of Biological and Agricultural Engineering since August 2005 and is presently a candidate for the degree of Master of Science in Biological and Agricultural Engineering.